

**The investigation of the mechanical properties of MAX phase and cubic boron nitride
ceramic composite made by spark plasma sintering**

By:

Tokoloho Rampai

School of Chemical and Metallurgical Engineering

University of the Witwatersrand

Supervisor:

Dr D. J. Whitefield

School of Chemical and Metallurgical Engineering

University of the Witwatersrand



UNIVERSITY OF THE
WITWATERSRAND,
JOHANNESBURG

August 2020

Thesis in full fulfilment of the requirements for the degree of Ph.D. (Metallurgical
Engineering)

PLAGIARISM DECLARATION

1. I know that plagiarism is wrong. Plagiarism is to use another's work and pretend that it is one's own.
2. I have used the Harvard system for citation and referencing. Each contribution to, and quotation in this thesis from the work(s) of other people has been attributed and has been cited and referenced.
3. This thesis is my own work.
4. I have not allowed, and will not allow, anyone to copy my work with the intention of passing it off as his or her own work.

Signature



Date



ACKNOWLEDGEMENTS

First and always, I would like to thank Heavenly father for his unwavering love and grace, and Jesus Christ for the atonement and the love and sacrifice given.

I would like to thank the DST-NRF centre of Excellence in Strong Materials for their financial support and general support during my PhD studies. I would also like to thank Element Six and University of Cape Town Research Office (ERP) for the financial support and faith in my skills. This work is based in the research supported in part by the National Research Foundation of South Africa (Grant number: 116801). I would like to thank my supervisor Dr David Whitefield for being supportive, always with guidance and constructive feedback on all things academic!

I would like to thank my late mother and father, Mamosiuwa and Puso Rampai for raising me with love, fun, happiness, understanding and forever believing in me. My children, Hopolang and Sabata Rampai for loving and supporting me, and for bearing with me through this period. To all my brothers and sisters, especially my sister, Lerato Rampai, who worked tirelessly to bridge the gap of parenting after our parents passed away. To my late brother Sehloho Moeketsi Rampai, who always made me laugh, this thesis is dedicated to you. To my adoptive family, the Thahane family, for lovingly helping me through the hardships of Grade 12.

My sincere gratitude goes to the Church of Jesus Christ of Latter-day Saints for being a great extended family and loving community for a lost soul like mine. For the support help, guidance, and loving service for our dedicated leaders.

Publications produced from this work

1. Utilization of moderate pressure elevated temperatures in the optimization of Ti_2AlC -cBN composites using SPS, by T. Rampai; D. Whitefield and I. Sigalas(requested revisions submitted 30/09/2020 to International Journal of Ceramic Engineering and Science).
2. Ti_3AlC_2 -cBN composite synthesis using SPS at elevated temperatures and moderate pressures, by control of cBN surface area and content, by T. Rampai; D. Whitefield and I. Sigalas (submitted 30/06/2020 to Journal of American Ceramics Society).

ABSTRACT

The MAX Phases, which are unique new carbide and nitride ternary ceramics, have the main advantages of both metals and ceramics: they are generally soft, machinable, heat-tolerant, strong and lightweight. Composites of MAX phases and Cubic boron nitride (cBN) could have a wide array of applications. The problem in making these composites lies in the reactivity of MAX phases and cBN. The cBN abrasive proportions used were 20 and 40 vol.%, and the average cBN particle sizes used were 10 and 100 μm cBN. Using the SPS method, the pressure was kept constant at 30 MPa throughout and temperatures varied from 700 to 1600°C. Successful samples in this study were defined as those that displayed abundant MAX phase and cBN in the sample, with minimum to no hBN presence.

The reactivity of the Ti_2AlC , Ti_3AlC_2 and Ti_3SiC_2 MAX phases with the cBN was determined to be the simultaneous hexagonalisation of cBN and reaction of the resultant hBN with the MAX phases. The resultant secondary phases were; hBN (in some cases), $\text{AlN}/\text{Ti}_a\text{Al}_b$, TiB_2 and TiC_xN_y (and/or TiC and TiN) from the Al based MAX phase composites. The phases present were hBN (in some cases), SiC , TiB_2 and TiC_xN_y (and/or TiC and TiN) from the Ti_3SiC_2 composites. It was observed that decreasing the surface area and/or increasing the volume fraction of the cBN had a stabilising effect on the MAX phase formation in the composites. The optimum conditions for synthesising Ti_2AlC based composites were 1250°C for 5 minutes for all sizes and fractions of cBN. For the Ti_3AlC_2 based composites, the optimum conditions were 1300°C for 10 minutes, for the 20 vol.% cBN composites, and 1350°C for 5 minutes for the 40 vol.% cBN composites. For the Ti_3SiC_2 based composites, the optimum conditions were 1250°C for 5 minutes for the 20 vol.% composites and 1300°C for 5 minutes for the 40 vol.% cBN composites. The SEM analysis of selected samples showed the cBN and MAX phases were both strongly bonded to the reaction area formed between the two phases. The Ti_3SiC_2 composites in general had the highest hardness and wear resistance followed by the Ti_2AlC composites and last was the Ti_3AlC_2 composites.

TABLE OF CONTENTS

LIST OF FIGURES	X
Figures in main thesis.....	x
Figures in Appendices	xviii
LIST OF TABLES.....	XXVII
Tables in main thesis.....	xxvii
Tables in Appendices	xxviii
 CHAPTER ONE: INTRODUCTION.....	 1
1.1 Background to the study	1
1.2 Problem Statement.....	2
1.3 Research Objectives	3
1.4 Overview of the Thesis	4
 CHAPTER TWO: LITERATURE REVIEW.....	 5
2.1 The MAX phase ceramics.....	5
2.1.1 Crystal structure and bonding	8
2.1.2 Kink bands and damage tolerance	10
2.1.3 Synthesis of MAX phases	12
2.1.3.1 Spark Plasma Synthesis Method	12
2.1.3.2 Ti ₂ AlC synthesis	14
2.1.3.3 Ti ₃ AlC ₂ synthesis	16
2.1.3.4 Ti ₃ SiC ₂ synthesis	18
2.1.4 Microstructure of the MAX phases	21
2.1.5 Physical properties.....	24
2.1.6 Oxidation.....	25
2.1.7 MAX phase composites.....	26
2.1.7.1 Ti ₂ AlC phase composites.....	26

2.1.7.2 Ti_3AlC_2 phase composites.....	27
2.1.7.3 Ti_3SiC_2 composites	29
2.1.7.4 Ti-Al phases formation.....	31
2.2 Cubic Boron Nitride	32
2.2.1 Applications of cBN	33
2.2.2 Decomposition studies	36
2.2.3 Composites of cBN	37
2.4 Grinding wheels.....	37
2.5 Rationale of study.....	40
CHAPTER THREE: METHODOLOGY	42
3.1 Powder preparation	42
3.2 MAX-cBN composites synthesis using spark plasma sintering furnace.....	43
3.3 MAX-cBN composite preparation and characterisation	45
3.3.1 MAX-cBN composites sample preparation	45
3.3.2 Density measurements (Archimedes' method)	46
3.3.3 X-ray diffraction (XRD)	47
3.3.4 Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDX).....	47
3.4 MAX-cBN mechanical properties evaluation	47
3.4.1 Vickers hardness measurements	47
3.4.2 Pin-on-belt wear tests	48
CHAPTER FOUR: RESULTS.....	50
4.1 Reaction temperature evaluation 20 vol.% of the 10 μm cBN	50
4.1.1 Ti_2AlC -cBN composites	55
4.1.2 Ti_3AlC_2 -cBN composites.....	65
4.1.3 Ti_3SiC_2 -cBN composites.....	73
4.2 Reaction temperature optimisation with 20 vol.% of the 10 μm cBN	81

4.2.1 Ti_2AlC -cBN composites	81
4.2.2 Ti_3AlC_2 -cBN composites	85
4.2.3 Ti_3SiC_2 -cBN composites	90
4.3 Investigation of cBN surface area effect on reaction temperatures using 100 μm cBN (20 vol.%)	94
4.3.1 Ti_2AlC -cBN composites	94
4.3.2 Ti_3AlC_2 -cBN composites	100
4.3.3 Ti_3SiC_2 -cBN composites	104
4.4 Investigation of cBN volume fraction effect on reaction temperatures using 40 vol.% cBN (100 μm)	110
4.4.1 Ti_2AlC -cBN composites	111
4.4.2 Ti_3AlC_2 -cBN composites	116
4.4.3 Ti_3SiC_2 -cBN composites	122
4.5 Evaluating of the mechanical properties of the MAX-cBN composites	127
4.5.1 Vickers hardness	129
4.5.2 Wear results	131
CHAPTER FIVE: DISCUSSION	134
5.1 Introduction	134
5.2 MAX-cBN composite synthesis	141
5.2.1 Ti_2AlC – cBN composites	141
5.2.1.1 Reaction Temperature evaluation for 20 vol.% of 10 μm cBN powder.	141
5.2.1.2 Increased particle size (10 to 100 μm) and volume fraction of the 100 μm cBN (20 to 40 vol.%)	148
5.2.2 Ti_3AlC_2 – cBN composites	152
5.2.2.1 Reaction Temperature evaluation for 20 vol.% of 10 μm cBN powder	152
5.2.2.2 Increased in particle size (10 to 100 μm) and volume fraction of the 100 μm cBN (20 to 40 vol.%)	157

5.2.3 Ti ₃ SiC ₂ - cBN composites.....	162
5.2.3.1 Reaction Temperature evaluation for 20 vol.% of 10 µm cBN powder	162
5.2.3.2 Increased particle size (10 to 100 µm) and volume fraction of the 100 µm cBN (20 to 40 vol.%)	167
5.2.4 Overall MAX cBN composites reactivity	170
5.3 Mechanical properties of the successful MAX-cBN composites	173
5.4 Suitability of the successful MAX-cBN composites for grinding wheels	175
CHAPTER SIX: CONCLUSIONS AND RECOMMENDATIONS	178
REFERENCES	183
APPENDICES.....	0
Appendix A: Supplementary individual XRD data for sintered samples.....	0
Appendix B: Supplementary phase peak lists for peaks assigned in the XRD analysis...	20
Appendix C: Supplementary Density data	0
Appendix D: Supplementary data for Rietveld analysis of samples	0
Appendix E: Supplementary SEM/EDX analysis of samples.....	9
Appendix F: Supplementary data for EDX reported averages.....	32
Appendix G: Supplementary data for mechanical test results	47
Appendix H: Paper publication done for Master's degree	56
Appendix I: First draft paper written from PhD work: submitted to International Journal of Ceramic Engineering and science after reviewer comment(15/07/2020)	57
Appendix J: Second Publication from PhD work: submitted to Journal of American Ceramics Society (30/06/2020)	88

LIST OF FIGURES

Figures in main thesis

Figure 2.1: Periodic table illustrating the designation of the MAX phases (Barsoum & El-Raghy, 2001).	5
Figure 2.2: Crystal structures of the three classes of MAX phases where M group atoms are red; A group atoms are blue and X group atoms are black. a) M_2AX phases, b) M_3AX_2 phases and c) M_4AX_3 phases (Barsoum & Randovic, 2011).	6
Figure 2.3: Kink bands in the microstructure of MAX phases a) schematic demonstrating the kink band formation, b) optical micrograph shows a typical macroscopic kink band and c) a transmission electron microscope image shows a microscopic kink band and its boundaries (Barsoum & El-Raghy, 2001).	10
Figure 2.4: Diagram showing the setup for a field assisted sintering technology/spark plasma sintering (FAST/SPS) (Chanthapan et al., 2011).	13
Figure 2.5: SEM (SE) image micrographs of the fracture surface of the Ti_2AlC sintered at (a) 1100°C, 30 MPa for 60 minutes with graphite as the carbon source (Zhou et al., 2005), (b) 1250°C, 1100 MPa for 8 minutes with carbon black as the carbon source (Mei et al., 2004), (c) 1200°C, 50 kN with CNT as the carbon source (Kulkarni et al., 2010) and (d) higher magnification of sample in (c).	15
Figure 2.6: SEM (SE) micrograph fracture surface of a polycrystalline Ti_3AlC_2 (a) obtained by SPS of mechanically alloyed 2Ti:1.1Al:2C powders (Yang et al., 2009) and (b) obtained by-SPS of Al_4C_3 , Ti and C (Zhou et al., 2003a).	17
Figure 2.7: SEM micrographs of the fracture surface of the Ti_3SiC_2 sintered at (a) (SE mode) 1250°C, 60 MPa for 10 min and (Gao et al., 2002), (b) (BSE mode) 1100°C, 30MPa for 5min of mechanically alloyed powders. (Liang et al., 2008).	19
Figure 2.8: Typical HRTEM images taken at a (a) Ti_2AlC grain boundary, (b) intergrowth of Ti_3AlC_2 with Ti_2AlC , (c) intergrowth of TiC with Ti_2AlC (Wang & Zhou, 2010 adapted from Lin et al., 2006a)..	22
Figure 2.9: HRTEM images of: (a) the incident beam parallel to the $[1210]$ direction of Ti_3AlC_2 , and (b) a basal plane stacking fault in Ti_3SiC_2 . The viewing direction is $[1120]$ (Lin et al., 2006a; Kooi et al., 2003).	23

Figure 2.10: SEM (SE) image of fractured surface of a TiAl/Ti ₂ AlC composite with 75 wt% MAX (Yang et al., 2014).	27
Figure 2. 11: Density and fracture toughness of the TiAl/Ti ₂ AlC composites with different vol.% of Ti ₂ AlC (Yang et al., 2014).	27
Figure 2.12: SEM images of Ti ₃ AlC ₂ –cBN composites processed under 4.5 GPa at 1100°C for 10 min. (a) (SE mode) Low magnification to show the distribution of cBN particles and (b) (SE mode) high magnification to show the layered structure of Ti ₃ AlC ₂ matrix (Li et al., 2012).	28
Figure 2.13: Graphs of (a) Hardness measurements of cBN–Ti ₃ AlC ₂ composites processed at different temperatures, (b) friction coefficients of cBN–Ti ₃ AlC ₂ composites processed at different temperatures and mass loss of corresponding Si ₃ N ₄ balls (Li et al., 2012).	29
Figure 2. 14: Young's modulus and Hardness of cBN-Ti ₃ SiC ₂ composites with different cBN contents (After Benko et al., 2004).	30
Figure 2.15: SEM(BSE) images of (a) Ti, SiC, C and cBN, (b)Ti ₃ SiC ₂ and cBN starting powders and (c) is a magnified image of (b) (Li et al., 2014).	31
Figure 2. 16: DTA heating curves of Ti:38 (wt%)Al powder mixture.	31
Figure 2.17: Structural transformation diamond and cBN at HTHP, (a) graphite to diamond and (b) hBN to cBN. (Monteiro et al., 2013).	33
Figure 2.18: Interface between cBN and sialon matrix-densified at 1575 °C. At the interface, the hBN grains embedded in the amorphous oxynitride grain boundary phase are clearly visible (light grey phase-sialon, bright phase-oxynitride liquid and dark grey-cBN/hBN)	36
Figure 3.1: The SPS furnace used to sinter cBN-MAX powders to synthesise the composite material.	44
Figure 3.2: Schematic diagram for the composite samples and the dimensions measured and calculated to determine wear.	49
Figure 4.1: SEM (BSE) image and EDX analysis of a Ti ₃ SiC ₂ -(20 vol.% 10µm) cBN sample sintered at 1500°C with 44 µm SiC.	53
Figure 4.2: SEM (BSE) images of Ti ₃ SiC ₂ -cBN composites sintered at 1300°C for 1 minute after a) original mixing method (20 vol.% of the 10 µm cBN), b) mixing by including 4 mm alumina balls in the	

dry mixing of cBN with Ti, Al and C (20 vol.% of the 10 μm cBN), c) doubling the mixing time to with the 4 mm alumina balls (20 vol.% of the 10 μm cBN) and d) same mixing as c) with 40 vol.% of the 100 μm cBN. Orange arrows point to areas lacking in cBN showing segregation of phases.	54
Figure 4.3: Ti_2AlC -cBN (20 vol.%,10 μm) curves from the SPS runs at 1 min and different temperatures. a) Piston displacement curves and b) Piston displacement time derivative curves.	57
Figure 4.4: Densities and open porosities of Ti_2AlC -cBN (20 vol.%,10 μm) samples sintered at different temperatures with 1-minute dwell time.	58
Figure 4.5: XRD traces of Ti_2AlC -cBN (20 vol.%, 10 μm) samples sintered at 30 MPa for 1 min and different temperatures (700°C and 1300°C).	59
Figure 4.6: XRD traces of Ti_2AlC -cBN (20 vol.%, 10 μm) samples sintered at 30 MPa for 1 minute and different temperatures (1300°C to 1500°C).	60
Figure 4.7: XRD traces of Ti_2AlC -cBN (20 vol.%, 10 μm) samples sintered at 30 MPa, 1 minute and different temperatures (1150°C to 1300°C).	61
Figure 4.8: SEM (BSE) images of Ti_2AlC -cBN (20 vol.%,10 μm) samples sintered at 30 MPa for 1 minute and different temperatures. The blue and red circles indicate the reaction area, between the two, occurring from reaction of cBN with MAX phase.	62
Figure 4.9: EDX analysis of Ti_2AlC -cBN (20 vol.%, 10 μm) sample sintered at 30 MPa, 1 minute and 1600°C.	64
Figure 4.10: Ti_3AlC_2 -cBN (20 vol.%,10 μm) curves from the SPS runs at 1 min and different temperatures. a) Piston displacement curves and b) Piston displacement time derivative curves.	66
Figure 4.11: Densities and open porosities of Ti_3AlC_2 -cBN (20 vol.%,10 μm) samples sintered at different temperatures with 1 minute dwell time.	67
Figure 4.12: XRD traces of Ti_3AlC_2 -cBN (20 vol.%, 10 μm) samples sintered at 30 MPa for 1 minute and different temperatures (700°C and 1360°C).	68
Figure 4.13: XRD traces of Ti_3AlC_2 samples sintered at 30 MPa for 1 minute and different temperature (1300°C to 1500°C).	69
Figure 4.14: XRD traces of Ti_3AlC_2 -cBN (20 vol.%, 10 μm) samples sintered at 30 MPa for 1 minute and different temperature profiles (1150°C and 1250°C).	70
Figure 4.15: SEM (BSE) of Ti_3AlC_2 -cBN (20 vol.%, 10 μm) samples sintered at 30 MPa, 1 minute and different temperatures.	71

Figure 4.16: EDX analysis of Ti_3AlC_2 -cBN (20 vol.%, 10 μm) samples sintered at 30 MPa, 1 minute and 1600°C.	72
Figure 4.17: Ti_3SiC_2 -cBN (20 vol.%, 10 μm) densification curves from the SPS experiments for the different temperatures.	74
Figure 4.18: Densities and open porosities of Ti_3SiC_2 -cBN (20 vol.%, 10 μm) samples sintered at different temperatures with 1-minute dwell time.	75
Figure 4.19: XRD traces of Ti_3SiC_2 -(20 vol.% of 10 μm) cBN samples sintered at 30 MPa, 1 minute and different temperatures (1150°C to 1300°C).	76
Figure 4.20: XRD traces of Ti_3SiC_2 -(20 vol.% of 10 μm) cBN samples sintered at 30 MPa, 1 minute and different temperatures (1400°C to 1600°C).	77
Figure 4.21: SEM (BSE) of Ti_3SiC_2 -cBN (20 vol.%, 10 μm) samples sintered at 30 MPa, 1 minute and different temperatures.	79
Figure 4.22: EDX analysis of Ti_3SiC_2 -cBN (20 vol.%, 10 μm) sample sintered at 30 MPa, 1 minute and 1600°C.	80
Figure 4.23: XRD traces of Ti_2AlC -cBN (20 vol.%, 10 μm) samples sintered at 30 MPa, 1250°C for different times.	82
Figure 4.24: Phase quantities, determined by Rietveld analysis, of Ti_2AlC -cBN (20 vol.%, 10 μm) samples sintered for different times at 1250°C.	83
Figure 4.25: Densities and open porosities of Ti_2AlC -cBN (20 vol.%, 10 μm) samples sintered at 1250°C for different dwell time.	83
Figure 4.26: SEM (BSE) of fractured (left column) and polished (right column) Ti_2AlC -cBN (20 vol.%, 10 μm) samples sintered at 30 and MPa 1250°C for different times. Blue arrows indicate crack propagation between cBN and matrix indicating strong bond between cBN and matrix and red arrows indicate crack propagating through the cBN.	84
Figure 4.27: XRD traces of Ti_3AlC_2 -(20 vol.% of 10 μm) cBN samples sintered at 30 MPa, 1250°C and different times.	86
Figure 4.28: XRD traces of Ti_3AlC_2 -cBN (20 vol.%, 10 μm) samples sintered at 30 MPa, 1300°C and different dwell/annealing times.	86
Figure 4.29: Phase quantities, determined by Rietveld analysis, of Ti_3AlC_2 -cBN (20 vol.%, 10 μm) samples sintered for different times at 1250°C.	87

Figure 4.30: Densities and open porosities of Ti_3AlC_2 -cBN (20 vol.%, 10 μm) samples sintered at different temperatures and for different dwell time.	88
Figure 4.31: SEM (BSE) of fractured (left) and polished (right) Ti_3AlC_2 -cBN (20 vol.%, 10 μm) samples sintered at 30 MPa 1300°C and different times. Blue arrows indicate crack propagation between cBN and matrix indicating strong bond between cBN and matrix, red arrows indicate crack propagating through the cBN and orange arrows indicate porosity in the matrix.	89
Figure 4.32: XRD traces of Ti_3SiC_2 -(20 vol% of 10 μm) cBN samples sintered at 30 MPa, 1150°C and different times.	90
Figure 4.33: XRD traces of Ti_3SiC_2 -cBN (20 vol.%, 10 μm) samples sintered at 30 MPa, 1250°C and different times.	91
Figure 4.34: Phase quantities, determined by Rietveld analysis, of Ti_3SiC_2 -cBN (20 vol.%, 10 μm) samples sintered for different times at 1250°C.	91
Figure 4.35: Densities and open porosities of Ti_3SiC_2 -cBN (20 vol.%, 10 μm) samples sintered at different temperatures and for different dwell time.	92
Figure 4.36: SEM (BSE) images of fractured (left) and polished (right) Ti_3SiC_2 -cBN (20 vol.%, 10 μm) samples sintered at 30 MPa 1250°C and different times. Blue arrows indicate crack propagation between cBN and matrix indicating strong bond between cBN and matrix, red arrows indicate crack propagating through the cBN and Green arrows indicate possible cBN pull-out.	93
Figure 4.37: XRD traces of Ti_2AlC -cBN (20 vol.%, 100 μm) samples sintered at 30 MPa, 1250°C and different times.	95
Figure 4.38: XRD traces of Ti_2AlC -cBN (20 vol%, 100 μm) cBN samples sintered at 30 MPa, 1300°C and different times.	96
Figure 4.39: Phase quantities, determined by Rietveld analysis, of Ti_2AlC -cBN (20 vol.%, 100 μm) samples sintered for different times at 1250°C.	96
Figure 4.40: Densities and open porosities of Ti_2AlC -cBN (20 vol.%, 100 μm) samples sintered at different temperatures for different dwell time.	97
Figure 4.41: SEM (BSE) images of Ti_2AlC -cBN (20 vol.%, 100 μm) samples sintered for different times at 1250°C (left column) and 1300°C (right column). Blue arrows indicate crack propagation between cBN and matrix, red arrows indicate crack propagating through the cBN and green arrows indicate possible cBN pull-out.	98

Figure 4.42: SEM (BSE) and EDX analysis of Ti_2AlC -cBN (20 vol.%, 100 μm) samples sintered at 30 MPa 1250°C 5 minutes.	99
Figure 4.43: XRD traces of Ti_3AlC_2 -cBN (20 vol.%, 100 μm) samples sintered at 30 MPa, 1300°C for different times.....	100
Figure 4.44: Phase quantities, determined by Rietveld analysis of Ti_3AlC_2 -cBN (20 vol.%,100 μm) samples sintered for different times at 1300°C.....	101
Figure 4.45: Densities and open porosities of Ti_3AlC_2 -cBN (20 vol.%,100 μm) samples sintered at different temperatures for different dwell time.....	102
Figure 4.46: SEM (BSE) images of Ti_3AlC_2 -cBN (20 vol.%, 100 μm) samples sintered for different times at 1300°C.....	103
Figure 4.47: SEM (BSE) and EDX analysis of Ti_3AlC_2 -cBN (20 vol.%, 100 μm) samples sintered at 30 MPa 1300°C 10 minutes.	103
Figure 4.48: XRD traces of Ti_3SiC_2 -(20 vol.% of 100 μm) cBN samples sintered at 30 MPa, 1250°C and different times.....	104
Figure 4.49: XRD traces of Ti_3SiC_2 -(20 vol% of 100 μm) cBN samples sintered at 30 MPa, 1300°C and different times.....	106
Figure 4.50: Phase quantities, determined by Rietveld analysis, of Ti_3SiC_2 -cBN (20 vol.%,100 μm) samples sintered for different times at 1250°C.....	106
Figure 4.51: Densities and open porosities of Ti_3SiC_2 -cBN (20 vol.%,100 μm) samples sintered at different temperatures for different dwell time.....	107
Figure 4.52: SEM (BSE) images of Ti_3SiC_2 -cBN (20 vol.%, 100 μm) samples sintered for different times at 1250°C (left column) and 1300°C (right column).	108
Figure 4.53: SEM (BSE) and EDX analysis of Ti_3SiC_2 -cBN (20 vol.%, 100 μm) samples sintered at 30 MPa, 1250°C for 1 minute.....	109
Figure 4.54: XRD traces of Ti_2AlC -cBN (40 vol.%, 100 μm) samples, and a pure Ti_2AlC sample for comparison, sintered at 30 MPa, for 5 min and different temperatures.....	111
Figure 4.55: XRD traces of Ti_2AlC -cBN (40 vol.%, 100 μm) samples, and a pure Ti_2AlC sample for comparison, sintered at 30 MPa, for 10 min and different temperatures.....	112
Figure 4.56: Phase quantities, determined by Rietveld analysis, of Ti_2AlC -cBN (40 vol.%,100 μm) samples sintered for 5 minutes at different temperatures.....	112

Figure 4.57: Densities and open porosities of Ti_2AlC -cBN (40 vol.%, 100 μm) samples sintered at different temperatures for different dwell time.....	113
Figure 4.58: SEM (BSE) images of Ti_2AlC -cBN (40 vol.%, 100 μm) samples sintered at 30 MPa and different temperatures for 5 minutes (left) and 10 minutes (right).....	114
Figure 4.59: SEM (BSE) and EDX analysis of Ti_2AlC -cBN (40 vol.%, 100 μm) samples sintered at 30 MPa, 1350°C and 5 minutes.	115
Figure 4.60: XRD traces of Ti_3AlC_2 -cBN (40 vol.%, 100 μm) samples sintered at 30 MPa for, 5 minutes and at different temperatures.	117
Figure 4.61: XRD traces of Ti_3AlC_2 -cBN (40 vol%, 100 μm) samples sintered at 30 MPa, 10 minutes and different temperatures.	117
Figure 4.62: Phase quantities, determined by Rietveld analysis, of Ti_3AlC_2 -cBN (40 vol.%, 100 μm) samples sintered for 5 minutes at different temperatures.....	118
Figure 4.63: Densities and open porosities of Ti_3AlC_2 -cBN (40 vol.%, 100 μm) samples sintered at different temperatures and dwell time.....	119
Figure 4.64: SEM (BSE) of Ti_3AlC_2 -cBN (40 vol.%, 100 μm) samples sintered at 30 MPa and different temperatures for 5 minutes (left) and 10 minutes (right).....	120
Figure 4.65: SEM (BSE) and EDX analysis of Ti_3AlC_2 -cBN (40 vol.%, 100 μm) samples sintered at 30 MPa, 1350°C for 5 minutes.	121
Figure 4.66: XRD traces of Ti_3SiC_2 -cBN (40 vol.%, 100 μm) samples sintered at 30 MPa, 5 min and different temperatures.	122
Figure 4.67: XRD traces of Ti_3SiC_2 -cBN (40 vol%, 100 μm) samples sintered at 30 MPa, 10 minutes and different temperatures.....	123
Figure 4.68: Phase quantities, determined by Rietveld analysis, of Ti_3SiC_2 -cBN (40 vol.%, 100 μm) samples sintered for 5 minutes at different temperatures.....	123
Figure 4.69: Densities and open porosities of Ti_3SiC_2 -cBN (40 vol.%, 100 μm) samples sintered at different temperatures for different dwell time.....	124
Figure 4.70: SEM (BSE) images of Ti_3SiC_2 -cBN (40 vol.%, 100 μm) samples sintered at different temperatures for 5 minutes (left) and 10 minutes (right).....	125
Figure 4.71: SEM (BSE) and EDX analysis of Ti_3SiC_2 -cBN (40 vol.%, 100 μm) samples sintered at 30 MPa, 1300°C for 5 minutes.	126

Figure 4.72: A chart showing decision making for the temperatures to use to synthesise Ti_2AlC -cBN composites. Selected optimal conditions from previous sections are highlighted in green.	128
Figure 4.73: A chart showing decision making for the temperatures to use to synthesise Ti_3AlC_2 -cBN composites. Selected optimal conditions from previous sections are highlighted in green.	129
Figure 4.74: A chart showing decision making for the temperatures to use to synthesise Ti_3SiC_2 -cBN composites. Selected optimal conditions from previous sections are highlighted in green.	129
Figure 4.75: Vickers microhardness results for the selected samples.	130
Figure 4.76: Vickers bulk hardness results for the selected samples.	131
Figure 4.77: Linear wear results for the selected samples, pin-on-belt wear tests.....	132
Figure 4.78: Wear rate results for the selected samples, pin-on-belt wear tests.....	132
Figure 4.79: SEM (BSE) images of wear scars for the selected samples, pin-on-belt wear tests. Orange arrows show the SiC particles worn from SiC counterphase by the composites.	133
Figure 4.79: Wear scar images for the selected samples, pin-on-belt wear tests.	133
Figure 5.1: XRD traces of Ti_2AlC -cBN samples sintered at 1250°C for 5 minutes, showing different volume fraction (20 or 40 vol.%) and different size (10 and 100 μm) cBN. The XRD traces are taken from Figure 4.23, 4.37 and 4.54.	149
Figure 5.2: XRD traces of Ti_3AlC_2 -cBN samples sintered at 1300°C for 10 minutes, showing different volume fraction (20 or 40 vol.%) and different size (10 and 100 μm) cBN, also included was the successful sample at the 40 vol.% cBN sample sintered at 1350°C for 5 minutes.	159
Figure 5.3: XRD traces of Ti_3SiC_2 -cBN samples sintered at 1250°C for 5 minutes, showing different volume fractions (20 or 40 vol.%) and different sized (10 and 100 μm) cBN; also included was the successful sample at the 40 vol.% cBN sample sintered at 1300°C for 5 minutes.	168
Figure 5.4: Graphs showing the rate of cBN hexagonalisation (left) and proportion of MAX phases formed (right) in all successful composites selected for mechanical tests.	172
Figure 5.5: Relationship between the Vickers hardness and linear wear of all MAX-cBN composites synthesised.	175

Figures in Appendices

Figure A 1: XRD analysis, of Ti_2AlC -cBN (20 vol.%,10 μm) samples sintered at 1300°C for 1 minute..	0
Figure A2: XRD analysis, of Ti_2AlC -cBN (20 vol.%,100 μm) samples sintered at 1500°C for 1 minute.	0
Figure A3: XRD analysis, of Ti_2AlC -cBN (20 vol.%,10 μm) samples sintered at 1250°C for 1 minute...	1
Figure A4: XRD analysis, of Ti_2AlC -cBN (20 vol.%,10 μm) samples sintered at 1250°C for 5 minutes.	1
Figure A5: XRD analysis, of Ti_2AlC -cBN (20 vol.%,10 μm) samples sintered at 1250°C for 10 minutes.	2
Figure A6: XRD analysis, of Ti_3AlC_2 -cBN (20 vol.%,10 μm) samples sintered at 1250°C for 1 minute.	2
Figure A7: XRD analysis, of Ti_3AlC_2 -cBN (20 vol.%,10 μm) samples sintered at 1250°C for 5 minutes.	3
Figure A8: XRD analysis, of Ti_3AlC_2 -cBN (20 vol.%,10 μm) samples sintered at 1250°C for 10 minutes.....	3
Figure A9: XRD analysis, of Ti_3AlC_2 -cBN (20 vol.%,10 μm) samples sintered at 1300°C for 1 minute.	4
Figure A10: XRD analysis, of Ti_3AlC_2 -cBN (20 vol.%,10 μm) samples sintered at 1300°C for 10 minutes.....	4
Figure A11: XRD analysis, of Ti_3SiC_2 -cBN (20 vol.%,10 μm) samples sintered at 1150°C for 1 minute.	5
Figure A12: XRD analysis, of Ti_3SiC_2 -cBN (20 vol.%,10 μm) samples sintered at 1250°C for 1 minute.	5
Figure A13: XRD analysis, of Ti_3SiC_2 -cBN (20 vol.%,10 μm) samples sintered at 1300°C for 1 minute.	6
Figure A14: XRD analysis, of Ti_3SiC_2 -cBN (20 vol.%,10 μm) samples sintered at 1300°C for 3 minutes.....	6
Figure A15: XRD analysis, of Ti_3SiC_2 -cBN (20 vol.%,10 μm) samples sintered at 1300°C for 10 minutes.....	7
Figure A16: XRD analysis, of Ti_2AlC -cBN (20 vol.%,100 μm) samples sintered at 1150°C for 1 minute.	7
Figure A17: XRD analysis, of Ti_2AlC -cBN (20 vol.%,100 μm) samples sintered at 1250°C for 1 minute.	8

Figure A18: XRD analysis, of Ti_2AlC -cBN (20 vol.%,100 μm) samples sintered at 1250°C for 5 minutes.....	8
Figure A19: XRD analysis, of Ti_2AlC -cBN (20 vol.%,100 μm) samples sintered at 1250°C for 10 minute.....	9
Figure A20: XRD analysis, of Ti_2AlC -cBN (20 vol.%,100 μm) samples sintered at 1300°C for 1 minute.	9
Figure A21: XRD analysis, of Ti_2AlC -cBN (20 vol.%,100 μm) samples sintered at 1300°C for 5 minutes.....	10
Figure A22: XRD analysis, of Ti_3AlC_2 -cBN (20 vol.%,100 μm) samples sintered at 1300°C for 1 minute.....	10
Figure A23: XRD analysis, of Ti_3AlC_2 -cBN (20 vol.%,100 μm) samples sintered at 1300°C for 5 minutes.....	11
Figure A24: XRD analysis, of Ti_3AlC_2 -cBN (20 vol.%,100 μm) samples sintered at 1300°C for 10 minutes.....	11
Figure A25: XRD analysis, of Ti_3SiC_2 -cBN (20 vol.%,100 μm) samples sintered at 1250°C for 1 minute.....	12
Figure A26: XRD analysis, of Ti_3SiC_2 -cBN (20 vol.%,100 μm) samples sintered at 1250°C for 5 minutes.....	12
Figure A27: XRD analysis, of Ti_3SiC_2 -cBN (20 vol.%,100 μm) samples sintered at 1250°C for 10 minutes.....	13
Figure A28: XRD analysis, of Ti_2AlC -cBN (40 vol.%,100 μm) samples sintered at 1250°C for 5 minutes.....	13
Figure A29: XRD analysis, of Ti_2AlC -cBN (40 vol.%,100 μm) samples sintered at 1250°C for 10 minutes.....	14
Figure A30: XRD analysis, of Ti_2AlC -cBN (40 vol.%,100 μm) samples sintered at 1300°C for 5 minutes.....	14
Figure A31: XRD analysis, of Ti_2AlC -cBN (40 vol.%,100 μm) samples sintered at 1300°C for 10 minutes.....	15
Figure A32: XRD analysis, of Ti_2AlC -cBN (40 vol.%,100 μm) samples sintered at 1350°C for 5 minutes.....	15

Figure A33: XRD analysis, of Ti_2AlC -cBN (40 vol.%,100 μm) samples sintered at 1350°C for 10 minutes.....	16
Figure A34: XRD analysis, of Ti_3AlC_2 -cBN (40 vol.%,100 μm) samples sintered at 1250°C for 5 minutes.....	16
Figure A35: XRD analysis, of Ti_3AlC_2 -cBN (40 vol.%,100 μm) samples sintered at 1250°C for 10 minutes.....	17
Figure A36: XRD analysis, of Ti_3AlC_2 -cBN (40 vol.%,100 μm) samples sintered at 1300°C for 5 minutes.....	17
Figure A37: XRD analysis, of Ti_3AlC_2 -cBN (40 vol.%,100 μm) samples sintered at 1300°C for 10 minutes.....	18
Figure A38: XRD analysis, of Ti_3AlC_2 -cBN (40 vol.%,100 μm) samples sintered at 1350°C for 5 minutes.....	18
Figure A39: XRD analysis, of Ti_3AlC_2 -cBN (40 vol.%,100 μm) samples sintered at 1350°C for 10 minutes.....	19
Figure D1: Rietveld analysis, of Ti_2AlC -cBN (20 vol.%,10 μm) samples sintered at 1250°C for 1 minute.....	0
Figure D2: Rietveld analysis, of Ti_2AlC -cBN (20 vol.%,10 μm) samples sintered at 1250°C for 5 minutes.....	0
Figure D3: Rietveld analysis, of Ti_2AlC -cBN (20 vol.%,10 μm) samples sintered at 1250°C for 10 minutes.....	1
Figure D4: Rietveld analysis, of Ti_3AlC_2 -cBN (20 vol.%,10 μm) samples sintered at 1300°C for 1 minute.....	1
Figure D5: Rietveld analysis, of Ti_3AlC_2 -cBN (20 vol.%,10 μm) samples sintered at 1300°C for 5 minutes.....	2
Figure D6: Rietveld analysis, of Ti_3AlC_2 -cBN (20 vol.%,10 μm) samples sintered at 1300°C for 10 minutes.....	2
Figure D7: Rietveld analysis, of Ti_2AlC -cBN (20 vol.%,100 μm) samples sintered at 1250°C for 1 minute.....	3

Figure D8: Rietveld analysis, of Ti_2AlC -cBN (20 vol.%, 100 μm) samples sintered at 1250°C for 5 minutes.....	3
Figure D9: Rietveld analysis, of Ti_2AlC -cBN (20 vol.%, 100 μm) samples sintered at 1250°C for 10 minutes.....	4
Figure D10: Rietveld analysis, of Ti_3AlC_2 -cBN (20 vol.%, 100 μm) samples sintered at 1300°C for 1 minute.....	4
Figure D11: Rietveld analysis, of Ti_3AlC_2 -cBN (20 vol.%, 100 μm) samples sintered at 1300°C for 5 minutes.....	5
Figure D12: Rietveld analysis, of Ti_3AlC_2 -cBN (20 vol.%, 100 μm) samples sintered at 1300°C for 10 minutes.....	5
Figure D13: Rietveld analysis, of Ti_2AlC -cBN (40 vol.%, 100 μm) samples sintered at 1250°C for 5 minutes.....	5
Figure D14: Rietveld analysis, of Ti_2AlC -cBN (40 vol.%, 100 μm) samples sintered at 1300°C for 5 minutes.....	6
Figure D15: Rietveld analysis, of Ti_2AlC -cBN (40 vol.%, 100 μm) samples sintered at 1350°C for 5 minutes.....	6
Figure D16: Rietveld analysis, of Ti_3AlC_2 -cBN (40 vol.%, 100 μm) samples sintered at 1250°C for 5 minutes.....	7
Figure D17: Rietveld analysis, of Ti_3AlC_2 -cBN (40 vol.%, 100 μm) samples sintered at 1300°C for 5 minutes.....	7
Figure D18: Rietveld analysis, of Ti_3AlC_2 -cBN (40 vol.%, 100 μm) samples sintered at 1350°C for 5 minutes.....	7
Figure D19: Rietveld analysis, of Ti_3SiC_2 -cBN (40 vol.%, 100 μm) samples sintered at 1250°C for 5 minutes.....	8
Figure D20: Rietveld analysis, of Ti_3SiC_2 -cBN (40 vol.%, 100 μm) samples sintered at 1300°C for 5 minutes.....	8
Figure D 21: Rietveld analysis, of Ti_3SiC_2 -cBN (40 vol.%, 100 μm) samples sintered at 1350°C for 5 minutes.....	8

Figure E 1: SEM (BSE) and EDX analysis of Ti_2AlC -(20 vol.% of 100 μm) cBN samples sintered at 30 MPa, 1250°C for 1 minute.....	9
Figure E 2: SEM (BSE) and EDX analysis of Ti_2AlC -(20 vol.% of 100 μm) cBN samples sintered at 30 MPa, 1250°C for 10 minutes.....	10
Figure E 3: SEM (BSE) and EDX analysis of Ti_3AlC_2 -cBN (20 vol.%, 100 μm) samples sintered at 30 MPa, 1300°C for 1 minute.....	11
Figure E4: SEM (BSE) and EDX analysis of Ti_3AlC_2 -cBN (20 vol.%, 100 μm) samples sintered at 30 MPa, 1300°C for 5 minutes.....	12
Figure E5: SEM (BSE) and EDX analysis of Ti_3SiC_2 -cBN (20 vol.%, 100 μm) samples sintered at 30 MPa, 1250°C for 1 minute.....	13
Figure E6: SEM (BSE) and EDX analysis of Ti_3SiC_2 -cBN (20vol.%, 100 μm) samples sintered at 30 MPa, 1250°C for 10 minutes.....	15
Figure E7: SEM (BSE) and EDX analysis of Ti_3SiC_2 -cBN (20 vol.%, 100 μm) samples sintered at 30 MPa, 1300°C for 1 minute.....	16
Figure E8: SEM (BSE) and EDX analysis of Ti_3SiC_2 -cBN (20 vol.%, 100 μm) samples sintered at 30 MPa, 1300°C for 5 minutes.....	17
Figure E9: SEM (BSE) and EDX analysis of Ti_3SiC_2 -cBN (20 vol.%, 100 μm) samples sintered at 30 MPa, 1300°C for 10 minutes.....	17
Figure E10: SEM (BSE) and EDX of Ti_2AlC -cBN (40 vol.%, 100 μm) samples sintered at 30 MPa, 1250°C and 5 minutes.....	18
Figure E11: SEM (BSE) and EDX of Ti_2AlC -cBN (40 vol.%, 100 μm) samples sintered at 30 MPa, 1250°C and 10 minutes.....	19
Figure E12: SEM (BSE) and EDX of Ti_2AlC -cBN (40 vol.%, 100 μm) samples sintered at 30 MPa, 1300°C and 5 minutes.....	20
Figure E13: SEM (BSE) and EDX of Ti_2AlC -cBN (40 vol.%, 100 μm) samples sintered at 30 MPa, 1300°C and 10 minutes.....	21
Figure E14: SEM (BSE) and EDX of Ti_2AlC -cBN (40 vol.%, 100 μm) samples sintered at 30 MPa, 1350°C and 10 minutes.....	22
Figure E15: SEM (BSE) and EDX analysis of Ti_3AlC_2 -cBN (40 vol.%, 100 μm) samples sintered at 30 MPa, 1250°C for 5 minutes.....	23

Figure E16: SEM (BSE) and EDX analysis of Ti_3AlC_2 -cBN (40 vol.%, 100 μm) samples sintered at 30 MPa, 1250°C for 10 minutes.....	24
Figure E17: SEM (BSE) and EDX analysis of Ti_3AlC_2 -cBN (40 vol.%, 100 μm) samples sintered at 30 MPa, 1300°C for 5 minutes.....	25
Figure E18: SEM (BSE) and EDX analysis of Ti_3AlC_2 -cBN (40 vol.%, 100 μm) samples sintered at 30 MPa, 1300°C for 10 minutes.....	26
Figure E19: SEM (BSE) and EDX analysis of Ti_3AlC_2 -cBN (40 vol.%, 100 μm) samples sintered at 30 MPa, 1350°C for 10 minutes.....	27
Figure E20: SEM (BSE) and EDX analysis of Ti_3SiC_2 -cBN (40 vol.%, 100 μm) samples sintered at 30 MPa, 1250°C for 5 minutes.....	28
Figure E21: SEM (BSE) and EDX analysis of Ti_3SiC_2 -cBN (40 vol.%, 100 μm) samples sintered at 30 MPa, 1250°C for 10 minutes.....	29
Figure E22: SEM (BSE) and EDX analysis of Ti_3SiC_2 -cBN (40 vol.%, 100 μm) samples sintered at 30 MPa, 1300°C for 5 minutes.....	30
Figure E23: SEM (BSE) and EDX analysis of Ti_3SiC_2 -cBN (40 vol.%, 100 μm) samples sintered at 30 MPa, 1300°C for 10 minutes.....	31
Figure F 1: EDX analysis of Ti_3SiC_2 -cBN (20 vol.%,10 μm) sample sintered at 30 MPa, 1 minute and 1600°C. Site 1.....	32
Figure F 2: EDX analysis of Ti_3SiC_2 -cBN (20 vol.%,10 μm) sample sintered at 30 MPa, 1 minute and 1600°C. Site 2.....	32
Figure F 3: EDX analysis of Ti_3SiC_2 -cBN (20 vol.%,10 μm) sample sintered at 30 MPa, 1 minute and 1600°C. Site 3.....	32
Figure F 4: EDX analysis of Ti_3SiC_2 -cBN (20 vol.%,10 μm) sample sintered at 30 MPa, 1 minute and 1600°C. Site 4.....	33
Figure F 5: EDX analysis of Ti_3SiC_2 -cBN (20 vol.%,10 μm) sample sintered at 30 MPa, 1 minute and 1250°C. Site 1.....	33
Figure F 6: EDX analysis of Ti_3SiC_2 -cBN (20 vol.%,10 μm) sample sintered at 30 MPa, 1 minute and 1250°C. Site 2.....	33

Figure F 7: EDX analysis of Ti_3SiC_2 -cBN (20 vol.%, 10 μm) sample sintered at 30 MPa, 1 minute and 1250°C. Site 3.	34
Figure F 8: EDX analysis of Ti_3SiC_2 -cBN (20 vol.%, 10 μm) sample sintered at 30 MPa, 1 minute and 1250°C. Site 4.	34
Figure F 9: SEM (BSE) and EDX analysis of Ti_3SiC_2 -cBN (20 vol.%, 100 μm) samples sintered at 30 MPa, 1250°C for 1 minute. Site 1.	34
Figure F 10: SEM (BSE) and EDX analysis of Ti_3SiC_2 -cBN (20 vol.%, 100 μm) samples sintered at 30 MPa, 1250°C for 1 minute. Site 2.	35
Figure F 11: SEM (BSE) and EDX analysis of Ti_3SiC_2 -cBN (20 vol.%, 100 μm) samples sintered at 30 MPa, 1250°C for 1 minute. Site 3.	35
Figure F 12: SEM (BSE) and EDX analysis of Ti_3SiC_2 -cBN (20 vol.%, 100 μm) samples sintered at 30 MPa, 1250°C for 1 minute. Site 4.	35
Figure F 13: SEM (BSE) and EDX analysis of Ti_3SiC_2 -cBN (20 vol.%, 100 μm) samples sintered at 30 MPa, 1250°C for 5 minute. Site 1.	35
Figure F 14: SEM (BSE) and EDX analysis of Ti_3SiC_2 -cBN (20 vol.%, 100 μm) samples sintered at 30 MPa, 1250°C for 5 minute. Site 2.	36
Figure F 15: SEM (BSE) and EDX analysis of Ti_3SiC_2 -cBN (20 vol.%, 100 μm) samples sintered at 30 MPa, 1250°C for 5 minute. Site 3.	36
Figure F 16: SEM (BSE) and EDX analysis of Ti_3SiC_2 -cBN (20 vol.%, 100 μm) samples sintered at 30 MPa, 1250°C for 5 minute. Site 4.	36
Figure F 17: SEM (BSE) and EDX analysis of Ti_3SiC_2 -cBN (20 vol.%, 100 μm) samples sintered at 30 MPa, 1250°C for 10 minute. Site 1.	37
Figure F 18: SEM (BSE) and EDX analysis of Ti_3SiC_2 -cBN (20 vol.%, 100 μm) samples sintered at 30 MPa, 1250°C for 10 minute. Site 2.	37
Figure F 19: SEM (BSE) and EDX analysis of Ti_3SiC_2 -cBN (20 vol.%, 100 μm) samples sintered at 30 MPa, 1250°C for 10 minute. Site 3.	37
Figure F 20: SEM (BSE) and EDX analysis of Ti_3SiC_2 -cBN (20 vol.%, 100 μm) samples sintered at 30 MPa, 1250°C for 10 minute. Site 4.	38
Figure F 21: SEM (BSE) and EDX analysis of Ti_3SiC_2 -cBN (20 vol.%, 100 μm) samples sintered at 30 MPa, 1250°C for 10 minute. Site 5.	38

Figure F 22: SEM (BSE) and EDX analysis of Ti_3SiC_2 -cBN (20 vol.%, 100 μm) samples sintered at 30 MPa, 1300°C for 1 minute. Site 1.	38
Figure F 23: SEM (BSE) and EDX analysis of Ti_3SiC_2 -cBN (20 vol.%, 100 μm) samples sintered at 30 MPa, 1300°C for 1 minute. Site 2.	39
Figure F 24: SEM (BSE) and EDX analysis of Ti_3SiC_2 -cBN (20 vol.%, 100 μm) samples sintered at 30 MPa, 1300°C for 1 minute. Site 3.	39
Figure F 25: SEM (BSE) and EDX analysis of Ti_3SiC_2 -cBN (20 vol.%, 100 μm) samples sintered at 30 MPa, 1300°C for 5 minute. Site 1.	39
Figure F 26: SEM (BSE) and EDX analysis of Ti_3SiC_2 -cBN (20 vol.%, 100 μm) samples sintered at 30 MPa, 1300°C for 5 minute. Site 2.	40
Figure F 27: SEM (BSE) and EDX analysis of Ti_3SiC_2 -cBN (20 vol.%, 100 μm) samples sintered at 30 MPa, 1300°C for 5 minute. Site 3.	40
Figure F 28: SEM (BSE) and EDX analysis of Ti_3SiC_2 -cBN (20 vol.%, 100 μm) samples sintered at 30 MPa, 1300°C for 10 minute. Site 1.	40
Figure F 29: SEM (BSE) and EDX analysis of Ti_3SiC_2 -cBN (20 vol.%, 100 μm) samples sintered at 30 MPa, 1300°C for 10 minute. Site 2.	41
Figure F 30: SEM (BSE) and EDX analysis of Ti_3SiC_2 -cBN (20 vol.%, 100 μm) samples sintered at 30 MPa, 1300°C for 10 minute. Site 3.	41
Figure F 31: SEM (BSE) and EDX analysis of Ti_3SiC_2 -cBN (40 vol.%, 100 μm) samples sintered at 30 MPa, 1250°C for 5 minute. Site 1.	41
Figure F 32: SEM (BSE) and EDX analysis of Ti_3SiC_2 -cBN (40 vol.%, 100 μm) samples sintered at 30 MPa, 1250°C for 5 minute. Site 2.	42
Figure F 33: SEM (BSE) and EDX analysis of Ti_3SiC_2 -cBN (40 vol.%, 100 μm) samples sintered at 30 MPa, 1250°C for 5 minute. Site 3.	42
Figure F 34: SEM (BSE) and EDX analysis of Ti_3SiC_2 -cBN (40 vol.%, 100 μm) samples sintered at 30 MPa, 1250°C for 5 minute. Site 4.	42
Figure F 35: SEM (BSE) and EDX analysis of Ti_3SiC_2 -cBN (40 vol.%, 100 μm) samples sintered at 30 MPa, 1250°C for 10 minute. Site 1.	43
Figure F 36: SEM (BSE) and EDX analysis of Ti_3SiC_2 -cBN (40 vol.%, 100 μm) samples sintered at 30 MPa, 1250°C for 10 minute. Site 2.	43

<i>Figure F 37: SEM (BSE) and EDX analysis of Ti_3SiC_2-cBN (40 vol.%, 100 μm) samples sintered at 30 MPa, 1250°C for 10 minute. Site 3.</i>	<i>43</i>
<i>Figure F 38: SEM (BSE) and EDX analysis of Ti_3SiC_2-cBN (40 vol.%, 100 μm) samples sintered at 30 MPa, 1250°C for 10 minute. Site 4.</i>	<i>44</i>
<i>Figure F 39: SEM (BSE) and EDX analysis of Ti_3SiC_2-cBN (40 vol.%, 100 μm) samples sintered at 30 MPa, 1300°C for 5 minute. Site 1.</i>	<i>44</i>
<i>Figure F 40: SEM (BSE) and EDX analysis of Ti_3SiC_2-cBN (40 vol.%, 100 μm) samples sintered at 30 MPa, 1300°C for 5 minute. Site 2.</i>	<i>44</i>
<i>Figure F 41: SEM (BSE) and EDX analysis of Ti_3SiC_2-cBN (40 vol.%, 100 μm) samples sintered at 30 MPa, 1300°C for 5 minute. Site 3.</i>	<i>45</i>
<i>Figure F 42: SEM (BSE) and EDX analysis of Ti_3SiC_2-cBN (40 vol.%, 100 μm) samples sintered at 30 MPa, 1300°C for 10 minute. Site 1.</i>	<i>45</i>
<i>Figure F 43: SEM (BSE) and EDX analysis of Ti_3SiC_2-cBN (40 vol.%, 100 μm) samples sintered at 30 MPa, 1300°C for 10 minute. Site 2.</i>	<i>45</i>
<i>Figure F 44: SEM (BSE) and EDX analysis of Ti_3SiC_2-cBN (40 vol.%, 100 μm) samples sintered at 30 MPa, 1300°C for 10 minute. Site 3.</i>	<i>46</i>

LIST OF TABLES

Tables in main thesis

<i>Table 2.1: $M_{n+1}AX_n$ phases (carbides) (Barsoum & Radovic, 2011).</i>	7
<i>Table 2.2: Comparison of damage tolerance (reported with no error bars) of other materials to Ti_3SiC_2, Ti_3AlC_2 and Ti_2AlC (adapted from Wang & Zhou, 2010).</i>	9
<i>Table 2.3: Typical thermal properties of Ti_2AlC, Ti_3AlC_2 and Ti_3SiC_2 (adapted from Barsoum et al., 1999; Barsoum et al., 2002; Wang & Zhou, 2010).</i>	24
<i>Table 2.4: Properties of cBN compared with other common ceramics and diamond (Monteiro et al., 2013).</i>	33
<i>Table 2.5: Properties of commercial registered marks of PcBN composites (Monteiro et al., 2013).</i>	35
<i>Table 2.6: Choice of grain size for desired surface finish (Link diamond, 2018).</i>	38
<i>Table 2.7: Choice of bond for operational conditions (Link diamond, 2018).</i>	39
<i>Table 2.8: Choice of abrasive concentration for operational conditions (Link diamond, 2018).</i>	39
<i>Table 3.1: Mass of powders used for MAX phase synthesis.</i>	43
<i>Table 4.1: Thermodynamic data obtained for the reaction of cBN with Ti_3SiC_2.</i>	77
<i>Table 4.2: Thermodynamic data obtained for the reaction of cBN with titanium.</i>	78
<i>Table 5.1: Density of phases found in the sintered samples (Springer, 2018).</i>	144
<i>Table 5.2: Density of the secondary phases, listed in descending order, found in the sintered samples, as well as cBN, hBN, and Ti_3SiC_2 phases under the triple border for comparison (Springer, 2018).</i>	163
<i>Table 3: Ti_2AlC-cBN composites naming convention.</i>	76
<i>Table 4: Density of the secondary phases, listed in descending order, found in the sintered samples, as well as cBN, hBN, Ti_2AlC and Ti_3AlC_2 phases near the triple border for comparison[26].</i>	109

Tables in Appendices

Table B 1: Peak lists for Ti_2AlC . Top are the calculated peak lists for the Co detector used in this work, bottom is the peak lists for the Mo detector as given by the PDF's sourced from the XRD program from the XRD machine used. Bold peaks are the primary peaks. _____ 20

Table B 2: Peak lists for Ti_2AlN . Top are the calculated peak lists for the Co detector used in this work, bottom is the peak lists for the Mo detector as given by the PDF's sourced from the XRD program from the XRD machine used. Bold peaks are the primary peaks. _____ 21

Table B 3: Peak lists for Ti_3AlC_2 . Top are the calculated peak lists for the Co detector used in this work, bottom is the peak lists for the Mo detector as given by the PDF's sourced from the XRD program from the XRD machine used. Bold peaks are the primary peaks. _____ 22

Table B 4: Peak lists for Ti_3SiC_2 . Top are the calculated peak lists for the Co detector used in this work, bottom is the peak lists for the Mo detector as given by the PDF's sourced from the XRD program from the XRD machine used. Bold peaks are the primary peaks. _____ 23

Table B 5: Peak lists for cBN. Top are the calculated peak lists for the Co detector used in this work, bottom is the peak lists for the Mo detector as given by the PDF's sourced from the XRD program from the XRD machine used. Bold peaks are the primary peaks. _____ 24

Table B 6: Peak lists for hBN. Top are the calculated peak lists for the Co detector used in this work, bottom is the peak lists for the Mo detector as given by the PDF's sourced from the XRD program from the XRD machine used. Bold peaks are the primary peaks. _____ 24

Table B 7: Peak lists for Ti_3Al . Top are the calculated peak lists for the Co detector used in this work, bottom is the peak lists for the Mo detector as given by the PDF's sourced from the XRD program from the XRD machine used. Bold peaks are the primary peaks. _____ 25

Table B 8: Peak lists for $TiAl_3$. Top are the calculated peak lists for the Co detector used in this work, bottom is the peak lists for the Mo detector as given by the PDF's sourced from the XRD program from the XRD machine used. Bold peaks are the primary peaks. _____ 25

Table B 9: Peak lists for $TiAl_2$. Top are the calculated peak lists for the Co detector used in this work, bottom is the peak lists for the Mo detector as given by the PDF's sourced from the XRD program from the XRD machine used. Bold peaks are the primary peaks. _____ 27

Table B 10: Peak lists for Ti_5Si_3 . Top are the calculated peak lists for the Co detector used in this work, bottom is the peak lists for the Mo detector as given by the PDF's sourced from the XRD program from the XRD machine used. Bold peaks are the primary peaks. _____ 28

Table B 11: Peak lists for $TiNb_6$. Top are the calculated peak lists for the Co detector used in this work, bottom is the peak lists for the Mo detector as given by the PDF's sourced from the XRD program from the XRD machine used. Bold peaks are the primary peaks. _____ 29

Table B 12: Peak lists for TiC_a . Top are the calculated peak lists for the Co detector used in this work, bottom is the peak lists for the Mo detector as given by the PDF's sourced from the XRD program from the XRD machine used. Bold peaks are the primary peaks. _____ 30

Table B 13: Peak lists for TiC_xN_y . Top are the calculated peak lists for the Co detector used in this work, bottom is the peak lists for the Mo detector as given by the PDF's sourced from the XRD program from the XRD machine used. Bold peaks are the primary peaks. _____ 31

Table B 14: Peak lists for SiC . Top are the calculated peak lists for the Co detector used in this work, bottom is the peak lists for the Mo detector as given by the PDF's sourced from the XRD program from the XRD machine used. Bold peaks are the primary peaks. _____ 33

Table B 15: Peak lists for TiB_2 . Top are the calculated peak lists for the Co detector used in this work, bottom is the peak lists for the Mo detector as given by the PDF's sourced from the XRD program from the XRD machine used. Bold peaks are the primary peaks. _____ 36

Table B 16: Peak lists for AlN . Top are the calculated peak lists for the Co detector used in this work, bottom is the peak lists for the Mo detector as given by the PDF's sourced from the XRD program from the XRD machine used. Bold peaks are the primary peaks. _____ 37

Table B 17: Peak lists for $TiAl$. Top are the calculated peak lists for the Co detector used in this work, bottom is the peak lists for the Mo detector as given by the PDF's sourced from the XRD program from the XRD machine used. Bold peaks are the primary peaks. _____ 38

Table C 1: Densities and open porosities of Ti_2AlC -cBN (20 vol.%, 10 μm) samples sintered at different temperatures and dwell times. _____ 0

Table C 2: Densities and open porosities of Ti_3AlC_2 -cBN (20 vol.%, 10 μm) samples sintered at different temperatures and dwell times. _____ 1

Table C 3: Densities and open porosities of Ti_3SiC_2 -cBN (20 vol.%, 10 μm) samples sintered at different temperatures and dwell times. _____ 2

<i>Table C 4: Densities and open porosities of Ti_2AlC-cBN (20 vol.%,100 μm) samples sintered at different temperatures and dwell times.</i>	3
<i>Table C 5: Densities and open porosities of Ti_3AlC_2-cBN (20 vol.%,100 μm) samples sintered at different temperatures and dwell times.</i>	3
<i>Table C 6: Densities and open porosities of Ti_3SiC_2-cBN (20 vol.%,100 μm) samples sintered at different temperatures and dwell times.</i>	3
<i>Table C 7: Densities and open porosities of Ti_2AlC-cBN (40 vol.%,100 μm) samples sintered at different temperatures and dwell times.</i>	4
<i>Table C 8: Densities and open porosities of Ti_3AlC_2-cBN (40 vol.%,100 μm) samples sintered at different temperatures and dwell times.</i>	4
<i>Table C 9: Densities and open porosities of Ti_3SiC_2-cBN (40 vol.%,100 μm) samples sintered at different temperatures and dwell times.</i>	5
<i>Table G1: Sample identification and sample naming designation</i>	47
<i>Table G2: Sample thicknesses for Ti_2AlC samples.</i>	48
<i>Table G3: Sample thickness for Ti_3SiC_2 samples.</i>	49
<i>Table G4: Sample thickness for Ti_3AlC_2 samples.</i>	50
<i>Table G5: Microhardness results for Ti_2AlC-cBN composites.</i>	51
<i>Table G6: Microhardness results for Ti_3AlC_2 -cBN composites.</i>	52
<i>Table G7: Microhardness results for Ti_3SiC_2 -cBN composites.</i>	53
<i>Table G8: Bulk hardness results for all composites.</i>	54
<i>Table G9: Wear results and calculations.</i>	55

CHAPTER ONE: INTRODUCTION

1.1 Background to the study

Ceramic materials are known to be the most suitable option for both high pressure and high temperature applications. They are also known to be inert to most chemicals, are hard, strong and lightweight. These material properties are advantageous, although there are some disadvantages which include poor fracture toughness, susceptibility to shattering when experiencing thermal shock or impact and poor machinability. Conversely, metals are generally machinable and have a much better fracture toughness than ceramics. The fact that metals can conduct heat efficiently means that they do not shatter when experiencing rapid changes in temperature or impact. However, most metals are heavy and do not tolerate high temperatures well.

The MAX Phases, which are unique new carbide and nitride ternary ceramics, have a combination of both the main advantages of metals and ceramics: soft, machinable, heat-tolerant, strong and lightweight. This combination of properties is mainly due to the crystal structures of these MAX phases which consist of layers, giving the materials high fracture toughness (**Barsoum, 2000; Barsoum and El-Raghy, 2001; Barsoum and Radovic, 2011**). Composites of MAX phases and traditional ceramics could have applications, such as cutting tools and grinding wheels, which may prove to be beneficial in industry.

Cutting tools used for removing solid material during machining consist of at least one, but usually several, abrasive bodies embedded partially or totally in a carrier material. The carrier material can be a partially rotationally symmetrical body, a brush, a pin or a disk (**Akyuz and El-Raghy, 2003**). Cubic boron nitride (cBN) is one of the materials most commonly used in abrasives, and it is ideal because it is exceeded in hardness only by diamond (**Vel et al., 1991**).

Unlike diamond, cBN is not chemically reactive with ferrous alloys, and is resistant to chemical attack in the presence of ferrous metals up to 1226-1327°C. Consequently, cBN is used to machine ferrous alloys by either making cutting tools with it, or by using it in the form of grit, as the cutting particles in grinding wheels (**Vel et al., 1991**). In the case of cutting tools, cBN is sintered together with a number of hard, binder ceramic phases in the form of polycrystalline cubic boron nitride (PcBN). The PcBN is cemented on top of a hard metal substrate during the high-pressure-high-temperature sintering process. The resulting compact is then used to fabricate cutting tool inserts. Alternatively, cBN grit is used to make grinding wheels. In the latter case, the cBN grit is bonded with a glass matrix, called a vitrified bond. Both cBN cutting tools and grinding wheels are used to machine hardened steels, cast irons and chilled cast irons (**Akyuz and El-Raghy, 2003**).

Grinding wheels with a vitrified bond find extensive application in precision grinding of hardened steel parts. The vitreous bond, being porous by design and of low density, allows these wheels to be used at very high cutting speeds. However, the nature of the bond used still makes the operation envelope of these tools very narrow, as this is a brittle material (**Akyuz and El-Raghy, 2003**). If an equally light, but much tougher and equally strong material bond could be achieved, it may be possible to make grinding wheels useable over a much wider range of operational parameters.

1.2 Problem Statement

- a. Is it possible to sinter cBN in a MAX phase matrix? The main problem, with promoting the cBN to react with the MAX phases at a mutually beneficial temperature. Thus, the challenge, was expected to occur in the sintering of these types of composites to ensure that cBN does undergo diffusion during sintering at the suitable synthesis temperatures for the MAX phases. Combining cBN with these MAX phases was

expected to present a problem in this respect, therefore, suitable sintering procedures and conditions were investigated.

- b. Can a suitable time, temperature and pressure combination be found to initiate and/or improve the diffusion processes in the cBN, while simultaneously not decomposing the MAX phases?
- c. Can a correct prediction of the optimal temperatures to react the 40 vol.% cBN be made from the 20 vol.% cBN experimental results? In this work, the cBN phase was used at 20 vol.% and 40 vol.% levels in the MAX phase matrix. The work started at the 20 vol% level. These were verified by experimental testing.
- d. Can a correct prediction of the optimal temperatures to react the 100 μm average size cBN particles composites be made for the 10 μm average cBN particles results? The work started by using cBN at 10 μm average grain size then 100 μm average particle sizes of cBN in the MAX phase matrix. These predictions were also verified by experimental testing.

1.3 Research Objectives

- a. Investigate the reactivity of cBN with Ti_2AlC , Ti_3AlC_2 and Ti_3SiC_2 MAX phases.
- b. Investigate the most favourable conditions for reacting the MAX phases and 20 vol.% of 10 μm cBN, where both phases were still clearly present after sintering.
- c. Determine the optimum time and temperature to react MAX phases with 20 vol.% of 100 μm cBN where both phases were still clearly present.
- d. Determine the best temperature to react MAX phases with 40 vol% of 100 μm cBN where both phases are still clearly present.
- e. Measure the mechanical and physical properties of the successfully synthesized composites. Successful samples in this study were defined as those that displayed abundant MAX phase and cBN in the sample, with minimum to no hBN presence.

1.4 Overview of the Thesis

This research work began with the background literature review of work already undertaken that was pertinent in some manner to this study. The undertaken methodology is then outlined with knowledge and understanding gained from literature and past work. The results and trends from the experiments, as per the methodology are presented, and thereafter discussed. Lastly, the conclusions are drawn, and recommendations outlined.

Figure 2.1: Periodic table illustrating the designation of the MAX phases (Barsoum & El-Raghy, 2001).

The last two classes of MAX phases with the larger n value were only recently discovered, these are the M_5AX_4 (Palmquist et al., 2004; Wang & Zhou, 2010) and 615 (Lin et al., 2006b; Wang & Zhou, 2010) phases. More than 70 known MAX phases of different chemical compositions share a common structure: $M_{n+1}X_n$ layers interleaved with pure A-group element layers, as illustrated in Figure 2.2 for structures with $n = 1-3$. It is seen in Figure 2.2 that for M_2AX ; two M layers are interleaved by an A layer, for M_3AX_2 three M layers are interleaved by an A layer and for M_4AX_3 four M layers are interleaved by an A layer (Barsoum & Radovic, 2011). Although Jeitschko & Nowotny (1967) determined the structures of the Ti_3SiC_2 and thus the M_3AX_2 compounds in the 1960s, the research into these compounds was neglected. It was only in 1996 that Barsoum & El-Raghy (1996) reported on the synthesis of phase-pure bulk Ti_3SiC_2 and its unusual properties. Since then, research on the MAX phases has increased (Wang & Zhou, 2010; Barsoum & M. Radovic, 2011).

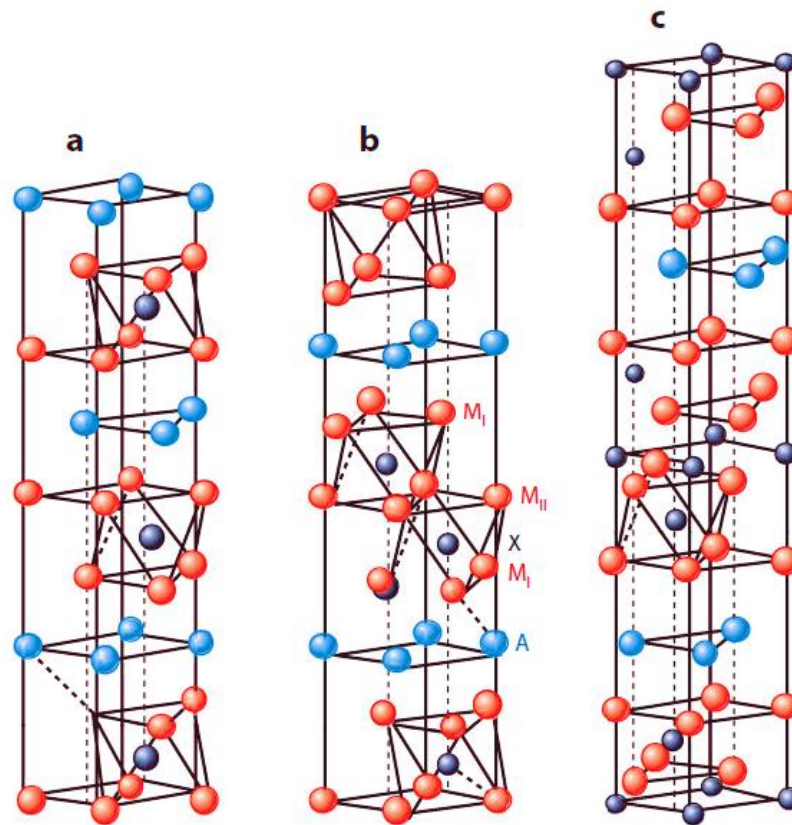


Figure 2.2: Crystal structures of the three classes of MAX phases where M group atoms are red; A group atoms are blue and X group atoms are black. a) M_2AX phases, b) M_3AX_2 phases and c) M_4AX_3 phases (Barsoum & Radovic, 2011).

There are more than fifty M_2AX phases, five M_3AX_2 phases and four M_4AX_3 phases, some of these are shown in Table 2.1 (Barsoum & Radovic, 2011; Magnuson & Mattesini, 2017).

Table 2.1: $M_{n+1}AX_n$ phases (carbides) (Barsoum & Radovic, 2011).

^aBold font denotes density of the MAX phase in g/cm^3 , a and c lattice parameters are in parentheses and measured in angstroms (Å), M_3AX_2 and M_4AX_3 phases are highlighted in yellow and blue.

IIIA	IVA	VA	VIA
Al	Si	P	S
Ti ₂ AlC, 4.11 (3.04, 13.60)	Ti ₃ SiC ₂ , 4.52 (3.07, 17.67)	V ₂ PC, 5.38 (3.08, 10.91)	Ti ₂ SC, 4.62 (3.22, 11.22)
V ₂ AlC, 4.82 (2.914, 13.19)		Nb ₂ PC, 7.09 (3.28, 11.50)	Zr ₂ SC, 6.20 (3.40, 12.13)
Cr ₂ AlC, 5.24 (2.86, 12.8)			Hf ₂ SC, (3.36, 11.99)
Nb ₂ AlC, 6.50 (3.10, 13.8)			
Ta ₂ AlC, 11.82 (3.07, 13.8)			
Ti ₃ AlC ₂ , 4.5 (3.075, 18.578)			
α -Ta ₄ AlC ₃ , 12.9 (3.11, 24.12)			
β -Ta ₄ AlC ₃ , 13.2 (3.087, 23.70)			
Nb ₄ AlC ₃ , 7.09 (3.123, 24.109)			
Ga	Ge	As	Se
Ti ₂ GaC, 5.53 (3.07, 13.52)	Ti ₂ GeC, 5.68 (3.07, 12.93)	V ₂ AsC, 6.63 (3.11, 11.30)	
V ₂ GaC, 6.39 (2.93, 12.84)	V ₂ GeC, 6.49 (3.00, 12.25)	Nb ₂ AsC, 8.03 (3.31, 11.90)	
Cr ₂ GaC, 6.81 (2.88, 12.61)	Cr ₂ GeC, 6.88 (2.95, 12.08)		
Nb ₂ GaC, 7.73 (3.13, 13.56)	Ti ₃ GeC ₂ , 5.55 (3.07, 17.76)		
Mo ₂ GaC, 8.79 (3.01, 13.18)			
Ta ₂ GaC, 13.05 (3.10, 13.57)			
In	Sn		
Ti ₂ InC, 6.2 (3.13, 14.06)	Ti ₂ SnC, 6.36 (3.16, 13.68)		
Zr ₂ InC, 7.1 (3.34, 14.91)	Zr ₂ SnC, 7.16 (3.36, 14.57)		
Nb ₂ InC, 8.3 (3.17, 14.37)	Nb ₂ SnC, 8.4 (3.24, 13.81)		
Hf ₂ InC, 11.57 (3.30, 14.73)	Hf ₂ SnC, 11.8 (3.32, 39)		
Tl	Pb		
Ti ₂ TlC, 8.63 (3.15, 13.98)	Ti ₂ PbC, 8.55 (3.20, 13.81)		
Zr ₂ TlC, 9.17 (3.36, 14.78)	Zr ₂ PbC, 9.2 (3.38, 14.66)		
Hf ₂ TlC, 13.65 (3.32, 14.62)	Hf ₂ PbC, 12.13 (3.55, 14.46)		

Like their parent binary MX (metal plus C or N) carbides and nitrides, the MAX phases are elastically stiff, thermally and electrically conductive (usually better than the pure parent metals), resistant to chemical attack, and have generally low thermal expansion coefficients (Barsoum & Radovic, 2011). Mechanically, however, they are different from the MX carbides

and nitrides. They are relatively soft (2-8 GPa) and easily machinable, thermally shock resistant, and damage tolerant. Also, some MAX phases are fatigue, creep, and oxidation resistant. At ambient temperatures, some can be compressed to high stresses and fully recover upon removal of the load **(Barsoum & Radovic, 2011; Magnuson & Mattesini, 2017)**. For example, the cyclic compression of polycrystalline Ti_3SiC_2 at room temperature to stresses up to 1 GPa can fully recover with the removal of the load, while dissipating about 25% (0.7 MJ.m^{-3}) of the mechanical energy. The stress–strain curves display fully reversible, rate-independent, closed hysteresis loops that are strongly influenced by grain size. The energy dissipated was significantly larger in the coarse-grained samples **(Barsoum et al., 2003)**. However, at higher temperatures, these materials undergo a Brittle-to-Plastic Transition (BPT), and their mechanical behaviour becomes a strong function of the deformation rate **(Barsoum et al., 2003; Barsoum & Radovic, 2011; Magnuson & Mattesini, 2017)**.

2.1.1 Crystal structure and bonding

The unit cells of the MAX phases are characterised by near close-packed M layers interleaved with layers of a pure A-group element, with the X atoms filling the octahedral sites between the former **(Barsoum & Radovic, 2011)**. The M_6X octahedra are identical to those found in the rock salt structure of the corresponding binary MX carbides. The A-group elements are located at the centres of trigonal prisms, which are slightly larger, and thus better able to accommodate the larger A atoms, than the octahedral sites. When $n = 2$, e.g. Ti_3SiC_2 , two M layers separate the A layers (Figure 2.2b). For $n = 3$, for e.g. Ti_4AlN_3 , there are four M layers (Figure 2.2c) **(Barsoum & Radovic, 2011; Magnuson & Mattesini, 2017)**.

It has been found that there are two types of vibrations present in MAX phases, low-energy ($<300 \text{ cm}^{-1}$) shear modes (along the a direction) involving the A and M atoms and higher-energy modes involving vibrations along the c axis involving the X atoms **(Barsoum &**

Radovic, 2011). These low energy modes are a manifestation of the weakness of the M-A bonds in shear relative to the M-X bonds.

The fundamental difference between the MAX phases and their corresponding MX phases is that in the MAX phases, basal plane dislocations are numerous, and as these dislocations increase their mobility increases from temperatures from as low as -196°C (**Kuronda et al., 2001; Barsoum & Radovic, 2011**). In typical ceramics at room temperature, the number of independent slip systems is essentially zero, or more technically accurately, the critical resolved shear stresses needed for dislocation motion are higher than the stresses at which they fail in a brittle manner, as indicated in Table 2.2. However, basal slip by itself yields fewer than the five slip systems needed for polycrystalline ductility (**Barsoum & Radovic, 2011**). The MAX phases are thus pseudo-ductile in constrained deformation modes, in highly oriented microstructures, and/or at higher temperatures. In unconstrained deformation, and especially in tension at lower temperatures, they behave in a more brittle fashion.

Table 2.2: Comparison of damage tolerance (reported with no error bars) of other materials to Ti_3SiC_2 , Ti_3AlC_2 and Ti_2AlC (adapted from **Wang & Zhou, 2010**).

	Fracture toughness ($\text{MPa}\cdot\text{m}^{1/2}$)	Bending Strength (MPa)	Elastic Modulus (GPa)	Vickers Hardness (GPa)	Damage Tolerance ($\text{m}^{1/2}$)
SiC	3.1	356	415	32	0.113
Si_3N_4	6.5	700	300	15.5	0.180
ZrO_2	12	950	200	13	0.194
Al_2O_3	2.2	180	300	12	0.366
TiB_2	6.2	400	565	25	0.350
Ti_3SiC_2	7.0	436	310	4.0	1.24
Ti_3AlC_2	6.9	340	288	3.0	1.95
Ti_2AlC	6.5	275	278	2.8	2.35

Only the basal plane dislocations are responsible for how the MAX phases respond to stress (**Barsoum & Radovic, 2011**). There are no reports that twins and/or non-basal dislocations participate in any meaningful manner in deformation. Thus, the number of slip systems active in MAX phases is less than the five independent slip systems needed for polycrystalline ductility.

2.1.2 Kink bands and damage tolerance

The microstructure of the MAX phases reveals a layered structure which forms kink boundaries when dislocations form and move across one another, in opposite directions under stress. Kink bands typically form when layered materials have stress applied parallel to the layers. Any cracks that start to separate the layers are halted by the kink boundaries, the cracks extend only into the area defined by the kink boundaries but not beyond them, shown in Figure 2.3 (Barsoum & El-Raghy, 2001). (The microstructure images in Figure 2.3a) and b) were reported without scale bars).

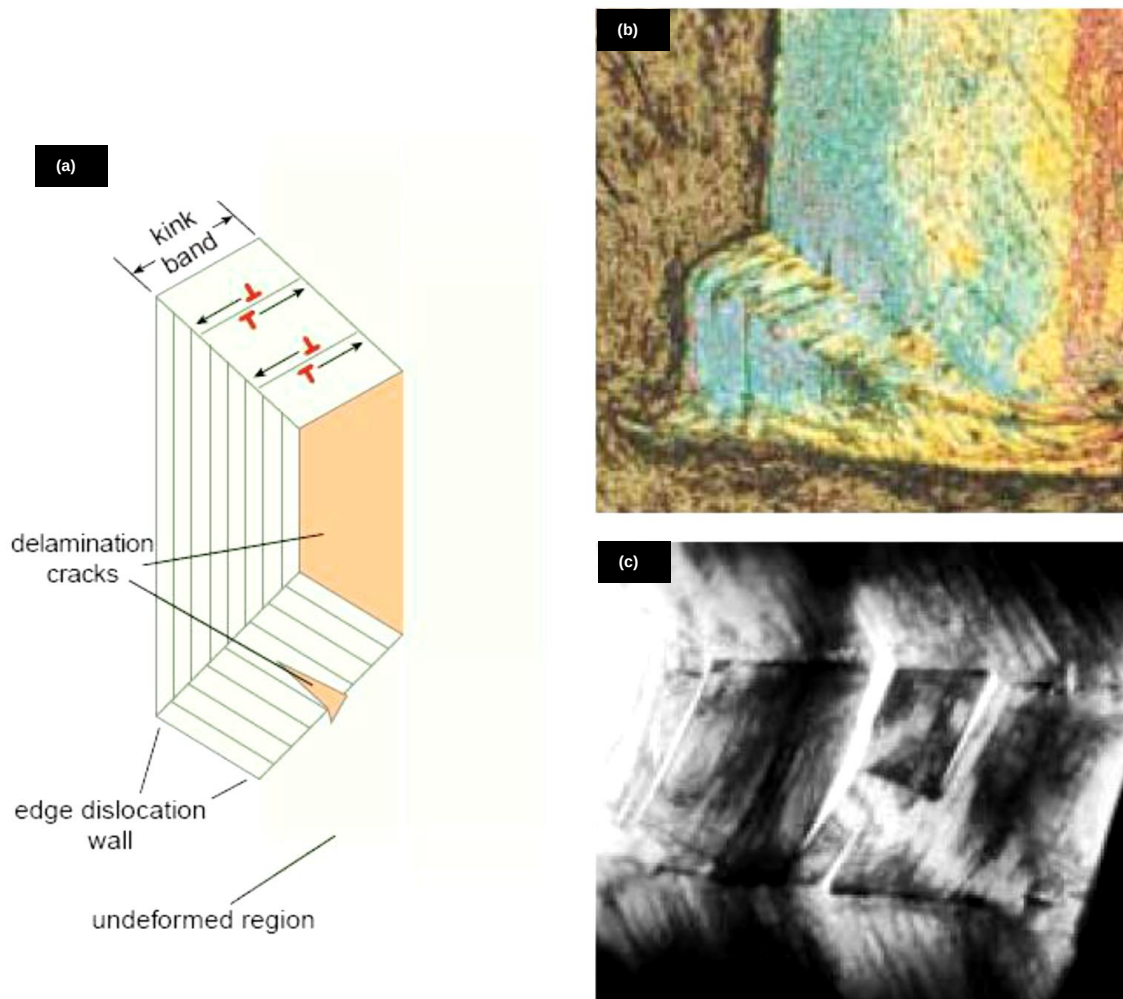


Figure 2.3: Kink bands in the microstructure of MAX phases a) schematic demonstrating the kink band formation, b) optical micrograph shows a typical macroscopic kink band and c) a transmission electron microscope image shows a microscopic kink band and its boundaries (Barsoum & El-Raghy, 2001).

Barsoum & El-Raghy (2001) described the formation of kink bands using this analogy: to form a kink band, stand a deck of cards on one end and carefully add weight on top. For small loads, the cards will buckle elastically (if the load is removed, the cards snap back to their original shape). However, at some maximal load, the cards will buckle irreversibly, forming one or more kink bands where the layers bend sharply and remain bent. For a kink band to form, part of the crystal that is forming the kink band must be able to glide relative to the stationary part. Furthermore, the layers must detach from each other (**Barsoum & El-Raghy, 2001**).

Unlike metals, MAX phases do not distort by plastic deformation, but rather by breaking from microscopic flakes at the surface (**Barsoum & El-Raghy, 2001**). Even after the initiation of damage, the MAX phases can still carry substantial loads because of the damage tolerance which is inherent to the structure at the atomic level. In most ceramic materials, once damage is initiated, the point of damage becomes weaker, resulting in further damage and further weakness and eventually rupture.

Transmission Electron Microscopy (TEM) (**Farber et al., 1998; Barsoum et al., 1999**) and High-Resolution Transmission Electron Microscopy (HRTEM) (**Farber et al., 1998, Farber, 1999**) studies of Ti_3SiC_2 revealed the presence of only perfect dislocations lying in the basal planes with a Burgers vector $b = \frac{1}{3}\langle 11\bar{2}0 \rangle$ and 1.54 Å in length. Every dislocation is of a mixed nature with an edge and screw component (**Farber, 1999; Kooi et al., 2003; Barsoum & Radovic, 2004**). **Barsoum & Radovic (2004)** stated that only basal plane dislocations influence the mechanical properties of the MAX phases. These dislocations are mobile and multiply, even at -196°C. Since the dislocations are confined to the basal planes, the dislocations arrange themselves either in arrays (pile-ups) on the same basal planes or in walls (low- and high-angle grain boundaries) normal to the basal planes (**Farber, 1999; Kooi et al. 2003; Barsoum & Radovic, 2004**).

2.1.3 Synthesis of MAX phases

2.1.3.1 Spark Plasma Synthesis Method

Since synthesis of bulk MAX phases has been achieved, a variety of synthesis methods have been investigated. These methods utilise high, moderate or no pressure, varying temperatures and sintering times that range from 1 minute to 24 hours. The pre-sintering steps can involve a simple milling/mixing step or a high energy milling to promote mechanical alloying of the starting powder. The methods range from hot pressing/hot isostatic pressing to spark plasma sintering/pulse discharge sintering to combustion sintering to slip casting. This work focused only on the SPS method, which was the method used for this research.

Field assisted sintering technology (FAST) is advantageous in ceramic processing as it requires only minutes for sintering time compared to hours, and in some cases, days when other sintering methods are used (**Chanthapan et al., 2011**). **They** stated that FAST can be described in different names such as: plasma assisted sintering (PAS), pulsed electric current sintering (PECS), electric pulse assisted consolidation (EPAC), plasma pressure compaction (P2C), and spark plasma sintering (SPS), all of which have the same principle and benefits of using the FAST method.

The FAST/SPS system utilises a graphite die, which contains the powder to be sintered, with the pressure applied by upper and lower punches (Figure 2.4). A DC current flows through the die and punches and can either be pulsed or continuous. This induces a radiant heat to the powder sample and current flows through the sample, instantly producing Joule heating. The combination of pressure, temperature, and localised heating at the particle boundaries results in a high sintering rate (**Chanthapan et al., 2011**), Figure 2.4.

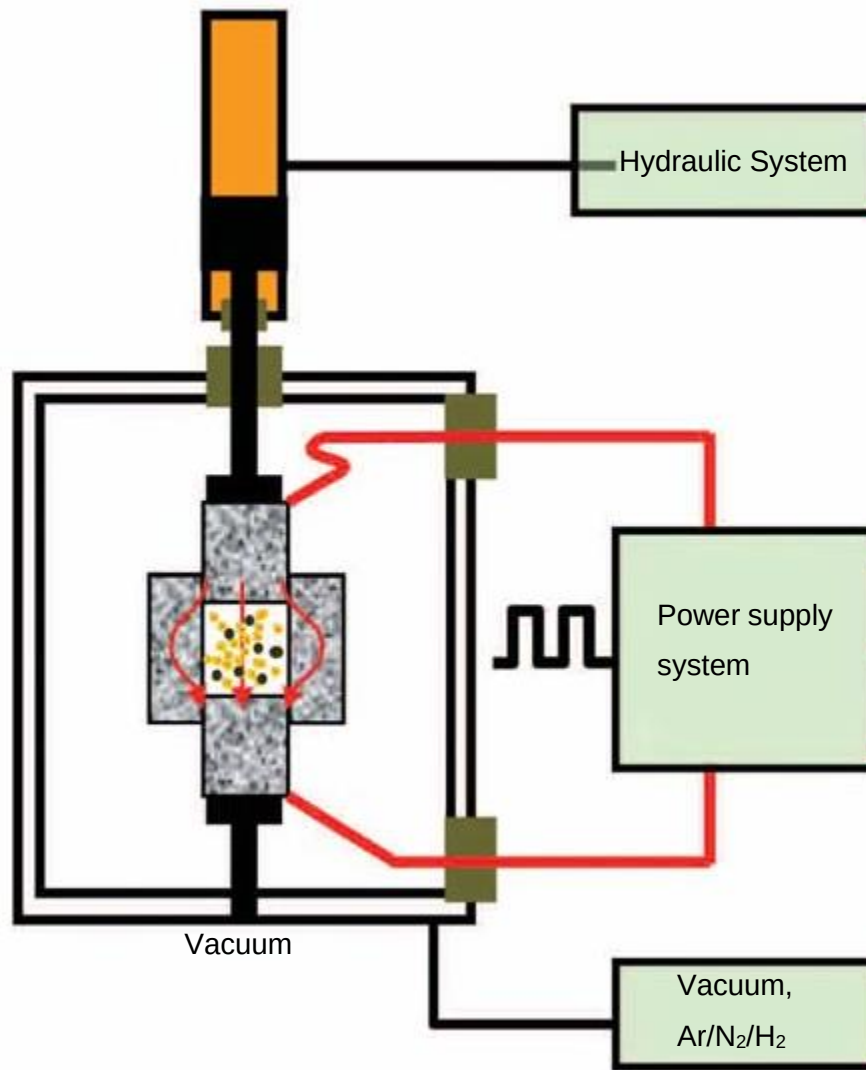


Figure 2.4: Diagram showing the setup for a field assisted sintering technology/spark plasma sintering (FAST/SPS) (Chanthapan et al., 2011).

Anselmi-Tamburini et al. (2005) noted that the temperature distribution, current distribution and the plunger positioning are some of the crucial factors that affect the sample during sintering. The positioning of the plunger in the die has an effect on the temperature and properties gradient. The temperature distribution in the sample and the die has an effect on the sample's homogeneity and the obtained reproducibility of the experiments. The current distribution in the die influences the heat generation distribution (**Anselmi-Tamburini et al., 2005**). The temperature gradient between the sample and the external surface of the die is caused by differential current distribution and radiation heat losses. These gradients are mainly

seen in temperatures from about 900°C. There is thus a need for an optical pyrometer focused on the external surface of the die, an estimation of the actual internal temperature of the sample can be made (**Anselmi-Tamburini et al., 2005**).

2.1.3.2 Ti₂AlC synthesis

Zhou et al. (2005) synthesised bulk, pure Ti₂AlC using a powder mixture of 2Ti:1.2Al:1C (graphite). The synthesis was done at 1100°C (80°C/min) and 30 MPa for 60 minutes. Excess Al was used because Al melts at about 660°C (**Massalski, 1990**), and at the reaction temperatures 1100°C some aluminium evaporates leaving the mixture Al deficient. The microstructure achieved by **Zhou et al. (2005)** was a laminar structure, Figure 2.5(a).

Mei et al. (2004) synthesised bulk, pure Ti₂AlC with powder mixture of 2Ti/1.2Al/1C (carbon black) at 1250°C (80°C/min) and 1100 MPa for 8 minutes. As the temperature increased to 1200°C and 1300°C, there was an increase in TiC and Ti₃AlC₂. The microstructure achieved by **Mei et al. (2004)** was a laminar structure, Figure 2.5(b).

Kulkarni et al. (2010) synthesised Ti₂AlC, with 90% purity, using powders of TiAl+2.06 wt% CNT (carbon nano-tubes) + 0.5 wt%Co (NO₃).6H₂O (as a catalyst to give a higher yield of the CNT). The powder mixture was heated to 1200°C at 50 kN, the dwell time was not specified, and this gave a high purity Ti₂AlC with TiC and Al₅Ti₂ as the resulting secondary phases. The microstructure found by **Kulkarni et al. (2010)** was a laminar structure, Figure 2.5(c) and (d).

Chen et al. (2009) showed that below 900°C a reaction occurred between the Ti and Al only. At 600°C, there were three phases: Ti, Al and TiAl₃, which indicated that a solid-state reaction occurred between the Ti and Al and generated TiAl₃ below the melting point of Al. At 700°C, the Al disappeared and TiAl₃ increased, so Al entirely reacted with Ti, generating the intermetallic TiAl₃ phase, but unreacted Ti still remained and TiAl and Ti₃Al were present together. When the temperature reached 800°C, the main phase present was TiAl while the

TiAl₃ phase disappeared completely and the Ti₃Al phase increased and some unreacted Ti remained. When sintering temperatures reached 900°C, the Ti was completely reacted, and the main phases present were TiAl and Ti₃Al. When sintering temperatures reached 1000°C and 1100°C, TiC formed and Ti was no longer present, so C participated according to Equation 2.1:

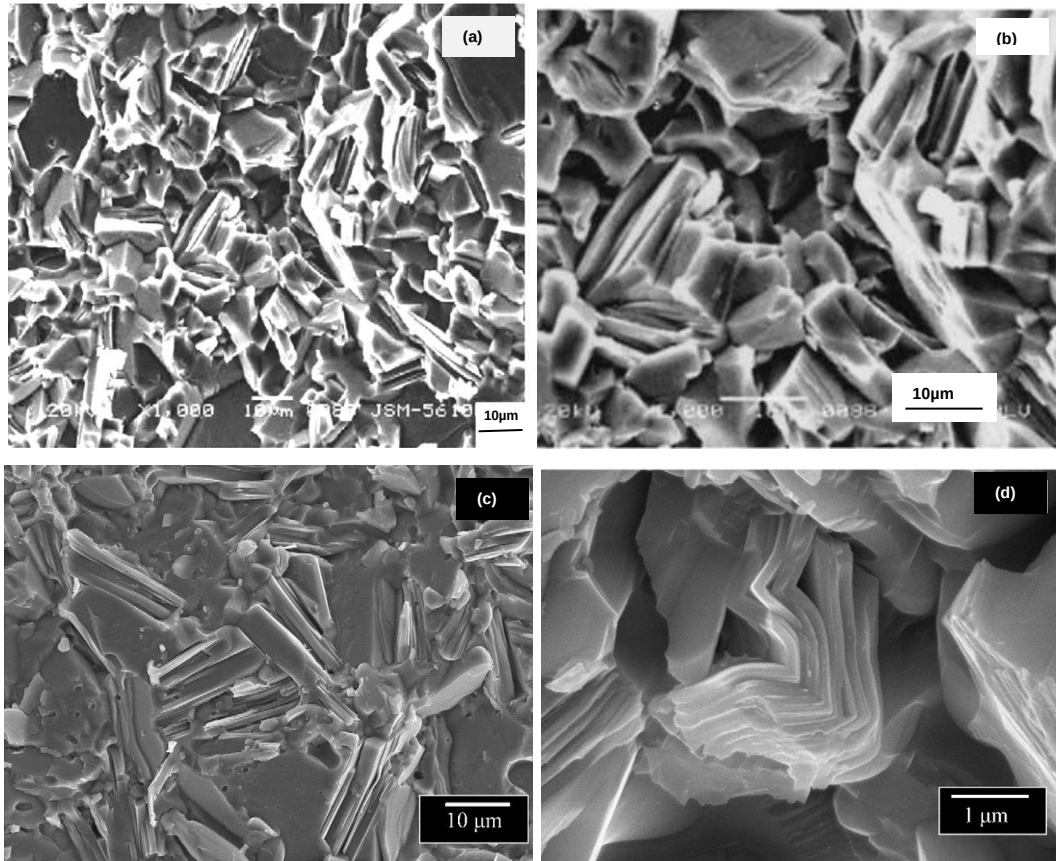
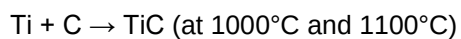
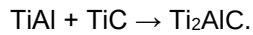


Figure 2.5: SEM (SE) image micrographs of the fracture surface of the Ti₂AlC sintered at (a) 1100°C, 30 MPa for 60 minutes with graphite as the carbon source (Zhou et al., 2005), (b) 1250°C, 1100 MPa for 8 minutes with carbon black as the carbon source (Mei et al., 2004), (c) 1200°C, 50 kN with CNT as the carbon source (Kulkarni et al., 2010) and (d) higher magnification of sample in (c).



Equation 2.1 (Chen et al., 2009)

At the same time, Ti₂AlC increased gradually. It was thought that the reaction in Equation 2.2 occurred:



Equation 2. 2 (Chen et al., 2009)

No TiC remained after sintering at 1200°C, which indicated that TiC participated completely during the reaction, with the TiAl content increased gradually. The TiAl content was highest after sintering at 1200°C and decreased when sintered at 1300°C, which means that the crystals of TiAl developed gradually by raising the sintering temperature and the optimum crystallinity of TiAl was obtained at 1200°C (**Chen et al., 2009**).

2.1.3.3 Ti_3AlC_2 synthesis

Yang et al. (2009) synthesised a fully dense bulk Ti_3AlC_2 with high purity (>99 wt%) at 1050°C (80°C/min), 35 MPa for 15–20 minutes by SPS of mechanically alloyed starting powder mixtures of 3Ti/1.1Al/2C. The mechanical alloying of these powders was achieved by milling the starting composition for 9.5 hours at 400 rpm. A large amount of Ti_3AlC_2 was formed with TiC as the secondary phase. The microstructure achieved by **Yang et al. (2009)** was a laminar structure, Figure 2.6 (a).

Zhou et al. (2003a) synthesised dense bulk Ti_3AlC_2 with high purity at 1250°C (600°C /min) and 22 MPa for 5 minutes. The method used was to first synthesise Al_4C_3 at 1400°C for 60 minutes in argon, then reacting the resulting Al_4C_3 powder with Ti and C (activated carbon), giving a Ti:Al:C ratio of 3:1.2:2 at the conditions specified. A large amount of Ti_3AlC_2 was formed with TiC as the secondary phase. The microstructure found by **Zhou et al. (2003a)** was a laminar structure, Figure 2.6(b).

Another method explored by **Zhou et al. (2003a)** involved using self-propagating high-temperature synthesis – spark plasma sintering (SHS-SPS). This process resulted in the formation of porous Ti_3AlC_2 by SHS from a mixture of Ti, Al and C, and then soaking the product by SPS with the conditions described in the previous paragraph. The SHS method resulted in predominantly Ti_3AlC_2 , with large amounts of Ti_2AlC and some TiC. Soaking the SHS product

powder with the SPS at the stipulated conditions caused the depletion of the Ti_2AlC phase and TiC , and a much higher purity Ti_3AlC_2 phase than the SPS method. The reason this method produced a higher purity phase will be explained shortly.

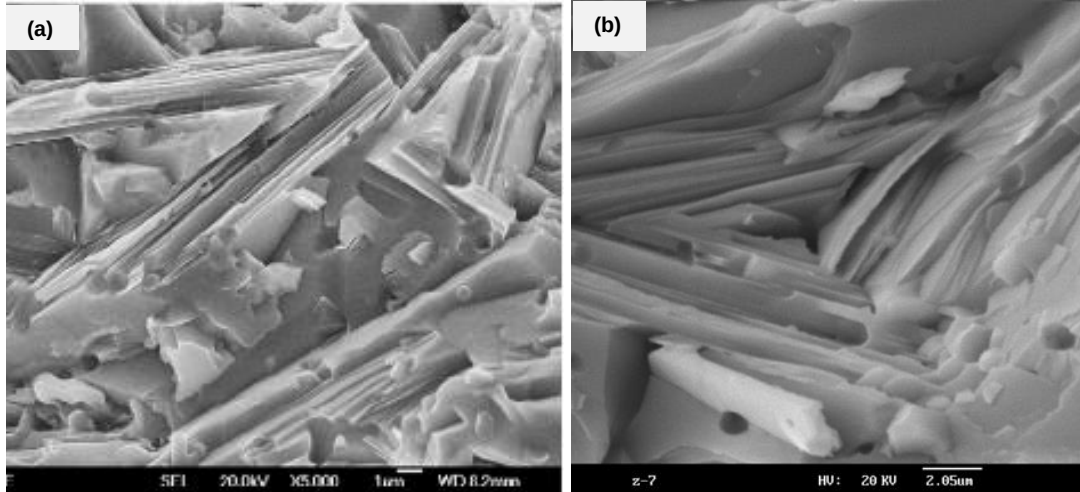
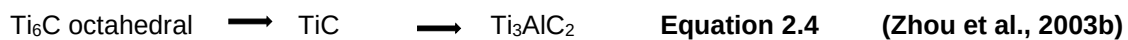
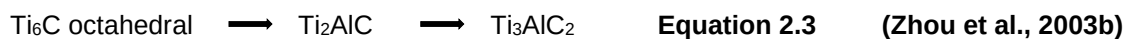


Figure 2.6: SEM (SE) micrograph fracture surface of a polycrystalline Ti_3AlC_2 (a) obtained by SPS of mechanically alloyed 2Ti:1.1Al:2C powders (Yang et al., 2009) and (b) obtained by-SPS of Al_4C_3 , Ti and C (Zhou et al., 2003a).

The fabrication of Ti_3AlC_2 is more dependent on kinetics rather than thermodynamics (Zhou et al., 2003b). The optimal synthesis conditions for Ti_3AlC_2 involves sintering at high temperature for a short time. Thus, the soaking time and temperature are the important factors for the synthesis of this phase. When the temperature was increased, significant amounts of Ti_6C octahedra were formed, due to the strong binding of Ti-C. TiC formation is an exothermic reaction, thus it was easier to form, although Ti_2AlC was easier to form from a kinetic point of view as the activation energy of formation is lower. This results in two reaction paths from the starting Ti_6C octahedral to form Ti_3AlC_2 :



The first reaction path, Equation 2.3, occurs because TiC crystals cannot be obtained directly from Ti_6C octahedra in a short time (**Zhou et al., 2003b**). At relatively low soaking temperature ($\sim 1300^\circ\text{C}$), the Ti_6C octahedra can only form edge-shared layers and every layer is linked together by an aluminium plane, Figure 2.2a, thus resulting in Ti_2AlC . Since Ti-Al bonding is weak, it may be replaced by stronger Ti-C bonding where using higher temperatures or longer soaking times under which conditions the Al evaporates from the system, and Ti_2AlC may lose half its aluminium planes and transform to Ti_3AlC_2 with these elevated high temperature conditions (**Zhou et al., 2003b**).

The second reaction path, Equation 2.4, occurs when the soak temperature is high enough for the TiC seed crystals to grow larger (**Zhou et al., 2003b**). Since TiC does not form below 1600°C , it was observed that if the soaking temperature was approximately 1600°C , the Ti_6C octahedra were easily linked together to form TiC crystals. These TiC crystals, however, cannot grow to perfect grains and often preferentially react with other phases. Due to the existence of an aluminium-rich liquid phase, Ti_6C octahedra in TiC crystals are separated by aluminium planes instead of directly linking together. Generally, every two layers of Ti_6C octahedra are separated by one aluminium plane, Figure 2.2, with a structure of Ti_3AlC_2 . Also, since Ti_3AlC_2 is a metastable phase at higher temperatures, and TiC is stable, this may cause an inverse reaction where the metastable phase decomposes into TiC as aluminium evaporates from the system (**Zhou et al., 2003b**).

2.1.3.4 Ti_3SiC_2 synthesis

Gao et al. (2002) synthesised bulk Ti_3SiC_2 by sintering Ti:Si:TiC powder mixtures resulted in Ti_3SiC_2 with 2 wt% TiC_x was produced in the temperature range $1250\text{--}1300^\circ\text{C}$ ($100^\circ\text{C}/\text{min}$ heating rate), and sintered at 60 MPa for 10 minutes, the microstructure was a laminar structure, Figure 2.7(a). The reason for the formation of the 3:1:2 phase from the molar ratio 2:1:1 of the starting powders may be explained using the same reasoning as for Ti_3AlC_2 . If the

Ti-Si bond is weaker in the material as well, at these conditions, there will be a loss of the Si from the system giving a 312 phase instead.

Liang et al. (2008) showed that the addition of suitable amounts of Al may increase the purity of Ti_3SiC_2 during mechanical alloying. High purity Ti_3SiC_2 bulk was synthesised by spark plasma sintering from mechanically alloyed powders. The addition of small amounts of Al accelerated the synthesis reaction of Ti_3SiC_2 with high purity, although excessive Al lowered the purity of Ti_3SiC_2 . Ti_3SiC_2 sintered bulk with a purity of 99.3 wt% was obtained by MA for 10 hours and subsequent SPS from a starting mixture of 3Ti:Si:2C:0.2Al at 1100°C (100°C/min heating rate), 30 MPa for 5 minutes. The Ti_3SiC_2 phase with a relative density of 98.9 % was obtained, with a microstructure was a laminar type structure, Figure 2.7(b).

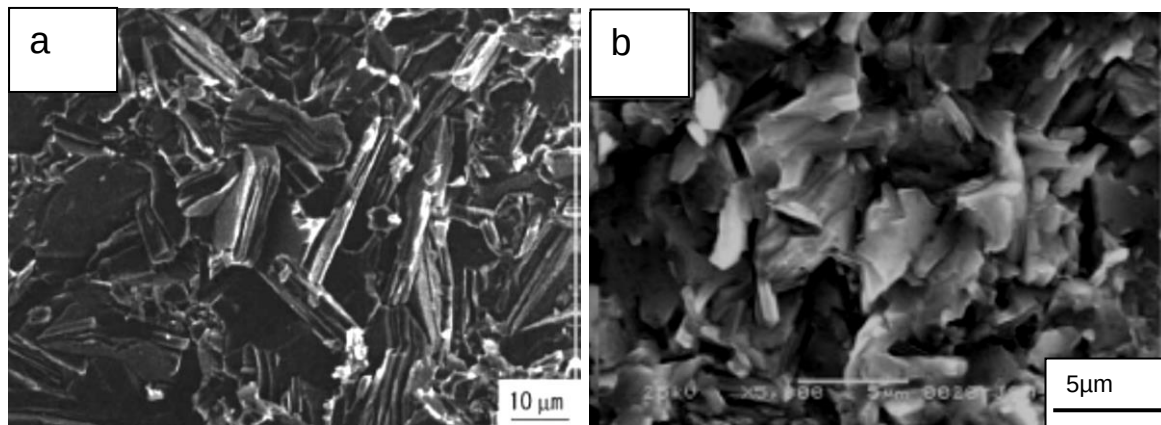
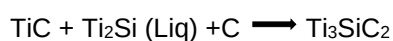


Figure 2.7: SEM micrographs of the fracture surface of the Ti_3SiC_2 sintered at (a) (SE mode) 1250°C, 60 MPa for 10 min and (**Gao et al., 2002**), (b) (BSE mode) 1100°C, 30 MPa for 5 min of mechanically alloyed powders. (**Liang et al., 2008**).

One possible reaction mechanism during synthesis of Ti_3SiC_2 from mechanically alloyed Ti, Si and C powders was given by **Li & Zhai (2005a)** as:



Equation 2. 5

In the Ti–Si–C system (in the 3:1:2 ratio), it is believed that a reaction between Ti and C occurs first because of the high chemical affinity of Ti for C (**Li & Zhai, 2005**). It is not possible for SiC to form first, because the heat of formation of TiC is over twice that of SiC. The reaction between Ti and C releases a large amount of heat, which leads to the formation of a Ti–Si eutectic (with two eutectic reactions for the Si–TiSi₂ and Ti–Ti₅Si₃ phases). Finally, as temperature increases, formation of the Ti–Si liquid spreads over the TiC particles, resulting in the rearrangement of particles. Ti₃SiC₂ was formed at the interfaces between the Ti–Si liquid and TiC, Equation 2.5.

Another possible reaction mechanism (Equations 2.6 to 2.10) with Ti, SiC and C powders was given by **El-Raghy & Barsoum (1999a)** as:



Free carbon reacts with titanium, forming TiC_{0.5} as shown in Equation 2.6. SiC reacts with titanium forming Ti₅Si₃C and rejecting carbon. The rejected carbon atoms from the reactions shown in Equations 2.6, and 2.7 diffuse into the Ti₅Si₃C, forming Ti₃SiC₂ (Equation 2.8) and rejecting excess silicon. The rejected silicone from the reaction shown in Equation 2.8 diffuse into TiC_{0.5} forming Ti₃SiC₂ and rejects carbon. The overall reaction is shown in Equation 2.10 (**El-Raghy & Barsoum, 1999a**).

The Ti_{n+1}AlC_n phases (in the 3:1:2 and 2:1:1 ratios) have a weaker Ti–Al bonds compared to the Ti–C bonds (**Barsoum et al., 1999**). Similarly, for the Ti_{n+1}SiC_n (in the 3:1:2 ratio) phase,

the strongest bonds, and hence smallest amplitudes of vibrations are those between the Ti and C atoms. Furthermore, in the M_3AX_2 phases the Ti–C bonds are not equal in strength. The central Ti_{II} (Figure 2.2) atoms are bonded on either side by C-atoms and do not vibrate as much as the Ti_I (Figure 2.2) atoms that are bonded to the Si and C atoms. The large amplitudes of vibration of the Si atoms are an indication that their bonding to Ti_I (Figure 2.2) is relatively weak compared to the Ti–C bonds.

2.1.4 Microstructure of the MAX phases

As discussed previously, $Ti_3AlC-TiC-Ti_2AlC$, $Ti_2AlC-TiC-Ti_3AlC_2$ and Ti_3SiC_2-TiC systems were a common result when synthesising the three phases under investigation (Ti_2AlC , Ti_3AlC_2 and Ti_3SiC_2).

Figure 2.8 shows HRTEM images where image simulations demonstrated that the white columns correspond to Al layers while the grey columns correspond to Ti layers (**Wang & Zhou, 2010**). Every three or two Ti layers are separated by Al layers in the same grain. In the crystal structure of Ti_3AlC_2 and Ti_2AlC , the number of Ti layers separated by Al layers is three and two respectively, therefore, intergrowth of Ti_3AlC_2 with Ti_2AlC was identified.

Most of the grain boundaries in Ti_2AlC have high-angles as shown in Figure 2.8(a)) and grains with misorientation of a few degrees were also present (**Zhou et al., 2003b; Lin et al., 2006a; Wang & Zhou, 2010**). Ti_3AlC_2 can intergrow with Ti_2AlC , Figure 2.8(b), and TiC can also intergrow with Ti_2AlC , Figure 2.8(c). The presence of these intergrown structures of $Ti_2AlC-Ti_3AlC_2$ -TiC and $Ti_2AlC-TiC-Ti_2AlC$ was found to be the result of local segregation of Ti and a lack of Al, as discussed in Section 2.1.3.

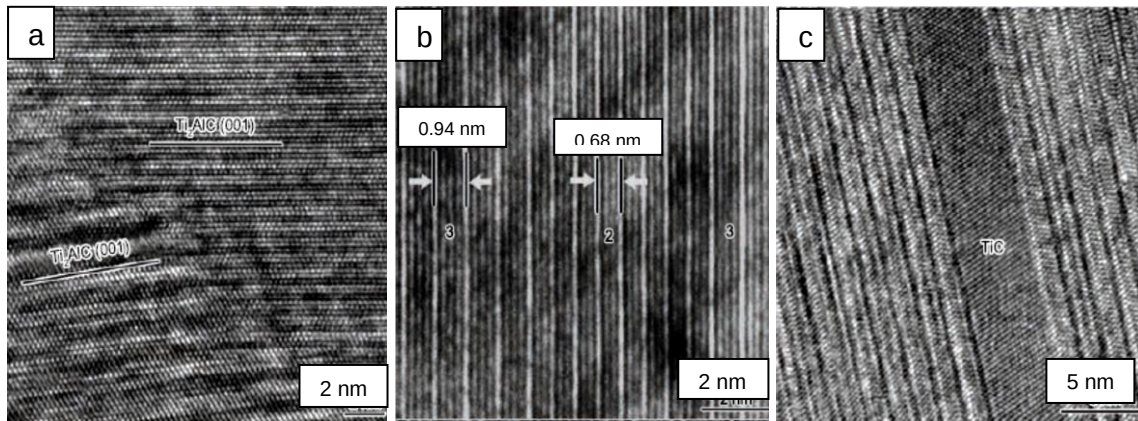


Figure 2.8: Typical HRTEM images taken at a (a) Ti_2AlC grain boundary, (b) intergrowth of Ti_3AlC_2 with Ti_2AlC , (c) intergrowth of TiC with Ti_2AlC (Wang & Zhou, 2010 adapted from Lin et al., 2006a)

In addition to TiC , TiAl was also found to be the intermediate phase during the synthesis of Ti_2AlC from elemental powders (Wang & Zhou, 2002a; 2010). Lin et al. (2006a) pointed out that the significant numbers of TiAl twin boundaries and two-dimensional defects provide rapid diffusion paths for carbon. Carbon was also found to accelerate dissolution of TiAl laths and led to the rapid formation of Ti_2AlC (Wang & Zhou, 2010).

The Ti_3AlC_2 grains, when imaged along the $[hki0]$ direction, exhibited elongated lamellae in the direction perpendicular to $[0001]$, Figure 2.9 (a) ((Kooi et al., 2003; Wang & Zhou, 2010). Most of the grains formed high-angle grain boundaries, where no amorphous phase was observed. Although the as-synthesized sample was predominantly single phase, thin platelets of cubic TiC intergrew with hexagonal Ti_3AlC_2 . TiC maintained a close orientational relationship with Ti_3AlC_2 . Such a relationship was also identified between Ti_3SiC_2 and TiC .

Together with the thin platelets of TiC intergrown with Ti_3AlC_2 , there was a minor amount of a tetragonal Al_3Ti phase present (Wang & Zhou, 2002b; 2010). No crystallographic relationship was observed between tetragonal Al_3Ti and hexagonal Ti_3AlC_2 , and no amorphous phase was found at the boundaries between Al_3Ti and Ti_3AlC_2 , nor between adjacent Ti_3AlC_2 grains.

Ti_3SiC_2 can be considered as thin TiC-like lamella consisting of 3 Ti and 2 C basal planes (indicated by the $\pm 20^\circ$ black lines in Figure 2.9 (b)) separated by Si basal planes around which the TiC layers were stacked with twinning symmetry (**Kooi et al., 2003**). A HRTEM image of a basal-plane stacking fault in Ti_3SiC_2 is shown in Figure 2.9 (b). At the core of the basal plane stacking fault a Si plane is missing and the remaining thin lamella consisted of 6 close-packed Ti planes, with 5 C planes between showing identical stacking as $\{111\}$ planes in TiC ($Fm3m$). The absence of the Si plane removed the twinning and led to 6 Ti and 5 C planes (indicated by the -20° white line at top of Figure 2.9 (b)) with normal stacking as if these were $\{111\}$ planes in TiC. Since these basal plane stacking faults were observed in non-deformed Ti_3SiC_2 samples, they were considered to be growth defects (**Lin et al., 2006a; Kooi et al., 2003**).

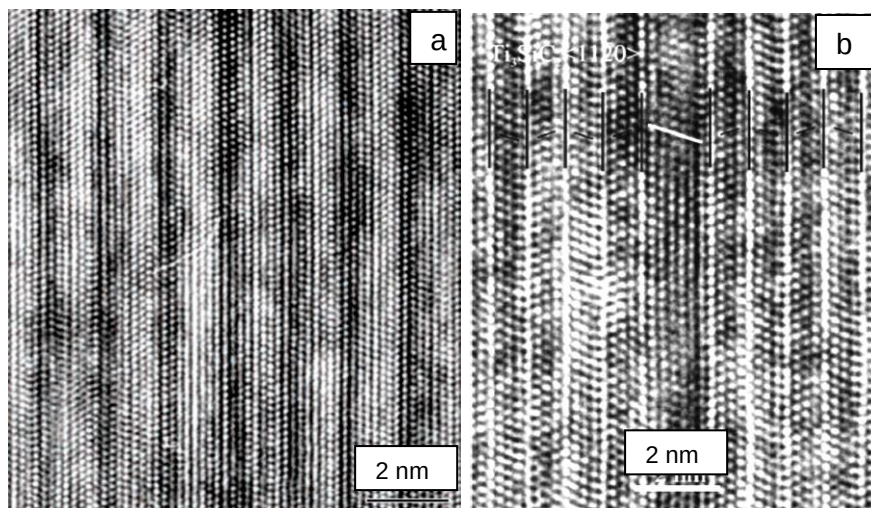


Figure 2.9: HRTEM images of: (a) the incident beam parallel to the $[1\bar{2}10]$ direction of Ti_3AlC_2 , and (b) a basal plane stacking fault in Ti_3SiC_2 . The viewing direction is $[1120]$ (**Lin et al., 2006a; Kooi et al., 2003**).

From Figure 2.9 and the microstructural characterizations, intergrown TiC is a common phenomenon in the synthesized Ti_2AlC , Ti_3AlC_2 and Ti_3SiC_2 phases (**Wang & Zhou, 2010**). The presence of TiC influenced the properties of these phases, for example, incorporating TiC in Ti_3AlC_2 can significantly increase flexural strength and hardness. In addition, TiC additions were detrimental to the oxidation resistance at elevated temperatures.

2.1.5 Physical properties

When considering the thermal conductivity of the MAX phases, Table 2.3, the thermal conductivities of Ti_2AlC , Ti_3AlC_2 and, Ti_3SiC_2 are larger than those of TiC and TiAl (**Barsoum et al., 1999; Barsoum et al., 2002; Wang & Zhou, 2010**). When considering the thermal expansion of the MAX phases, Table 2.3, it was evident that the thermal expansion coefficient in increasing order are: $\text{Ti}_3\text{SiC}_2 < \text{Ti}_3\text{AlC}_2 < \text{Ti}_2\text{AlC}$. This order was expected since there are two typical bonds, i.e. Ti-C and Ti-Al (-Si), in the 312 phases and there are more Ti-C bonds, which are the stronger bonds (**Wang & Zhou, 2010**).

Table 2.3: Typical thermal properties of Ti_2AlC , Ti_3AlC_2 and Ti_3SiC_2 (adapted from **Barsoum et al., 1999; Barsoum et al., 2002; Wang & Zhou, 2010**).

	Heat capacity ($\text{J.mol}^{-1}.\text{K}^{-1}$)	Thermal Conductivity ($\text{W.m}^{-1}.\text{K}^{-1}$)	Thermal Expansion Coefficient ($10^{-6}\text{K}^{-1}[\text{25-1200}^\circ\text{C}]$)
Ti_3SiC_2	110	37-43	7.1
Ti_3AlC_2	125.4	40.0 - 27.5	9.0 - 9.2
Ti_2AlC	80.1 - 82.0	46	8.2-9.6
TiC	35	16	8.5
TiAl	44.9	15	11.8*

Note:* Temperature range is 27-475°C.

MAX phases show a relatively low hardness. The reported values of the Vickers hardness of Ti_2AlC , Ti_3SiC_2 and Ti_3AlC_2 shown in Table 2.2 range from 2.8 to 4 GPa.

Theoretical and experimental work has demonstrated that MAX phases show both low shear moduli and shear strengths (**Barsoum & Radovic, 2011**). The low hardness is associated with an easy basal plane slip resulting from the layered structure and the relatively weak coupling between MX slabs and A planes (discussed in Section 2.1.2) (**Wang & Zhou, 2010; Barsoum & Radovic, 2011**).

2.1.6 Oxidation

Cui et al. (2011) investigated the microstructural development during high-temperature oxidation of Ti_2AlC . They found that below 1300°C , a discontinuous outer TiO_2 layer and a dense continuous inner $\alpha\text{-Al}_2\text{O}_3$ layer was gradually formed. After heating at 1200°C , two types of planar defect were identified in the surface TiO_2 grains: twins with (200) twin plane and stacking faults bounded by partial dislocations. The formation of planar defects is believed to be related to thermal stresses generated in TiO_2 grains, arising from thermal expansion mismatch of phases in the oxide scale. After heating at 1400°C , a mixed outer layer of TiO_2 and Al_2TiO_5 and a cracked $\alpha\text{-Al}_2\text{O}_3$ inner layer were formed.

The planar defects could be removed by annealing at 1400°C (**Cui et al., 2011**). After heating to 1400°C , the large thermal expansion coefficient (TEC) mismatch of $\text{TiO}_2\text{--Al}_2\text{TiO}_5$, the TEC anisotropy in Al_2TiO_5 grains, together with the large volume changes associated with the reactions resulted in cracks in the TiO_2 grains which propagated into the $\alpha\text{-Al}_2\text{O}_3$ layer. An atomistic model was proposed to describe the formation mechanism of oxide scale on Ti_2AlC , in which the growth of oxide scale is caused by inward diffusion of O^{2-} and the outward diffusion of Al^{3+} and Ti^{4+} . The weakly bound aluminium leaves the Al atom plane in the layered structure of Ti_2AlC , and diffuses outward to form a protective inner $\alpha\text{-Al}_2\text{O}_3$ layer between 1100°C and 1300°C . However, due to crack propagating through the $\alpha\text{-Al}_2\text{O}_3$ layer at 1400°C , channels are formed for quick access of oxygen through the sample, leading to significant oxidation (**Cui et al., 2011**).

Wang & Zhou (2010) studied the isothermal oxidation behaviour of Ti_3AlC_2 between 1000°C and 1400°C for 20 h. It was found that Ti_3AlC_2 had excellent oxidation resistance. The types of scales formed below 1300°C were densely layered, adherent and resistant to cyclic oxidation. The inner layer of these scales formed below 1300°C consisted of continuous $\alpha\text{-Al}_2\text{O}_3$.

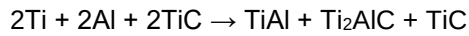
Al_2O_3 . The outer layer changed from rutile, TiO_2 , at temperatures below 1200°C to a mixture of Al_2TiO_5 and TiO_2 at 1300°C . For the samples oxidized at 1400°C , the scale consisted of a mixture of Al_2TiO_5 and, predominantly $\alpha\text{-Al}_2\text{O}_3$, while the adhesion of the scales to the substrates was less than that at the lower temperatures. The carbon monoxide at the scale/substrate was involved in the formation of the continuous Al_2O_3 layers.

As in Ti_3AlC_2 , TiC_x was also found to be detrimental to the oxidation resistance of Ti_3SiC_2 (Wang & Zhou, 2010). By removing TiC from Ti_3SiC_2 by introducing the appropriate amounts of Al in the starting elemental powders, the oxidation resistance of TiC-free Ti_3SiC_2 was much improved (Zhang et al., 2004; Wang & Zhou, 2010).

2.1.7 MAX phase composites

2.1.7.1 Ti_2AlC phase composites

Yang et al. (2014) reported that $\text{TiAl}/\text{Ti}_2\text{AlC}$ composites (with up to 75wt% MAX phase) could be obtained from the starting powders of TiC, Ti and Al by hot pressing. The reaction in Equation 2.11 takes place above 1100°C , while TiC decreased with an increase in temperature, but was not depleted. The optimum temperature chosen for sintering the samples was 1300°C , the sintered samples' mechanical properties were evaluated, Figure 2.10 and Figure 2.11. The resultant composites exhibited increased density and hardness, because Ti_2AlC has a greater density and higher hardness than TiAl. However, the maximum bending strength was $7.78 \text{ MPa}\cdot\text{m}^{1/2}$ and fracture toughness was 486 MPa at 15 wt% Ti_2AlC due to fewer Ti_2AlC particles reinforcing TiAl. This was due to the second phase strengthening, giving a hardness of 2.92 GPa. With the correct content of *in situ* formed Ti_2AlC , small particle sizes, and higher deformation resistance and residual stress toughening can be achieved. The toughening of the composite was a result of diminishing the residual compressive stress intensity at the tip of the deflected crack.



Equation 2. 11 (Yang et al., 2014)

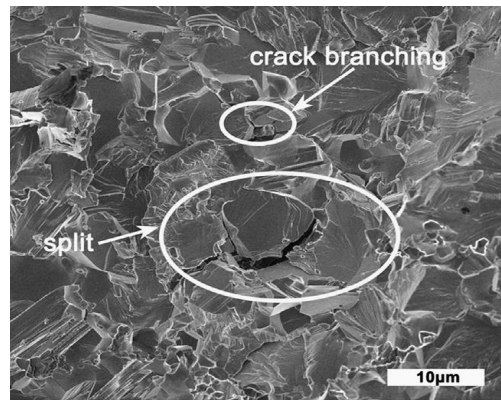


Figure 2.10: SEM (SE) image of fractured surface of a TiAl/Ti₂AlC composite with 75 wt% MAX (Yang et al., 2014).

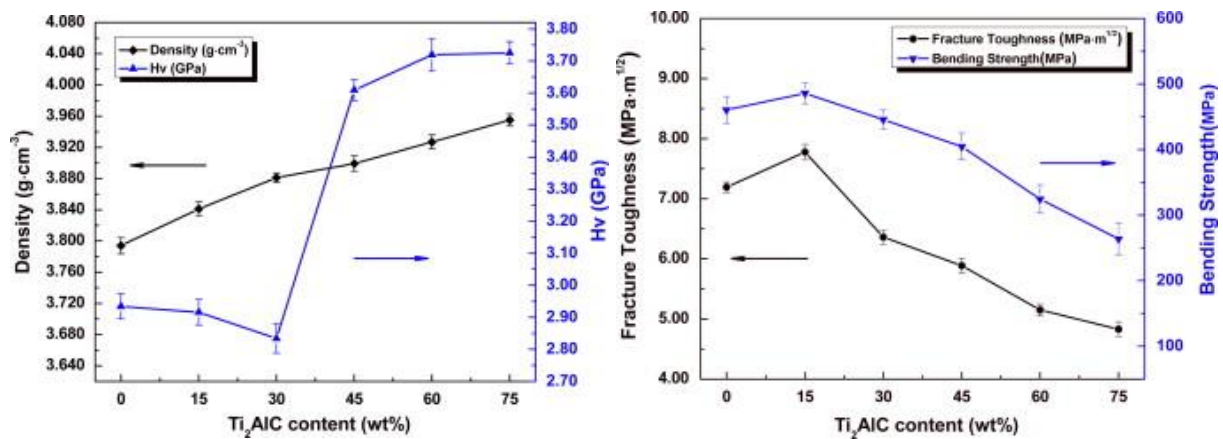


Figure 2. 11: Density and fracture toughness of the TiAl/Ti₂AlC composites with different vol.% of Ti₂AlC (Yang et al., 2014).

2.1.7.2 Ti₃AlC₂ phase composites

Weibing et al. (2009) synthesised dense Ti₃AlC₂-TiB₂ composites from B₄C:TiC:Ti:Al by spark plasma sintering under a uniaxial pressure of 30 MPa in an Ar atmosphere at 1250°C for 8 minutes. The introduction of TiB₂, especially 10 vol.% content, raised the hardness, flexural strength and toughness of the composite. However, the fracture toughness of Ti₃AlC₂- 20 vol.% TiB₂ composite began to decrease because of TiB₂ agglomeration.

Composites of cBN and Ti_3AlC_2 have also been investigated by other researchers. **Yang et al. (2016)** and **Yue et al. (2018)** reported the syntheses of these composites at 1350°C , under 5.5 GPa for 12 minutes sintering time. The starting powders were Ti_3AlC_2 and cBN (60-95 wt% of $1\ \mu\text{m}$ particles). The XRD results for both cases displayed no MAX phase in the final samples which showed only TiC, $\text{TiC}_{0.7}\text{N}_{0.3}$ cBN, TiB_2 , AlN and hBN.

Li et al. (2012) showed that Ti_3AlC_2 and cBN composites could be synthesised at 1050°C , under 4.5 GPa for 10 minutes by cubic anvil high-pressure apparatus from the starting powders 3Ti:1.2Al:2C:cBN. The reaction products at this temperature were cBN, Ti_3AlC_2 , TiC, TiAl, hBN and TiN. Using 3Ti:1.2Al:2C:cBN the reaction to form Ti_3AlC_2 started at 1200°C with the resultant phases cBN, Ti_3AlC_2 , TiC, TiAl and TiN, and hBN only found from 1250°C . Figure 2.12 shows SEM SE images of one of the composites sintered at 4.5 GPa at 1100°C for 10 minutes. The optimum sintering temperature was 1150°C to synthesise highly pure Ti_3AlC_2 by high pressure-high temperature (HPHT). The material processed at 1200°C had the highest friction coefficient and hardness (Figure 2.13), which resulted in the largest mass loss of Si_3N_4 . Either decreasing or increasing the temperature reduced the grinding performance of the as-prepared cBN– Ti_3AlC_2 composite (**Li et al., 2012**). The large errors observed in the hardness of the composites may be due to the indenter landing on cBN, Ti_3AlC_2 or the secondary phases.

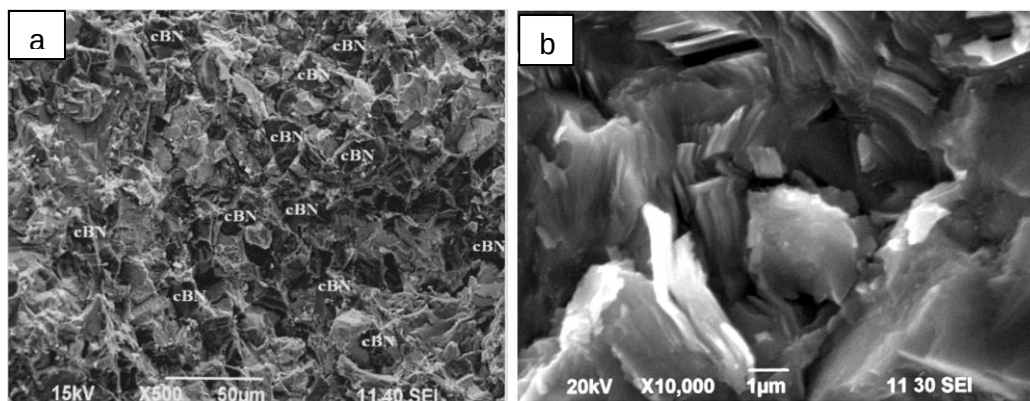


Figure 2.12: SEM images of Ti_3AlC_2 –cBN composites processed under 4.5 GPa at 1100°C for 10 min. (a) (SE mode) Low magnification to show the distribution of cBN particles and (b) (SE mode) high magnification to show the layered structure of Ti_3AlC_2 matrix (**Li et al., 2012**).

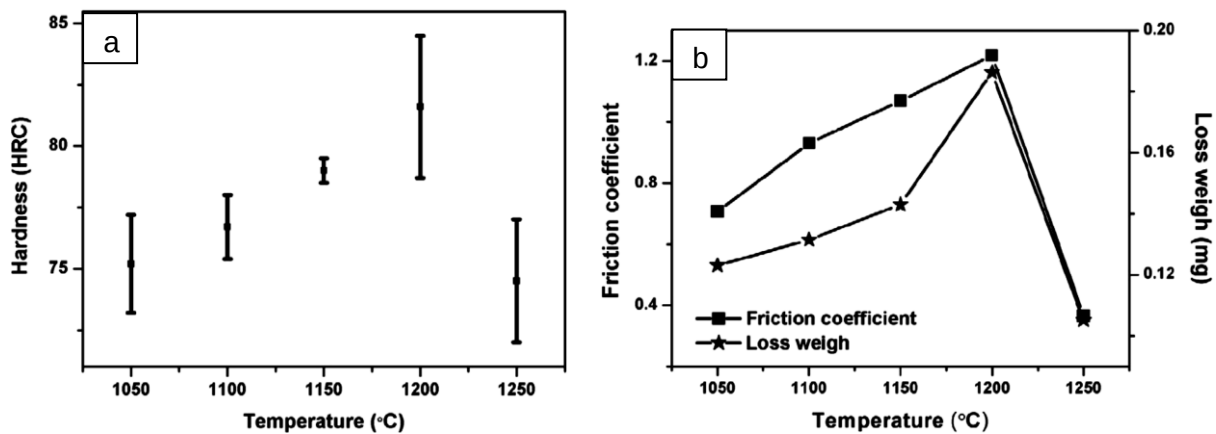


Figure 2.13: Graphs of (a) Hardness measurements of cBN-Ti₃AlC₂ composites processed at different temperatures, (b) friction coefficients of cBN-Ti₃AlC₂ composites processed at different temperatures and mass loss of corresponding Si₃N₄ balls (Li et al., 2012).

2.1.7.3 Ti₃SiC₂ composites

Composites of cBN and Ti₃SiC₂ have also been investigated by **Kolabylina et al. (2017)** and **Yue et al. (2018)**. **Yue et al. (2018)** reported the syntheses of these composites at 1350°C, under 5.5 GPa for 12 minutes. The starting powders were Ti₃SiC₂ and cBN (60-95 wt% of 1 µm particles). The XRD results for both cases displayed no MAX phase in the final samples which showed only TiC, SiC, Ti(C,N) cBN, TiB₂ and TiS₂ and hBN. **Kolabylina et al. (2017)** reported the syntheses of these composites at 1400-2400°C, under 8 GPa pressure for 45 seconds. The starting powders were Ti₃SiC₂, TiC and cBN (60-90 wt% of 1-3 µm particles). The XRD for both cases displayed no MAX phase in the final samples, which showed only TiC, SiC, Ti(C,N) cBN, TiB₂ and TiS₂.

Benko et al. (2004) reacted Ti₃SiC₂ and cBN powders, in 0.5:0.5 and 0.25:0.75 volume ratios of cBN:Ti₃SiC₂, at 7 GPa pressure and 1750°C. From these experiments cBN, TiC, SiC and TiB₂ were found by TEM studies. No Ti₃SiC₂ existed in the final composite. From the microscopic observation, the samples exhibited a porous, not fully dense structure. Phases such as TiB₂, SiB₄, TiC and SiC, with vacancies in TiB₂, formed in the cBN-Ti₃SiC₂ interface.

The cBN samples sintered with the addition of Ti_3SiC_2 exhibited Young's moduli in the range of 400–650 GPa, depending on the Ti_3SiC_2 contents. The highest values obtained were for samples with a low content of the Ti_3SiC_2 phase. These materials exhibited hardness values from 11 to 28 GPa. From these measurements, it was found that the composites sintered with higher Ti_3SiC_2 contents showed the highest hardness. The results of the hardness measurements of the samples of cBN sintered with different amounts of Ti_3SiC_2 are shown in Figure 2.14 (Benko et al., 2004)

Qin & He (2013) and Li et al. (2014) reported that Ti_3SiC_2 decomposed under pressure and high temperature after showing that the decomposition at 5 GPa started at 800°C. Li et al. (2014) also stated that the decomposition temperature decreased with increasing pressure. Li et al. (2014) thus sintered the composite with a 1:1 ratio of the two phases from either Ti, SiC, C and cBN or from Ti_3SiC_2 and cBN at 1150°C and 4 GPa using a cubic anvil high-pressure apparatus. The result was that for both combinations the MAX phase and the cBN were present together with some TiC, Figure 2.15. The first combination, however, also resulted in $\text{TiN}_{0.5}$ TiN, hBN, graphite and SiC, although this might have been caused by the unreacted SiC from the starting powders.

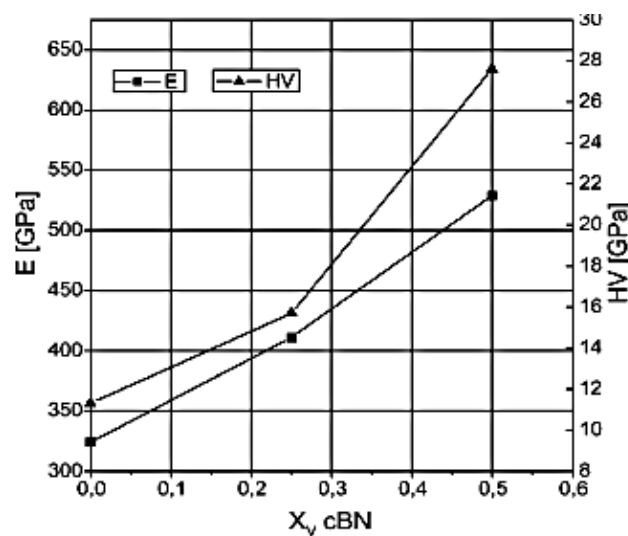


Figure 2.14: Young's modulus and Hardness of cBN- Ti_3SiC_2 composites with different cBN contents (After Benko et al., 2004).

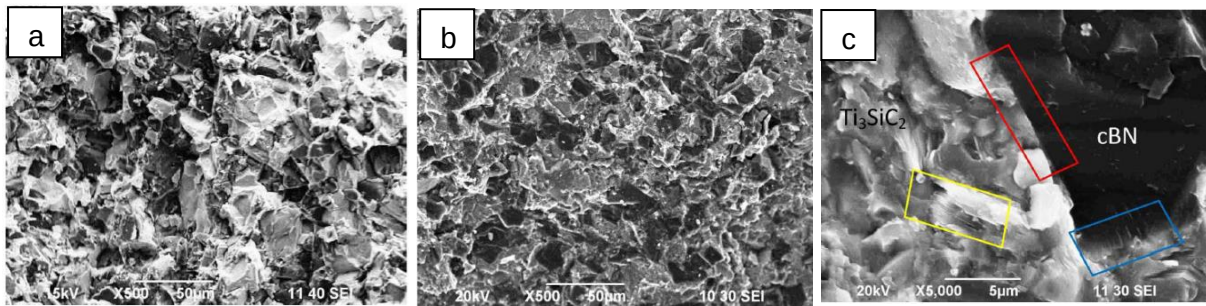


Figure 2.15: SEM(BSE) images of (a) Ti, SiC, C and cBN, (b) Ti₃SiC₂ and cBN starting powders and (c) is a magnified image of (b) (Li et al., 2014).

2.1.7.4 Ti-Al phases formation

Skolakova et al. (2018) used SHS method to investigate the formation of Ti-Al phases using Ti and Al powders. The experiments were carried out at different heating rates (15, 48, 70, and 98°C/min) under argon atmosphere with the sintering temperature of 1100°C. In this work, it was found that the resultant phases were Ti₃Al, unreacted titanium, TiAl, TiAl₂, TiAl₃, and Ti₂Al₅ for all heating rates. It was shown by **Skolakova et al. (2018)** that there was one significant SHS reaction peak at 680°C starting immediately at the melting point of Al and hence the endothermic reaction peak was not noticeable (Figure 2.16).

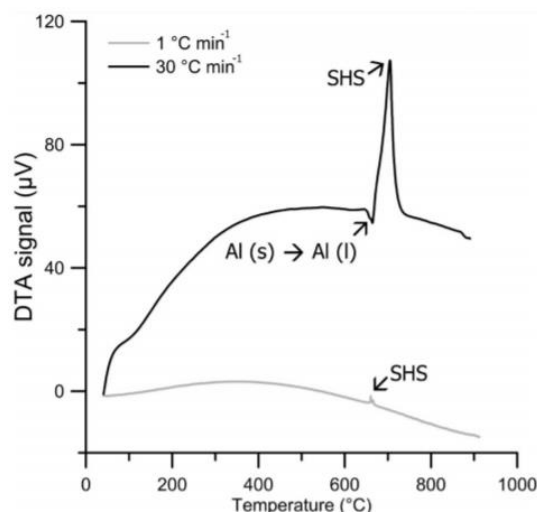


Figure 2. 16: DTA heating curves of Ti:38 (wt%)Al powder mixture.

The endothermic peak was associated with the melting of aluminium at 660°C, thus the SHS reaction is not initiated until the temperature reaches Al melting point at high heating rate. The melting of aluminium is not necessary for the SHS reaction to initiation at low heating rates; however, the exothermic reaction peak is negligible. The exothermic peak was associated with the formation of a number of Ti-Al phases however, it was challenging to determine which phases form preferentially.

2.2 Cubic Boron Nitride

Cubic boron nitride or cBN is one form of a group of synthetic materials developed in the early 19th century (**Vel et al., 1991; Element Six, 2008; Monteiro et al., 2013**). As boron and nitrogen are elements that are close neighbours to carbon in the periodic table, boron nitride and carbon exhibit similarities in their crystal structure. In the same way that carbon exists as graphite and diamond, boron nitride can be synthesised in hexagonal and cubic forms.

It was reported that HPHT conditions like those used for diamond synthesis were also suitable for the manufacture of hexagonal structure of boron nitride (hBN) to be converted into the diamond-like cubic structure of cBN, as illustrated in Figure 2.16 (**Monteiro et al., 2013**). Cubic boron nitride has a zinc blende structure with a tetrahedral symmetry (space group Td_2) i.e. a cubic structure without an inversion centre. In this diamond-like cubic structure, B-N bonds are strongly covalent, boron and nitrogen being tetrahedrally co-ordinated (sp^3) (**Vel et al., 1991; Monteiro et al., 2013**). It consists of cubic closest-packed layers of boron and nitrogen, illustrated in Figure 2.16.

Cubic boron nitride is the second hardest known material, the first is diamond, which possesses many excellent physical and chemical properties such as thermal stability up to 1200°C (**Monteiro et al., 2013**). cBN possesses a high resistance to chemical attack and good

mechanical properties (high H and E values close to those of diamond materials), as shown in Table 2.4.

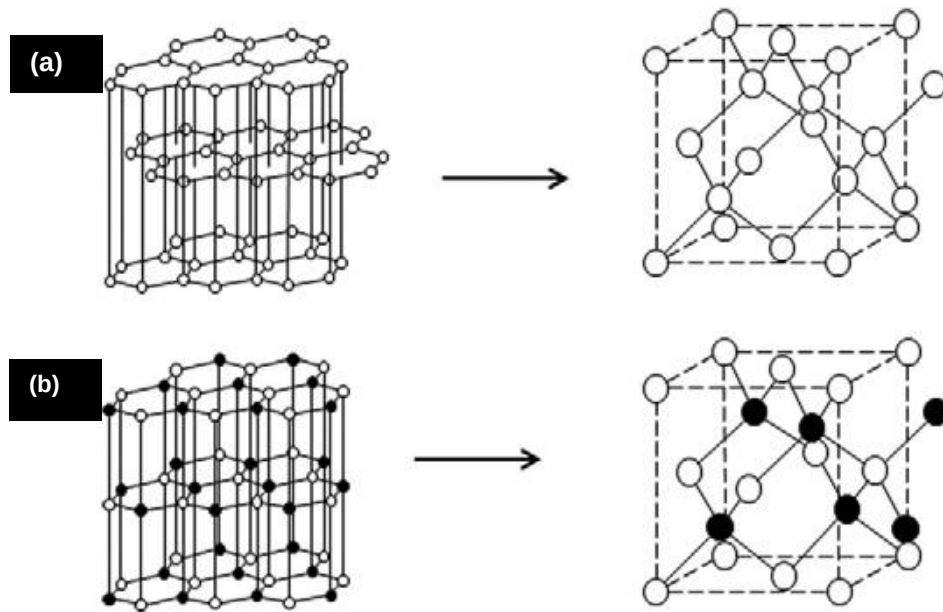


Figure 2.17: Structural transformation diamond and cBN at HTHP, (a) graphite to diamond and (b) hBN to cBN. (Monteiro et al., 2013).

Table 2.4: Properties of cBN compared with other common ceramics and diamond (Monteiro et al., 2013).

	Density (g/cm ³)	Knoop hardness (GPa)	Compressive strength (GPa)	Thermal conductivity (W/m.K)	Thermal expansion (10 ⁻⁶ .K ⁻¹)
cBN	3.45	45	5.33	740	1.2
Diamond	3.51	57 – 104	8.68	600 – 2,000	1.5 – 4.8
SiC	3.20	32	3.9	120	4.0
WC	14.7	13	4.5	100	5.4

2.2.1 Applications of cBN

Super-hard materials such as diamond and cBN are widely used for grinding, tooling and as abrasives (Monteiro et al., 2013). There is an increase in interest for cBN as a potential substitute for diamond in industrial applications, the reasoning being that cBN, unlike diamond, is stable up to 2000°C. Also, the hardness of diamond starts decreasing from 500°C, becoming inferior to that of cBN which only starts to decrease from 800°C.

The low chemical reactivity of cBN with the iron group metals and its high thermal stability, particularly in oxidizing conditions, make it a better candidate for engineering cutting materials than diamond (Vel et al., 1991; Monteiro et al., 2013). It is used as a powder for abrasive processes (i.e. with a wheel set-up) and as a sintered ceramic for sawing, cutting or crushing applications. The cBN reinforced ceramic or metal composites produced under high pressure and temperature, and the tools made from them, are inserted into high speed machining equipment for machining hardened steels, chilled cast iron, carbides and nickel or cobalt based superalloys.

Cubic boron nitride is much harder than the conventional abrasive materials such as Al_2O_3 , SiC and WC (Table 2.4), thus the grinding performance of cBN wheels is considerably improved over the conventional SiC or Al_2O_3 wheels in grinding chilled cast irons, hardened and high-speed steels (Vel et al., 1991; Monteiro et al., 2013). Diamond tools cannot be used in these cases because of the chemical reactivity with ferrous metals, whereas cBN is resistant to chemical attack in the presence of ferrous metals up to 1227-1327°C.

In most cases, compacted cBN powder is cemented on tungsten carbide or ceramic substrates. The machining speed is augmented, and the tool life is increased by a factor of 7-50 (in comparison to WC tools) (Vel et al., 1991). The high quality of the surface finish dispenses with further grinding and polishing actions in many cases.

Thus, depending on the combination of binder composition, the market offers many registered trademarks of PcBN composites, the following are among the most important as listed by Monteiro et al. (2013):

- BZN compact®, GE (USA)
- Sumboron®, Sumitomo (Japan)
- Sunnit®, Amborite® and Ambrasit®, Element Six (South Africa)

- Elbor®, Saint Petersburg Abrasive (Russia)
- Belbor®, IFTT (Belarus)
- Kiborit®, ISM (Ukraine).

The Amborite Company supplied the PcBN, and the properties of this PcBN (shaded grey) composite were compared to others are shown in Table 2.5.

Like synthetic diamond powder, the crystal particles of synthesized cBN cannot be directly used in any kind of tool, except as embedded particles in polishing pastes for finishing purposes (**Monteiro et al., 2013**). Two sintering procedures may be used, the first is direct under HPHT; the second binder assisted which serves to allow much lower temperatures and pressures. In the second method, the fast diffusion and the possibility of non-equilibrium phase transformation significantly improved the binder interaction with the cBN particles. Consequently, continuous solid solutions of borides and nitrides were formed. The choice of binder, in combination with the cBN particle characteristics, influences the resultant composite material properties (**Monteiro et al., 2013**).

Table 2.5: Properties of commercial registered marks of PcBN composites (**Monteiro et al., 2013**).

	Knoop hardness (GPa)	Density (g/cm ³)	Compressive strength (GPa)	Toughness, KIC (MPa·m ^{1/2})	Elastic Modulus (GPa)	Thermal conductivity (Btu/m·K)
BZN Compact®	35 – 45	3.48	3.1 – 4.8	8.6	740 – 870	50-80
BN 100®	40 – 45	4.25	4.6	7.0	830	34-38
BN 200®	30 – 35	4.25	4.3	6.6	814	24-36
Amborite®	28.5	3.37	3.7	13.1	680 – 720	110-135
Elbor®	32 – 38	3.31	2.3 – 3.2	3.7 – 4.2	660 – 750	60-80
Belbor®	39	3.42	4.0 – 5.0	10.8	730	70-85
Kiborit®	32 - 36	3.20	2.6 – 3.2	13.5	850 - 910	100

2.2.2 Decomposition studies

In air, cBN does not oxidize up to 1297-1397°C, as a B_2O_3 layer produced by slight oxidation protects against further oxidation. **Vel et al. (1991)** reported that there was no evidence of a conversion to hBN at 1397°C, although there was some conversion in nitrogen at 1525°C for 12 hours and under vacuum (10^{-7} Torr) between 1547°C and 1597°C. The cubic to hexagonal transformation conditions can be calculated using Equation 2.12:

$$P \text{ (kbar)} = 0.030 T(K) - 10.3, \text{ (1 kbar}=0.1 \text{ GPa)}$$

$$\text{Equation 2. 12 (Vel et al., 1991)}$$

Wolfrum et al. (2018) investigated the stability of cBN particles in a ceramic matrix. The particle size of the cBN used was 30 vol.% of 20 μm in oxide glasses in the range of 1100°C to 1400°C for 1 to 10 hours. The cBN to hBN conversion happened at temperatures as low as 1200°C. The probable transformation mechanism in the work was found to be dissolution of the metastable cBN in the glass or melt, and diffusion and precipitation of the stable hBN. Thus, the process occurred in ceramic-matrix composites in which a liquid phase dissolving hBN exists during densification. The formation of hBN was found on the surfaces of the cBN, Figure 2.18, this caused a weak bonding of c-BN in the matrix.

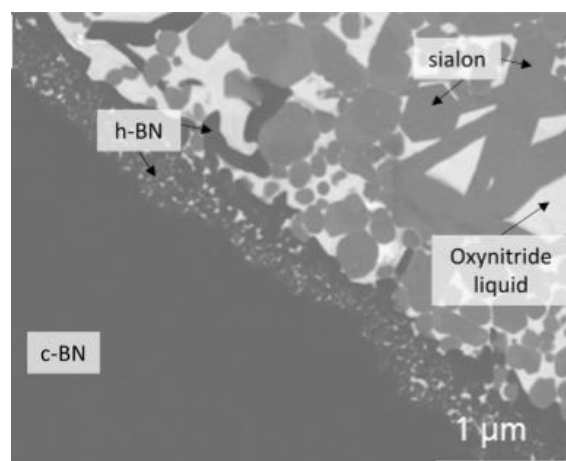


Figure 2.18: Interface between cBN and sialon matrix-densified at 1575 °C. At the interface, the hBN grains embedded in the amorphous oxynitride grain boundary phase are clearly visible (light grey phase-sialon, bright phase-oxynitride liquid and dark grey-cBN/hBN)

Garrett et al. (2015) also investigated the stability of cBN using 10 and 100 μm cBN at 30 MPa to make composites with Sialon. The hexagonalisation rates for the composites containing 10 and 100 μm cBN were different. The Sialon-cBN composites exhibited hexagonalisation of cBN at temperatures as low as 1550°C and extensive hexagonalisation was observed at 1625°C. This occurred at the cBN-matrix interface and at internal defects and grain boundaries of the cBN twins. **Garrett et al. (2015)** also found that hexagonalisation decreased with sintering temperature.

2.2.3 Composites of cBN

In addition to cBN composites mentioned in Section 2.1.7, **Rong et al. (2002)** reported that the microhardness increased with increasing cBN content at both 1200°C and 1400°C, and the highest microhardness of 30.7 GPa was achieved for the 75 vol.% cBN–13 vol.% TiN–12 vol.% Al composition specimen. Most of the samples sintered at 1200°C had higher micro hardness than the same composition specimen sintered at 1400°C. During high-pressure sintering, reactions occurred between cBN, TiN and Al, and new compounds, TiB_2 and AlN , were formed. TEM analysis indicated that all cBN and TiN grains were surrounded with an AlN layer of different thickness, and small TiB_2 and AlN grains co-existed to form clusters (**Rong et al., 2002**).

2.4 Grinding wheels

Diamond and cBN are a common choice for abrasives in grinding wheels due to their relatively high performance in machining materials (**Link diamond, 2018**). As mentioned in Section 2.2.1, cBN is second only to diamond in hardness and is more advantageous as an abrasive when machining ferrous metals and at higher temperatures up to 1200°C. These properties

translate to cBN tools achieving greater stock removal of a workpiece and thus shorter grinding times and also a longer working life (**Link diamond, 2018**).

There are many factors to consider when selecting a grinding tool for a specific material and use (**Link diamond, 2018**). These include the type of abrasives, binder, the type of grinding wheel, operational speeds, need for lubrication, concentration of the abrasive and size of the abrasive grain.

Choice of grain size is determined by the extent of the machining intended for a specific workpiece, thus the stock removal capacity and the surface finish capability of the cBN grit size is essential (**Link diamond, 2018**). The greater the grain size, the greater the stock removal, however, the smaller grain size yields better quality of the surface finish. **Link diamond (2018)** recommends the combination in Table 2.6, depending on the contact conditions and the size of the surface that will be machined.

Table 2.6: Choice of grain size for desired surface finish (**Link diamond, 2018**).

Type of grinding	Size of abrasive grain (μm)
Rough grinding	126-181
Finish grinding	75-107
Fine and precision grinding	20-54

Link diamond (2018) recommends the combination in Table 2.7, depending on the contact conditions and the size of the surface that will be machined. Choice of bonding media is determined by the operational conditions such as the two extremes outlined below (**Link diamond, 2018**):

- need for cool grinding with a good grip, high stock removal rate and low contact pressure, but these are coupled with a shorter useful tool life.
- need for hard grinding with increased heat generation, lower stock removal rate and high contact pressure, these are combined with longer useful tool life.

Table 2.7: Choice of bond for operational conditions (Link diamond, 2018).

Type of bonding media	Working conditions
Hard bond	Narrow grinding coatings
	Long working life
	Wet grinding
	Specific profile required
Soft bond	Wide grinding coatings
	Work pieces sensitive to heat
	Dry grinding

The choice of bond medium concentration of the abrasive is determined by the surface finish required; also, the efficiency of the cBN grinding wheel depends on the concentration of the cBN abrasive. Link diamond (2018) recommends the combination in Table 2.8, depending on the contact conditions and the size of the surface to be machined. Table 2.8 shows that the concentration of the abrasive is coupled with the size of the abrasive and the type of bond for the working conditions. These combinations can also influence the cBN grinding wheel surface and thus its performance (Link diamond, 2018). For instance, having a bond that is too soft and a low concentration of grains that are too fine can result in wear of the bond being too great, and thus the grains of cBN will be pulled out. Having a bond that is too hard and a high concentration of cBN grains that are too coarse can result in wear of the bond being too low and thus a low stock removal. Ideal combinations result in grains protruding from the bond, with large chip clearance and no pull-out.

Table 2.8: Choice of abrasive concentration for operational conditions (Link diamond, 2018).

Concentration of cBN grains	Working conditions
Low	Polishing
	In combination with extremely fine grit ($\leq 30 \mu\text{m}$)
	Special process, large contact area
Standard	Surface grinding
	In combination with fine grit ($\sim 76 \mu\text{m}$)
	Higher coatings widths
High	Profile grinding, form holding, slitting
	In combination with coarse grit ($\sim 252 \mu\text{m}$) and hard bond
	Small contact area

2.5 Rationale of study

The origin of this study was the idea to use MAX phase composites for grinding wheel applications. MAX phases, as discussed in Sections 2.1.2, 2.1.5 and 2.1.6, have advantageous properties for high temperature, wear and abrasion applications. The synthesis of MAX phases is outlined in Section 2.1.3 and demonstrates the feasibility of using the moderate temperatures and pressures approach for this study. The expected secondary phases are also outlined in Section 2.1.4 demonstrating how these phases intergrow with the MAX phases on a microstructural level. The advantages of using cBN, instead of diamond, in the composites for the intended application are also shown in Section 2.2.1, with the hexagonalisation conditions noted in Section 2.2.2. The composites of the Max phases as well as cBN further shows the feasibility of the approach of moderate temperatures and pressure that were used in this study.

A few researchers had used high temperatures/pressures and failed to show the presence of either, or both cBN and MAX phase in the final samples. While others demonstrated success with Ti_3AlC_2 high pressure-moderate temperature method. The Ti_2AlC MAX phase has, however, never been attempted with cBN as a composite, while Ti_3SiC_2 had failed attempts by all investigations of composites with cBN. Generally, the average size of cBN used was $\sim 10\mu\text{m}$ and the volume fraction would be varied. Equation 2.12 shows that at moderate pressures, cBN would hexagonalise at relatively low temperatures, possibly lower than that of the sintering temperatures to be used.

Thus, the rational for using moderate pressures and temperature is that, since cBN does not participate easily in the diffusion processes at lower temperatures, lowering the pressure will allow a certain degree of hexagonalisation, and thus the hBN could then participate in forming the desired secondary phases that would be compatible with both the cBN and MAX phase. These moderate pressures would also allow the sintering of the MAX phase as higher

pressures may promote the decomposition of the MAX phases. The degree of hexagonalisation would have to be closely monitored, not to deplete the cBN, and not to have excess hBN in the system, while forming the desired secondary phases. The effect of surface area on the degree of hexagonalisation will be investigated, as larger particles sizes of $>10\mu\text{m}$ have not been investigated. The effect of both surface area of cBN and content of cBN on the stability of the MAX phases will be investigate, which has also not been done.

CHAPTER THREE:

METHODOLOGY

3.1 Powder preparation

The powders that were used in this project were titanium, aluminium, activated carbon, titanium carbide, silicon carbide and cubic boron nitride. The properties and suppliers of these powders are shown in Table 3.1. The powder preparation method outlined in this section was adapted from previous work by the author **Rampai et al. (2013)** where it was demonstrated that the mixing methods yielded a homogenous powder mixture.

Table3. 1: Powders used for the experimental work.

Powder	Purity (%)	Supplier	Average Size (µm)
Ti	99,00	Alfa Aesar	45
Al	99,97	Alfa Aesar	45
C	99,00	ABCR	45
SiC	99,00	Alfa Aesar	45
cBN	Unknown	Element 6	10
cBN	Unknown	Element 6	100

The powders were first weighed to obtain the relevant molar ratios for the respective MAX phases as indicated in Table 3.2. For the aluminium based MAX phase composites, 1.2 moles of aluminium were used instead of 1 mole to allow for the evaporation of some aluminium, as was recommended by **Zhou et al. (2005)**. The weighed powders were milled in zirconia milling pots containing 2 mm alumina milling balls and hexane, with a ball to powder ratio of 2:1. A planetary ball mill was used to mill the powder for six hours at 300 rpm.

After milling, the milling pot was placed in a glove bag and air was removed using a vacuum pump. The bag was filled with argon and again evacuated; this was repeated several times to eliminate as much air as possible. The contents of the milling pot were sieved to separate the milling balls from the hexane and powder, then the suspension was concentrated into a slurry by decanting excess hexane. Drying the slurry was done at room temperature and promoted by circulating argon in a glove bag to remove the hexane.

Table 3.1: Mass of powders used for MAX phase synthesis.

	Ti₂AlC (g)	Ti₃AlC₂ (g)	Ti₃SiC₂ (g)
Ti	9,576	14,364	14,364
Al	2,698	2,698	0
C	1,200	2,400	1,200
SiC	0	0	4,009
cBN (20 vol.%)	12,555	24,297	24,441
cBN (40 vol.%)	25,110	48,594	73,324

After drying, the MAX powders were mixed in one of three different ways with cBN to achieve different sizes and fractions of cBN in the composites; adding 20 vol.% of 10 µm size cBN, or 20 vol.% of 100 µm size cBN, or 40 vol.% of 100 µm size cBN. The “MAX”-cBN powders were mixed using a turbula mixer at 67 rpm for four hours. Four 10 mm alumina balls were used in the case of the 10 µm cBN powders to break the agglomerates that formed.

3.2 MAX-cBN composites synthesis using spark plasma sintering furnace

The MAX-cBN powder mixture was compacted into a graphite die, then sintered in a spark plasma sintering furnace (SPS), shown in Figure 3.1. Sintering of the 10 µm of the 20 vol.% cBN composites was first done at 1500°C (at 100°C/min) for 1 minute, since it was noted that the highest decomposition temperature for the MAX phases under investigation (**Rampai &**

Lang, 2011). This was done in order to evaluate the SPS traces for any notable changes in the chamber temperatures (indicative of reactions) in that temperature range.



Figure 3.1: The SPS furnace used to sinter cBN-MAX powders to synthesise the composite material.

Then the sintering of the powder was carried out at the observed peaks, Figures 4.3b, 4.9b and 4.15b, (two observed for the Al based MAX phases and one for the Si based MAX phase) to evaluate which reactions took place at these temperatures. This was followed by sintering at 1150°C, 1250°C (and 1300°C for the M_3AX_2) to evaluate the optimum sintering temperature and to note any phase changes. Finally, sintering was done from the higher reaction temperatures to 1500°C, at 100°C increments, to evaluate the phase distribution changes that may have occurred. To optimise the quantity of the MAX phases and cBN in the composites, the synthesis temperature(s) that displayed the most cBN and MAX content in the 1 minute runs were used, and time increased to 5 and 10 minutes. The pressure in this work was kept constant at 30 MPa, as this work's novelty is using moderate pressures to synthesise the required composites. In addition to other work by the author (**Rampai et al., 2013**), it was demonstrated that full densification could be reached at this pressure.

The optimum time and temperature obtained from the samples containing 10 μm of 20 vol.% cBN were used as the starting conditions to sinter and evaluate optimum sintering conditions for 100 μm of 20 vol.% cBN composites. The optimum time and temperature obtained from the samples containing 100 μm of 20 vol.% cBN were used as the starting conditions to sinter and evaluate optimum sintering conditions for the 100 μm of 40 vol.% cBN composites.

3.3 MAX-cBN composite preparation and characterisation

3.3.1 MAX-cBN composites sample preparation

A sand blaster was used to remove the graphite and hBN coating on the sintered samples, then they were ground and polished for characterisation. Manual grinding was done using a grinding machine at 375 rpm with water as a lubricant. Diamond grinding wheels were used first with 200 grit then 800 grit, and finally 1200 grit SiC grinding paper. The ground surface was then polished by hand at 150 rpm, using 6 μm , then 3 μm and 1 μm diamond paste. An

oxide particle suspension was used for final polishing after which the samples were subjected to density measurements and XRD.

3.3.2 Density measurements (Archimedes' method)

The density measurements were carried out in a water medium, the boiling and suspending of the samples was also done in water, hence the ρ_{H_2O} in Equation 3.1 is density of water. The dry mass (m_D) for all samples was measured before and after boiling the samples for four hours. The samples were left to cool down after boiling, then the wet mass (m_W) was measured, finally the suspended mass (m_S) was also measured five times. The three masses were then used to calculate the absolute density and the open porosity of the samples using Equation 3.1 and 3.2.

$$\text{Density of sample} = \frac{m_D \times \rho_{H_2O}}{m_W - m_S} \quad \text{Equation 3.1}$$

$$\text{Open porosity} = \frac{m_W - m_D}{m_W - m_S} \quad \text{Equation 3.2}$$

The samples were then fractured into two pieces by a three-point bend jig, after notching the sample in the middle, and only one fracture surface was further ground and polished. The rough fracture surface piece was used for SEM imaging of the fracture surface from the edge of the sample, to the core, to determine the fracture mode of the sample. The polished half of the sample was used for phase distribution, reaction area evaluations and XRD

The samples for XRD were ground flat on the cross-section fracture surface and polished using the apparatus and procedures specified above. The half of the fractured sample set aside for SEM was first ultrasonically cleaned to remove any dust particles or micro-particles which might have attached to the fracture surface.

3.3.3 X-ray diffraction (XRD)

The cross-sections were then analysed using a Bruker AXS D2 PHASER desktop powder diffractometer using Co (K α) radiation produced at 40 KV and 20 mA. Diffractograms were collected over a range of 2θ between 10 to 70° using a “60,1 min, sample rotation” profile.

3.3.4 Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDX)

Using the Philips XL 30 ESEM-FEG (scanning electron microscope) the fracture surfaces were imaged using an accelerating voltage of 20 kV. The fracture mode was analysed using the secondary electron mode of the SEM machine. The samples were also analysed by energy dispersive spectroscopy (EDX) to determine the composition of the samples using the back-scatter electron mode of the SEM machine. The occurring reaction area width between the matrix and cBN particles in the relevant samples was estimated by taking 10 randomly selected and measuring 4 opposite sites around each particle and taking the average of the 40 measurements.

3.4 MAX-cBN mechanical properties evaluation

Samples that were considered to be the optimum from each size cBN and volume fraction were reproduced into batches of 20 samples each for the mechanical tests described hereafter.

3.4.1 Vickers hardness measurements

A HWDM-3 micro hardness indenter test machine was used for the micro hardness measurements. The applied load was 19,6 N for 15 seconds. As the indenter is a square based diamond pyramid, the arithmetic means of the two diagonals (d) gives the Vickers number (kgf/mm^2) using Equation 3.3. Three samples were selected for Vickers micro hardness for

each optimum composite as described. Six readings were taken for each sample using a minimum distance between each indentation of 2,5 times the length of the diagonal (**ASTM E92, 1997**).

$$HV = 1.854 \frac{F}{d^2}$$

Equation 3.3 (ASTM E92, 1997)

Bulk hardness tests were also done on one of each sample; this was completed to evaluate whether cracking would occur in the samples or not. In this case; Zwick Roell ZHV machine was used for the tests. The load was progressively increased from 29,4 N, 49 N, 98 N, 196 N and finally 294 N; each load was applied for 10 seconds.

The hardness machine gave an output value of Vickers number, and for the conversion of the hardness to SI units of Pascals, Equation 3.4 (Gordon England, 2018) was used:

$$1 \text{ HV} = 0,009807 \text{ GPa}$$

Equation 3.4

3.4.2 Pin-on-belt wear tests

An erosion abrasive wearing machine using a 120 grit SiC belt as the counter phase on the surface, was used to measure abrasion resistance. The rotational speed, v_t , of the belt was 60 rpm, with a contact force, F_N , of 4,28 N, and a travel distance of 17 m. No lubricant was used throughout the experiments. The pin was made of 30 mm diameter MAX-cBN composites of varying thicknesses, the mass loss was determined, and the linear wear and wear rate were calculated. Figure 3.2 illustrates the different variables used in the calculations.

From Figure 3.2, L was the measured length across the cross-sectional area of the worn surface after each test. R was the radius of the samples, all set at 15 mm for every sample, r was the calculated length of a line from the centre of the sample to L, and is perpendicular to

L. The calculated value h was the linear wear documented in the results section and is the linear reduction in R due to wear. The dimensions shown were determined as follows:

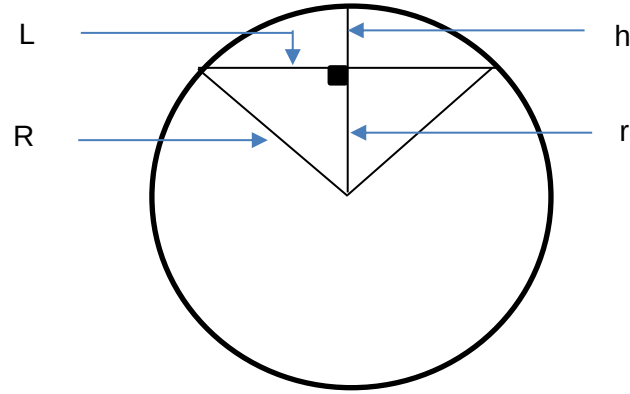


Figure 3.2: Schematic diagram for the composite samples and the dimensions measured and calculated to determine wear.

L was measured for each sample after each wear test, then r was calculated using Pythagoras, Equation 3.5:

$$r^2 = R^2 - (0,5h)^2 \quad \text{Equation 3.5}$$

Then h was determined from the difference as shown in Equation 3.6:

$$h = R - r \quad \text{Equation 3.6}$$

The two-dimensional area of the arc representing the worn material was calculated using Equation 3.7:

$$A = R^2 \cos^{-1} \left(R - \frac{h}{R} \right) - (R - h) \times \sqrt{2Rh - h^2} \quad \text{Equation 3.7}$$

Finally, volume loss and wear rate were determined by Equations 3.8 and 3.9, respectively.

$$V_{\text{loss}} = A \times \text{thickness of the sample} \quad \text{Equation 3.8}$$

$$\text{Wear rate} = V_{\text{loss}} / \text{Applied load} \quad \text{Equation 3.9}$$

CHAPTER FOUR: RESULTS

4.1 Reaction temperature evaluation 20 vol.% of the 10 μm cBN

This chapter starts with a description of the homogeneity of the mixed powders particularly the resultant distribution of the cBN in the sintered composites. The reaction mechanisms of the respective MAX phases with cBN were evaluated and the distribution of the phases resulting from these reactions assessed. Then optimisation conditions were investigated to find time-temperature combinations that resulted in the highest MAX phase contents in the respective composites, while minimising the content of hBN. Then, the effect of reducing the surface area of the cBN particles on MAX phase synthesis and cBN stabilisation were reported using these optimum conditions. In addition, the effect of the increase in cBN fraction on the MAX phase synthesis and cBN stability were also investigated. Finally, the mechanical properties of the optimal samples were evaluated; particularly Vickers Hardness and wear properties. Optimal samples in this study were considered to be those that contain the relevant MAX phase, cBN presence and minimal to no hBN in the samples.

In an attempt to find the optimum temperature for sintering MAX-cBN composites, where both phases were present in relatively high proportions, the dwell time was kept constant at 1 minute, and the temperatures were varied. The sintering pressure was kept constant at 30 MPa for all experiments in this work as the aim of this study was to use moderate pressures for sintering, and 30 MPa was found to be sufficient for densification from work by **Rampai et al., (2013)**.

The XRD diffractograms were plotted on one axis, offset, in order to easily evaluate the phase changes due to varying temperature/time in samples of the same starting powders. Due to plotting multiple diffractograms on one graph and subtracting the background from the

diffractograms, some of the peaks of phases that were present in small quantities appeared to be negligible and thus not reliable. To clarify the presence of these peaks, the actual XRD diffractograms of each individual sample are given in Appendix A. For instance, the presence of TiN_b in Figure 4.14 for the sample sintered at 1250°C seems unlikely, however Figure A6 shows clearly the presence of TiN_b , where $b = 0.98$ in this case. The XRD data in Appendix A were also used to prove the presence of the different phases assigned to these peaks.

EDS analysis was done for all samples under investigation, however, only one sample per sub-section is shown in this chapter, with justifications of the selected sample given in each sub-section. The EDS analyses of the remaining samples are given in Appendix E. The resultant EDS analysis data shown in this chapter and in Appendix E was an average of at least 5 measurements of phases with the same contrasts. Every effort was made to minimise any systematic error for this analysis, therefore the large error associated with some of the EDX results could only be attributed to random errors. These would result from the fluctuation of the values due to the limitation of the equipment used to do the EDS analyses. For example, the resultant phases in the matrix were mostly less than $\sim 2\text{ }\mu\text{m}$ in size, which is the approximate size of the incident beam which would likely also generate x-rays for neighbouring phases in this case. Every effort was made in these cases to analyse the phase in the centre and to pick larger phases of the same contrast. The EDS analysis was thus done with the phases seen in XRD results, and the EDX results were more indicative of the migration of elements in cBN and MAX phases.

The density, phase quantities and hardness & wear results are plotted on single graphs for ease of interpretation with the actual values given in Appendices C, D and F respectively. The Rietveld analysis from the Topas software gave the phase quantities in wt.%, these values were converted to vol.% for the Rietveld graphs in this section. This was done as the cBN inclusion in the composites was calculated in vol.%, therefore it would be more relevant to assess the resultant cBN fraction in the samples after reaction in vol.%.

The justification of the observed XRD, EDX, density, Rietveld and mechanical properties results found in this chapter are discussed in Chapter 5.

In addition to the reactivity studies, the effective mixing of the starting powders, to achieve a homogeneous material, was also considered in this study. This was undertaken in order to minimise the final composite having differential phase composition, and thus material behaviour, within the sample through agglomeration of different powders. Previous work (**Rampai & Lang, 2011**) demonstrated that the current methods used to mix the “MAX phase” powders were sufficient to yield a homogeneous powder mixture of the different powders. However, the study by **Rampai & Lang, 2011** did not include the mixing of the “MAX phase” powders with cBN powder. But rather synthesising MAX phases first, then crushing the MAX phase samples then mixing the resultant powder with cBN powder for further sintering. The additional mixing of the MAX phase powders and cBN powders is outlined in Section 3.1. The success of this mixing method, to maintain the homogeneity of the powders, was evaluated post-sintering with fracture surfaces of the composites assessed for the distribution of the cBN in the sample, seen as the black phases in Figures 4.1 and 4.2. Figure 4.1 shows the SEM BSE image and EDX analysis of the Si based MAX-cBN composites sintered with the 44 μm (average size) SiC advised from previous work (**Rampai & Lang, 2011**) and outlined in Section 3.1. It was observed that the SiC remained in the samples even at temperatures as high as 1500°C, and did not adequately participate in the reaction to form Ti_3SiC_2 in the composite. This problem was not experienced with the Al based MAX-cBN composites as these composites used Al powder and the Ti_3SiC_2 composites used SiC instead of Si. This is because Al is a metal and reacted much easier at the moderate temperatures used in this study than the SiC which is a ceramic and did not react as easily under the same conditions.

In all SEM (BSE) images the phases containing heavier atoms are brighter as they scatter a greater number of electrons back which are then picked up by the detector (such as Ti in this

case). The phases containing lighter atom elements will thus show up darker in the image as less electrons are scattered to the detector (B in this case). So, phases such as a BN will be the darkest as it contains a combination of the lightest elements, and the MAX phase will have the brightest contrast as it contains the heaviest element Ti. There were cBN particles as small as 2 μm and as large as 20 μm observed in the sintered composite shown in Figure 4.1 and 4.2a to 4.2c. Thus, the observed size distribution of cBN powder that is noted as “10 μm cBN” throughout this report was rather an approximation of the size which ranged from 2 – 20 μm .

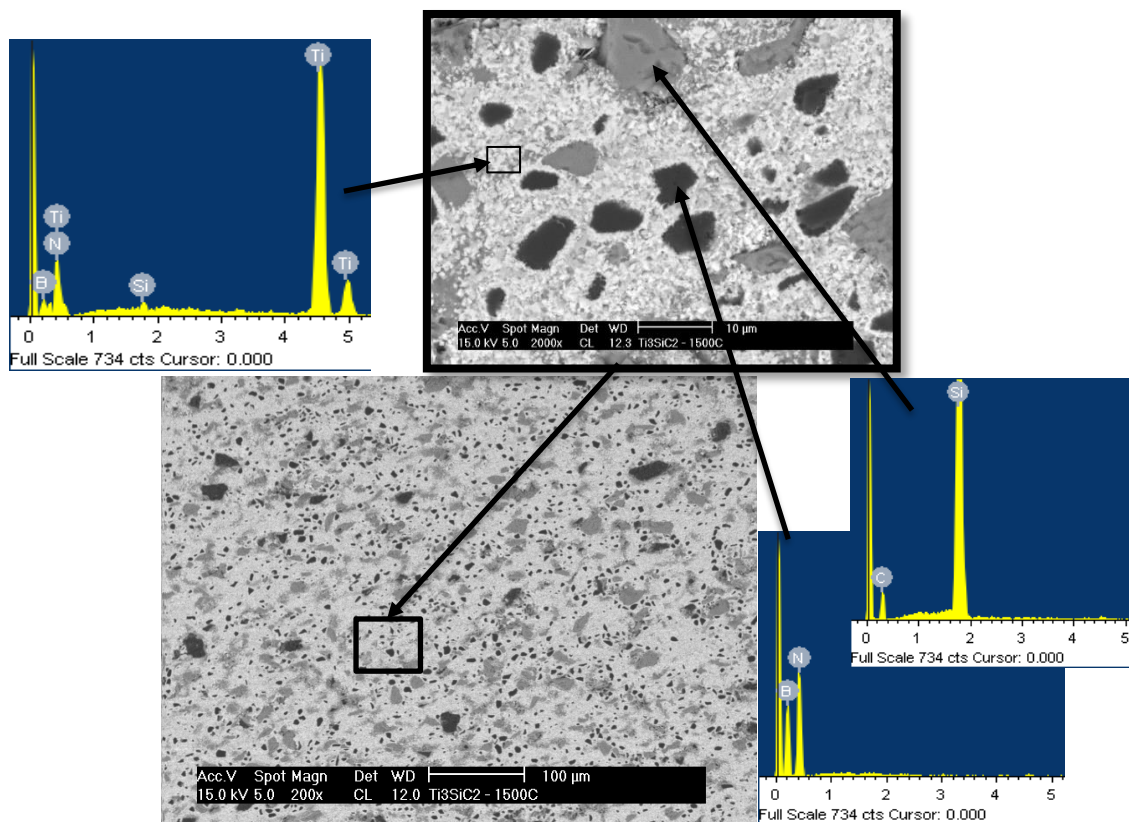


Figure 4.1: SEM (BSE) image and EDX analysis of a Ti_3SiC_2 -(20 vol.% 10 μm) cBN sample sintered at 1500°C with 44 μm SiC.

Figure 4.2 shows the SEM (BSE) images of Ti_3SiC_2 composites images with 10 μm (a to c) and 100 μm (d) cBN particles. These samples were all sintered at 1300°C for 1 minute and show the outcome of different mixing parameters. Only Ti_3SiC_2 was shown in Figure 4.2, however, the same behaviours were observed in the Al bases MAX phase composites. The

mixing of the “MAX phase” powders using the methods in previous work (**Rampai & Lang, 2011**) yielded good mixing of the Ti, C and SiC/Al powders, with no mechanical alloying.

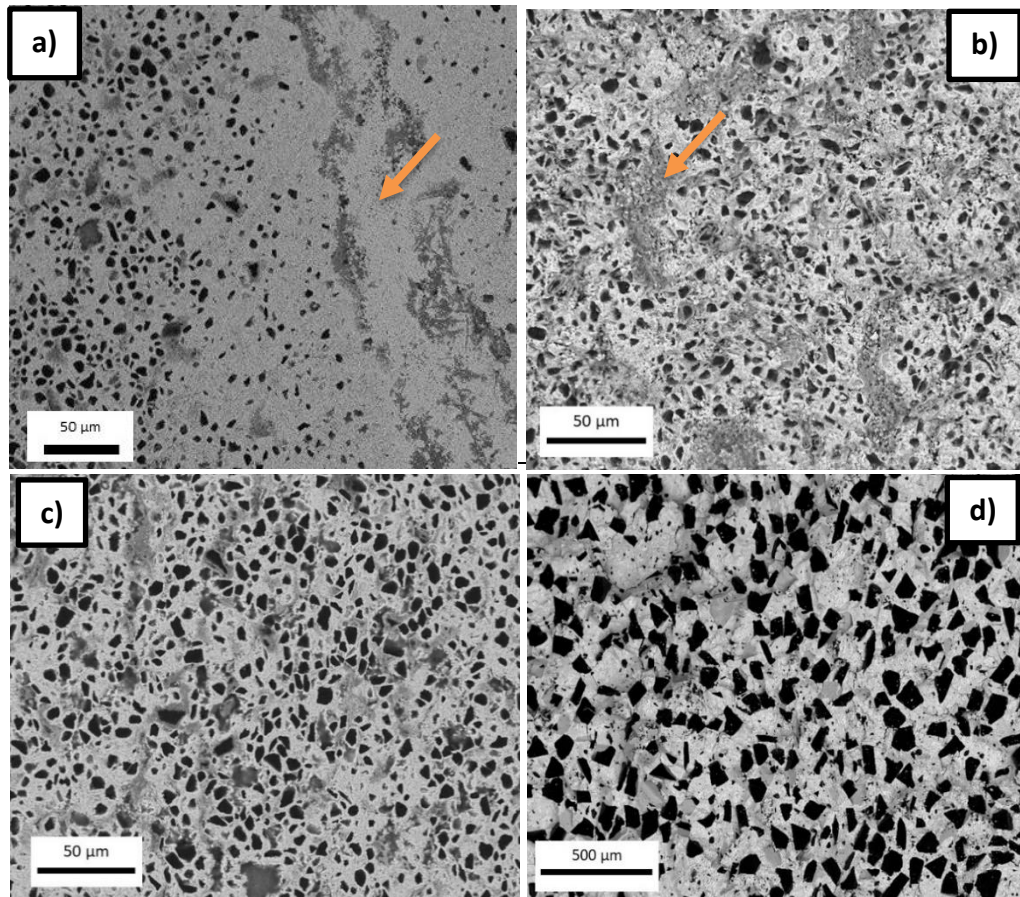


Figure 4.2: SEM (BSE) images of Ti_3SiC_2 -cBN composites sintered at 1300°C for 1 minute after a) original mixing method (20 vol.% of the $10\ \mu\text{m}$ cBN), b) mixing by including 4 mm alumina balls in the dry mixing of cBN with Ti, Al and C (20 vol.% of the $10\ \mu\text{m}$ cBN), c) doubling the mixing time to with the 4 mm alumina balls (20 vol.% of the $10\ \mu\text{m}$ cBN) and d) same mixing as c) with 40 vol.% of the $100\ \mu\text{m}$ cBN. Orange arrows point to areas lacking in cBN showing segregation of phases.

The “MAX” powders were initially mixed with the cBN in a tubular mixer with 1 mm alumina balls. The result of this mixing on the sintered composites are shown in Figure 4.2a as an example of all samples, which shows severe segregation of the cBN powders yielding cBN deficient zones (orange arrow). This was attributed to the agglomeration of the cBN due to its high surface area. It was decided to use larger alumina balls to break up the agglomerates. When using 10 mm alumina balls for the same milling time, the composites showed an

improvement, but there were still some cBN deficient areas (orange arrow), Figure 4.2b. Doubling the mixing time (from 2 to 4 hours) successfully homogenised the cBN distribution in the sintered Si based MAX phase composite samples (Figure 4.2c), thus this method was adopted going forward. All composites containing 100 μm cBN also showed a good homogeneity of cBN in the matrix of the sintered samples, as seen in Figure 4.2d (taken at higher magnification than the other images) as representative of what was seen in all similar samples.

4.1.1 Ti_2AlC -cBN composites

This section evaluated the reactivity of BN in the Ti-Al-C system, in the ratio 2:1:1.

Figure 4.3 shows the sintering profiles of the Ti_2AlC -cBN composites from the SPS sintering runs obtained at different temperatures as discussed in Section 3.2, the temperature indicated was the chamber temperature during sintering. The temperature curves, indicated on both Figure 4.3a and 4.3b, show the rate of increase of temperature for all samples was consistent. They also indicate the final sintering temperature for each run, ending in a vertical line which indicates the dwell time (1 minute) at the sintering temperature. In both figures, it was observed that the chamber temperature spiked at two temperatures (~ 680 and $\sim 1300^\circ\text{C}$). This may indicate an exothermic reaction as the sudden increase in temperature was not due to the SPS as it was set to increase the temperature at a fixed rate. Therefore, the spike can only be attributed to the sample itself giving off heat, thus an exothermic reaction was indicated.

Figure 4.3a shows the piston displacement curves (traces at the bottom of the graph), which indicate the relative piston movement with increase in temperature. This may be used as an indication of volume changes of the samples with increase in temperature, and in some sense the densification or density changes in the samples with increase in temperature. Figure 4.4 shows the densities of samples with increase in temperature, this was used to corroborate the density changes observed in Figure 4.3a. The errors associated with the density

measurements were very small, indicating that the average densities obtained for these samples were very consistent. Figure 4.3b shows SPS traces indicating piston displacement-time-derivative curves (traces at the bottom of the graph), these indicate the rate of travel of the piston with increase in temperature. These curves, in combination with the temperature curves, were utilised to estimate temperatures where reactions in the Ti_2AlC -cBN composites may have occurred. Figure 4.5 shows the XRD traces for samples sintered at or near the reaction temperature, the XRD data was used to show the resultant phases of the reactions observed in Figure 4.3b.

In Figure 4.3, a peak indicating the melting of aluminium was not clearly observed at 660°C as it was dwarfed by the immediate exothermic reaction peak. This occurred as the endothermic reaction was significantly less intense, but an essential precursor to the resulting exothermic reaction. It was seen that the exothermic peak was at $\sim 680^\circ\text{C}$ with T_{onset} 660°C and T_{offset} 686°C . An analysis of samples sintered at 700°C (Figure 4.5) shows the resultant phases; Ti, Ti_3Al , TiAl_2 from these simultaneous reactions. Figure 4.3a show the movement of the pistons relative to one another moving at a faster rate, also indicating the formation of phases with a lower density than the starting powder, further supporting the abovementioned, and XRD data.

Figure 4.3a further shows that the 1150°C and the 1250°C curves do not have the ~ 1 mm (orange circle) increase at about 14 minutes, this only occurred for samples sintered at 1300°C and above. Figure 4.4 confirms this observation as densities of the samples increase with temperature until 1300°C where after it stayed constant. The open porosity in this case was also observed to follow the same trend as the density, except the outlier at 1250°C . The trend observed with the open porosity of the samples could be due to the formation of the denser phases from the less dense phases, leaving some vestiges in the samples. This sudden ~ 1 mm (orange circle) increase was attributed to the reaction peaks observed in Figure 4.3b for these samples which correlate to the complete degradation of the MAX phase in these

composites (Figure 4.6). This indicated the formation of major phases found in these samples (TiC_xN_y and TiB_2), which were denser than the major phases in the samples sintered at 1250°C and below (Ti_2AlC and cBN) Figures 4.5 and 4.7.

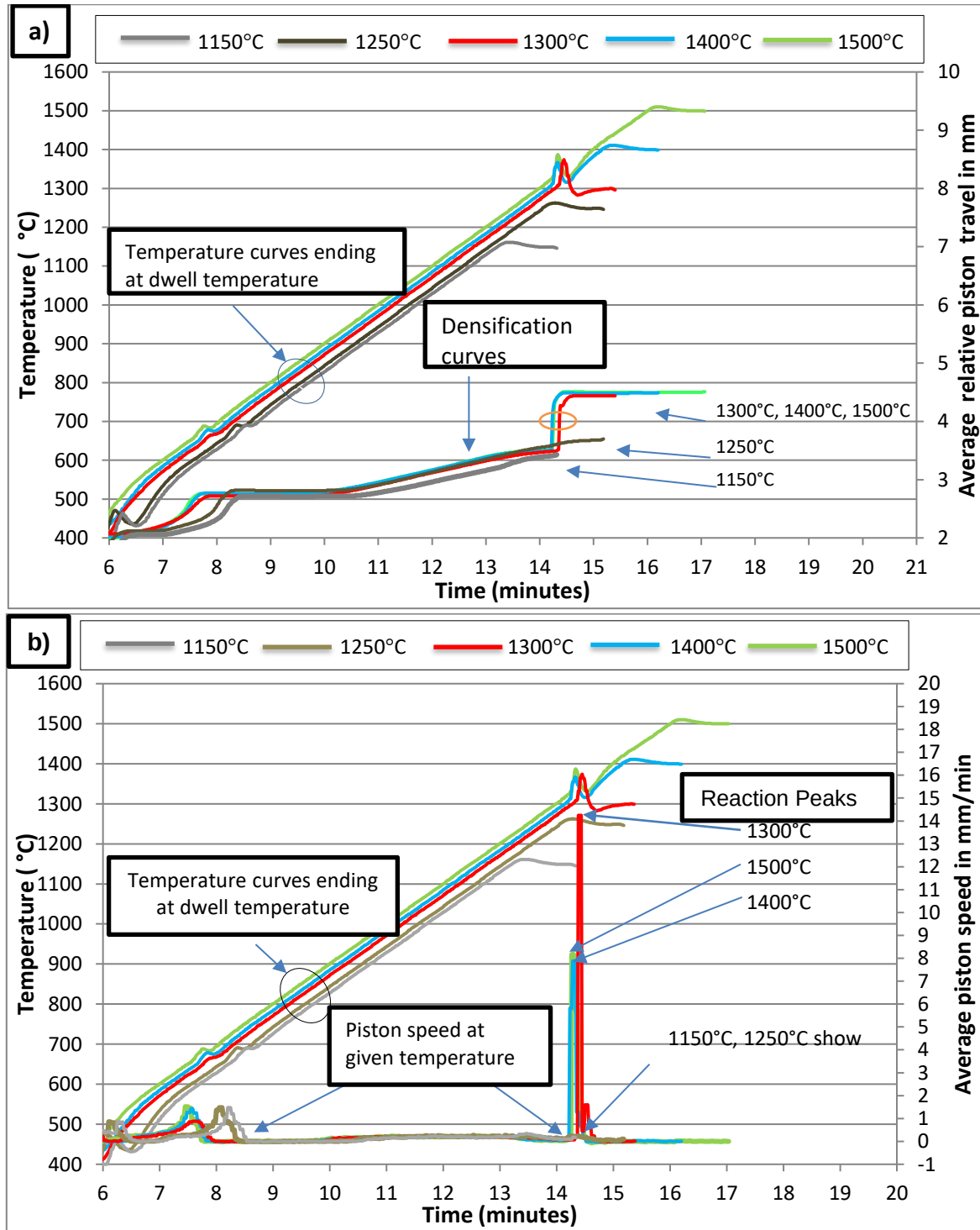


Figure 4.3: Ti_2AlC -cBN (20 vol.%, 10 μm) curves from the SPS runs at 1 min and different temperatures.

a) Piston displacement curves and b) Piston displacement time derivative curves.

For the samples sintered at 1300°C and above (densities of 4.21, 4.18 and 4.25 g/cm³ respectively, Figure 4.4), the traces in Figure 4.3a were a flat line after the observed 1 mm increase (orange circle). This indicated that the pistons of the SPS machine (during sintering) were no longer moving relative to each other, and that the samples had reached relative full densification. The sample sintered at 1150°C (density of 3.86 g/cm³) showed the opposite, indicating that full densification had not been reached. The sample sintered at 1250°C (density of 3.99 g/cm³) showed some level of flat line, indicating the sample was approaching full densification. Figure 4.4 shows that the open porosity of the samples was relatively low and increased at 1400°C. Since the densities are similar in these samples, this could have been due to the low density hBN reacting to form the higher density secondary phases (AlN, TiN_b, TiB₂), and thus may form some pores in the samples.

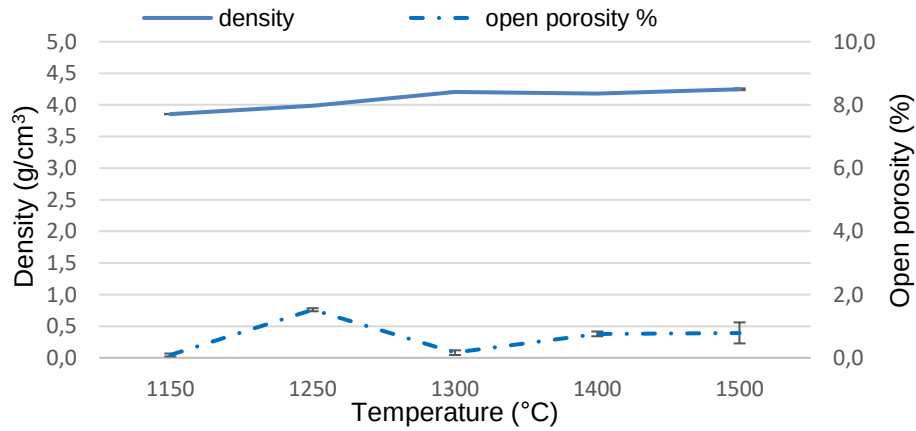


Figure 4.4: Densities and open porosities of Ti₂AlC-cBN (20 vol.%, 10 μm) samples sintered at different temperatures with 1-minute dwell time.

Figure 4.7 shows XRD results for samples sintered at 1150°C, 1250°C and 1300°C. There was a clear presence of the Ti₂AlC phase and cBN in the samples sintered at 1150°C and 1250°C, and secondary phases present included TiC_a, TiN_b, TiB₂, Ti₃Al and TiAl₂. The content of N and C in the TiN and TiC fluctuated with increased in temperature (a=0.65 to 1 and b = 0.9 to 1). The TiC peak shifted to the left with increase in C in the phase, and the TiN peak shifted to the

right with the increase of N in the phase. The TiC_xN_y phase observed at temperatures above 1250°C also displayed similar trends. The peak shifted to the right with increase in N and to the left with increase in the C. It was also observed, from this XRD analysis (Figure 4.7), that Ti_2AlN was present in these samples.

In this study it was observed that the thermodynamically favourable phases were Ti_3Al , TiAl_2 and TiAl_3 . Both the TiAl_2 and TiAl_3 showed varying, non-stoichiometric, fractions of the Al in the system with changing temperature. The respective peaks shifted to the right with a decrease in the Al in each phase. A crude estimation of the phase development at different temperatures was made using the relative peak intensity ratio of the phase of interest compared to the other phases. A more detailed analysis, Rietveld, was used in the optimisation study in Sections 4.2 onwards, where phase quantification was more crucial. Using this method, it was found that TiAl_2 occurs as one of the major phases as a result of the exothermic reaction at 680°C (Figure 4.5). This phase then decreased with increase in temperature and finally depleted at 1300°C (Figure 4.7), with the same trend observed with Ti_3Al . TiAl_3 , however, was initially one of the minor phases (Figure 4.5) and remained even after the reaction at 1300°C .

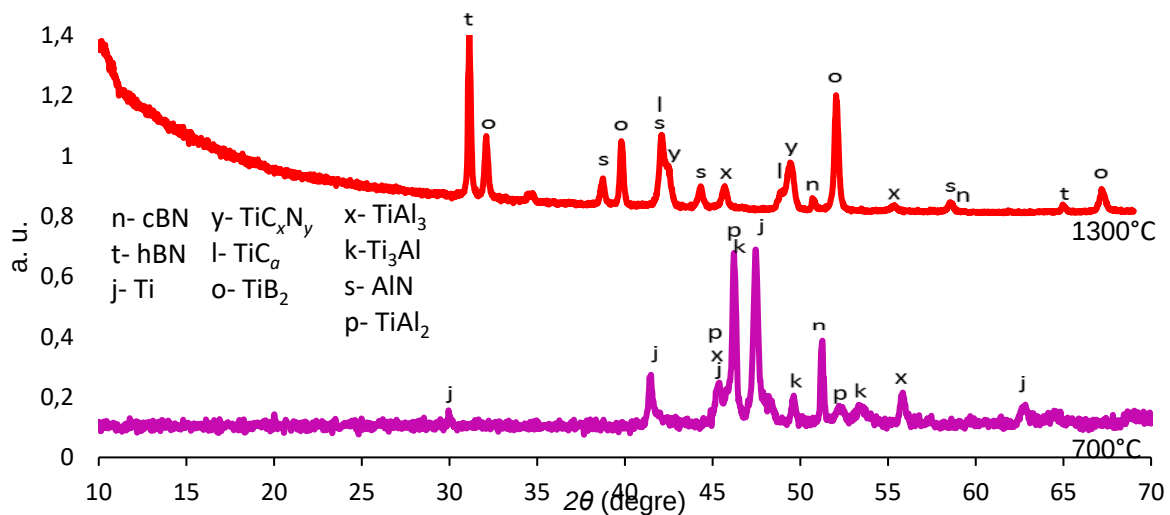


Figure 4.5: XRD traces of Ti_2AlC -cBN (20 vol.%, 10 μm) samples sintered at 30 MPa for 1 min and different temperatures (700°C and 1300°C).

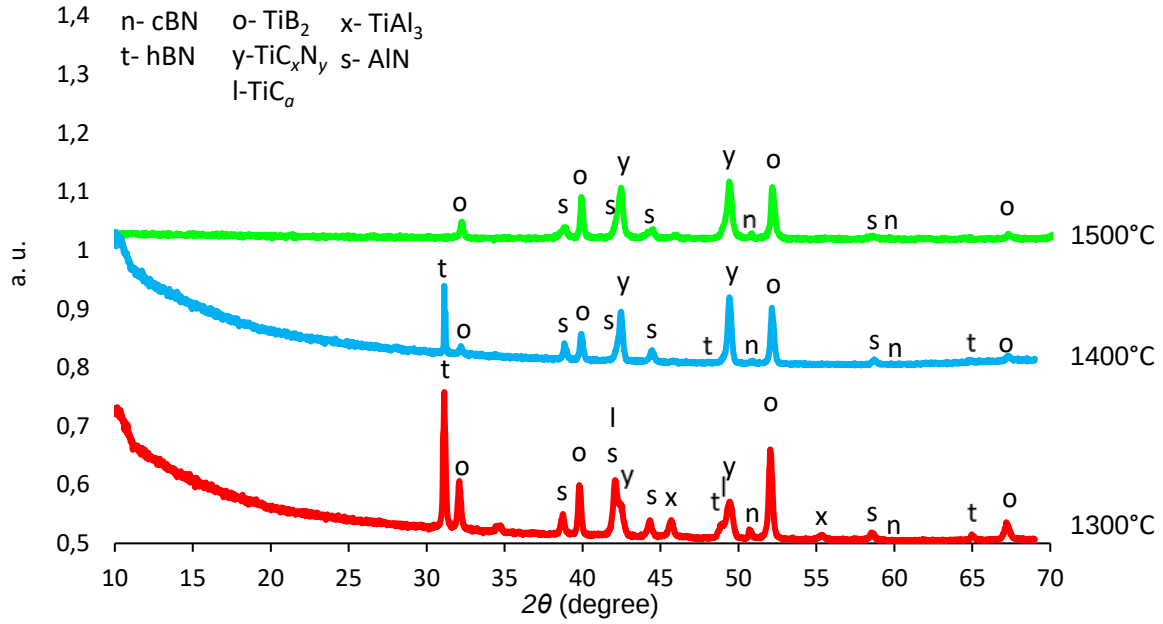


Figure 4.6: XRD traces of Ti_2AlC -cBN (20 vol.%, 10 μm) samples sintered at 30 MPa for 1 minute and different temperatures (1300°C to 1500°C).

The formation of both the Ti_2AlC and Ti_2AlN phases occurred in this study (Figure 4.7), with both phases present at 1150°C, along with TiN, TiC and Ti-Al intermetallics. However, the formation of Ti_2AlN was limited by the available hBN, thus Ti_2AlC formed more extensively as there was a higher content of C. Both these phases increased with increased temperature, Figure 4.7, until 1250°C. At low angles, the XRD peaks of Ti_2AlC and Ti_2AlN coincide because of the similar structure and chemical makeup. However, at higher angles (46/47° and 63/64°) the peaks start to be separate, but still close forming broad peaks with a shoulder if the two MAX phases are present in the sample (Figure 4.7).

The exothermic reaction at 1300°C caused a $\text{cBN} \rightarrow \text{hBN}$ transformation and the decomposition of both Ti_2AlC and Ti_2AlN . This forms TiC_xN_y , AlN and more TiB_2 . The TiC and TiAl_3 still remain in the system from 1300°C. In this case, unlike for temperatures below

1300°C, there was an excess of hBN observed in the composites which reduced and was finally depleted as Ti forms the N and B phases.

Figure 4.8 shows the SEM-BSE images of the samples sintered at 1250°C, 1300°C, 1400°C, and 1500°C. The images confirm the XRD results, in Figure 4.6 and 4.7 that the cBN quantities decreased with increased temperature. The hexagonalisation of cBN occurred from the surface of the cBN and migrated inwards, indicating the shrinking core model for the transformation of cBN to hBN. This was observed from the outline of the reaction area, which was the original outline of the cBN (red circles, Figure 4.8) staying constant at approximately 10 µm throughout all samples. The outline of the actual cBN after the hexagonalisation was some distance from the original position (indicated by the blue circles, Figure 4.8).

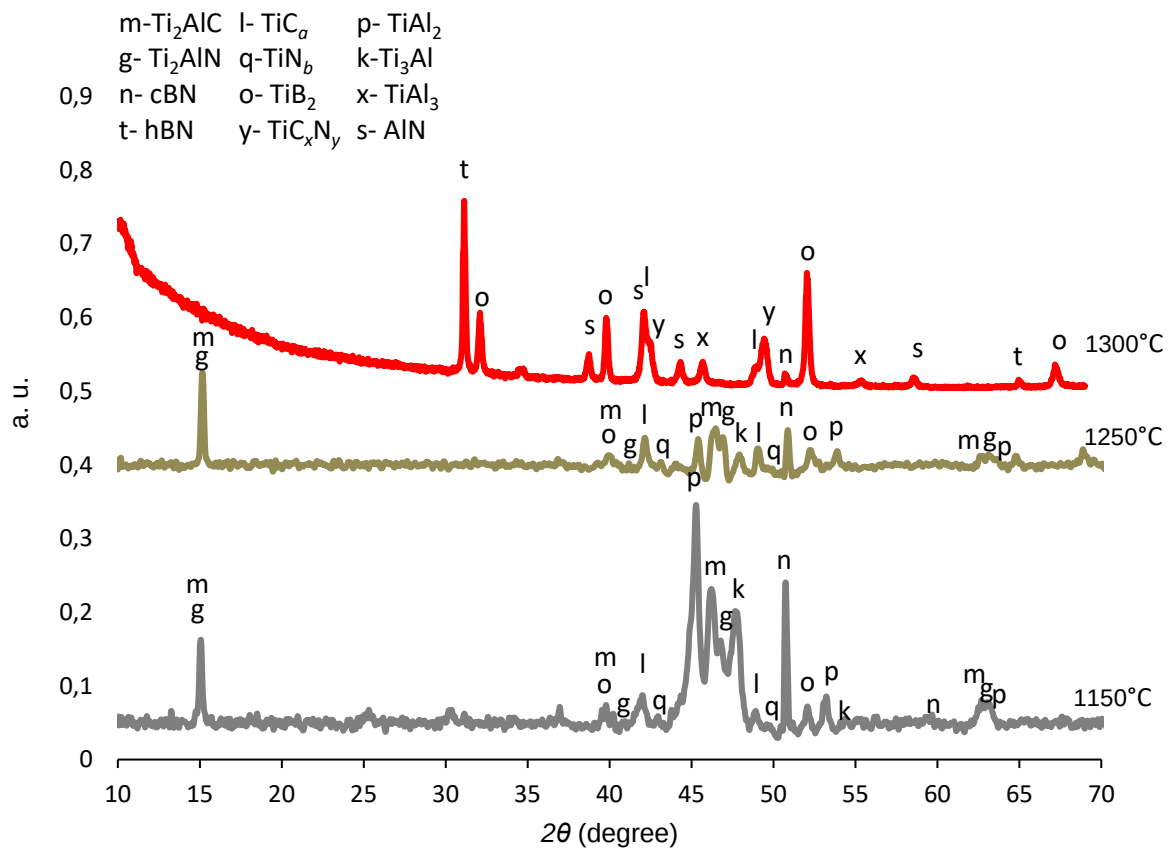


Figure 4.7: XRD traces of Ti_2AlC -cBN (20 vol.%, 10 µm) samples sintered at 30 MPa, 1 minute and different temperatures (1150°C to 1300°C).

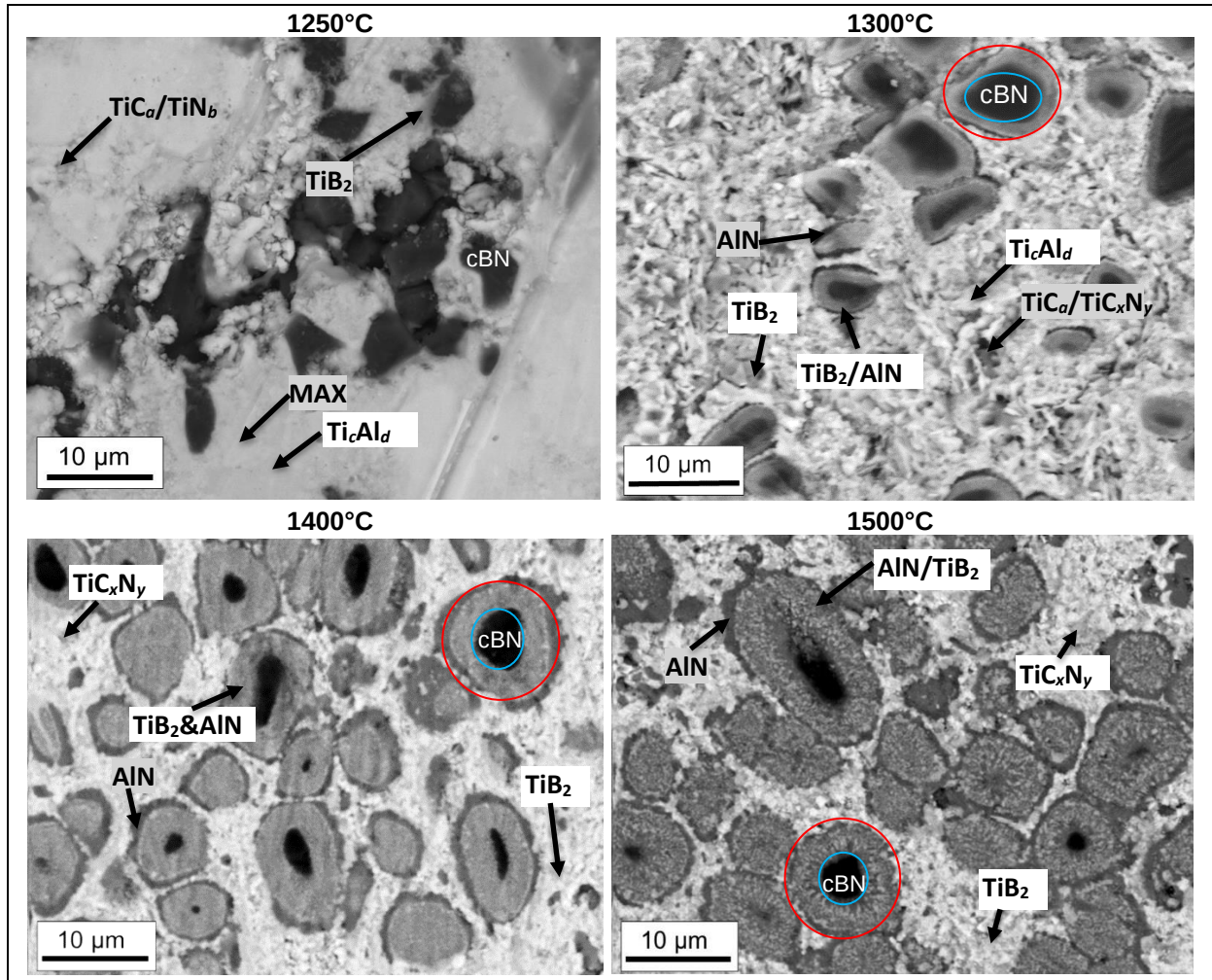
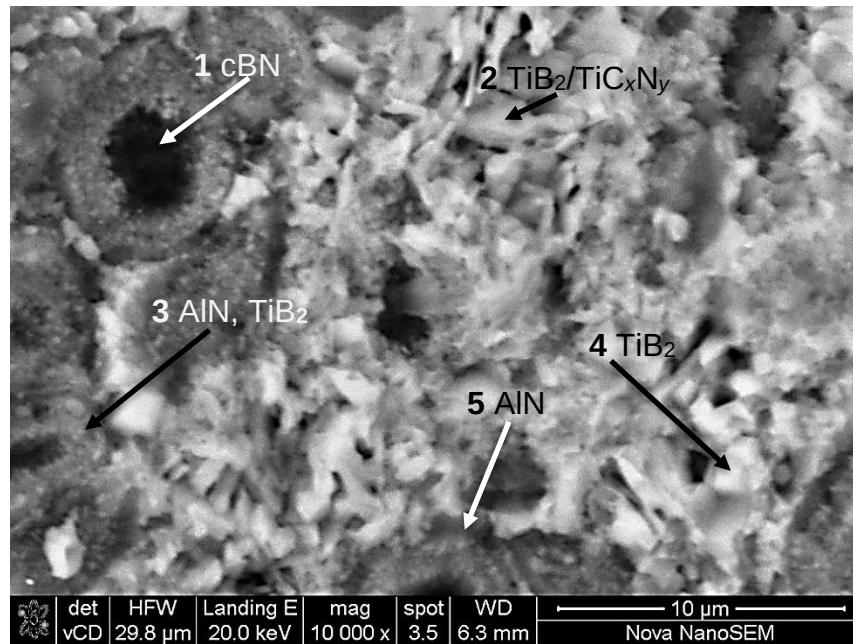


Figure 4.8: SEM (BSE) images of Ti_2AlC -cBN (20 vol.%, 10 μm) samples sintered at 30 MPa for 1 minute and different temperatures. The blue and red circles indicate the reaction area, between the two, occurring from reaction of cBN with MAX phase.

The sample sintered at 1250°C had no apparent reaction area (Figure 4.8), and therefore the cBN original size was the same as the outline after sintering. This looked like there may not have been any reaction between cBN and the MAX phase. However, from the XRD scans in Figure 4.7, it was observed that some of the secondary phases included TiN_b and TiB_2 which indicate that the cBN phase has participated in some reactions. The likely reason for the observation would be that the reaction area was very thin and was not readily apparent from the SEM images. The reaction area width (between the blue and red circle), thereafter, increased with increased temperature, it started at $\sim 1\ \mu\text{m}$ at 1300°C, then $\sim 3\ \mu\text{m}$ and finally $\sim 3.5\ \mu\text{m}$ at 1500°C. The different phases that occurred in the matrix, are shown as different

shades of grey (and assigned with XRD analysis phase present in each sample), seen after sintering at temperatures above 1300°C and are generally less than 1 µm. This may be due to the FAST (SPS) method facilitating the sintering times as low as 1 minute.

Figure 4.9 shows the EDX analysis of the sample sintered at 1500°C for 1 minute. This was done in order to determine the distribution of the secondary phases given by XRD analysis. The error associated with the given EDX data was significantly high for some elements found in the measurements made per phase. Therefore, ten or more measurements were made for phases that look similar, and 5 of those that gave the lowest standard deviation were reported. This still resulted in high errors in some cases, such as those in Site 2 where N varies from 1,2 to 30,8 at.%. However, the EDX analyses was useful for evaluating where some elements were concentrated. For example; Al, N, more concentrated in the sites near cBN (Sites 3 and 5) and Ti, B were seen near the cBN (Site 3) and in the matrix (Sites 2 and 4). This proved the migration of certain element during the reaction of cBN and the MAX phases. The assignment of the specific phases to each site was done using XRD results of the present phases, EDX analysis and the principles of SEM-BSE images with different contrasts indicating electron densities of different elements withing the phases. The sample sintered at 1500°C was analysed because the secondary phases in this sample are more pronounced. The EDX was taken with a beam intensity of 20keV because the sample was thick. However, because of the small sizes of the phases analysed, the beam could also have picked up the x-ray signals reflected from the neighbouring and/or underlying phases. The level of C was also observed to be high even in phases that were not expected to contain C (such as cBN), thus the presence/content of C in each scan was cautiously considered. There was only one phase containing Al in the sample analysed in Figure 4.9 as seen in the XRD analysis of the samples, Figure 4.7. This phase is AlN, and since it occurs in small proportions, this suggests that some Al evaporated out of the system during sintering.



		B	C	N	Al	Si	Ti	Total
	atomic %							
site 1	average	46,0	19,4	34,0	0,5	0,0	0,1	100,0
	std deviation	6,8	12,8	6,6	0,3	0,0	0,1	
site 2	average	40,9	32,3	16,0	3,5	0,1	7,1	100,0
	std deviation	1,1	13,1	14,8	1,1	0,2	2,1	
site 3	average	52,3	15,5	21,7	6,8	0,0	3,6	100,0
	std deviation	4,1	3,7	3,6	0,2	0,0	0,2	
site 4	average	40,8	46,1	0,0	0,6	0,1	12,4	100,0
	std deviation	4,2	6,1	0,0	0,4	0,2	2,3	
site 5	average	50,7	13,8	24,2	7,6	0,0	3,8	100,0
	std deviation	2,9	1,2	3,5	1,8	0,0	1,5	

Figure 4.9: EDX analysis of Ti_2AlC -cBN (20 vol.%, 10 μm) sample sintered at 30 MPa, 1 minute and 1600°C.

Site 1 was observed to be cBN as expected since B and N both have low densities and the presence of the other elements may be due to the cBN size being so small ($\sim 3\mu\text{m}$) the beam could have picked up elements from the surrounding phases. Site 2 displayed more Ti, Al, N, C and B which could come from the TiB_2 and/or TiC_xN_y phases. The observed B may be due to a nearby cBN (in addition to N present) as a result of the teardrop effect of the incident beam, also some AlN could have been picked up as AlN surrounds the reaction area around

the cBN. Sites 3 and 5 containing more Al than Ti, this could be where the AlN was found. This is not unlikely as AlN was determined to be present in samples sintered at 1300°C and above (Figures 4.6 and 4.7). The phases in and around the reaction area were only observed in samples sintered at and above 1300°C (Figure 4.8). The Al was the first to leave the Ti_2AlC layered structure to form migrating towards the BN to form AlN (Site 5). The two different contrasts observed in the reaction are likely to be TiB_2 and AlN (Site 3), with a possible contribution from cBN. Site 5 is more likely to contain only AlN with the x-rays from the nearby TiB_2 and BN picked up as well. Site 4 displays high contents of Ti, B and C. This could not be TiC_a in the sample as Figure 4.6 shows that TiC_a was not present in the sample and could not be TiC_xN_y as there was no N to pick up. This was possibly only TiB_2 with other elements picked up from the x-rays of the neighbouring phases. These results suggest that Al migrates towards the BN, and the B would migrate to react with the Al deficient MAX phase to form TiB_2 and TiC_a . However, there was also a presence of B within the reaction area (Site 3), and a little N in the matrix as well (Site2).

The reaction temperature evaluations showed that the optimisation of the Ti_2AlC – cBN composite would be at 1250°C since there was more Ti_2AlC in the system and no hBN observed (Figure 4.7).

4.1.2 Ti_3AlC_2 -cBN composites

In this section the reactivity of Ti_3AlC_2 and BN were considered. Since the elements in Section 4.1.1 were the same as those under investigation in this section, Ti-Al-C, similar reaction trends were expected to be similar. The differences that might occur would be due to the excess Ti and C in this case. Therefore, in this section the similarities as discussed in Section 4.1.1 will just be noted and the differences elaborated upon.

Figure 4.10 shows the sintering profiles of the Ti_3AlC_2 -cBN composites from the SPS sintering runs obtained for different temperatures. Figure 4.10a shows the densification curves (traces at the bottom of the graph) and Figure 4.10b shows SPS traces indicating reaction temperatures of the Ti_3AlC_2 -cBN composites.

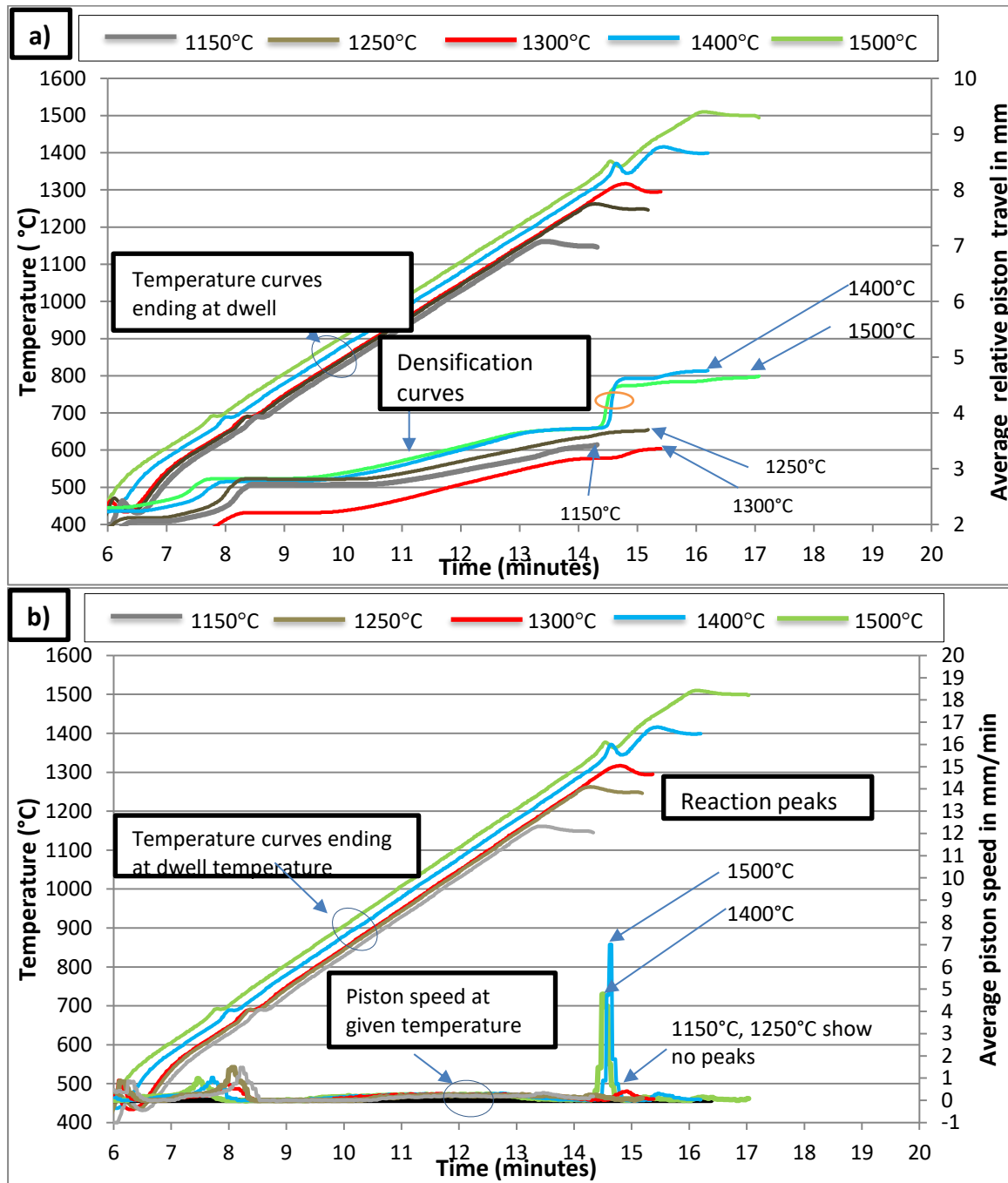


Figure 4.10: Ti_3AlC_2 -cBN (20 vol.%, 10 μm) curves from the SPS runs at 1 min and different temperatures. a) Piston displacement curves and b) Piston displacement time derivative curves.

The densification curves and the reaction curves observed in Figure 4.10 were offset on the x-axis in order to clearly see the behaviour of the different curves as the temperature was increased. Figure 4.11 shows the resulting densities of the samples sintered at the respective temperatures in the SPS furnace. The densification behaviour in Figure 4.10a was similar to those observed for Ti_2AlC composites. The endothermic melting of Al (660°C) followed by a simultaneous exothermic formation of Ti-Al intermetallics was also observed. There were two exothermic peaks observed, one at $\sim 680^\circ\text{C}$ with $T_{\text{onset}} 660^\circ\text{C}$ and $T_{\text{offset}} 686^\circ\text{C}$, and a second larger peak at $\sim 1350^\circ\text{C}$. In these composites, the second exothermic peak occurred at 50°C higher than that noted in the Ti_2AlC system, Figure 4.3.

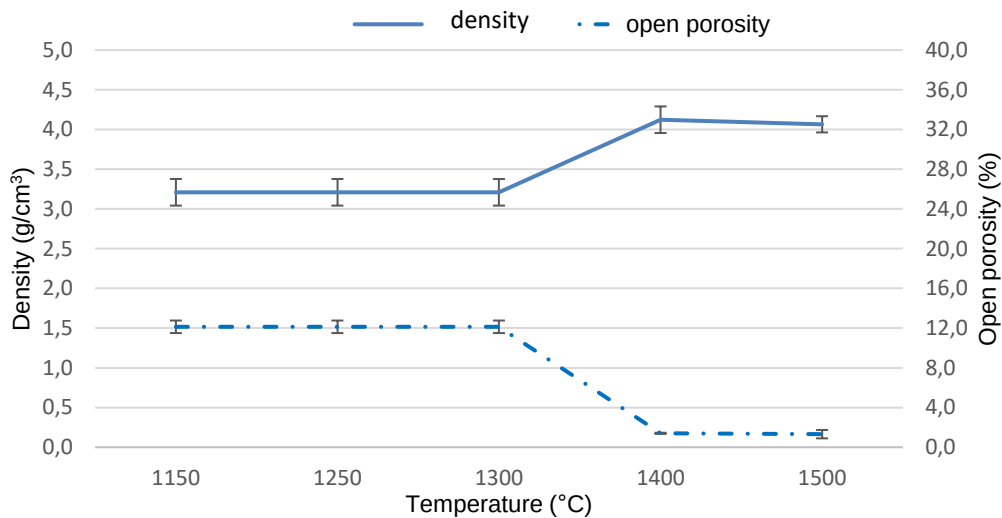


Figure 4.11: Densities and open porosities of $\text{Ti}_3\text{AlC}_2\text{-cBN}$ (20 vol.%, 10 μm) samples sintered at different temperatures with 1 minute dwell time.

Figure 4.11 shows the densities of the samples sintered as shown in Figure 4.10, the densities evaluated here had some variations in the average densities and open porosity which would indicate that there were problems with the scale that was used to measure the different masses, the likely problem would be the stability of the scale as these scales were calibrated on a regular basis. However, the variations are within 5 % of the indicated averages which were statistically acceptable. This was observed for every sample except the open porosity measured for the sample sintered at 1500°C . In Section 4.1.1, it was observed that the density

generally increased with increase in sintering temperature. In this section the density of the samples remained the same ($\sim 3.2 \text{ g/cm}^3$), with a sudden increase above the reaction temperature ($\sim 4.2 \text{ g/cm}^3$) and stayed the same again thereafter. The open porosity displayed the opposite, decreasing (12 % to 1.4%) after the exothermic peak (1350°C).

Figure 4.12 shows the XRD diffractograms of the Ti_3AlC_2 -cBN composites sintered just above the two exothermic reaction temperatures observed in Figure 4.10, 700°C and 1360°C . It was observed that, as in the Ti_2AlC -cBN composites, the resultant phases from the two SPS reaction peaks are the same. Ti, cBN, TiAl_2 , TiAl_3 and Ti_3Al from the reaction at 660°C ; and TiC_a , TiC_xN_y , TiB_2 , AlN , cBN and hBN from the reaction at 1350°C (1300°C for Ti_2AlC -cBN composites). The difference in this case was the amount (only estimated from the relative intensity of the phases) of the present phases.

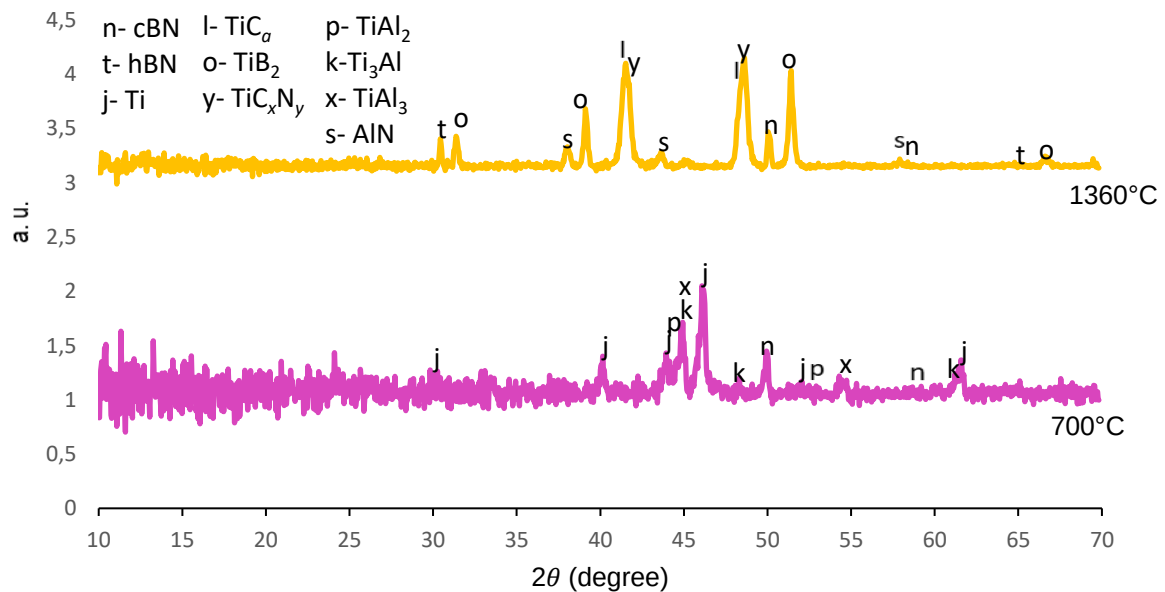


Figure 4.12: XRD traces of Ti_3AlC_2 -cBN (20 vol.%, 10 μm) samples sintered at 30 MPa for 1 minute and different temperatures (700°C and 1360°C).

In the Ti_2AlC -cBN composites the second reaction peak (Figure 4.3b) was twice that of the Ti_3AlC_2 -cBN composites (Figure 4.10b). This indicated that the increase in temperature during this reaction in the Ti_3AlC_2 -cBN composites was not as much as in the Ti_2AlC -cBN composites.

Thus, the Ti_3AlC_2 -cBN composites resulted in less hBN formation. In addition, because of the higher Ti-C content in the Ti_3AlC_2 -cBN composites, more TiC_a was also observed in the system under investigation.

Figure 4.13 shows the XRD analysis of the Ti_3AlC_2 -cBN composites sintered from 1300°C to 1500°C. It was found that the phase content was the same for Ti_3AlC_2 -cBN composites and Ti_2AlC -cBN composites. Even though in this case the molar ratio of the T-Al-C powders was 3:1:2 instead of 2:1:1, Ti_2AlC was still found in the current composites instead of Ti_3AlC_2 . For the same reasons given in Section 2.1.1, Ti_2AlN was also found in these samples. Also, the excess hBN formed also decreased with increased temperature above 1250°C. The other notable difference observed in this system was the complete lack of the TiAl_3 at elevated temperatures (Figure 4.14).

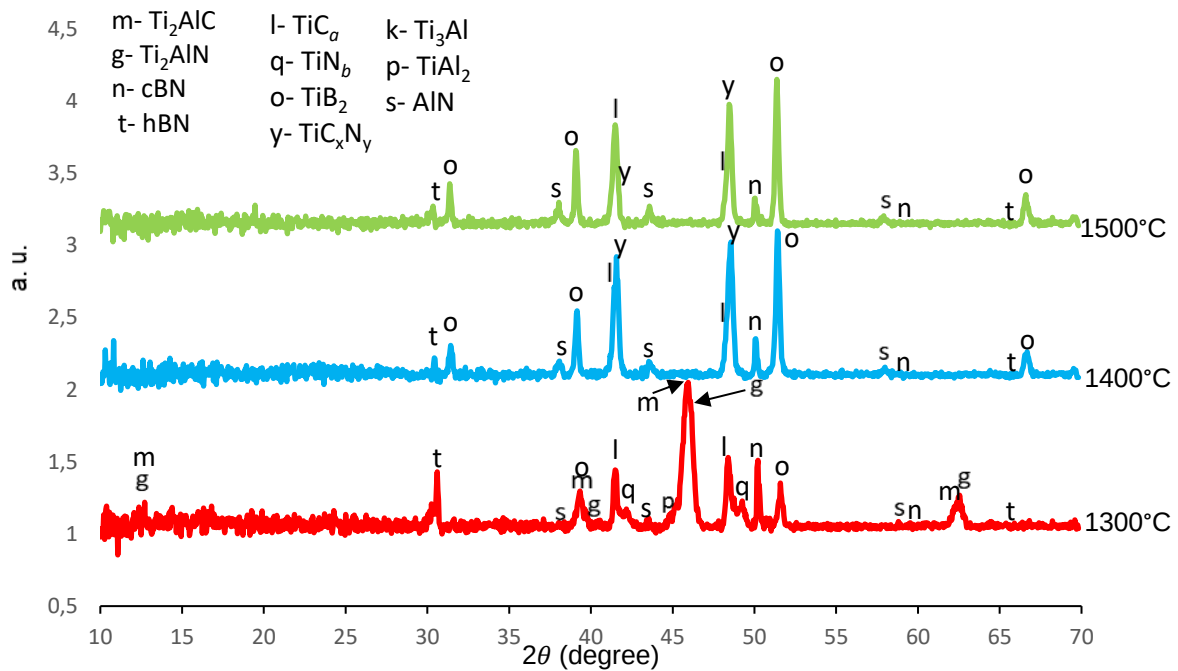


Figure 4.13: XRD traces of Ti_3AlC_2 samples sintered at 30 MPa for 1 minute and different temperature (1300°C to 1500°C).

Figure 4.15 shows the SEM BSE images of the samples sintered at 1250°C, 1300°C, 1400°C, and 1500°C for 1 minute. The images confirm the XRD results in Figure 4.13 and 4.14 that the cBN (indicated with the red/blue circles) decreased with increase in sintering temperature but was still present up to 1600°C. Similar to the Ti_2AlC system, the $\text{cBN} \rightarrow \text{hBN}$ transformation occurred at the surface of the cBN (red circle, Figure 4.15) and continued inwards with an increase in temperature (blue circle, Figure 4.15). The only difference observed in the SEM images of the two systems was that the reaction area was only observed in samples sintered above 1300°C, which resulted due to the reaction in this case only having occurred at 1350°C. The phases present and their distribution were also observed to be similar to those found in the Ti_2AlC composites. This was not unexpected since the formed MAX phase in these composites was Ti_2AlC instead of the expected Ti_3AlC_2 .

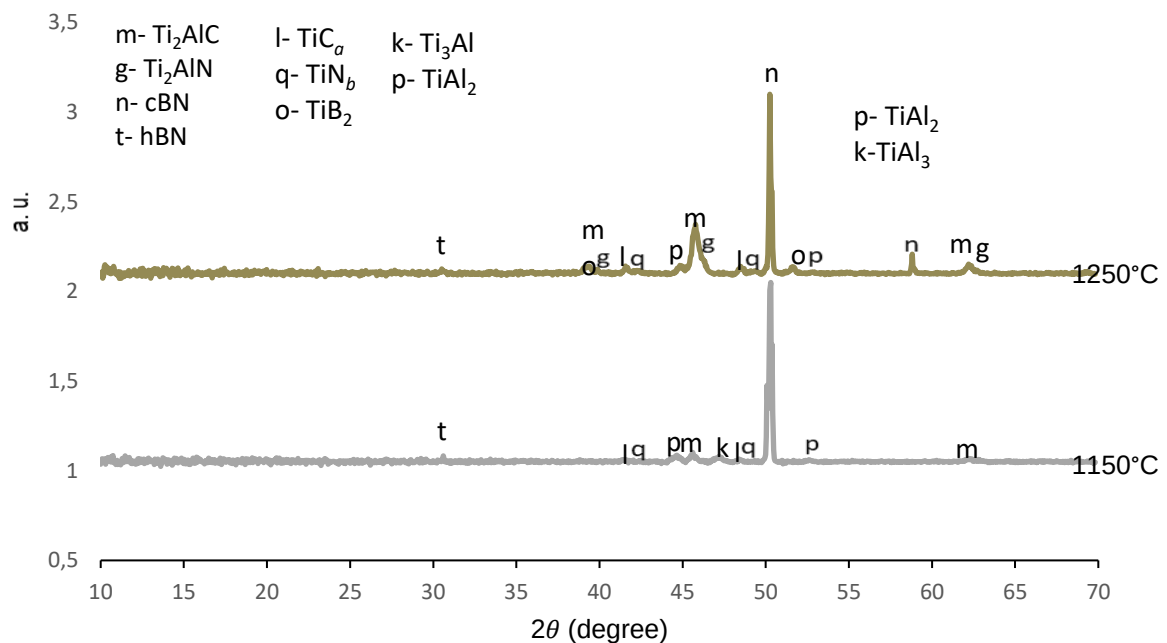


Figure 4.14: XRD traces of Ti_3AlC_2 -cBN (20 vol.%, 10 μm) samples sintered at 30 MPa for 1 minute and different temperature profiles (1150°C and 1250°C).

Figure 4.16 shows the EDX analysis of the sample sintered at 1500°C for 1 minute used to ascertain the secondary phases and their distribution in the sample. The composition distributions in these samples were significant, which signifies that the analysis of one phase

in this case was not very accurate as the variation can be due to detected x-rays from neighbouring phases. Thus, the analysis was considered with caution and the same challenges experienced in the EDX analysis of Ti_2AlC -cBN composites (section 2.1.1) were experienced in the Ti_3AlC_2 system. The resultant secondary phases in this case were found to be about $1\text{ }\mu\text{m}$ or less (Figure 4.16), which was a result of the lowered extent of thermal exposure using the SPS method. This prevented grain growth and resulted in a fine-grained composite. This was the desired outcome but presented a problem for EDX analysis, as analyses of phases $2\text{ }\mu\text{m}$ or less results in high errors and should be considered with caution. In these composites, as in section 2.1.1, the EDX analysis is more useful in identifying the migration of different elements, such as Al in the reaction phase near the cBN and B in the matrix.

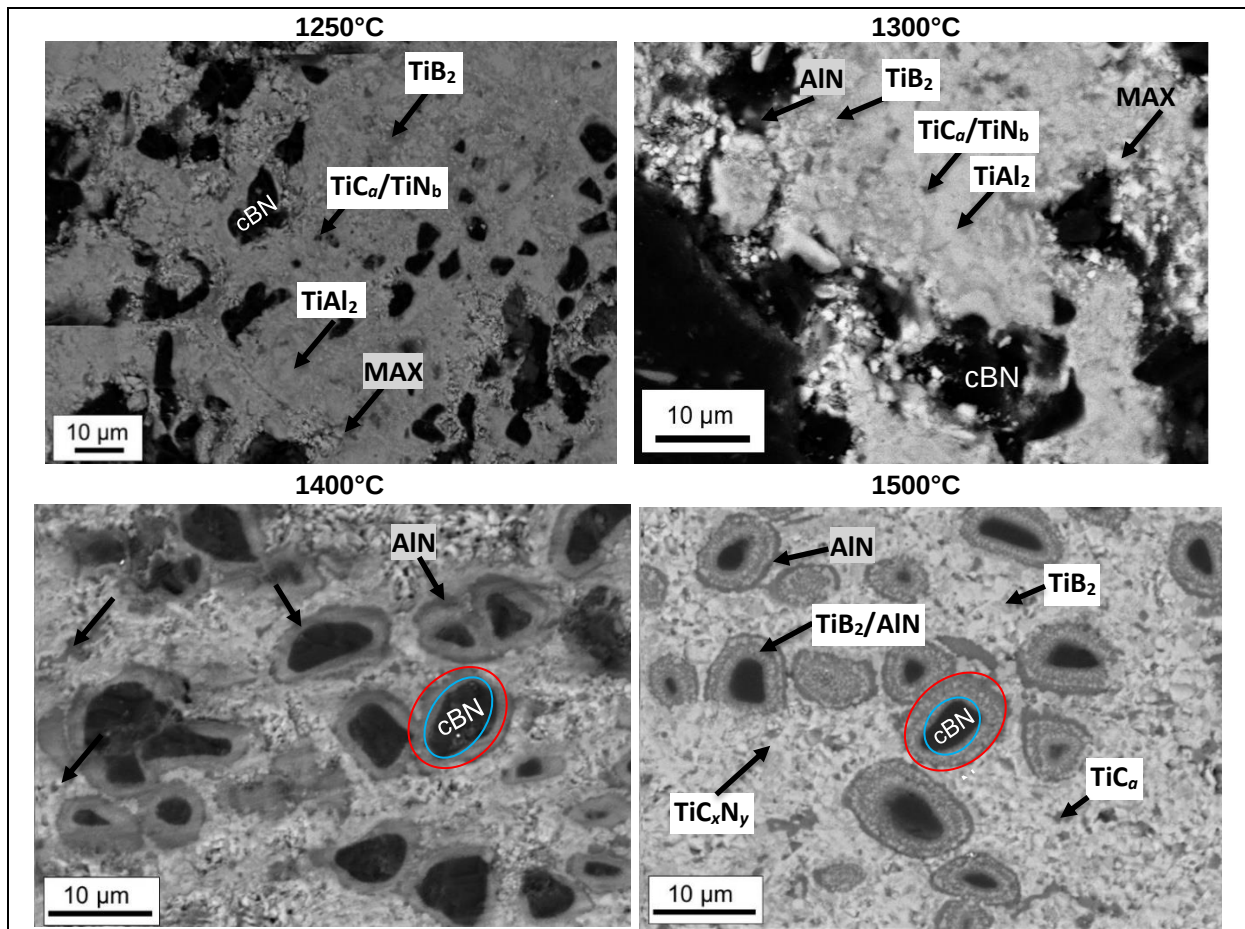
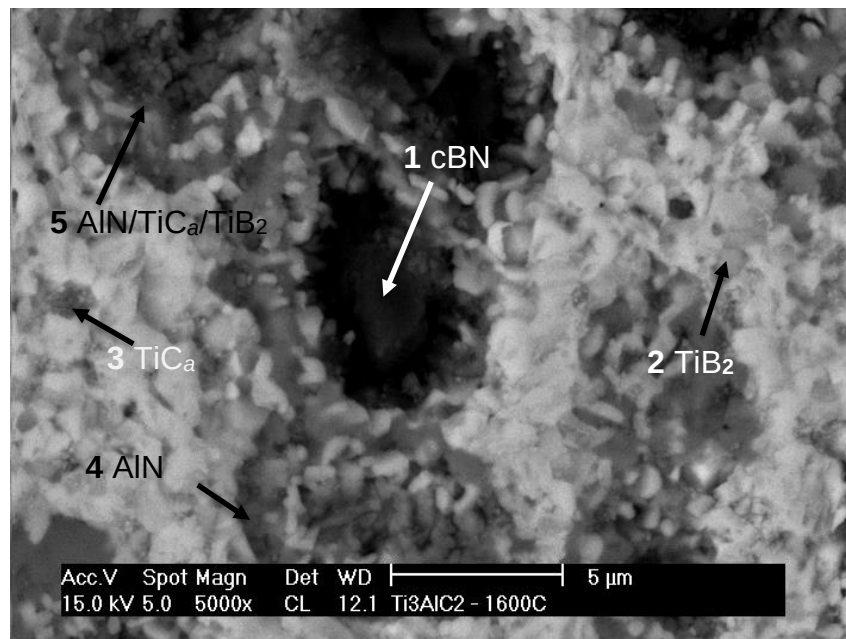


Figure 4.15: SEM (BSE) of Ti_3AlC_2 -cBN (20 vol.%, 10 μm) samples sintered at 30 MPa, 1 minute and different temperatures.



		B	C	N	O	Al	Si	Ti	Total
		atomic %							
site 1	average	50,2	8,4	32,1	0,6	5,7	0,0	3,0	100,0
	std deviation	8,0	7,3	13,6	1,3	4,3	0,0	2,8	
site 2	average	22,8	41,5	0,0	11,3	2,2	0,0	22,1	100,0
	std deviation	18,8	6,3	0,0	16,5	1,6	0,1	16,5	
site 3	average	15,7	35,5	0,0	12,5	2,0	0,2	34,1	100,0
	std deviation	19,6	12,5	0,0	15,8	1,2	0,2	14,8	
site 4	average	24,3	32,3	6,8	0,0	5,6	0,1	30,9	100,0
	std deviation	21,0	16,0	13,6	0,0	4,6	0,2	24,1	
site 5	average	29,1	20,9	19,9	1,3	6,4	0,1	22,4	100,0
	std deviation	24,5	16,8	17,1	1,7	2,7	0,1	24,5	

Figure 4.16: EDX analysis of Ti_3AlC_2 -cBN (20 vol.%, 10 μm) samples sintered at 30 MPa, 1 minute and 1600°C.

Similar to the Ti_2AlC -cBN system, AlN and TiB_2 were found closer to the cBN, Sites 4 and 5. Site 1 shows the presence of BN, there were other elements detected and the proportion of B to N was not 1:1 indicating that the x-rays from surrounding phases were also picked up. TiB_2 and TiC_α were found in the matrix, Site 2 and 3 respectively. In the case of excess Ti and C in

Site 2, this could be the x-rays from neighbouring phases, this was similar to Site 3 containing TiCa, the Ti and C ratios coincided, thus the other elements may have also resulted from the neighbouring phases. Site 4 contained AlN, TiC_a and TiB₂, it is likely that this site is AlN as there is only one contrast which implies it is most likely AlN. Site 5 showed some AlN, TiB₂ and TiC_a, thus it is likely that all of these phases are present in the reaction area as there are 3 contrasts seen. There is some evidence of cBN, however, this may be due to the cBN being so near to this site that the cBN x-rays were also picked up. In these composites, it was also observed that the reactivity of the phases resulted in the migration of the Al, out of the Ti-Al-C phase towards the BN (hence the AlN layer outlining the reaction area around the BN). Some TiB₂ and TiC_a were also found in the reaction area indicating that the Ti would also migrate inwards when there was a deficiency of Al in the Ti₂AlC structure.

4.1.3 Ti₃SiC₂-cBN composites

Figure 4.17 shows the sintering profiles of the Ti₃SiC₂-cBN composites from the SPS sintering runs obtained for different temperatures. Figure 4.17a shows the densification curves (traces at the bottom of the graph) and Figures 4.17b shows SPS traces indicating reaction temperatures of the composites. Figure 4.19 and 4.20 show the XRD diffractograms of the Ti₃SiC₂-cBN composites sintered at different temperatures shown in Figure 4.11.

Figure 4.17a shows that the 1150°C, 1250°C, 1300°C and 1400°C curves do not have the approximate 1 mm increase (orange circle) after 15 minutes; this only occurred for samples sintered at 1500°C and above. This sudden increase was attributed to the reaction observed in Figure 4.17b, reaction peaks indicated. This indicated the degradation of the MAX phase and reduction of the cBN as seen in Figure 4.19.

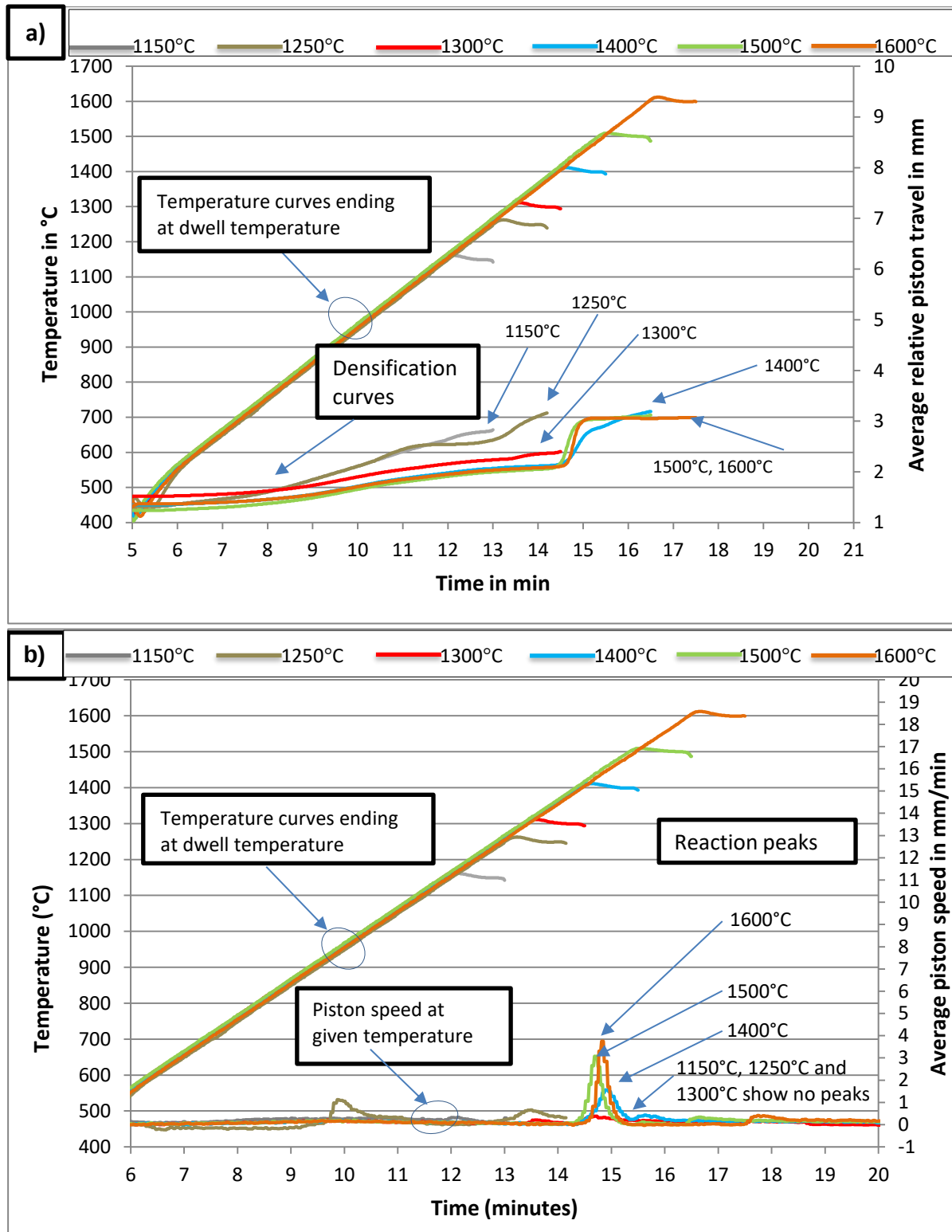


Figure 4.17: $\text{Ti}_3\text{SiC}_2\text{-CBN}$ (20 vol.%, 10 μm) densification curves from the SPS experiments for the different temperatures.

For the samples sintered at 1500°C and above, the trace was a flat line after the 1 mm increase, Figure 4.17a. This indicates that the pistons of the SPS machine (during sintering)

were no longer moving relative to each other and that the samples had reached relative full densification. The samples sintered at 1150°C, 1250°C, 1300°C and 1400°C showed the opposite, indicating full densification had not yet been reached, Figure 4.17a. Figure 4.17b shows that for all sintering temperatures there was a peak at around 1400°C, this exothermic reaction correlates to the complete degradation of the MAX phase by reacting with cBN to form the secondary phases (Figure 4.20).

Figure 4.18 shows the density of the samples sintered in Figure 4.17. The error associated with the given average density was acceptable, however, the open porosity errors were large, but acceptable as they do not overlap. Figure 4.19 shows the XRD spectra of samples sintered from 1150°C to 1300°C.

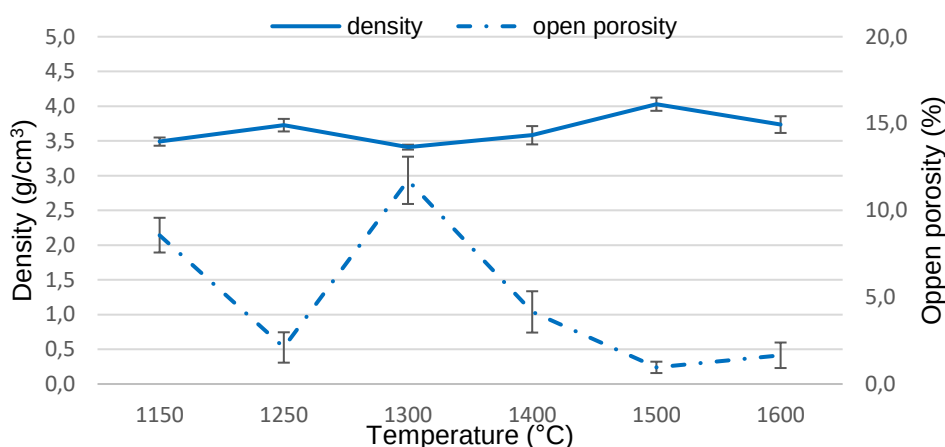


Figure 4.18: Densities and open porosities of Ti_3SiC_2 -cBN (20 vol.%, 10 μm) samples sintered at different temperatures with 1-minute dwell time.

As observed in Figure 4.18 that the density of the samples remained similar ($\sim 3.6 \text{ g/cm}^3$), an increase was observed (to $\sim 3.9 \text{ g/cm}^3$) in samples sintered at 1400°C and above. The exception observed was for the composite sintered at 1600°C which displayed a decrease in the density. This was corroborated by the densification curves in Figure 4.17, where the samples sintered at 1400°C and above displayed an approximate 1 mm increase at 1400°C.

In the case for the Ti_3SiC_2 system under investigation here, an increase in the chamber temperature was not observed as in the Ti-Al-C systems.

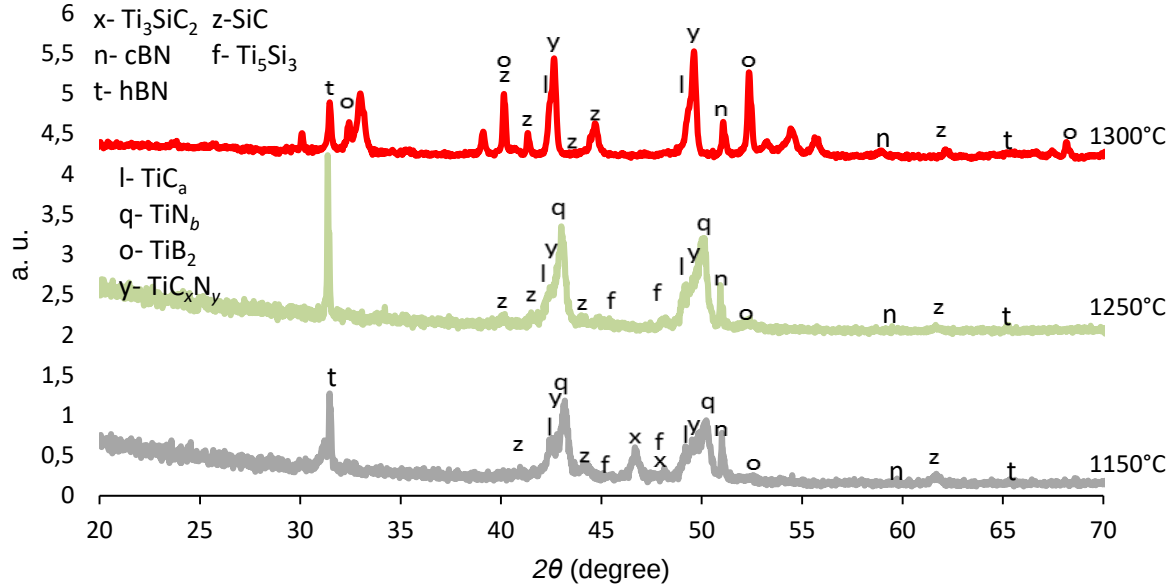


Figure 4.19: XRD traces of Ti_3SiC_2 -(20 vol.% of 10 μm) cBN samples sintered at 30 MPa, 1 minute and different temperatures (1150°C to 1300°C).

As seen in Figure 4.19, Ti_3SiC_2 was only seen in the sample sintered at 1150°C, whereas cBN was seen in all samples. Also present, in significant quantities, were TiC_a , TiC_xN_y , and TiN_b phases in all samples up to 1400°C, with TiC_xN_y remaining even at 1600°C. All samples had hBN, with samples sintered at 1250°C (Figure 4.19) to 1400°C (Figure 4.20) having a significant amount. As observed in Figures 4.19 and 4.20, increasing the temperature increased SiC and TiB_2 secondary phases whereas Ti_5Si_3 was only found in samples sintered at 1150°C and 1250°C. An evaluation of the reactivity of the BN phase with Ti_3SiC_2 (Table 4.1) and with Ti (Table 4.2) was done using a thermodynamic assessment program. Table 4.1 shows that the reaction of the Ti_3SiC_2 phase with BN was not thermodynamically favoured over the temperature ranges studies here (positive Gibbs free energies at all temperatures used). However, the reaction of Ti with BN was favoured as shown by the large negative Gibbs free energies ranging from -440kJ to -390kJ (Figure 4.20).

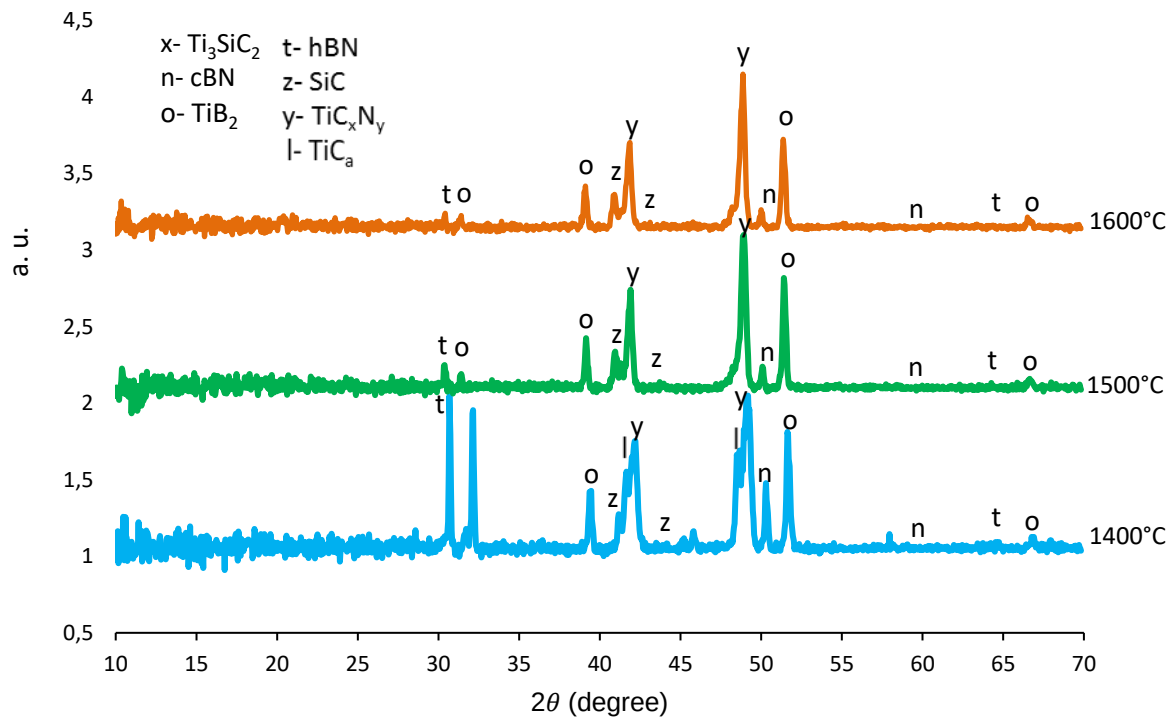
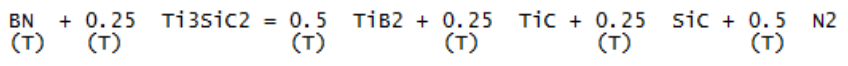


Figure 4.20: XRD traces of Ti_3SiC_2 -(20 vol.% of 10 μm) cBN samples sintered at 30 MPa, 1 minute and different temperatures (1400°C to 1600°C).

Table 4.1: Thermodynamic data obtained for the reaction of cBN with Ti_3SiC_2 .



BN(s-SGPS) Ti_3SiC_2 (s-SGTE) TiB_2 (s-SGPS) TiC (s-SGPS) SiC (s-SGPS) N_2 (g-SGPS)

T(C)	Delta_H(J)	Delta_G(J)	Delta_vol(litre)	Delta_S(J/K)	Delta_cp(J/K)	Delta_A(J) T
100.00	183958.3	153459.0	1.5310E+01	81.735	2.633	151907.8
200.00	184145.5	145259.1	1.9413E+01	82.186	1.125	143292.1
300.00	184178.6	137034.4	2.3516E+01	82.255	-0.517	134651.7
400.00	184036.3	128818.1	2.7619E+01	82.029	-2.300	126019.6
500.00	183723.6	120635.3	3.1722E+01	81.599	-3.913	117421.1
600.00	183262.8	112502.5	3.5824E+01	81.040	-5.258	108872.6
700.00	182680.4	104429.6	3.9927E+01	80.410	-6.352	100384.0
800.00	182000.7	96421.7	4.4030E+01	79.746	-7.211	91960.3
900.00	181245.8	88480.8	4.8133E+01	79.073	-7.848	83603.7
1000.00	180442.2	80606.5	5.2236E+01	78.416	-8.164	75313.7
1100.00	179616.5	72796.4	5.6339E+01	77.792	-8.339	67087.8
1200.00	178775.7	65047.0	6.0442E+01	77.201	-8.473	58922.7
1300.00	177922.7	57355.1	6.4545E+01	76.641	-8.584	50815.2
1400.00	177059.1	49717.9	6.8648E+01	76.109	-8.687	42762.2
1500.00	176198.2	42132.4	7.2750E+01	75.609	-8.508	34760.9
1600.00	175353.6	34594.9	7.6853E+01	75.145	-8.400	26807.7

Table 4.2: Thermodynamic data obtained for the reaction of cBN with titanium.
$$2 \text{ BN} + 3 \text{ Ti} = \text{TiB}_2 + 2 \text{ TiN}$$

(T) (T) (T) (T)

BN(s-SGPs) Ti(s-SGPs) TiB₂(s-SGPs) TiN(s-SGPs)

T(°C)	Delta_H°(J)	Delta_G°(J)	Delta_vol(litre)	Delta_S°(J/K)	Delta_cp(J/K)	Keq	T
100.00	-452355.7	-440583.8	0.0000E+00	-31.547	7.410	4.7062E+61	
200.00	-451527.6	-437528.7	0.0000E+00	-29.586	8.569	1.9995E+48	
300.00	-450739.3	-434651.2	0.0000E+00	-28.070	6.772	4.0870E+39	
400.00	-450228.3	-431891.3	0.0000E+00	-27.241	3.417	3.2566E+33	
500.00	-450055.8	-429183.6	0.0000E+00	-26.996	0.072	9.8914E+28	
600.00	-450200.4	-426478.1	0.0000E+00	-27.169	-2.872	3.2557E+25	
700.00	-450615.2	-423740.8	0.0000E+00	-27.616	-5.372	5.5471E+22	
800.00	-451258.4	-420949.0	0.0000E+00	-28.243	-7.432	3.0818E+20	
881.85	-451924.5	-418613.2	0.0000E+00	-28.841	-8.790	8.5353E+18	
881.85	-464434.5	-418613.2	0.0000E+00	-39.672	6.291	8.5353E+18	
900.00	-464319.9	-417894.1	0.0000E+00	-39.574	6.331	4.0394E+18	
1000.00	-463670.2	-413963.4	0.0000E+00	-39.042	6.694	9.6296E+16	
1100.00	-462990.2	-410085.0	0.0000E+00	-38.528	6.855	3.9742E+15	
1200.00	-462309.8	-406256.5	0.0000E+00	-38.050	6.699	2.5386E+14	
1300.00	-461661.0	-402473.3	0.0000E+00	-37.624	6.223	2.3085E+13	
1400.00	-461078.1	-398729.5	0.0000E+00	-37.264	5.360	2.8039E+12	
1500.00	-460601.6	-395017.7	0.0000E+00	-36.987	4.109	4.3292E+11	
1600.00	-460268.9	-391329.0	0.0000E+00	-36.804	2.480	8.1718E+10	

Figure 4.21 shows the SEM BSE images of the samples sintered at 1250°C, 1300°C, 1400°C, and 1500°C for 1 minute. The images were not a good indicator to confirm the XRD results in Figure 4.19 and 4.20 that the cBN quantities decreased with increased sintering temperature, the surface of the BN phase shown here might be the hBN, but this could not be confirmed with SEM as the SEM BSE method cannot differentiate between the two BN phases.

There was no clear reaction area observed in these samples as observed in the Ti-Al-C systems. However, the sample sintered at 1250°C for 1 minute looked a different in the area around BN phase (between the red and blue outlined, Figure 4.21) and the matrix. This was assumed to be the reaction area, since it was discussed in Section 4.1.1 that the hBN formation occurs at the surface of the cBN, and this was where the formation of the B and N phases would first occur. The estimated reaction area was shown between the red and blue circles, and it seemingly did not change with increase in temperature. In addition, in the Ti₃SiC₂-cBN composites the phase contrasts were not as clear as the Al based MAX-cBN composites. For example, there are 8 phases in the XRD result for the sample sintered at 1250°C, but these

phases cannot be easily recognised by contrast in the SEM-BSE images (Figure 4.21). Thus, phase assignment with the XRD results and contrast input method cannot be used effectively in this case.

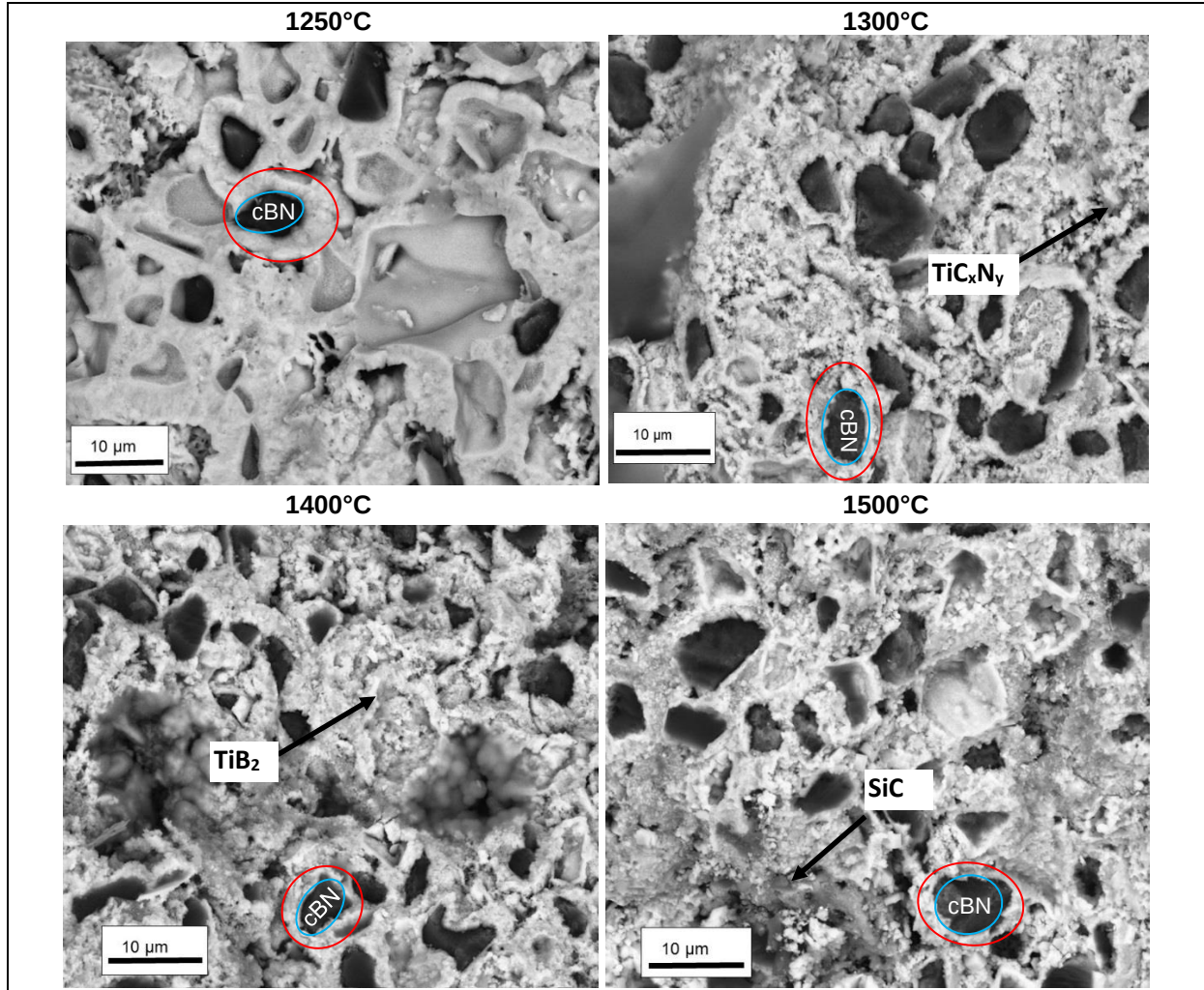


Figure 4.21: SEM (BSE) of Ti_3SiC_2 -cBN (20 vol.%, 10 μm) samples sintered at 30 MPa, 1 minute and different temperatures.

Figure 4.22 shows the EDX analysis of the sample sintered at 1600°C for 1 minute to ascertain the secondary phases and their distribution. The error for the present phases in the Ti_3SiC_2 -cBN composite samples were also large as in the previous two composites, thus the results observed were to be considered with caution in this case too. The reasoning for this is the same as given in Sections 4.1.1 and 4.1.2, thus the EDX results were mostly valuable in evaluating the migration of the present elements within the phases with increase in temperature.

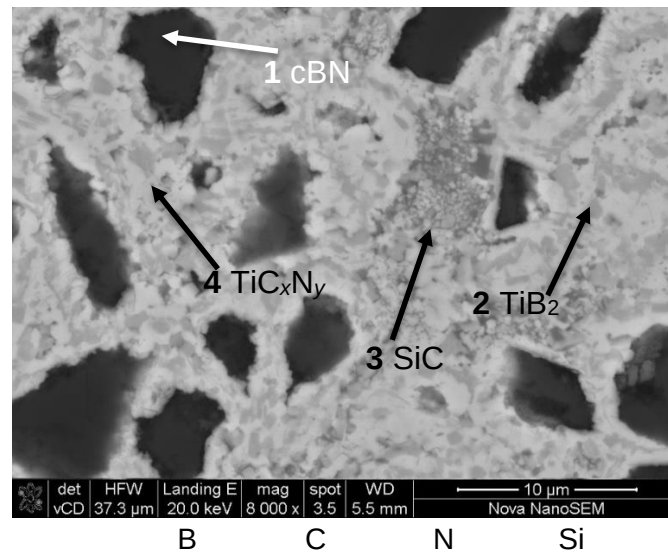


Figure 4.22: EDX analysis of $\text{Ti}_3\text{SiC}_2\text{-cBN}$ (20 vol.%, 10 μm) sample sintered at 30 MPa, 1 minute and 1600°C.

In Figure 4.22, the Si and N contents at site 3 showed a high variability, which means the presence and content of these elements in the site were considered with caution. Site 1 was interpreted as BN phase, sites 2, 3 and 4 all displayed similar contents of Ti, B, N, C and Si, which may be caused by the beam picking up reflected x-rays from the neighbouring phases. This suggests that the TiC_xN_y , TiB_2 and SiC phases are found distributed within the matrix. Therefore, using the XRD results for this samples (Figure 4.20) for the phases present and the principles of SEM (BSE) for different shaded based on electron densities of the present elements, the following was assumed. Site 2 was TiB_2 , Site 3 was SiC and Site 4 was TiC_xN_y .

The present phases (as shown in different shades of grey) seem to be 1 μm or less. This fine grain structure was achieved due to the short thermal exposure time of 1 min.

4.2 Reaction temperature optimisation with 20 vol.% of the 10 μm cBN

From the results in Section 4.1.1, it was decided that the optimum temperature to work with for the Ti_2AlC -cBN composites was 1250°C, since there was more MAX phase in the sample (compared to samples sintered at 1300°C and above), but also less TiAl_2 compared to samples sintered at 1150°C. The SEM analysis showed that at this temperature, a much thinner reaction area was present, which correlates with less secondary phases. From the results in Section 4.1.2, it was decided that the best temperature to optimise the Ti_3AlC_2 -cBN composites was 1300°C, since there was more MAX phase in the sample compared to other samples. The SEM analysis of this sample also showed that the large reaction area (in samples sintered at 1400°C and higher) was absent in this composite. Since the main MAX phase that resulted was Ti_2AlC instead of Ti_3AlC_2 , the main aim of the optimisation studies for the Ti_3AlC_2 -cBN composites was to drive transformation for the resultant Ti_2AlC to Ti_3AlC_2 . From the results in Section 4.1.3, it was decided that the best temperature to work on optimising Ti_3SiC_2 -cBN composites was 1250°C, since there was more MAX phase in this sample compared to samples sintered at 1300°C and above, but also less SiC compared to samples sintered at 1150°C.

4.2.1 Ti_2AlC -cBN composites

Figure 4.23 shows the XRD diffractograms of the samples sintered at a constant temperature of 1250°C and a pressure of 30 MPa for 1, 5 and 10 minutes. Figure 4.24 shows the Rietveld analysis of the samples analysed in Figure 4.23, with the raw data analysis shown in Appendix C. This was done to optimise the Ti_2AlC phase in the sample without compromising the cBN

content. For all three dwell times, Ti_2AlC and cBN phases were present, with Ti_2AlC as the major phase at 1- and 10-minute dwell times (Figure 4.25).

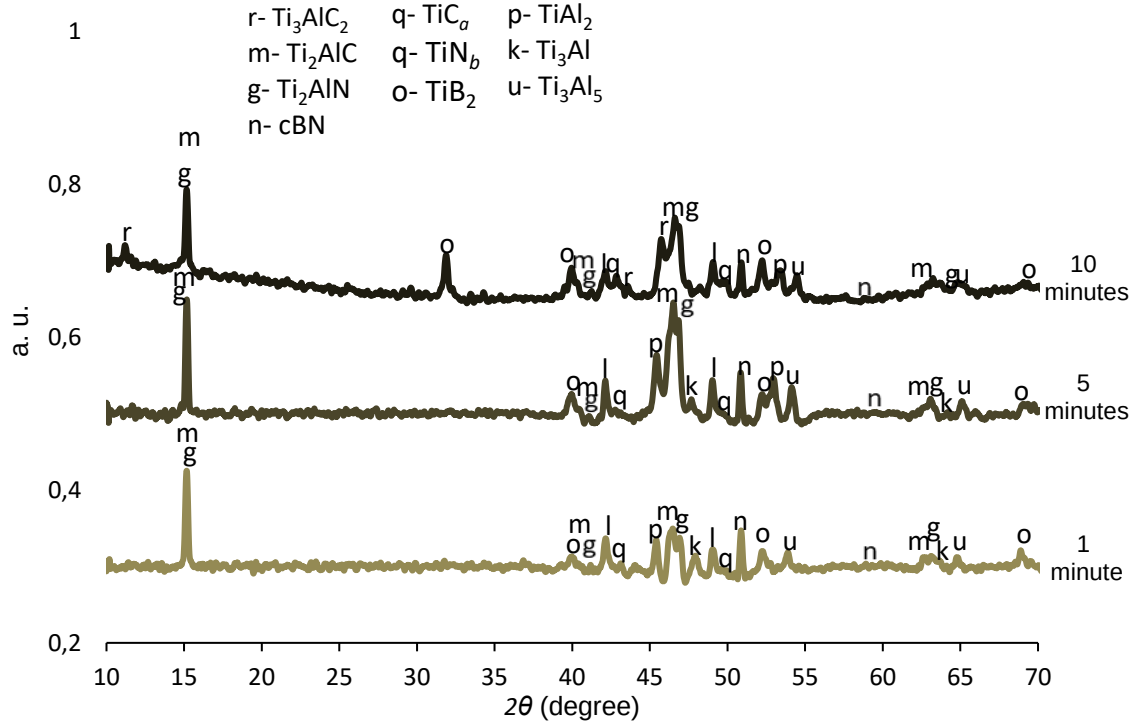


Figure 4.23: XRD traces of Ti_2AlC -cBN (20 vol.%, 10 μm) samples sintered at 30 MPa, 1250°C for different times.

Ti_2AlN was observed to increase with dwell time, as shown in Figure 4.24. TiC_α and TiB_2 , also increased with increased dwell time. TiNb content stayed the same in all samples, whereas Ti_3Al , TiAl_2 and cBN decreased with increased dwell time. However, at 10 minutes dwell time Ti_3AlC_2 and Ti_3Al_5 were found in the sample with no TiAl_2 and Ti_3Al . In the sample sintered for 5 minutes there was less Ti_2AlC phase present than in the other samples. TiB_2 was only found in samples sintered at 5 minutes and 10 minutes according to the Rietveld analysis, however XRD analysis shows that it was seen in all samples. The total content of M_2AX phase in the sample (Ti_2AlC and Ti_2AlN) increase from 32 % to 30 % and finally 52 %.

Figure 4.25 shows the densities of the samples sintered at 1250°C at different dwell times. And Figure 4.26 shows the SEM-BSE images of the sample sintered at 1250°C, both polished and untreated fracture surfaces are shown. The error for the densities was very small, which indicates that the reported average values are reliable. This was also observed for the open porosity except the value for the sample sintered for 5 minutes, meaning that this value was not as reliable.

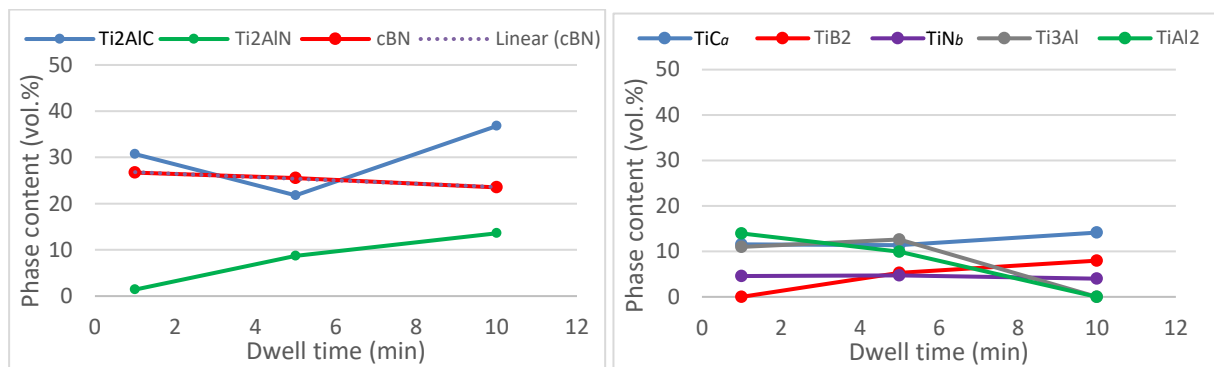


Figure 4.24: Phase quantities, determined by Rietveld analysis, of Ti_2AlC -cBN (20 vol.%, 10 μm) samples sintered for different times at 1250°C.

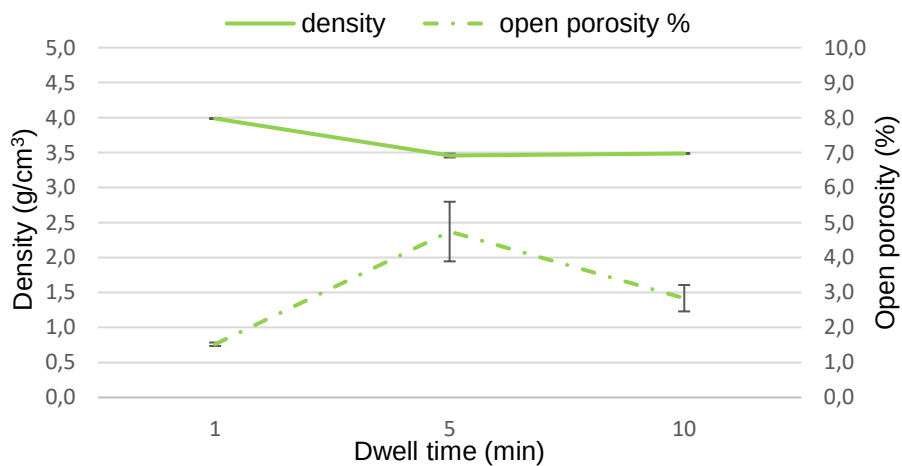


Figure 4.25: Densities and open porosities of Ti_2AlC -cBN (20 vol.%, 10 μm) samples sintered at 1250°C for different dwell time.

Since the same procedure was used for density measurements by the same person and the sample sintered for 1 minute and 5 minutes have similar phases, the error observed is likely

to be due to the equipment on the particular day the sample was measured. However, the errors of all three samples do not overlap, thus the results are reliable.

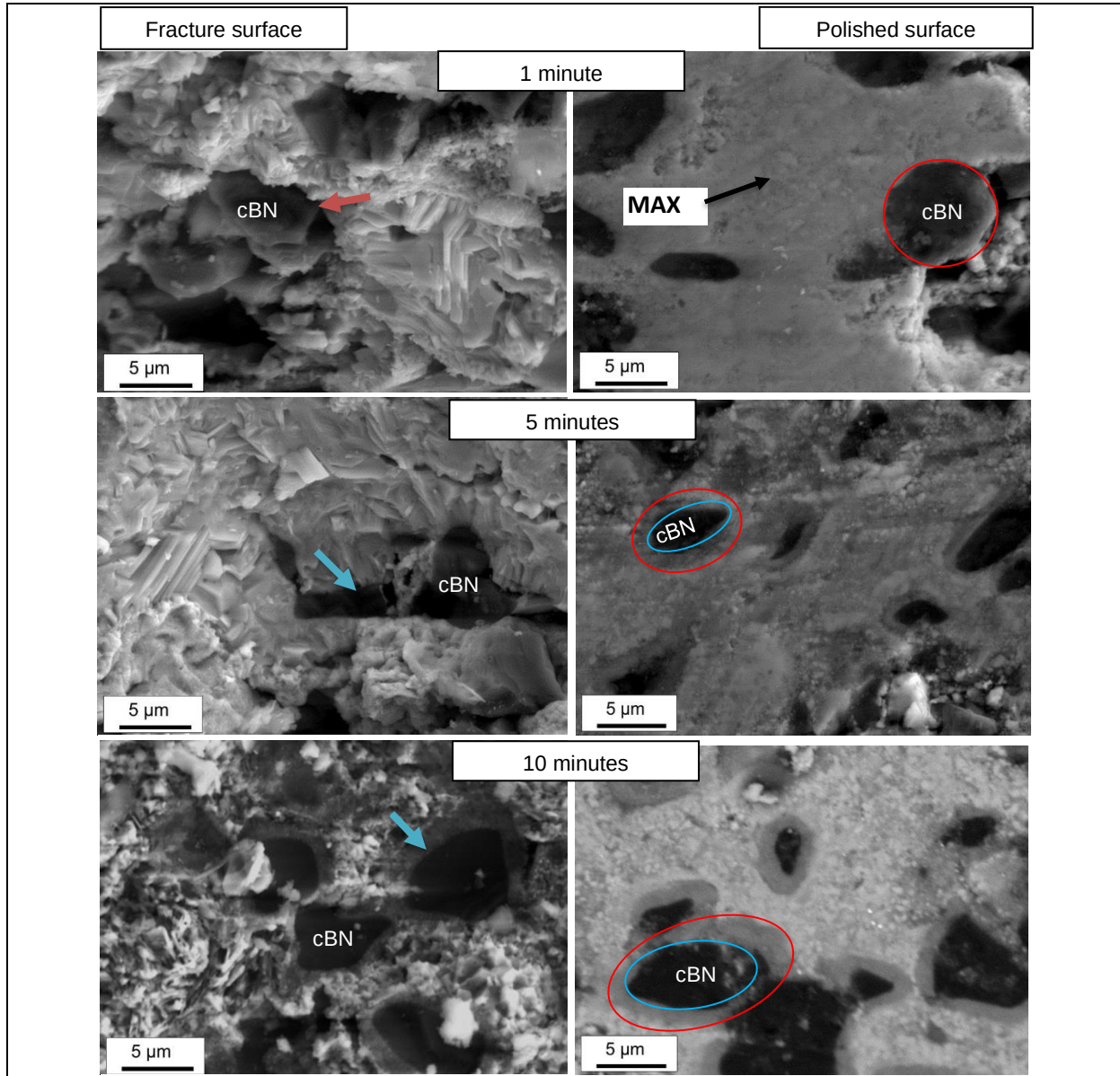


Figure 4.26: SEM (BSE) of fractured (left column) and polished (right column) Ti_2AlC -cBN (20 vol.%, 10 μm) samples sintered at 30 and MPa 1250°C for different times. Blue arrows indicate crack propagation between cBN and matrix indicating strong bond between cBN and matrix and red arrows indicate crack propagating through the cBN.

The density of the samples decreased from 1 minute to 5 minutes dwell time and stayed constant to 10 minutes. The open porosity increased with increased dwell time from 1 minute

to 5 minutes and then decreased again. The decrease in density observed can be attributed to the increase in the phases of lower density (Ti_2AlC and Ti_2AlN) and the decrease of the higher density phases (Ti_3Al and TiAl_2).

For the sample sintered for 1 minute the fracture seemed to have propagated around the cBN particles (red arrow), with the samples sintered for 5 and 10 minutes displaying the fracture crack propagation through the cBN (blue arrows). The polished surfaces show the reaction area (between the red and blue circles), with the sample sintered at 5 minutes having a reaction width of about $1\text{ }\mu\text{m}$, and that of the sample sintered for 10 minutes about $2\text{ }\mu\text{m}$. The fracture of the samples sintered for 1 and 5 minutes show a laminar structure within the matrix, this was not as pronounced for the sample sintered for 10 minutes.

4.2.2 Ti_3AlC_2 -cBN composites

Figures 4.27 and 4.28 show the XRD results of samples sintered at 1250°C and 1300°C , for different times. Figure 4.29 shows a summary of the Rietveld analysis of the samples analysed in Figure 4.28, and the actual analysis data shown in Appendix C. At 1250°C (Figure 4.27), no Ti_3AlC_2 was found, however there was a clear presence of Ti_2AlC and Ti_2AlN , cBN and hBN. In addition, TiC_a , TiN_b , TiAl_2 , Ti_3Al and TiB_2 were also present in all samples. AlN was only found in the sample sintered for 1 minute, and Ti_3Al was seen to reduce for 5 and 10 minutes dwell times. The samples sintered at 1300°C (Figure 4.27), however, showed a transformation of Ti_2AlC to Ti_3AlC_2 in the sample sintered for 10 minutes. For all three dwell times Ti_2AlC , Ti_2AlN , cBN, TiN_b , TiC_xN_y and TiB_2 were present, with Ti_3AlC_2 phase only found in the samples sintered for 10 minutes. Ti_2AlC was the dominate phase for samples sintered for 1 and 5 minutes with Ti_3AlC_2 and cBN becoming the dominant phases in the sample sintered for 10 minutes (Figure 4.29). TiAl_2 and Ti_3Al were only found in samples sintered for 1 and 5 minutes, and hBN was only observed in the sample sintered for 5 minutes.

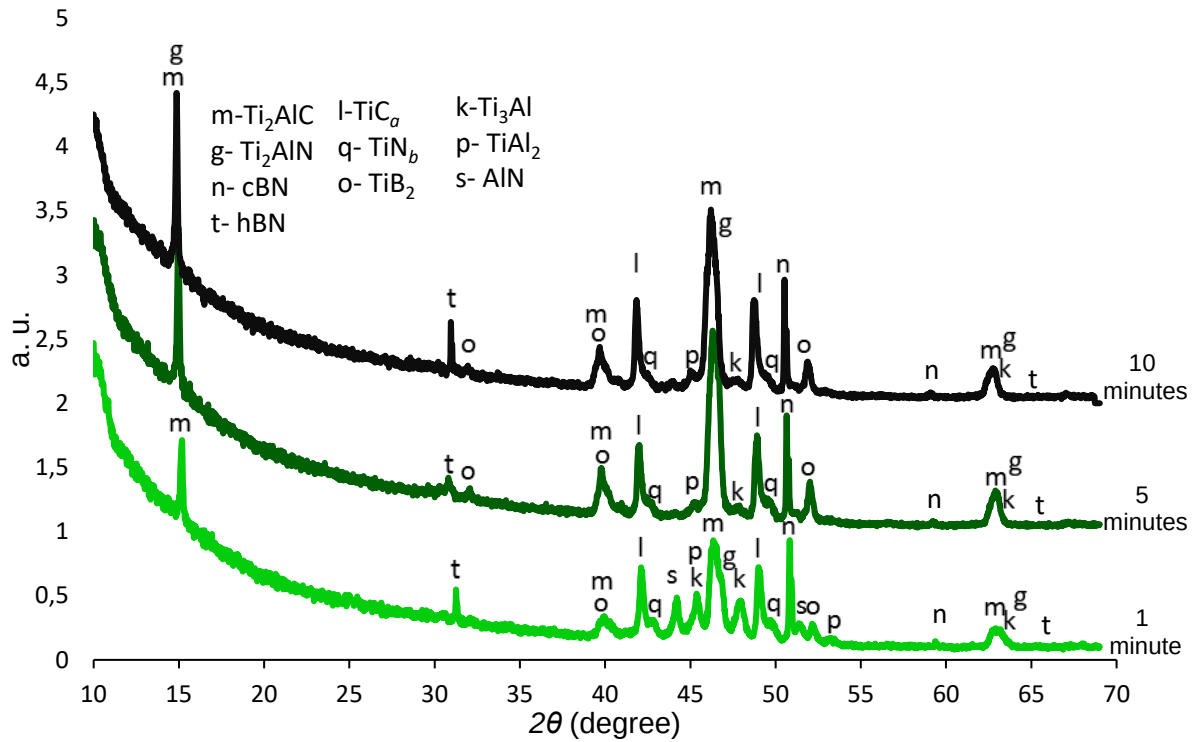


Figure 4.27: XRD traces of Ti_3AlC_2 -(20 vol.% of 10 μm) cBN samples sintered at 30 MPa, 1250°C and different times.

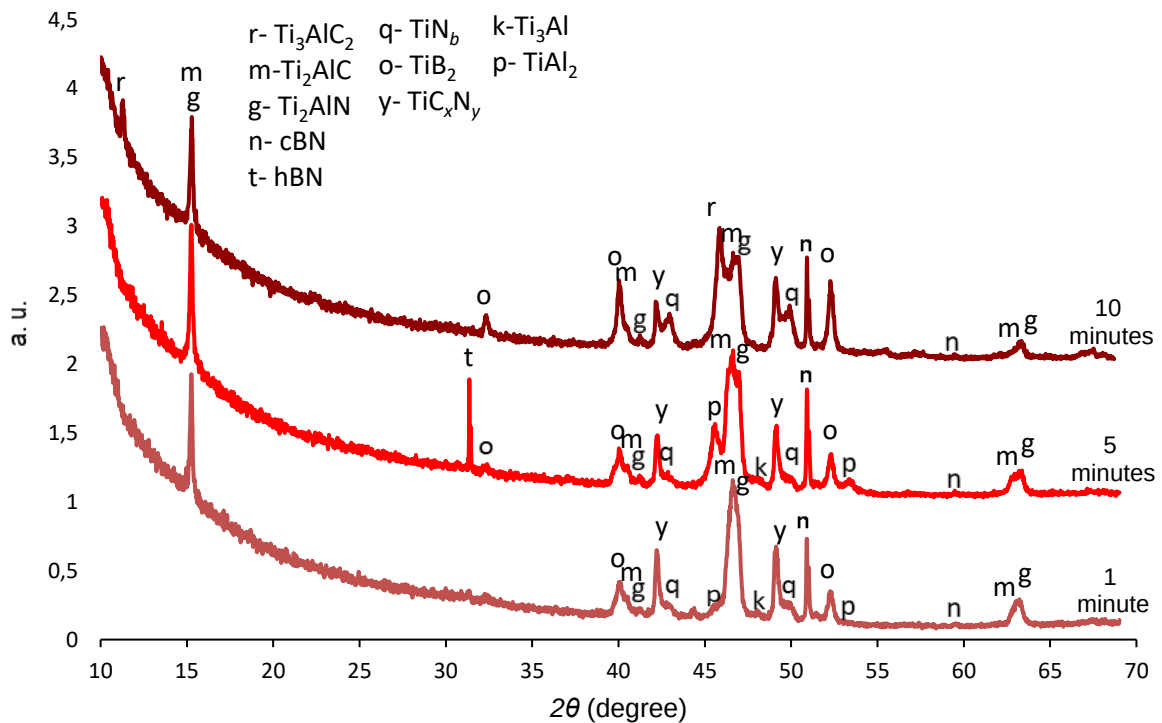


Figure 4.28: XRD traces of Ti_3AlC_2 -cBN (20 vol.%, 10 μm) samples sintered at 30 MPa, 1300°C and different dwell/annealing times.

Figure 4.29 shows the Rietveld analyses of the phase content of the samples sintered at 1300°C (Figure 4.28). The Ti_2AlC and TiAl_2 phases decreased with increase in temperature whereas cBN decreased initially, then stayed approximately the same up to 10 minutes dwell time. Ti_2AlN and hBN increased then decreased with dwell time, TiCa displayed the opposite behaviour and TiB_2 increased with dwell time. In the sample sintered for 5 minutes, there was hBN, however, this was not observed at samples sintered at 10 minutes. This shows that the hBN formed at 5 minutes dwell time could have participated in the reactions to form the B and N containing phases, such as TiB_2 which increased with time, until it was depleted at 10 minutes.

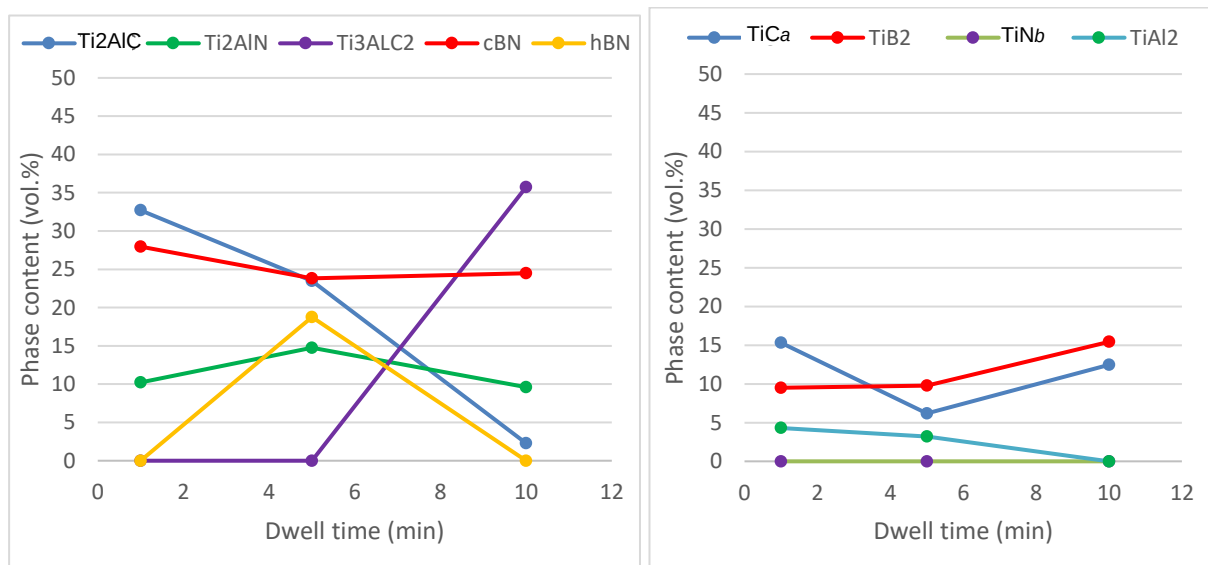


Figure 4.29: Phase quantities, determined by Rietveld analysis, of Ti_3AlC_2 -cBN (20 vol.%, 10 μm) samples sintered for different times at 1250°C.

Figure 4.30 shows the densities of the samples sintered at 1250°C and 1300°C. It was observed that the error in these samples were not too large, indicating that the values reported were reliable. However, there was an overlap in the errors for the densities of the samples sintered at 1250 and 1300 for 1 minute, this could be attributed to the similarity of the major phases of these samples, hence the densities are generally the same. The densities and open

porosities of all samples sintered at 1200°C remained the same and 3.2 g/cm³ and 12 %, respectively. This was expected since there were no major phase changes within these samples. The samples sintered at 1300°C showed an increase in the density at 5 minutes from 3.4 to 4.2 g/cm³ and back down to 3.4 g/cm³. This can be attributed to the fact that at 5 minutes, the sample has more TiAl₃ than in the other samples, this has a higher density than the other major phases at 1 and 10 minutes dwell times.



Figure 4.30: Densities and open porosities of Ti₃AlC₂-cBN (20 vol.%, 10 µm) samples sintered at different temperatures and for different dwell time.

Figure 4.31 shows the SEM (BSE) images of the samples sintered at 1300°C, both for polished and untreated fracture surfaces. For the samples sintered for 1 minute, the fracture seems to have propagated around the cBN particles (red arrow) in an intergranular manner. The samples sintered for 5 and 10 minutes display the crack propagating through (transgranular) the cBN (blue arrow). The polished surfaces show there was a reaction area (between the red and blue circles) only for the sample sintered for 10 minutes, which was approximately 2 µm thick. The fracture of the samples sintered for 1 and 5 minutes show a laminar structure within

the matrix, this was not as pronounced in the sample sintered for 10 minutes and a severe extent of porosity was also observed (orange arrow) throughout the matrix.

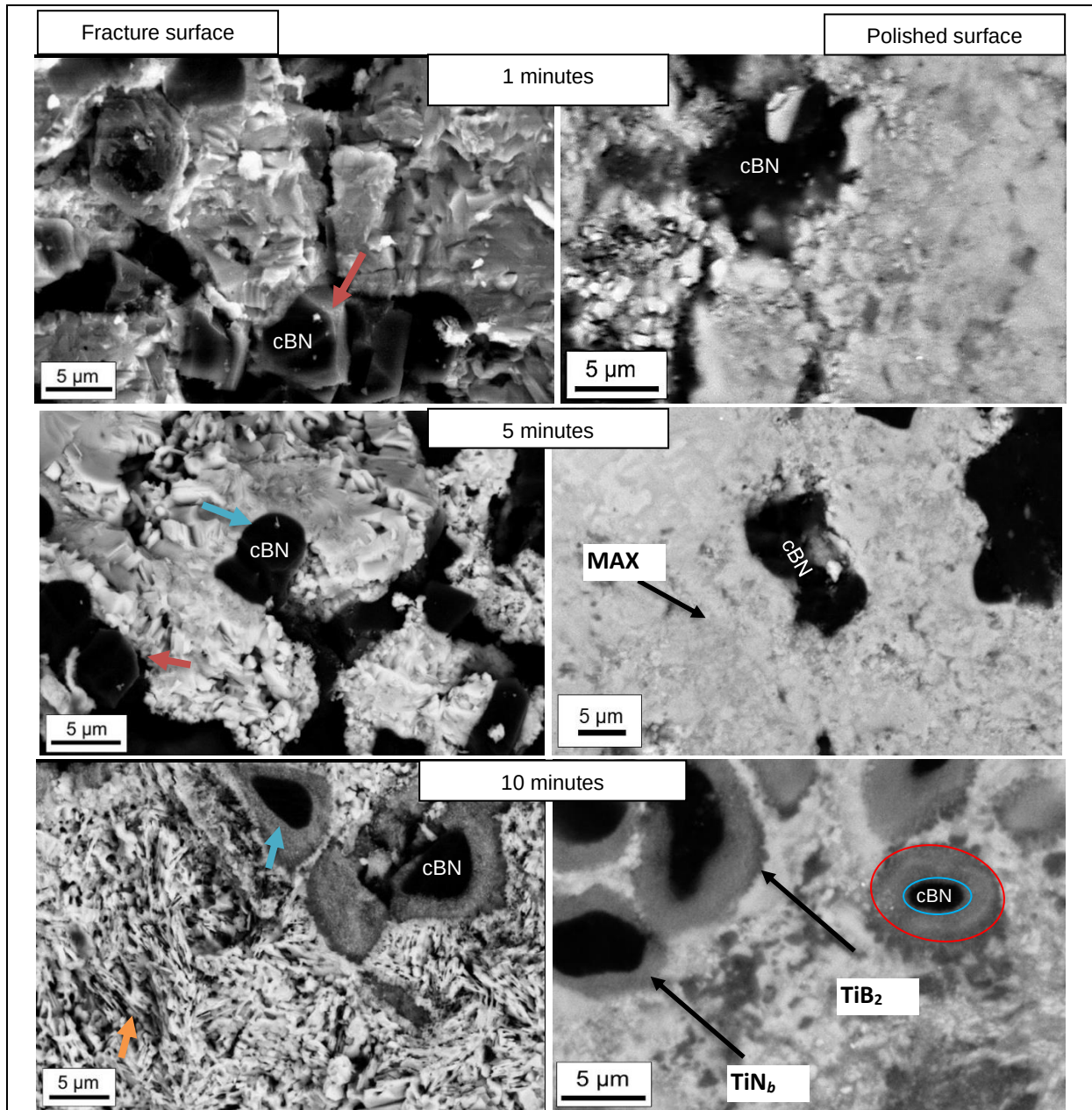


Figure 4.31: SEM (BSE) of fractured (left) and polished (right) Ti_3AlC_2 -cBN (20 vol.%, 10 μm) samples sintered at 30 MPa 1300°C and different times. Blue arrows indicate crack propagation between cBN and matrix indicating strong bond between cBN and matrix, red arrows indicate crack propagating through the cBN, and orange arrows indicate porosity in the matrix.

4.2.3 Ti_3SiC_2 -cBN composites

Figures 4.32 and 4.33 shows the XRD diffractograms of the samples sintered at 1150°C and 1250°C at constant pressure of 30 MPa and 1, 5 and 10 minutes. Figure 4.34 shows the Rietveld analysis of the samples analysed in Figure 4.33, with the actual analysis data collected shown in Appendix C. The increase in dwell time was carried out to optimise the Ti_3SiC_2 phase in the sample without compromising the cBN content.

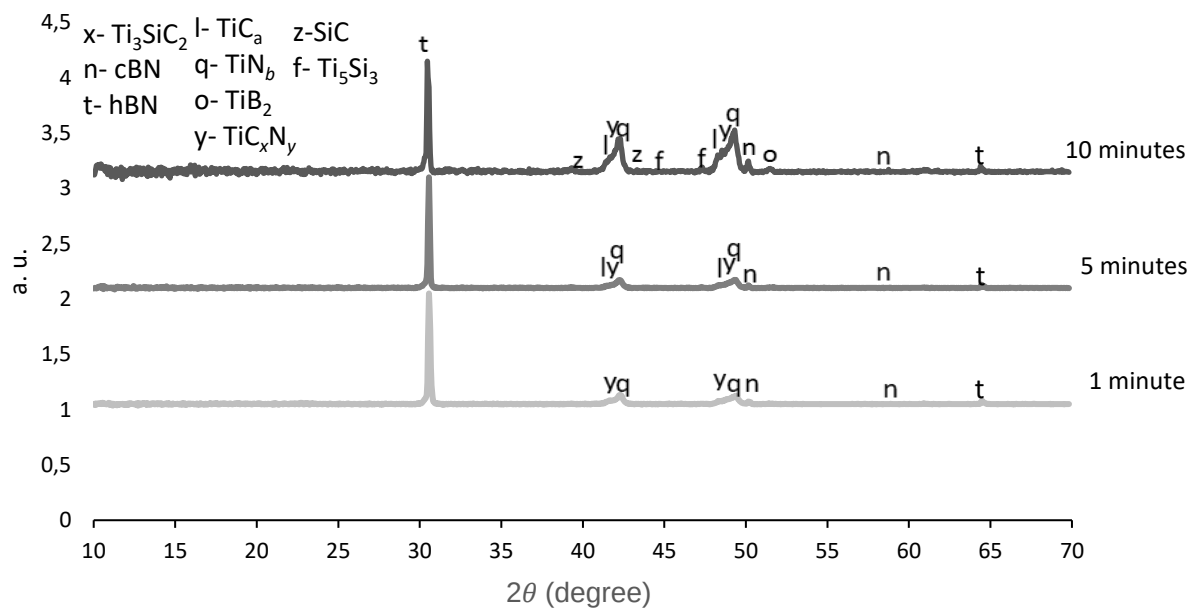


Figure 4.32: XRD traces of Ti_3SiC_2 -(20 vol% of 10 μm) cBN samples sintered at 30 MPa, 1150°C and different times.

The samples sintered at 1150°C did not contain any Ti_3SiC_2 , and very little cBN and hBN as the major phase. All samples contained TiC_xN_y , TiN_b , with TiC_a and Ti_5Si_3 seen in samples sintered for 5 and 10 minutes. Samples sintered at 1250°C (Figure 4.33) also displayed lack of Ti_3SiC_2 with very little cBN. The exception was the sample sintered for 10 minutes, as there was a little Ti_3SiC_2 found. TiC_xN_y , TiB_2 , TiN_b , TiC_a and Ti_5Si_3 were found in all samples. SiC was not found in the sample sintered for 10 minutes. The hBN phase was present in all samples and was the major phase in the samples sintered for 1 and 10 minutes.

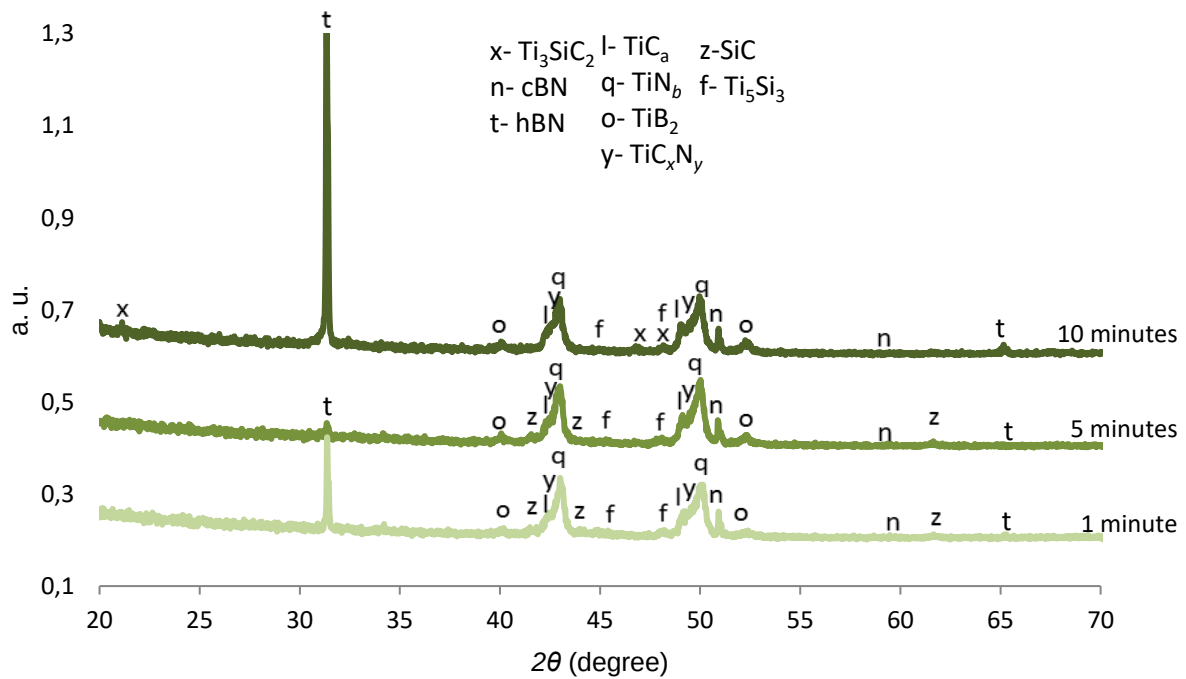


Figure 4.33: XRD traces of Ti_3SiC_2 -cBN (20 vol.%, 10 μm) samples sintered at 30 MPa, 1250°C and different times.

Figure 4.34 shows the Rietveld analysis of the samples analysed in Figure 4.33. It was seen that there was a steady decrease in the cBN content, whereas hBN decreased and then increased. This might be that the other B and N containing phases, TiN_b , TiB_2 and TiC_xN_y all increased until 5 minutes with not much cBN reduction. Meaning that the reduction of the hBN was due to the formation of these phases, not that cBN hexagonalisation reduces with time.

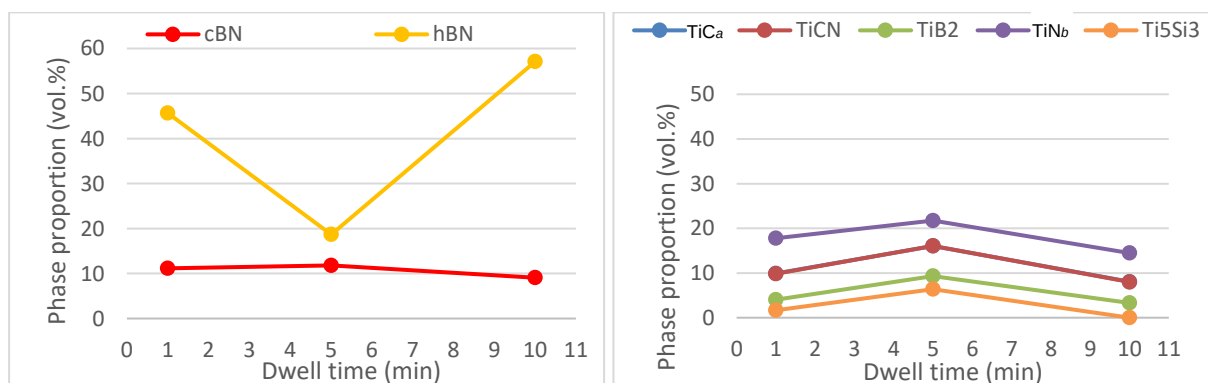


Figure 4.34: Phase quantities, determined by Rietveld analysis, of Ti_3SiC_2 -cBN (20 vol.%, 10 μm) samples sintered for different times at 1250°C.

Figure 4.35 shows the density and open porosity for samples shown in Figure 4.32 and 4.33. It was observed that the errors for the density measurements were small, but for those of the open porosity, they were more significant. This means that the density values here are more reliable than the open porosity values. The densities of the samples remain generally the same as the dwell time increased. This was expected since the different composites had similar phases throughout. The open porosities also showed a general constant value as well, with the exception of the porosity for the sample sintered at 1300°C which first showed a decrease in the open porosity from 1 to 5 minutes, then a constant negligible porosity.

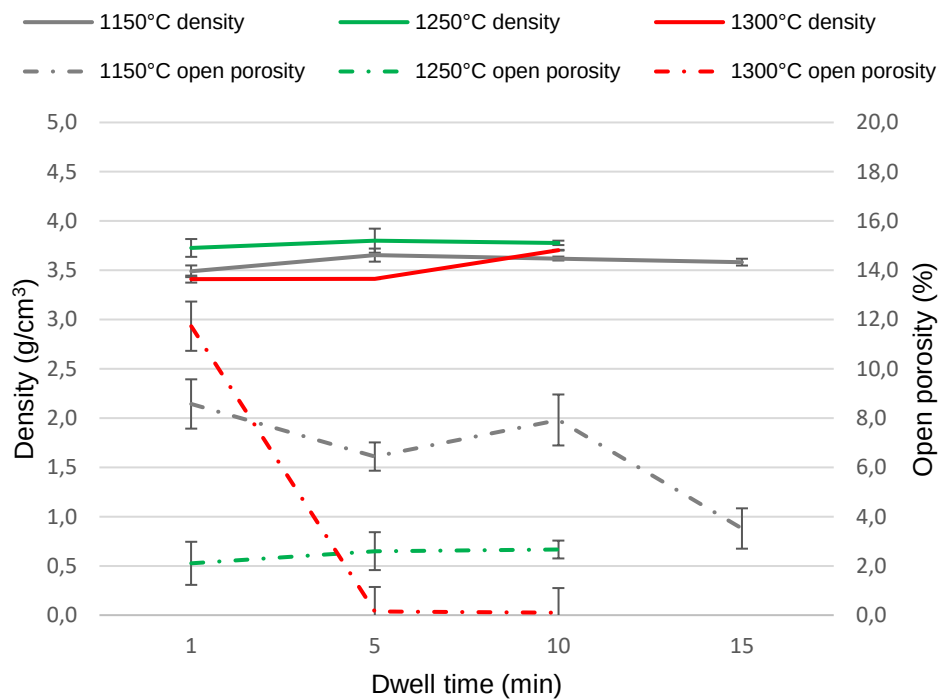


Figure 4.35: Densities and open porosities of Ti_3SiC_2 -cBN (20 vol.%, 10 μm) samples sintered at different temperatures and for different dwell time.

Figure 4.36 shows the SEM (BSE) images of the fracture of the samples sintered at 1250°C for different times. All samples showed that the fracture seems to have propagated around the cBN particles (red arrows) with a significant amount of cBN pull-out was observed (green arrow).

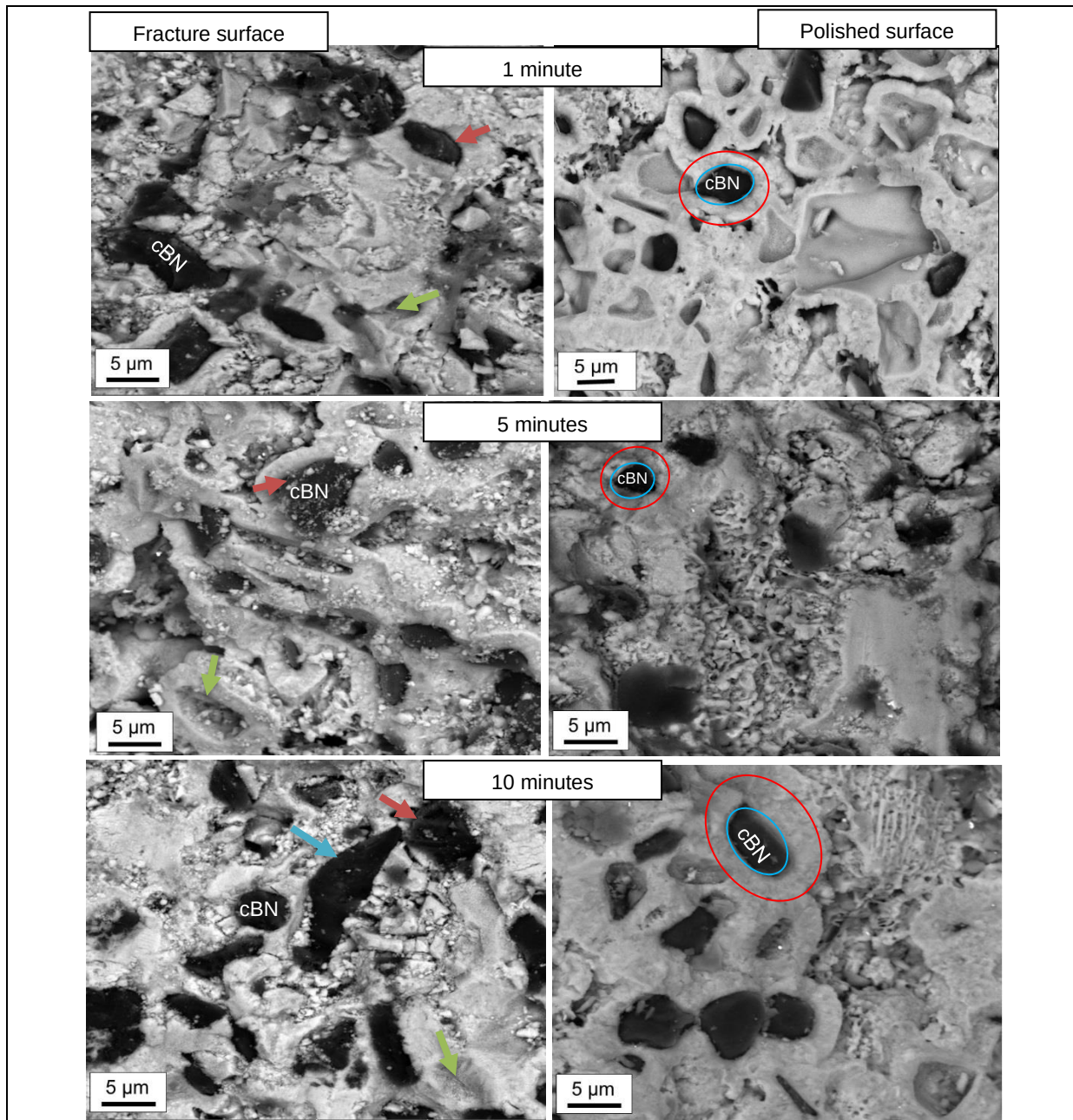


Figure 4.36: SEM (BSE) images of fractured (left) and polished (right) Ti_3SiC_2 -cBN (20 vol.%, 10 μm) samples sintered at 30 MPa 1250°C and different times. Blue arrows indicate crack propagation between cBN and matrix indicating strong bond between cBN and matrix, red arrows indicate crack propagating through the cBN, and Green arrows indicate possible cBN pull-out.

The polished samples in Figure 4.36 show that there was an apparent reaction area around the cBN (between red and blue circles) in all samples with the width increasing from $\sim 1 \mu\text{m}$ to $\sim 3 \mu\text{m}$ to $\sim 5 \mu\text{m}$ with the respective increase in dwell time.

4.3 Investigation of cBN surface area effect on reaction temperatures using 100 μm cBN (20 vol.%)

From Section 4.2 the reaction temperatures of different MAX phases and 10 μm cBN for the optimal conditions for sintering were identified.

For the Ti_2AlC -cBN composites, the 1250°C temperature, sintered for 5 minutes condition was used, but 1300°C was also used in anticipation that, for the larger cBN, a similar reaction to the previous section could occur at a slightly higher temperature or a longer dwell time.

For the Ti_3AlC_2 -cBN composites, the 1300°C temperature, 10 minutes condition was used to sinter the samples as recommended in the previous section. Different dwell times were also investigated in order to evaluate whether there was a difference in the kinetics to transform Ti_2AlC into Ti_3AlC_2 when the surface area of the cBN was reduced.

For the Ti_3SiC_2 -cBN composites, the 1250°C temperature, 10 minutes was used to sinter these samples as recommended in the previous section, but 1300°C was also used in anticipation that, for the larger cBN, a similar reaction to the previous section could occur at a slightly higher temperature.

4.3.1 Ti_2AlC -cBN composites

Figure 4.32 shows the XRD diffractograms of the samples sintered at a constant temperature of 1250°C and a pressure of 30 MPa and three different dwell times. This was done to both obtain and optimise the Ti_2AlC phase in the sample without compromising the cBN content. Ti_2AlC and Ti_2AlN were present only in samples sintered for 5 and 10 minutes with the former dominating in these samples. The phases present in all samples were TiC_a , TiN_b , TiB_2 , and cBN. Ti_3Al and TiC_xN_y were only found in samples sintered for 1 and 5 minutes, with TiAl_2 only

found in the sample sintered for 5 minutes. Ti_3AlC_2 and hBN were only found in the sample sintered for 10 minutes. In contrast, all the samples sintered at 1300°C , Figure 4.38, showed a clear presence of Ti_2AlC , Ti_2AlN , cBN and significant amounts of hBN. TiC_a , TiC_xN_y , TiB_2 , TiAl_2 and Ti_3Al were also present in all samples with TiN_b only found in samples sintered for 1 and 5 minutes. Finally, no Ti_3AlC_2 phase was formed in any of the samples sintered at all three dwell times.

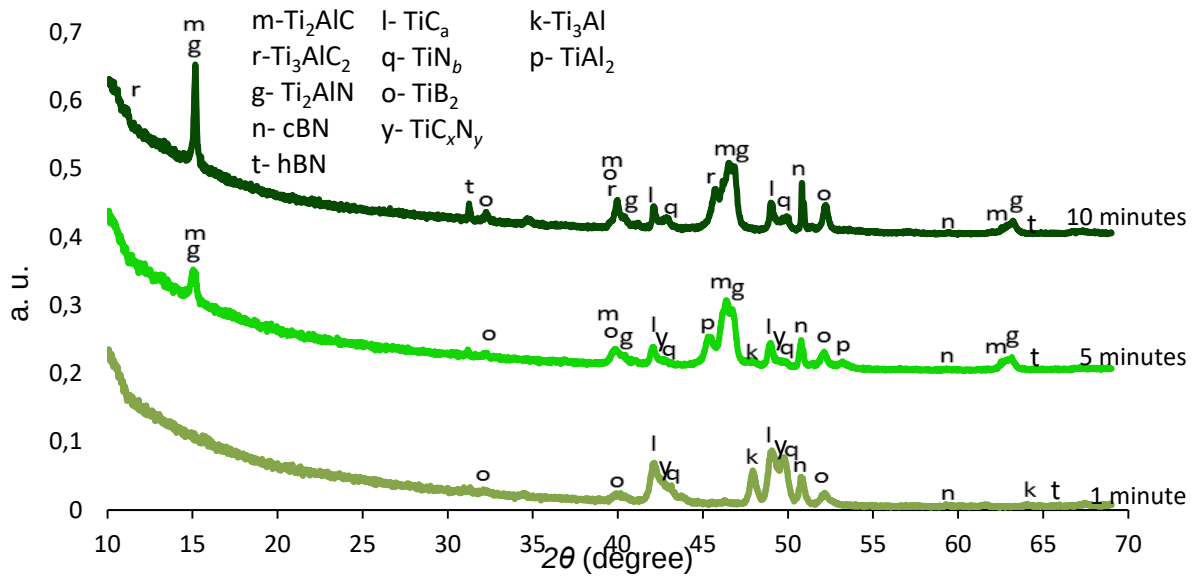


Figure 4.37: XRD traces of Ti_2AlC -cBN (20 vol.%, 100 μm) samples sintered at 30 MPa, 1250°C and different times.

Figure 4.39 shows the Rietveld analysis of the samples analysed in Figure 4.37, with the actual analysis shown in Appendix C. Ti_2AlC was the major phase in samples sintered for 5 and 10 minutes with TiC_a being the major phase in the sample sintered for 1 minute. Ti_2AlN increased with increase in dwell time with cBN first decreasing then unusually increasing with increase of dwell time to 10 minutes. Ti_2AlC and TiB_2 first increased, then decrease with increased dwell time. TiC_a first significantly decreased with increased dwell time, then stayed generally the same amount, while TiN_b decreased with increased dwell time.

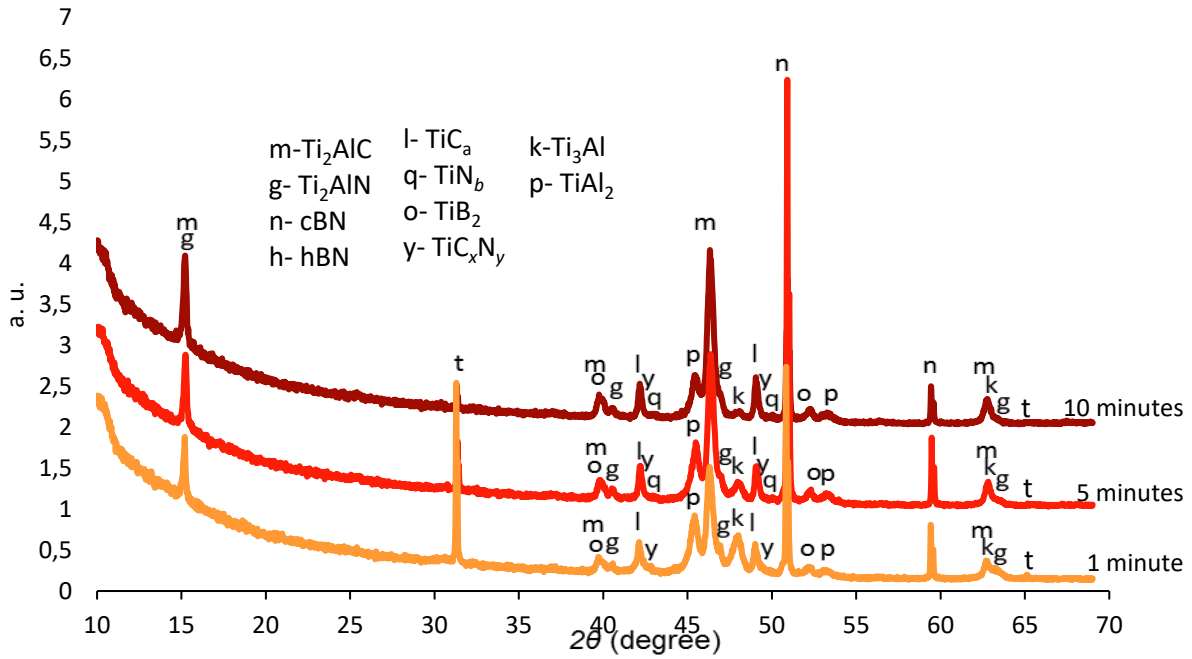


Figure 4.38: XRD traces of Ti_2AlC -cBN (20 vol%, 100 μm) cBN samples sintered at 30 MPa, 1300°C and different times.

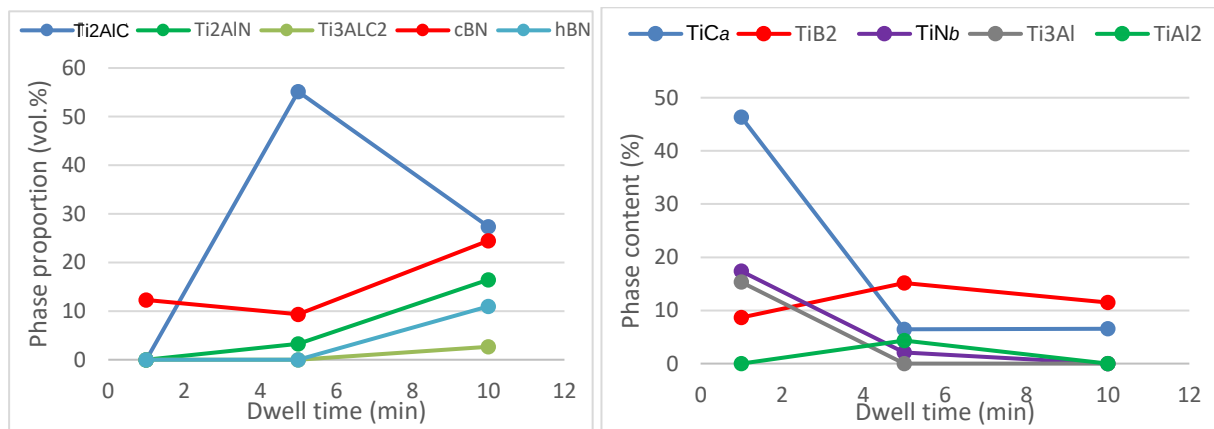


Figure 4.39: Phase quantities, determined by Rietveld analysis, of Ti_2AlC -cBN (20 vol.%, 100 μm) samples sintered for different times at 1250°C.

Figure 4.40 shows the densities of samples sintered at 1300°C and 1250°C from 1 to 10 minutes. The error for the densities of all samples was small, thus the average densities reported are reliable. The open porosity error, however, was large but they did not overlap, this can be taken as reliable. The densities of all samples sintered at 1300°C were the same (3.64 g/cm^3), and the open porosity as well (~1.2 %). This was because the phase content of all

sample was the same, the only difference was the fraction of each phase. The difference in the quantity of each phase may have only caused negligible density changes, thus no change was observed. The densities of the samples sintered at 1250°C initially remained the same and increased from 5 minutes to 10 minutes dwell time (3.54 g/cm³). This may be because when TiC_a decreases from being the major phase, TiAl₂ increased to become the major phase at 5 minutes dwell time, Figure 4.39. These two phases have similar densities, thus the change in the sample density was not observed from 1 to 5 minutes. The density then displayed a slight increase to 3.60 g/cm³, this was only a slight change as the major phase also increased only slightly. The open porosities for these samples increased from 1 to 5 minutes, then decreased again. The increase may be due to the major phase change which may cause some porosity in regions where the higher density phase was formed. Then the decrease would be due to the dwell time at high temperatures and 30 MPa pressure promoting densification.

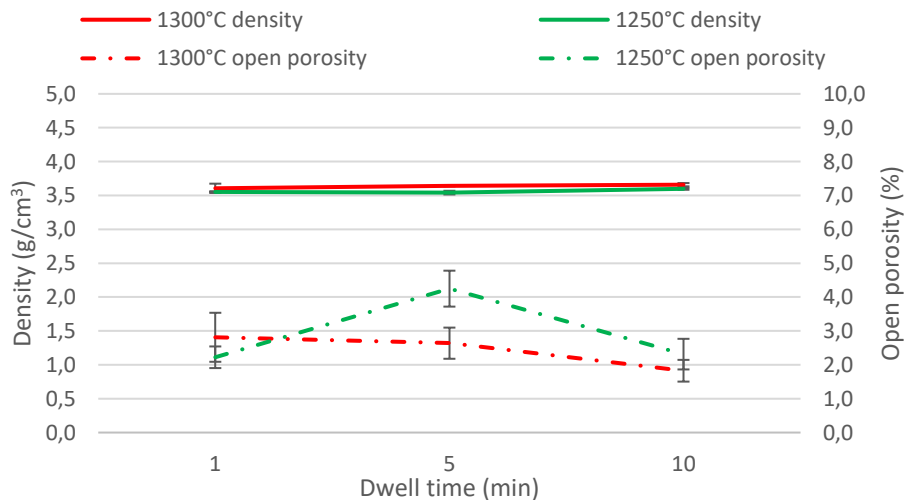


Figure 4.40: Densities and open porosities of Ti₂AlC-cBN (20 vol.%, 100 μm) samples sintered at different temperatures for different dwell time.

Figure 4.41 shows the SEM (BSE) images of the Ti₂AlC-cBN samples sintered at 1250°C and 1300°C. All samples showed that the cracks propagated through the cBN (blue arrow), indicating that the bond between the cBN and the MAX phase was strong. All samples

displayed cBN and phases in the matrix that displayed different morphologies. The analysis of the phases was shown in the EDX analysis in Figure 4.42.

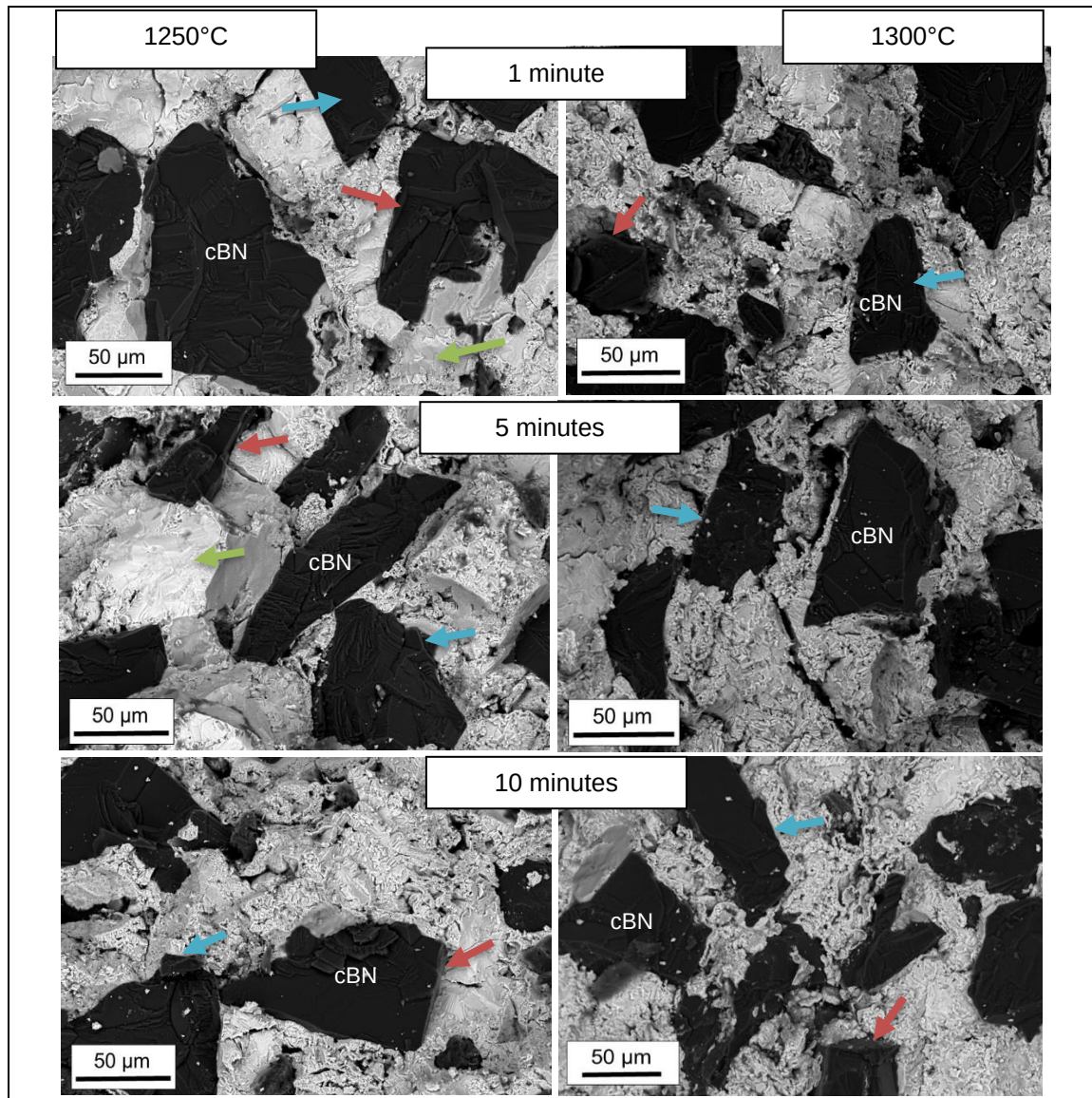
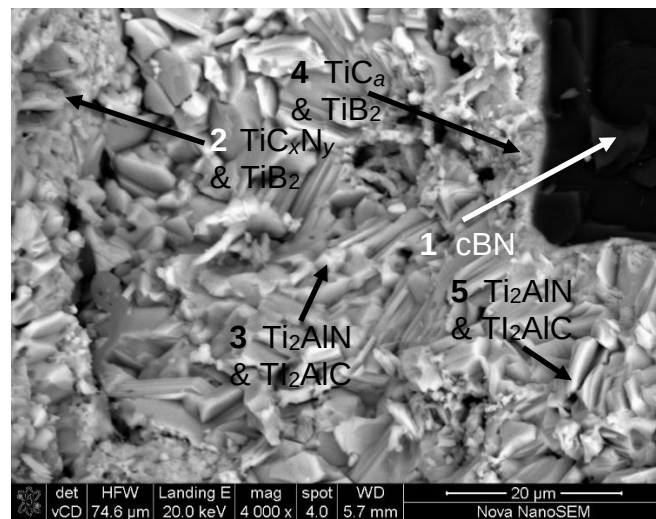


Figure 4.41: SEM (BSE) images of Ti_2AlC -cBN (20 vol.%, 100 μm) samples sintered for different times at 1250°C (left column) and 1300°C (right column). Blue arrows indicate crack propagation between cBN and matrix, red arrows indicate crack propagating through the cBN and green arrows indicate possible cBN pull-out.

Figures 4.42 shows the EDX analysis of the sample sintered at 1250°C for 5 minutes which had a combination of high MAX phase content with minimal hBN (Figure 4.37). The EDX results for sites 3, 4 and 5 displayed high errors. In these sites, there might have been phases

that are 2 μm and below, as seen in samples analysed in previous sections. Thus, these results should be considered cautiously, but are still valuable in evaluating the migration of the different elements within the phases with increase in dwell time. The EDX analysis of the reaction area (Site 4) showed a high content of B; this could be because the cBN was close to the area detected. There was high Ti content observed, this was where the TiC_a and TiB_2 were also found. Sites 3 and 5 was Ti_2AlN and more TiB_2 and TiC_xN_y were found in the matrix (Site 2). A similar phase distribution was observed in the other samples sintered at 1250°C and sintered at 1300°C, all shown in Appendix D.



		B	C	N	Al	O	Ti	Total
		atomic %						
site 1	average	48,8	6,4	43,7	0,9	0,1	0,1	100,0
	std deviation	1,5	1,8	1,0	0,3	0,1	0,0	
site 2	average	23,7	26,5	0,0	5,5	9,8	34,5	100,0
	std deviation	1,7	0,4	0,0	1,8	2,2	2,1	
site 3	average	23,8	48,5	0,0	6,3	3,7	17,6	100,0
	std deviation	1,4	5,5	0,0	0,8	3,7	2,0	
site 4	average	44,0	16,7	13,7	2,7	4,8	18,2	100,0
	std deviation	8,7	5,1	2,0	0,9	2,3	3,7	
site 5	average	32,8	33,8	0,0	5,5	8,8	19,1	100,0
	std deviation	4,5	5,1	0,0	0,1	0,7	1,3	

Figure 4.42: SEM (BSE) and EDX analysis of Ti_2AlN -cBN (20 vol.%, 100 μm) samples sintered at 30 MPa 1250°C 5 minutes.

4.3.2 Ti_3AlC_2 -cBN composites

Figure 4.43 shows the XRD diffractograms of the samples sintered at a constant temperature of 1300°C and a pressure of 30 MPa and three different dwell times (1, 5 and 10 minutes); this was done to obtain and optimise the Ti_3AlC_2 phase in the samples without compromising the cBN content. For all three dwell times, cBN, AlN, TiN_b , TiC_xN_y and TiB_2 were present, with TiC_xN_y , TiC_a and TiB_2 becoming the dominant phases in the sample sintered for 10 minutes (Figure 4.43). The peak for TiC_xN_y shifted to the right as the N content within the sample increased, and the TiN_b content remained lower than 1.5 vol.% in all samples (Figure 4.44). Ti_2AlC was the dominant phase for samples sintered for 1 and 5 minutes with Ti_2AlN also present in these samples, and both phases diminished in the sample sintered for 10 minutes. The hBN phase was only found in the samples sintered for 5 and 10 minutes. The Ti_3AlC_2 phase was seen only in the sample sintered for 10 minutes and was the only MAX phase in the sample.

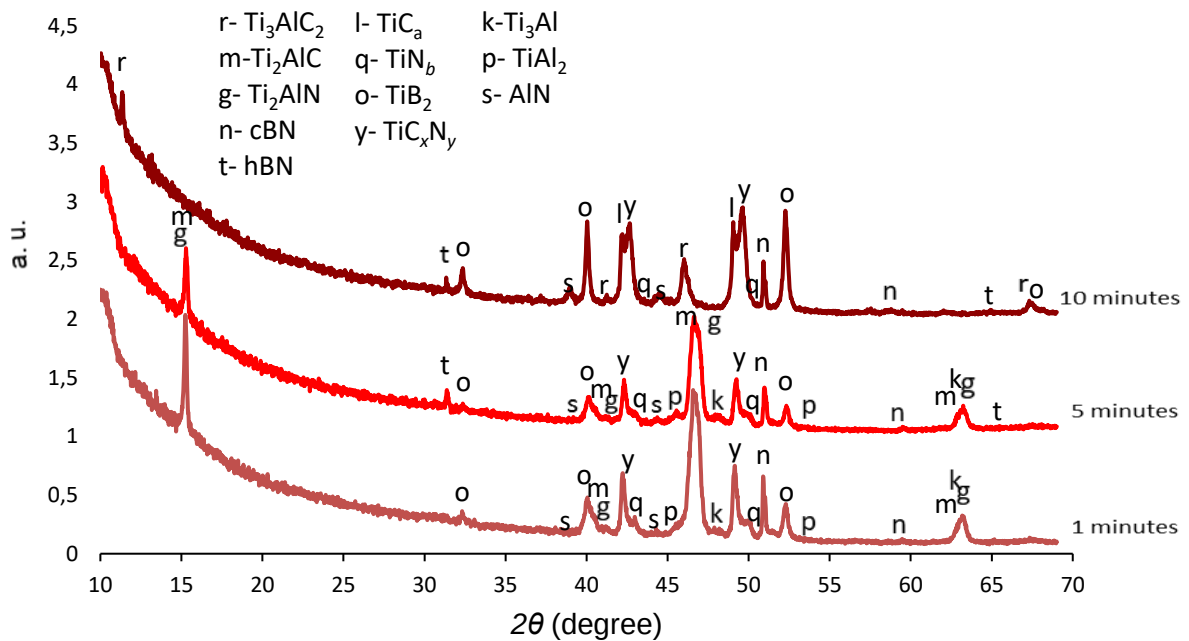


Figure 4.43: XRD traces of Ti_3AlC_2 -cBN (20 vol.%, 100 μm) samples sintered at 30 MPa, 1300°C for different times.

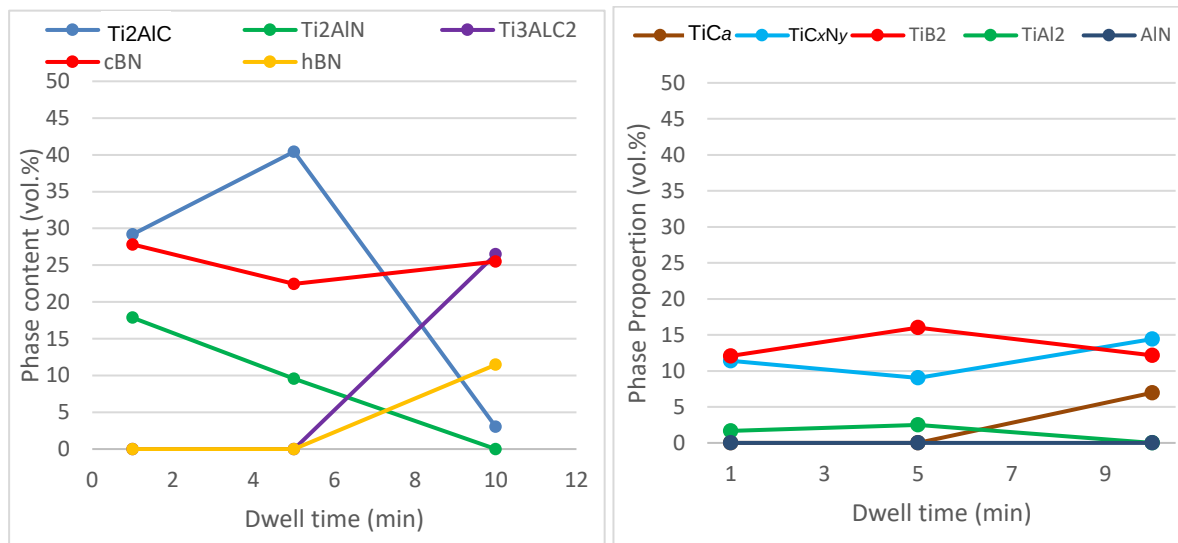


Figure 4.44: Phase quantities, determined by Rietveld analysis of Ti_3AlC_2 -cBN (20 vol.%, 100 μm) samples sintered for different times at 1300°C.

Figure 4.45 shows the density of these samples. In Figure 4.45 it was observed that the error for the densities was small and thus the reported values are reliable. However, the error for the open porosities was large, and this indicates that the values should be considered with caution. These large errors may be an indicator of the scale that was used was not stable or needed calibration. The density of the samples increased (3.83 to 4.00 g/cm^3) with the dwell time increased to 5 minutes and decreased again (3.54 g/cm^3) as the time was increased to 10 minutes.

This trend seemed to follow that of the Ti_2AlC phase, as shown in Figure 4.44, where the phase increased from 29 vol.% to 40 vol.% from 1 to 5 minutes. Then it reduced again to less than 2 vol.% as the time increased to 10 minutes and Ti_3AlC_2 phase was present at 26 vol.%. Since these are the dominant phases in the respective samples, they have the most significant effect on the density of the samples. The open porosity of all samples remained generally the same as the temperature was increased for 1 to 10 minutes, Figure 4.45. There was a decrease in Ti_2AlN with increase in dwell time, an increase then a decrease for cBN and TiAl_2 .

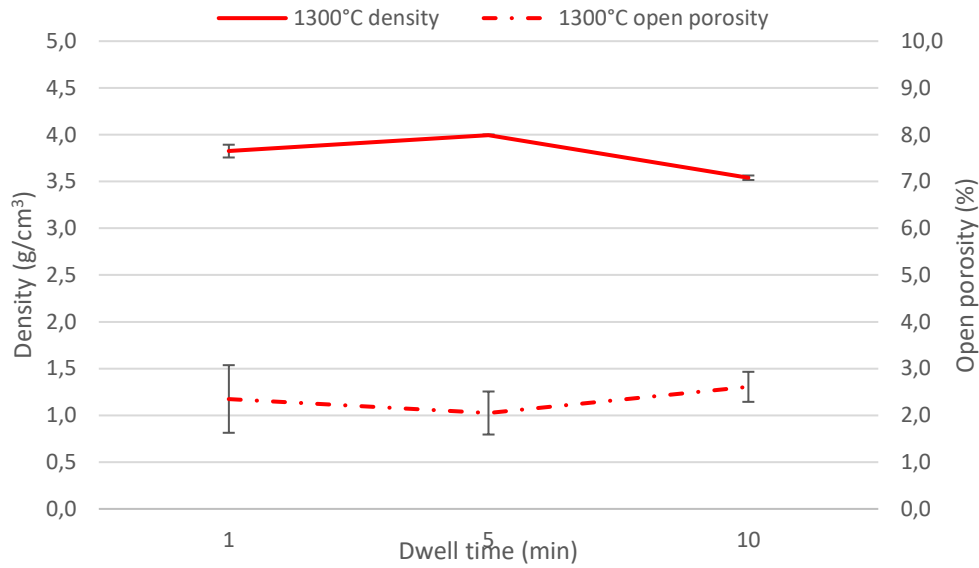


Figure 4.45: Densities and open porosities of Ti_3AlC_2 -cBN (20 vol.%, 100 μm) samples sintered at different temperatures for different dwell time.

Figure 4.46 shows the SEM (BSE) images of the Ti_3AlC_2 -cBN samples sintered at 1300°C. All samples showed that there were cracks propagating through the cBN (blue arrow), which may be an indicator that the bond between the cBN and the matrix was strong. There also seemed to be cracks propagating between the cBN and matrix (red arrow) in addition to possible cBN pull-out (green arrow). In these cases, the crack propagation was indicative of the bond between the cBN and the matrix was not strong. In all samples there seemed to be both strong and weak bonds between the matrix and cBN. All samples displayed cBN and a phase with a layered structure further away from the cBN.

Figure 4.47 shows the EDX analysis the sample sintered at 1300°C for 10 minutes. The EDX analysis of the reaction area, Site 2, consisted mainly of TiC and that Site 1 was BN phase. Site 3 showed a Ti, Al and carbon distribution in the approximate ratio of 2:1:1, which indicated the Ti_2AlC MAX phase. Similar phase distributions were detected in the rest of the samples sintered for 1 and 5 minutes as shown in Appendix E.

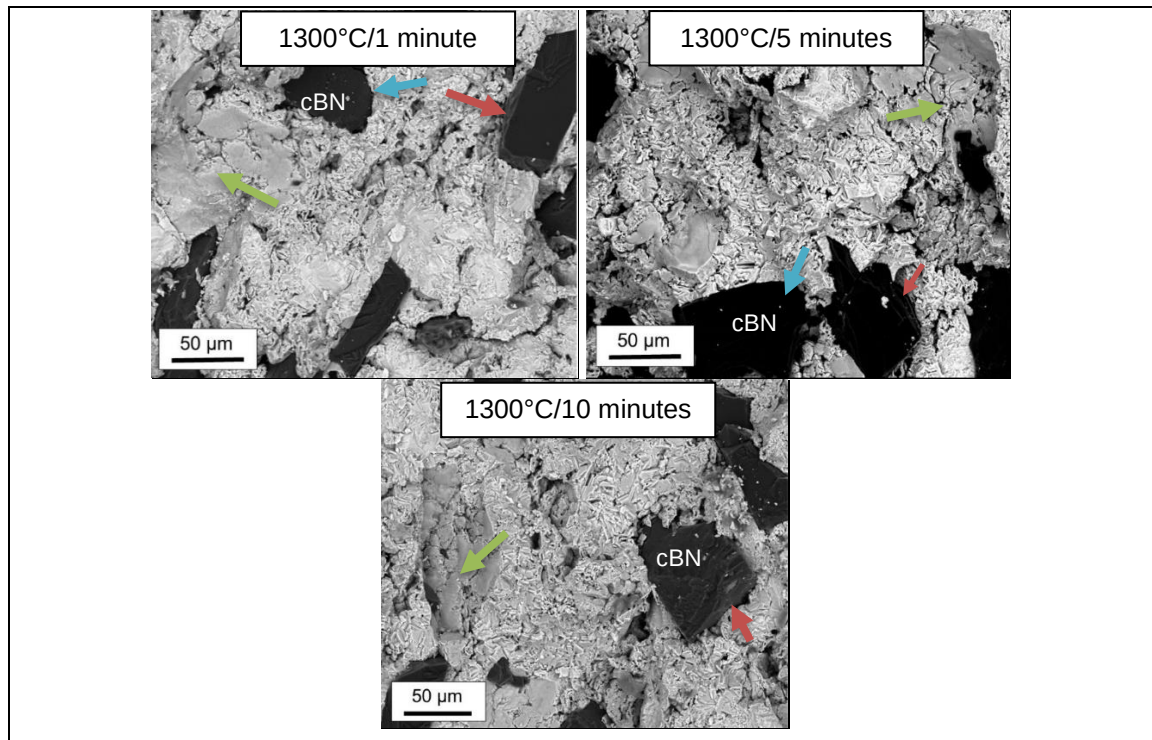
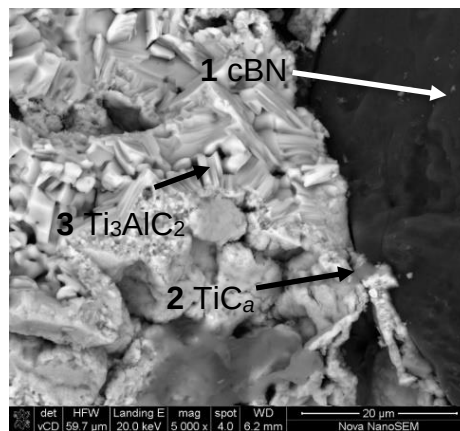


Figure 4.46: SEM (BSE) images of Ti_3AlC_2 -cBN (20 vol.%, 100 μm) samples sintered for different times at 1300°C.



		B	C	N	O	Al	Ti	Total
		atomic %						
site 1	average	54,3	0,0	43,5	2,2	0,0	0,2	101,5
	std deviation	1,7	0,0	3,9	2,1	0,0	0,2	
site 2	average	0,0	53,8	0,0	0,0	2,0	44,2	100,0
	std deviation	0,0	10,3	0,0	0,0	3,1	10,3	
site 3	average	0,0	30,5	0,0	0,0	22,6	46,9	100,0
	std deviation	0,0	6,8	0,0	0,0	4,7	2,9	

Figure 4.47: SEM (BSE) and EDX analysis of Ti_3AlC_2 -cBN (20 vol.%, 100 μm) samples sintered at 30 MPa 1300°C 10 minutes.

4.3.3 Ti_3SiC_2 -cBN composites

Figure 4.48 shows the diffractograms of Ti_3SiC_2 -cBN composite samples sintered at 1250°C for different times. Figure 4.49 shows the diffractograms of Ti_3SiC_2 -cBN composite samples sintered at 1300°C for different times. All samples sintered at 1250°C showed presence of Ti_3SiC_2 unlike the samples that were sintered at 1300°C which only contained Ti_3SiC_2 in the sample sintered for 1 minute.

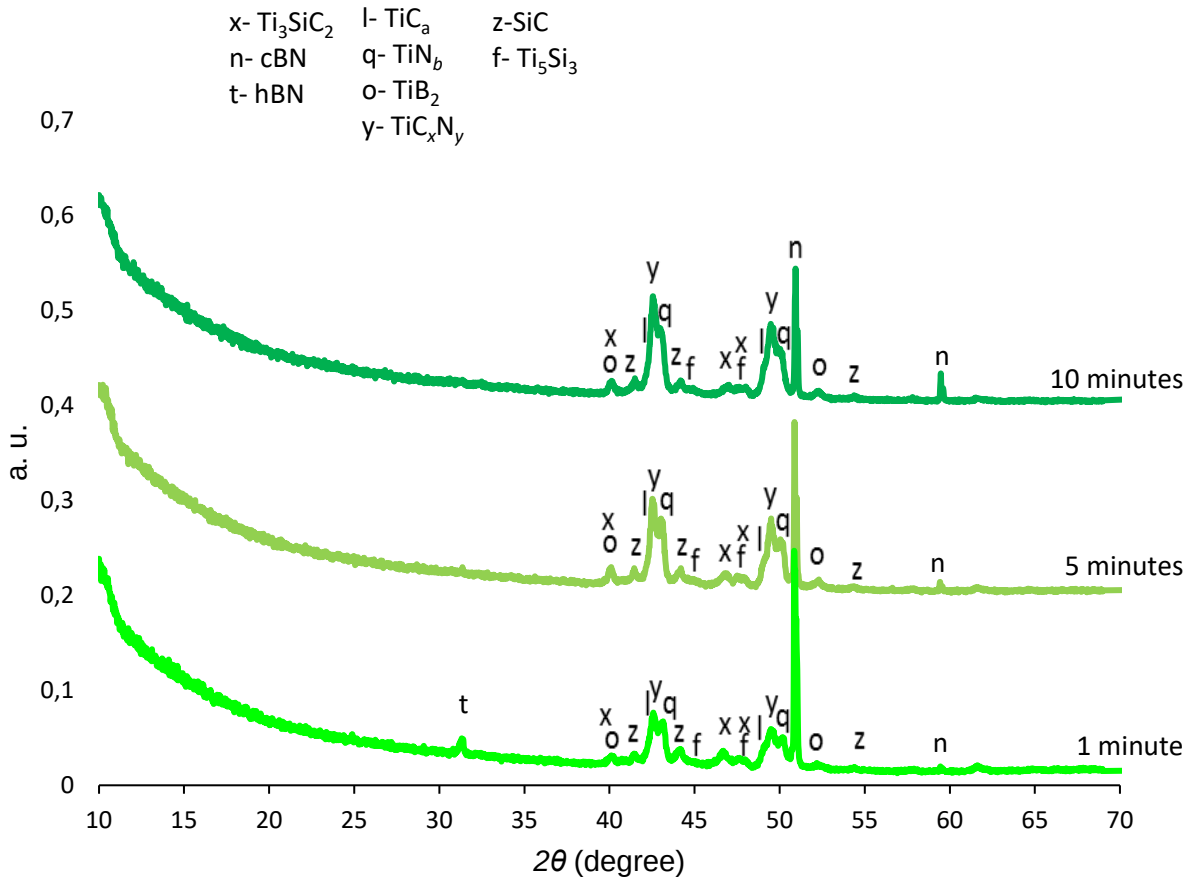


Figure 4.48: XRD traces of Ti_3SiC_2 -(20 vol.% of $100\ \mu\text{m}$) cBN samples sintered at 30 MPa, 1250°C and different times.

Rietveld analysis of the samples sintered at 1250°C, Figure 4.50, shows that there was less than 10 vol.% of Ti_3SiC_2 present in all. The highest quantity of Ti_3SiC_2 was found in the sample sintered for 1 minute and decreased with sintering dwell time. The TiC_a , TiN_b , TiC_xN_y and cBN were present in large quantities in all samples sintered at 1250°C and 1300°C. The TiB_2 , SiC, Ti_5Si_3 phases were also found in all samples sintered at 1250°C and 1300°C but in very small quantities. The hBN phase was only observed in the sample sintered at 1250°C for 1 minute and at 1300°C for 10 minutes.

Figure 4.50 shows the Rietveld analyses of the phase proportion of the samples analysed in Figure 4.48. The cBN, Ti_5Si_3 and Ti_3SiC_2 decreased with increase in dwell time whereas TiC_a and TiN_b increased with increased dwell time. TiC_xN_y increased then decreased with dwell time and SiC seem to have had no change with temperature.

Figure 4.51 shows the density of the samples sintered at 1250°C and 1300°C, the error for both the densities and open porosities were small. The exception was open porosities for samples sintered for 10 minutes, the densities at 1300°C for 5 minutes and 1250°C for 1 minute. Again, these values were considered with caution. The densities and open porosities of the samples sintered at 1250°C remained the same for all dwell times. The density of the samples sintered at 1300°C, however, stayed the same and only decreased with increasing of dwell time to 10 minutes. The open porosity stayed the same until 5 minutes, then increased with increased dwell time. The change in density in this case may be due to the increase in open porosity, not necessarily changes in phases on the samples, the increase of the TiN which has a higher density, than BN phases (lowered densities) may be the reason for this.

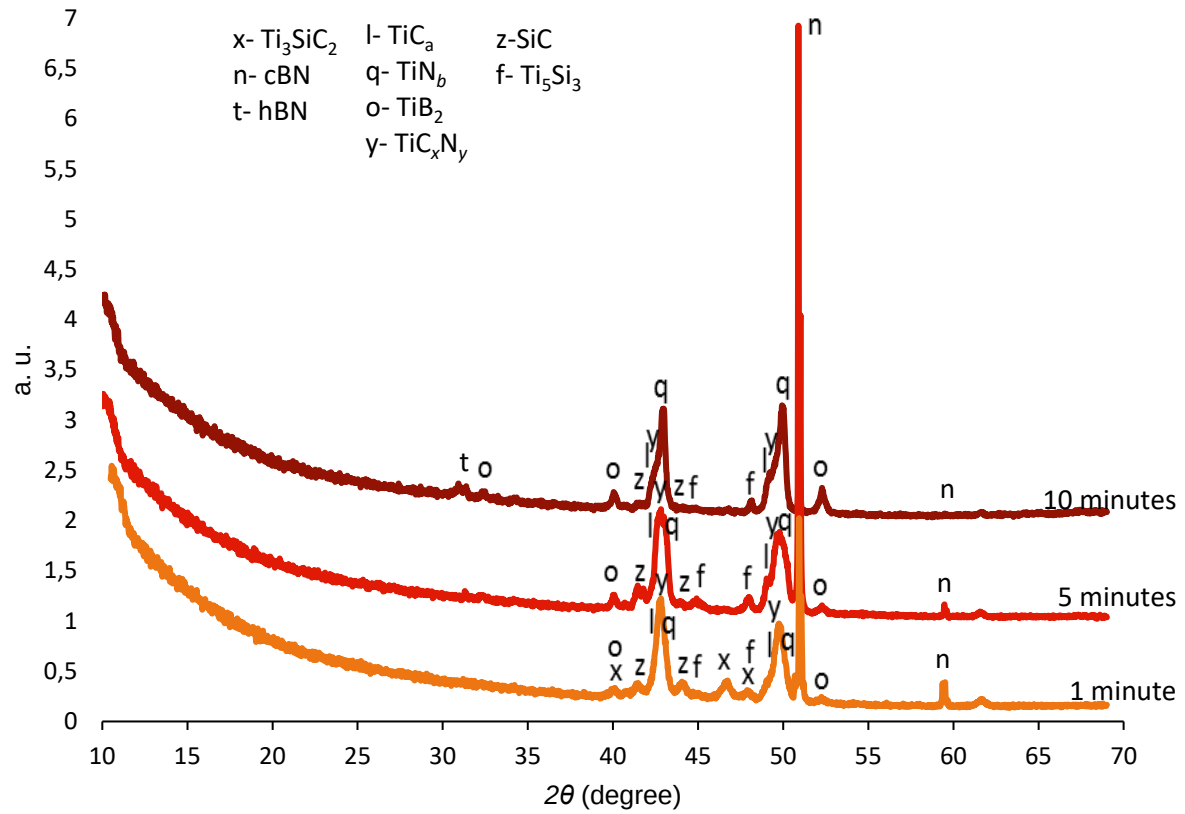


Figure 4.49: XRD traces of Ti_3SiC_2 -(20 vol% of 100 μm) cBN samples sintered at 30 MPa, 1300°C and different times.

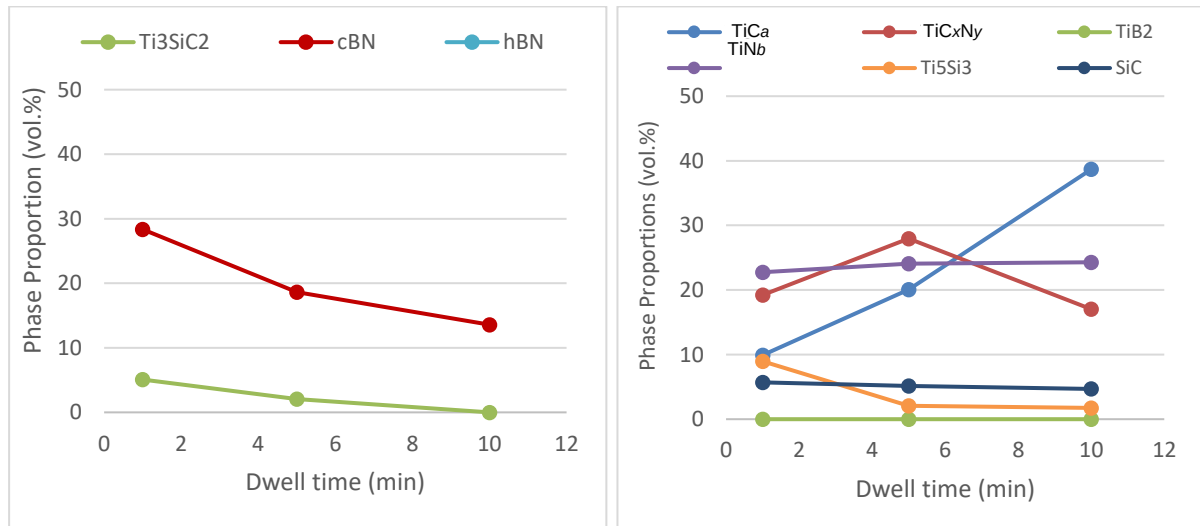


Figure 4.50: Phase quantities, determined by Rietveld analysis, of Ti_3SiC_2 -cBN (20 vol.%, 100 μm) samples sintered for different times at 1250°C.

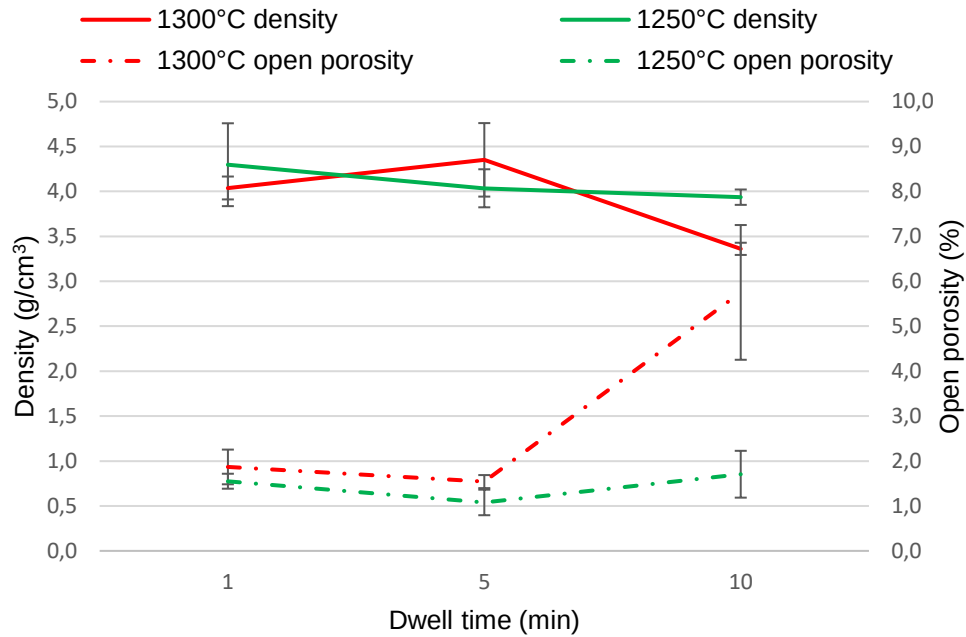


Figure 4.51: Densities and open porosities of Ti_3SiC_2 -cBN (20 vol.%, 100 μm) samples sintered at different temperatures for different dwell time.

Figure 4.52 shows the SEM (BSE) images of the Ti_3SiC_2 -cBN samples sintered at 1250°C and 1300°C. For all samples sintered at 1250°C and 1300°C for 1 minute, there were cracks propagating between the cBN and matrix (red arrows) seen, indicating that the bond between the cBN and the MAX phase may not be strong.

The sample sintered at 1300°C for 5 minutes had the crack propagated through the cBN (blue arrows), indicating that the bond between the matrix and the cBN was stronger. In the sample sintered at 1300 for 1 minute there was a region of possible cBN pull-out (green arrow), but in this sample also some crack propagated through the cBN (red arrow) which may indicate mixed modes of fracture. This implies that there were some cBN bonds strongly bonded and some that were not.

Figures 4.53 shows the EDX analysis of the sample sintered at 1250°C for 1 minute. Site 1 shows that this was cBN with some C, but B and N were the major elements. The B:N ratio was not 1:1, but from the principles of SEM-BSE analysis cBN will appear as the darkest phase

as the elements in the phase have the lowest electron density to the other phases in the sample, thus this was taken as cBN. The other phases were difficult to differentiate with contrast, rather the differentiation was done based on different morphologies.

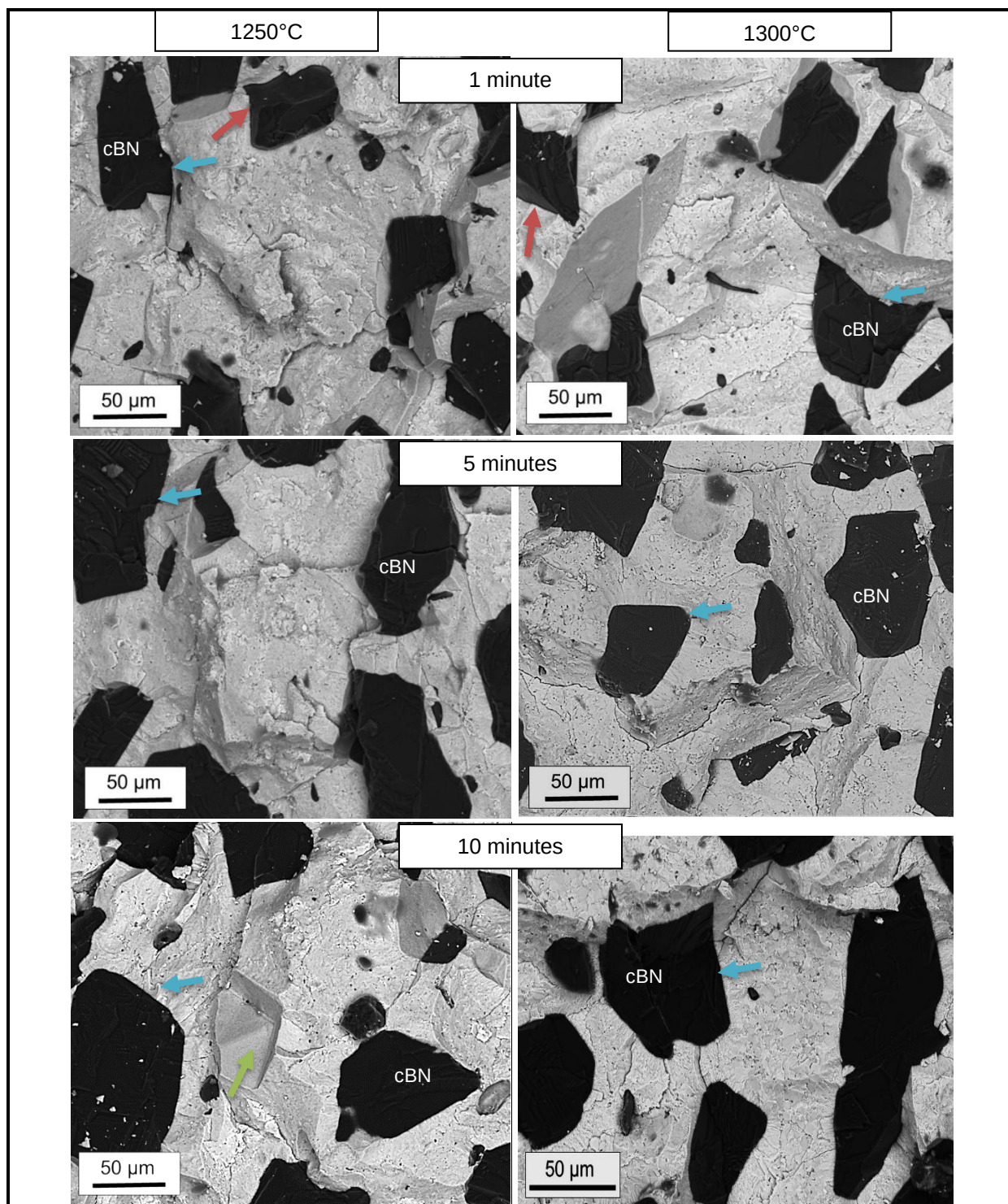
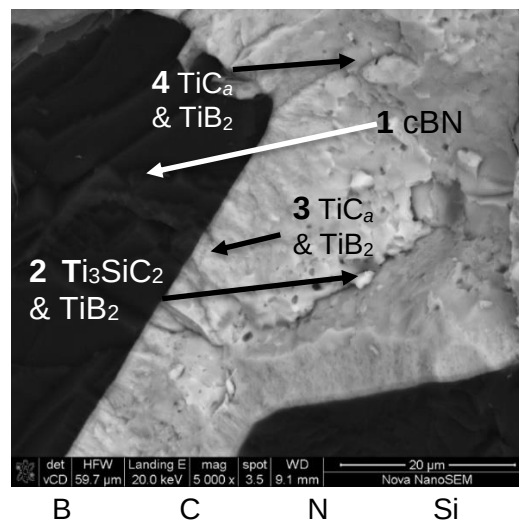


Figure 4.52: SEM (BSE) images of Ti_3SiC_2 -cBN (20 vol.%, 100 μm) samples sintered for different times at 1250°C (left column) and 1300°C (right column).

Sites 3 and 4 in Figure 4.53 had similar elemental composition with Ti, B and carbon present in both. It could be that this was where TiC_a and TiB_2 were found (both in the matrix and reaction area). Site 2 contained Ti, C, B and a small amount of Si, the error for the Si is relatively high and this could be due to the selection of similar phases being based solely on the morphologies in this case. This could have resulted in some selected phases having Si and other not as 5 different sites with similar morphologies were selected for analysis.



		B	C	N	Si	Ti	Total
		atomic %					
site 1	average	50,6	11,7	37,6	0,0	0,1	100,0
	std deviation	0,8	0,6	0,6	0,0	0,1	
site 2	average	54,1	27,8	0,0	2,5	15,6	100,0
	std deviation	4,8	4,9	0,0	2,0	2,2	
site 3	average	61,9	20,8	0,0	0,0	17,3	100,0
	std deviation	3,1	6,6	0,0	0,0	4,7	
site 4	average	62,1	21,7	0,0	0,0	16,2	100,0
	std deviation	1,1	3,7	0,0	0,1	3,3	

Figure 4.53: SEM (BSE) and EDX analysis of Ti_3SiC_2 -cBN (20 vol.%, 100 μm) samples sintered at 30 MPa, 1250°C for 1 minute.

Some sites selected could have Ti_3SiC_2 and since this phase was found in small amounts in the sample (Figure 4.48) the Si content in these phases would be low. If it is assumed that

Ti_3SiC_2 is one of the components in these sites, then the at.% from the site analysis contributing to the MAX phase would be 7,5:2,5:5 for Ti:Si:C assuming that all the Si would be for Ti_3SiC_2 . This would leave 8,1 at.% Ti, 22,8 at.% C and 54,1 at.% B indicating that more TiB_2 could be found in these site.

4.4 Investigation of cBN volume fraction effect on reaction temperatures using 40 vol.% cBN (100 μm)

From the study in the previous sections of reaction/optimisation temperatures of different MAX phases and 20 vol.% of the 100 μm cBN, the optimal/best conditions for sintering a successful composite were recommended, as outlined below, for the 40 vol.% of the 100 μm cBN composite.

For the Ti_2AlC -cBN composites, the 1250°C, sintered for 5 minutes the conditions were once again 1300°C and 1350°C temperatures were also used in anticipation that for the larger cBN, higher volume cBN, a similar reaction to the previous section would occur at a higher temperature or a longer dwell time.

For the Ti_3AlC_2 -cBN composites, the 1300°C, 10 minutes condition was once again used to sinter the samples as recommended in the previous section. Composites were also sintered at 1350°C in anticipation that the higher volume cBN would require higher temperatures for favourable conditions to occur to yield a successful composite. Samples were also sintered at 1250°C to assess the reactivity of these composites at a wider range of temperature.

For the Ti_3SiC_2 -cBN composites, the 1250°C, 5 minutes was also once again used to sinter these composites of a higher volume fraction of cBN as recommended in the previous section, but 1300°C and 1350°C were also used in anticipation that for the larger and higher volume

fraction of the cBN in these composites, more optimal reactions to form Ti_3SiC_2 , could occur at the selected reaction temperatures.

4.4.1 Ti_2AlC -cBN composites

Figure 4.54 shows the XRD diffractograms of the samples sintered at a constant time of 5 minutes and a pressure of 30 MPa and three different temperatures. This was done to obtain and optimise the Ti_2AlC phase in the sample without compromising the cBN content. For all three sintering temperatures, TiC_a , TiC_xN_y , TiB_2 and cBN phases were present. The Ti_3Al , TiAl_2 , Ti_2AlC and Ti_2AlN were only seen in samples sintered at 1250°C and 1300°C, with the sample sintered at 1350°C containing small amounts of Ti_3AlC_2 and TiN_b and significant amounts of hBN. The TiC_xN_y peak shifted with change in values for x and y , the larger the y the further right the peaks were. Similar trends were observed for samples sintered for 10 minutes, Figure 4.55, the only difference was that hBN was observed in samples sintered at 1300°C and 1350°C and no MAX phase was found in the samples sintered at 1350°C.

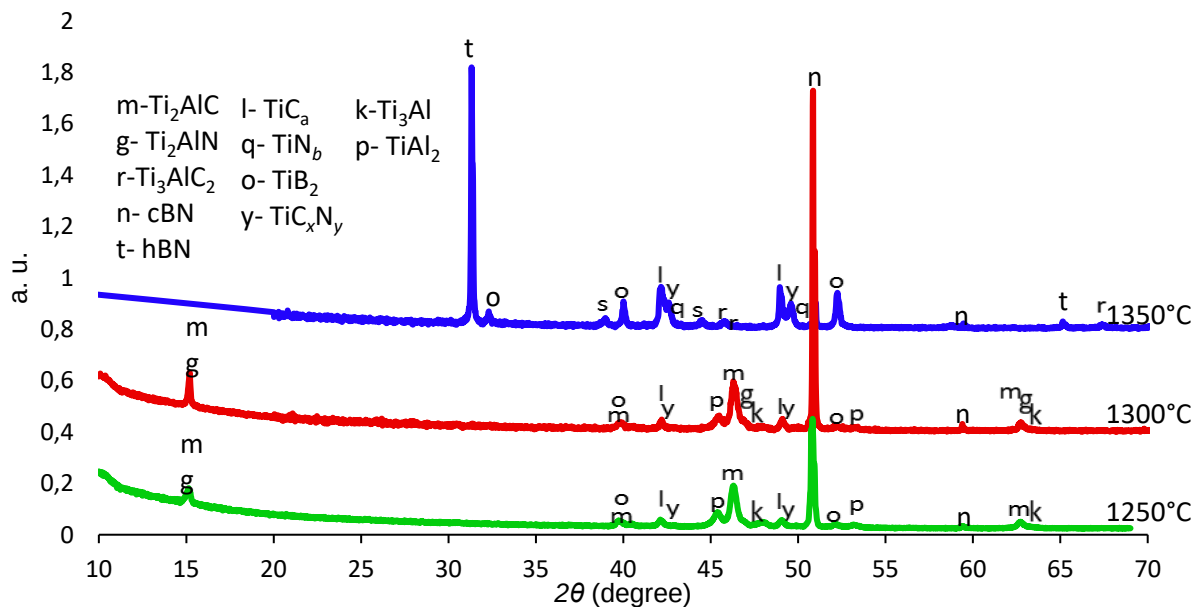


Figure 4.54: XRD traces of Ti_2AlC -cBN (40 vol.%, 100 μm) samples, and a pure Ti_2AlC sample for comparison, sintered at 30 MPa, for 5 min and different temperatures.

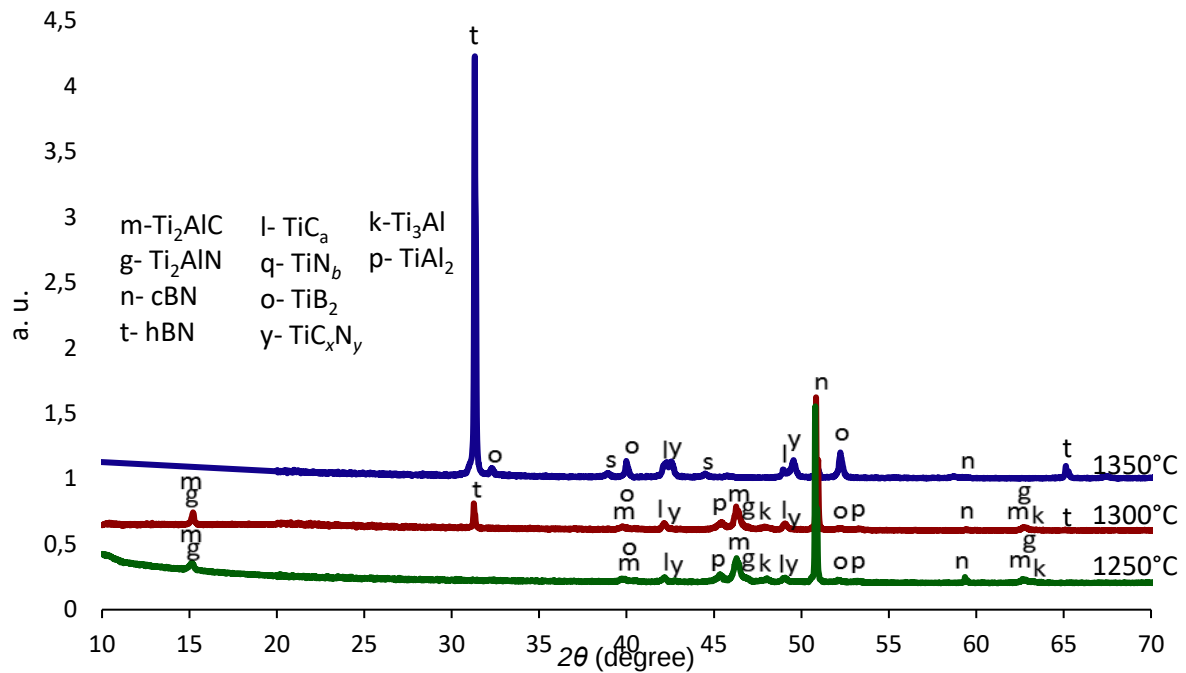


Figure 4.55: XRD traces of Ti_2AlC -cBN (40 vol.%, 100 μm) samples, and a pure Ti_2AlC sample for comparison, sintered at 30 MPa, for 10 min and different temperatures.

Figure 4.56 shows the phase contents of the samples analysed in Figure 4.54. Ti_2AlN and cBN decreased with increased temperature, whereas Ti_2AlC and TiAl_2 first increased then decreased with increased temperature. TiB_2 and TiC_xN_y first decreased then increased with increased temperature. The cBN phase remained the major phase in all samples except samples sintered at 1350°C where TiB_2 and TiC_xN_y become the major phases. The analysis done here agrees with the observations in Figure 5.54.

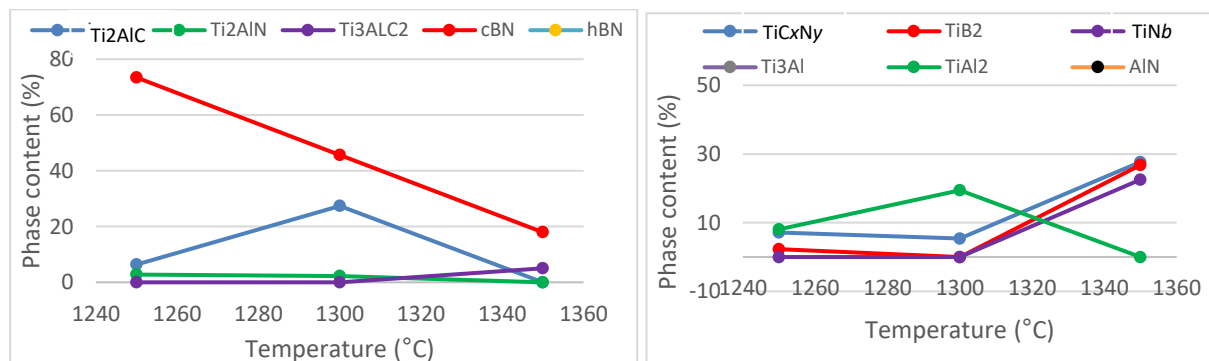


Figure 4.56: Phase quantities, determined by Rietveld analysis, of Ti_2AlC -cBN (40 vol.%, 100 μm) samples sintered for 5 minutes at different temperatures.

Figure 4.57 shows the densities and open porosities of the samples sintered for 5 and 10 minutes. The densities for the samples sintered for 5 and 10 minutes were the same (3.5 g/cm³) for all sintering temperatures. Samples sintered at 1250°C and 1300°C also had the same densities (3.5 g/cm³), and the density increased (3.9 g/cm³) when the sintering temperature increased to 1350°C. The open porosities have a large error associated with them, so the values are not reliable, however the open porosities remain the same until a decrease at 1350°C. The difference in the density and open porosities for the sample sintered at 1350°C can be attributed to the phase change that was observed, Figures 4.54 and 4.55, where the sample sintered for 5 minute had Ti₃AlC₂ and the one sintered for 10 minutes did not.

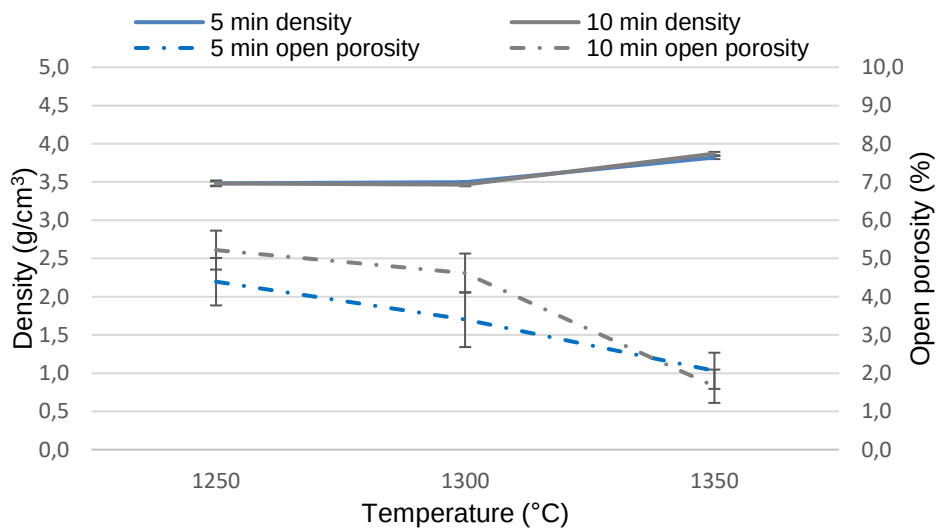


Figure 4.57: Densities and open porosities of Ti₂AlC-cBN (40 vol.%, 100 µm) samples sintered at different temperatures for different dwell time.

Figure 4.58 shows the SEM (BSE) images of the Ti₂AlC-cBN samples sintered for 5 minutes and 10 minutes. Samples sintered at 1250°C and 1300°C were similar in terms of the matrix and cBN morphology, however, the samples sintered at 1350°C had a clear reaction area (between red and blue circles). The reaction area had two clear layers and was approximately

8-9 μm thick for the sample sintered for 5 minutes and approximately 10-12 μm thick for the sample sintered for 10 minutes.

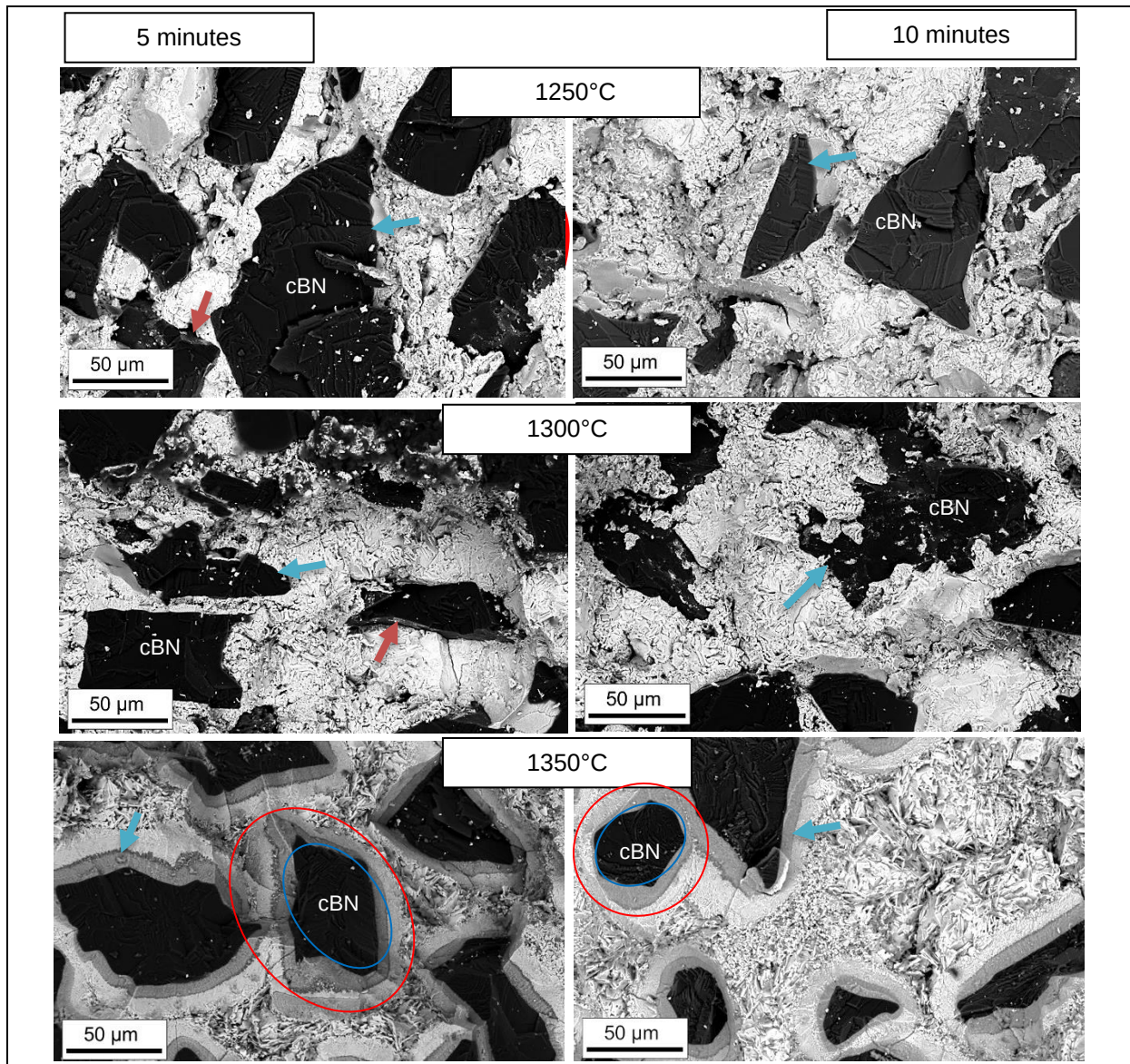
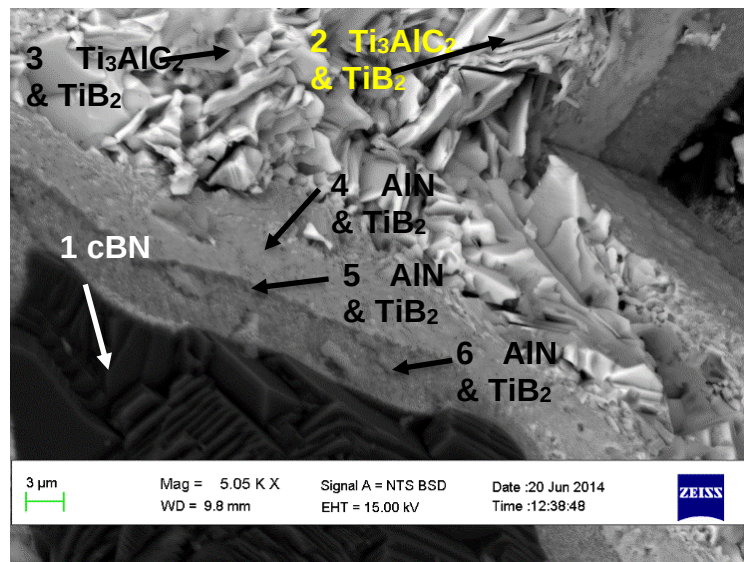


Figure 4.58: SEM (BSE) images of Ti_2AlC -cBN (40 vol.%, 100 μm) samples sintered at 30 MPa and different temperatures for 5 minutes (left) and 10 minutes (right).

In all samples it was observed that there was evidence of crack propagation through cBN (blue arrow) which indicates that the bond of the matrix to the cBN was strong. It was also observed in samples sintered for 5 minutes at 1250°C and 1300°C had some evidence of crack propagating between the cBN and the matrix (blue arrow) indicating that, in these cases, the bond was weak.

Figures 4.59 shows the EDX analysis of the samples sintered at 1350°C for 5 minutes as the samples sintered at 1250°C and 1300°C were similar in morphology as the samples presented in Section 4.3.1.



		B	C	N	Al	Ti	Total
		atomic %					
site 1	average	46,0	9,2	44,1	0,4	0,3	100,0
	std deviation	3,9	5,5	2,9	0,4	0,3	
site 2	average	24,2	26,9	1,8	6,3	40,7	100,0
	std deviation	4,9	16,9	4,0	2,6	18,2	
site 3	average	22,1	22,9	18,7	6,4	29,8	100,0
	std deviation	3,3	8,8	12,0	2,3	11,4	
site 4	average	45,4	18,7	11,4	4,4	20,1	100,0
	std deviation	3,5	2,2	1,9	1,2	3,1	
site 5	average	45,1	7,8	26,9	13,2	7,0	100
	std deviation	0,2	0,7	1,1	1,0	0,6	
site 6	average	37,7	20,1	18,7	12,7	10,8	100
	std deviation	3,5	7,6	3,9	5,4	4,8	

Figure 4.59: SEM (BSE) and EDX analysis of Ti_2AlC -cBN (40 vol.%, 100 μm) samples sintered at 30 MPa, 1350°C and 5 minutes.

The EDX analysis shows that in Site 1 there was a BN phase and some C observed from the EDX data, this could be due to the x-rays from the neighbouring phases. Site 2 shows that the elements present in the at.% can be Ti_3AlC_2 and TiB_2 , there is a large error associated with the carbon content which could be due to some of the 5 sites chosen for EDX analysis having very little carbon, meaning they could have contained more TiB_2 . Site 3 also showed shows that the ratios of the elements could have been Ti_3AlC_2 and TiB_2 , in this case the large error was associated with the N content could be due to some of the 5 sites chosen for EDX analysis containing TiN_b , but with high uncertainty in this case. Site 4 shows some evidence of possible AlN and TiB_2 . Sites 5 show evidence of AlN , TiB_2 and evidence that some cBN x-rays might have been picked up by the detector as the analysed site is thin and close to cBN. Site 6 also shows signs of AlN and TiB_2 and more evidence of BN phase for the same reasoning for site 5. Sites 4, 5 and 6 within the reaction area seem to contain the same phases, the difference in shade may be due to a difference in ratio of TiB_2 and AlN . For instance, site 5 May contain more AlN than the other sites, and site 6 less AlN than the other sites.

4.4.2 Ti_3AlC_2 -cBN composites

Figure 4.60 shows the XRD diffractograms of the samples sintered for a constant time of 5 minutes and a pressure of 30 MPa and three different temperatures. Figure 4.61 shows the XRD diffractograms of the samples sintered at the same temperatures and pressures as the samples in Figure 4.60 but sintered for 10 minutes. This was done to obtain and optimise the Ti_3AlC_2 phase in the sample without compromising the cBN content. For samples (Figures 4.60 and 4.61), TiC_xN_y and cBN phases were present, with Ti_2AlC and Ti_3Al present in all samples sintered at 1250°C and 1300°C. The Ti_3AlC_2 , TiN_b AlN and TiC_a phases were observed in the sample sintered at 1350°C, and TiAl_2 observed only in sample sintered at 1250°C (Figures 4.60 and 4.61). TiB_2 was observed in all samples sintered for 10 minutes (Figure 4.61), whereas in the samples sintered for 5 minutes, it was only observed in the sample sintered at 1350°C (Figure 4.60). The hBN phase was present in small amounts in all samples sintered

for 10 minutes (Figure 4.61). The TiC_xN_y peak shifted to the left as the N content decreased in the phase, the exact ratios of x and y in this phase for each sintering temperature can be seen in Appendix B.

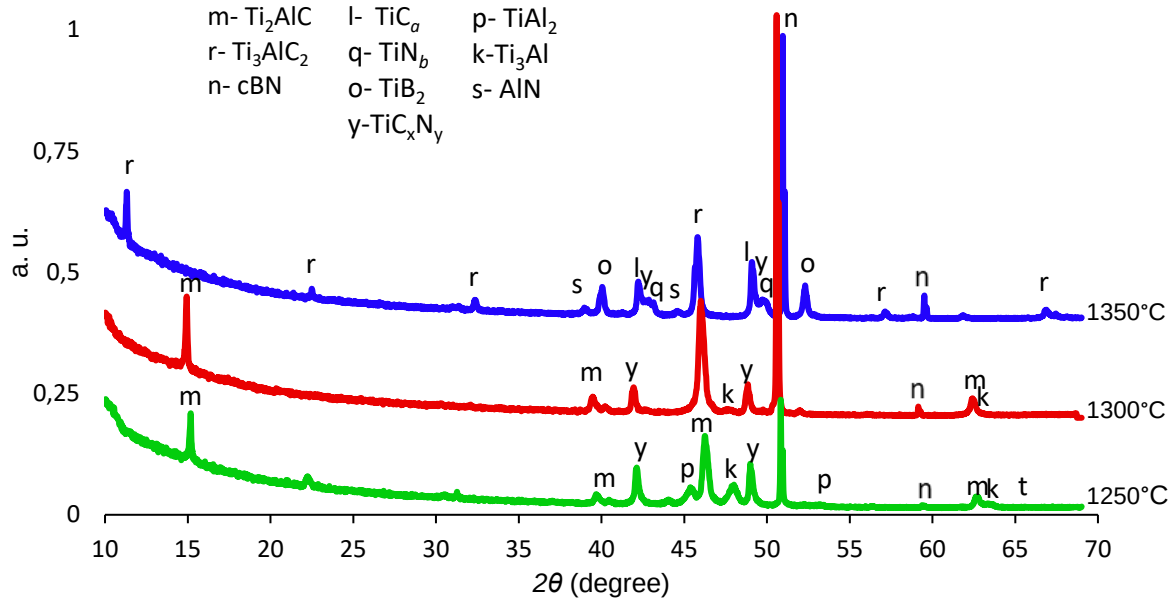


Figure 4.60: XRD traces of Ti_3AlC_2 -cBN (40 vol.%, 100 μm) samples sintered at 30 MPa for, 5 minutes and at different temperatures.

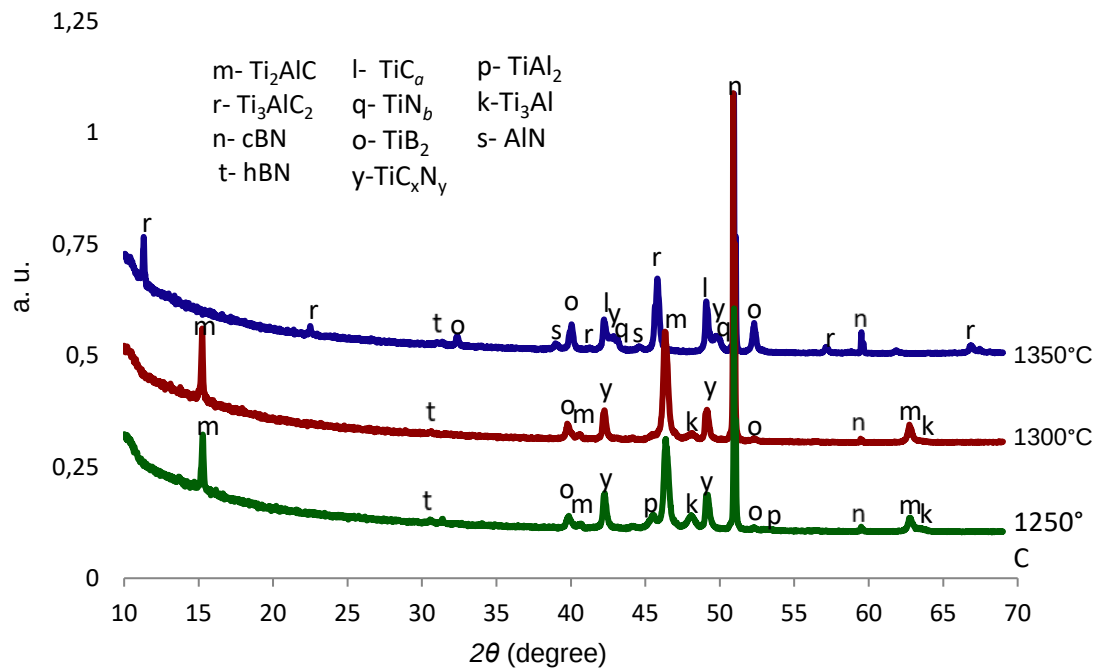


Figure 4.61: XRD traces of Ti_3AlC_2 -cBN (40 vol%, 100 μm) samples sintered at 30 MPa, 10 minutes and different temperatures.

Figure 4.62 shows the results of the Rietveld analysis of the samples analysed in Figure 4.60. Ti_3AlC_2 , TiNb , TiCa , TiB_2 and AlN were only seen in the sample sintered at 1350°C . Ti_2AlC first increased with temperature then decreased until it was depleted in the sample sintered at 1350°C . However, cBN and Ti_3Al decreased with increasing in temperature and TiC_xN_y had only a slight increase with temperature.

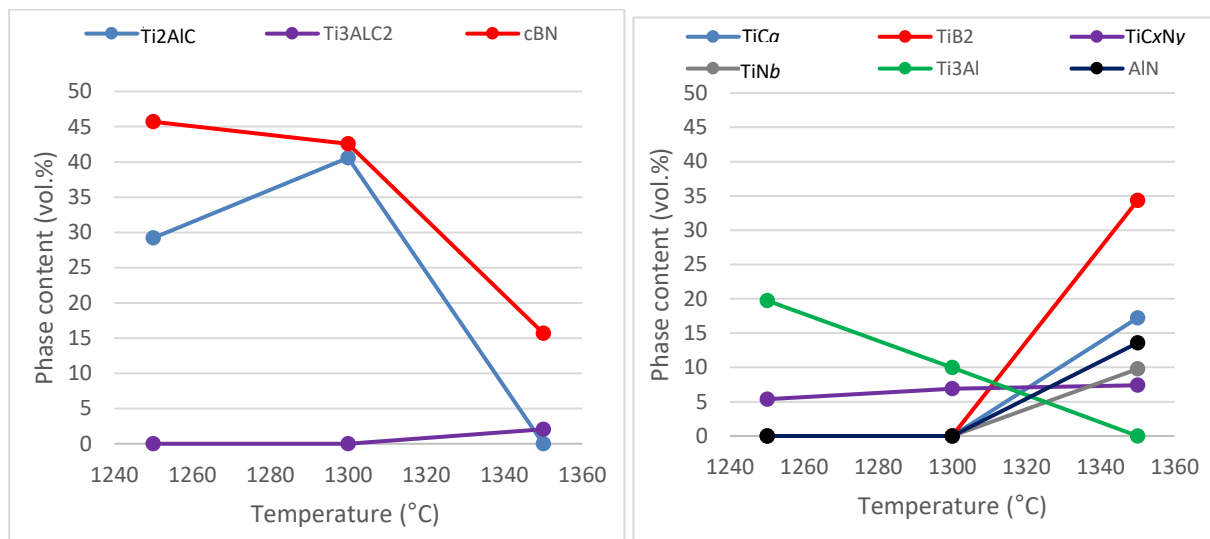


Figure 4.62: Phase quantities, determined by Rietveld analysis, of Ti_3AlC_2 -cBN (40 vol.%, 100 μm) samples sintered for 5 minutes at different temperatures.

Figure 4.63 shows the density of samples sintered at all temperatures and for all dwell times. The densities of the samples sintered at both 5 and 10 minutes dwell times were the same. Also, samples sintered at 1250°C to 1350°C had similar densities, this was not unexpected as the phase content of the samples was very similar. The open porosities for all samples displayed a large error due to the scale instability, thus the values observed were considered with caution. For samples sintered for 10 minutes, the open porosity decreased with increased sintering temperature, whereas, the samples sintered for 5 minutes the open porosity first increased then decreased. The decreased porosity with temperature was expected as the increase in temperature promoted densification and thus decreased porosity.

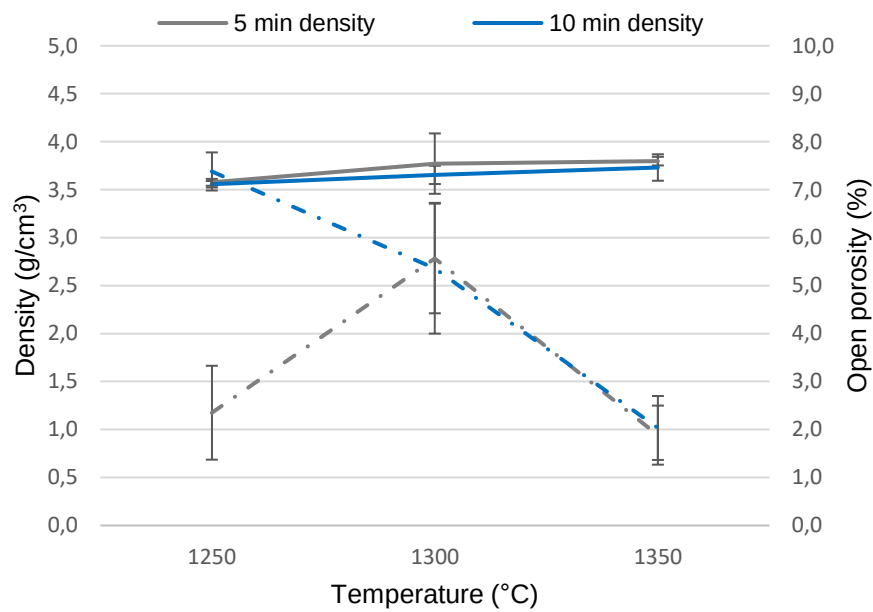


Figure 4.63: Densities and open porosities of Ti_3AlC_2 -cBN (40 vol.%, 100 μm) samples sintered at different temperatures and dwell time.

Figure 4.64 shows the SEM (BSE) analysis of the Ti_2AlC -cBN samples sintered for 5 minutes and 10 minutes. The samples sintered at 1250°C and 1300°C had similar morphology to the samples in Sections 4.2.2 and 4.3.2. However, the samples sintered at 1350°C had a clear reaction area (between red and blue circles) which was approximately 25 μm thick for both samples sintered for 5 and 10 minutes.

It was also observed in Figure 4.64 that in all samples, there were instances where the crack propagated through the cBN (blue arrow) indicating that the bond between the cBN and the matrix was strong. In samples below 1350°C showed evidence of the crack propagating between the cBN and the matrix (red arrows) which indicated that the bond between the cBN and the matrix was not strong in these cases.

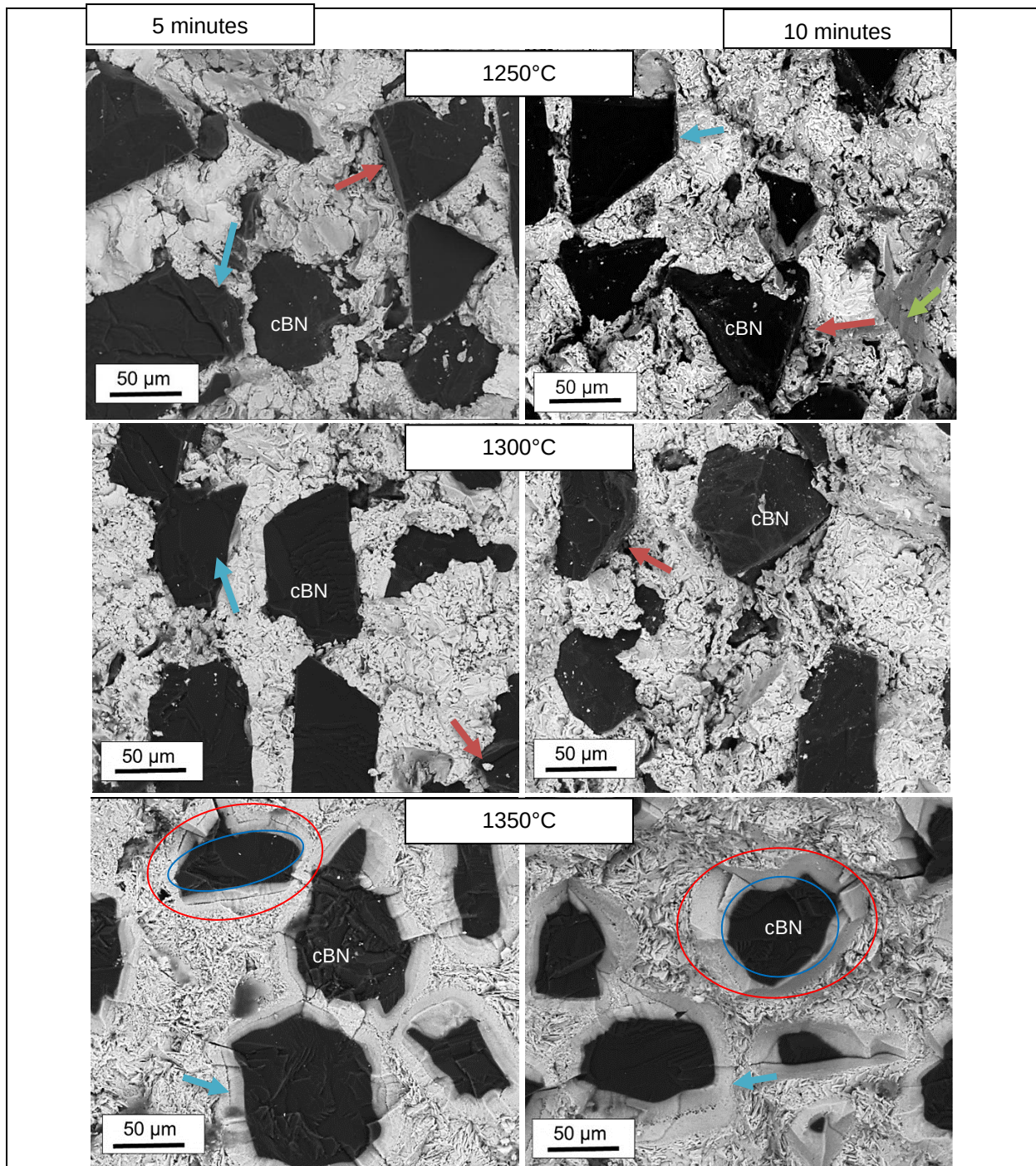
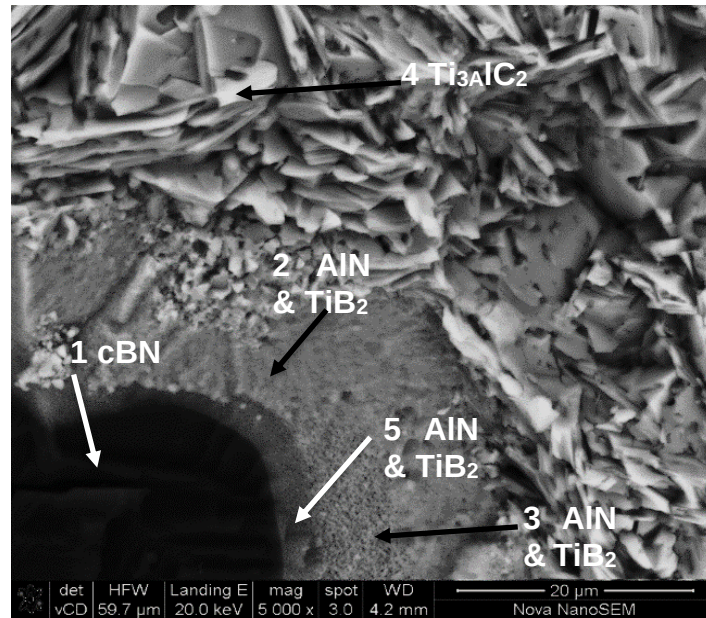


Figure 4.64: SEM (BSE) of Ti_3AlC_2 -cBN (40 vol.%, 100 μm) samples sintered at 30 MPa and different temperatures for 5 minutes (left) and 10 minutes (right).

Figures 4.65 shows the EDX analysis of the sample sintered at 1350°C for 5 minutes as the samples sintered at 1250°C and 1300°C look similar morphology in relation presented in Sections 4.3.2. The EDX analysis for Site 1 shows that this is the cBN phase, the B:N ratios

are not 1:1, however using the principles of SEM-BSE analysis: the darkest phase of all the phases present in the sample (Figure 4.60) is cBN.



		B	C	N	Al	Ti	Total
		atomic %					
site 1	average	50,0	16,8	32,9	0,0	0,3	100,0
	std deviation	4,7	14,1	15,0	0,0	0,5	
site 2	average	56,2	20,3	10,4	1,3	11,8	100,0
	std deviation	6,3	13,3	11,6	0,6	3,4	
site 3	average	62,2	22,1	3,0	1,2	11,5	100,0
	std deviation	5,2	5,2	7,3	0,5	2,2	
site 4	average	51,1	33,3	0,0	3,1	12,5	100,0
	std deviation	4,0	4,7	0,0	1,5	1,8	
site 5	average	62,6	24,3	3,0	0,6	9,6	100,0
	std deviation	4,6	11,6	6,7	0,6	6,0	

Figure 4.65: SEM (BSE) and EDX analysis of Ti_3AlC_2 -cBN (40 vol.%, 100 μm) samples sintered at 30 MPa, 1350°C for 5 minutes.

Sites 2, 3 and 5 had similar phase content with the exception of Site 2, which showed a little less B and slightly more N. These Sites had a high error for N, this may have been due to one some of the 5 phases that were analysed per area containing no N and some sites with high

N content. These sites may have contained TiB_2 and a little AlN with BN x-ray signals detected as these sites were close to cBN. The contrasts and morphologies of these sites may have been due to the different ratios of the present phases in each site. Site 4 shows evidence of Ti_3AlC_2 and a large amount of B which could have been detected from the neighbouring phases.

4.4.3 Ti_3SiC_2 -cBN composites

Figure 4.66 shows the XRD diffractograms of the samples sintered for a constant time of 5 minutes, at 30 MPa and three different temperatures, in order to optimise and cBN contents in the sample. For all three sintering temperatures Ti_3SiC_2 , TiC_a , TiB_2 , cBN and hBN phases were present. Ti_5Si_3 was only found in the sample sintered at 1250°C and 1300°C with TiC_xN_y only in the sample sintered at 1350°C . Similar trends were observed for samples sintered for 10 minutes at 1250°C and 1300°C with the hexagonalisation of the cBN more pronounced and SiC present in the sample sintered at 1250°C , Figure 4.67.

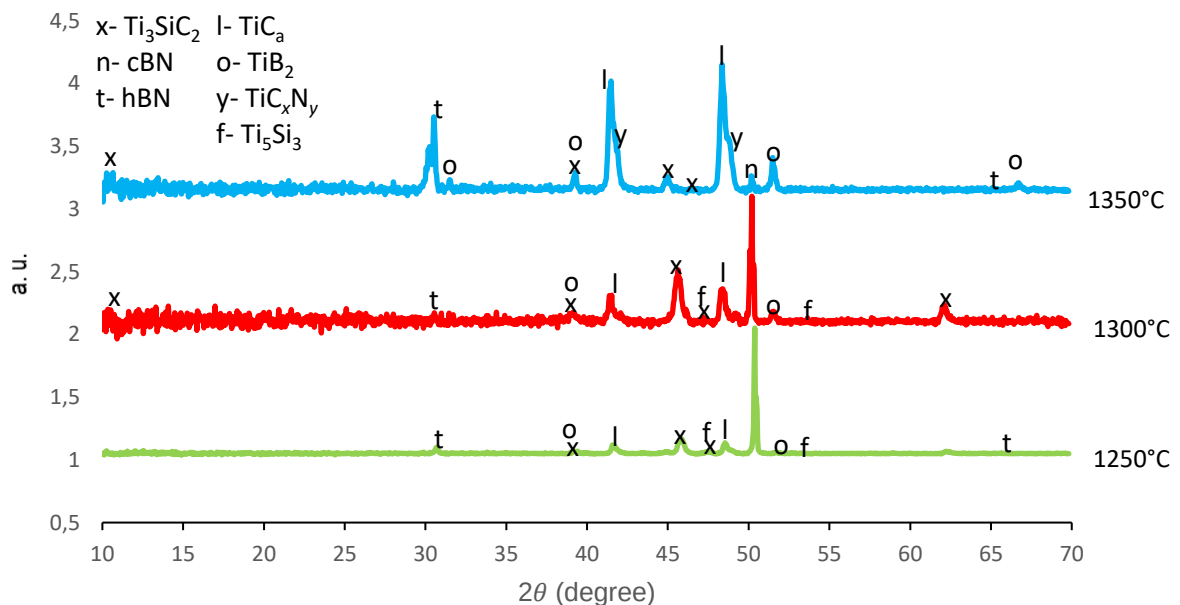


Figure 4.66: XRD traces of Ti_3SiC_2 -cBN (40 vol.%, 100 μm) samples sintered at 30 MPa, 5 min and different temperatures.

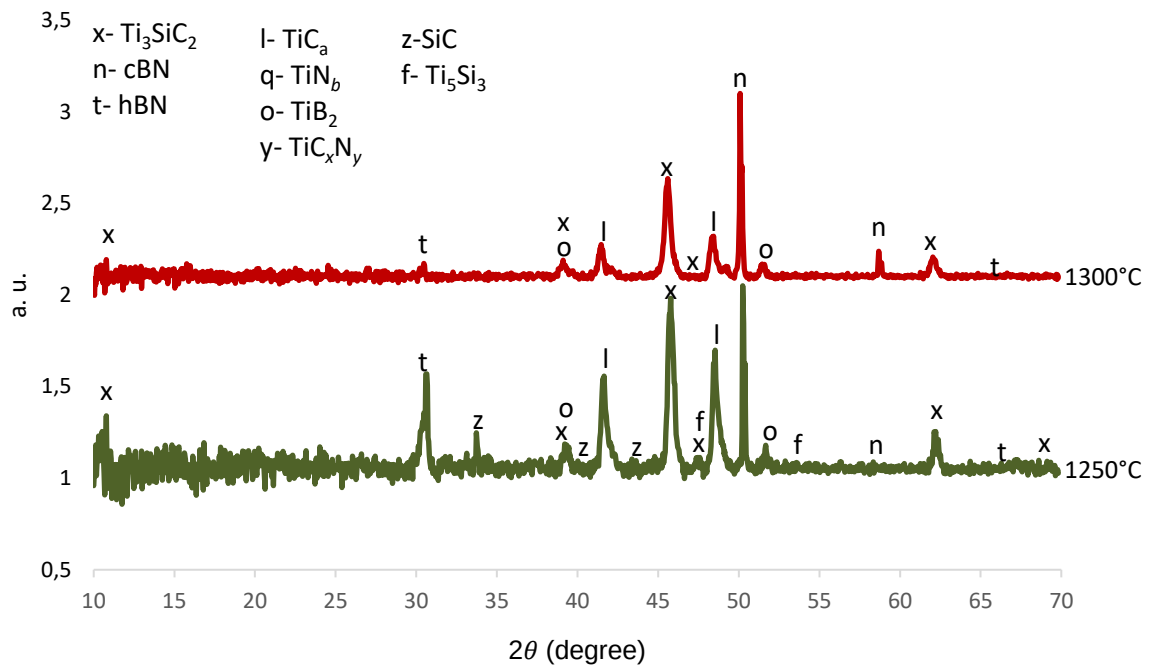


Figure 4.67: XRD traces of Ti_3SiC_2 -cBN (40 vol%, 100 μm) samples sintered at 30 MPa, 10 minutes and different temperatures

Figure 4.68 shows the Rietveld analyses of the phase proportions of the samples analysed in Figure 4.66. The cBN, and Ti_3SiC_2 phases decreased with increased temperature whereas TiC_a increased with temperature. Ti_5Si_3 first increased then decreased with temperature, TiB_2 and TiC_xN_y were only seen in samples sintered at 1350°C cBN and Ti_3SiC_2 were the major phases at 1250°C and 1300°C, then TiB_2 and TiC_a became the major phases in samples sintered at 1350°C.

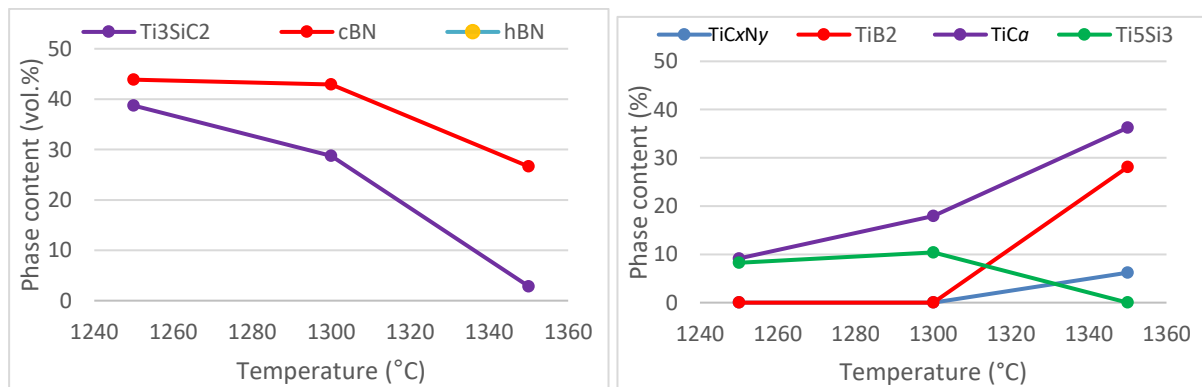


Figure 4.68: Phase quantities, determined by Rietveld analysis, of Ti_3SiC_2 -cBN (40 vol.%, 100 μm) samples sintered for 5 minutes at different temperatures.

Figure 4.69 shows the density of samples sintered at all temperatures and for all dwell times. The densities of the samples sintered at both 5 and 10 minutes dwell times were similar for each sintering temperature, this was reasonable as the phase content of the samples was very similar at each temperature. The densities for the samples sintered for 5 and 10 minutes increased with temperature, and the open porosity decreased with increased temperature. This was due to the increase of the higher density secondary phases and the reduction of the lower density major phases (Figure 4.68). The errors for both the densities and open porosities of all the samples was low, meaning these results in Figure 4.69 were reliable.

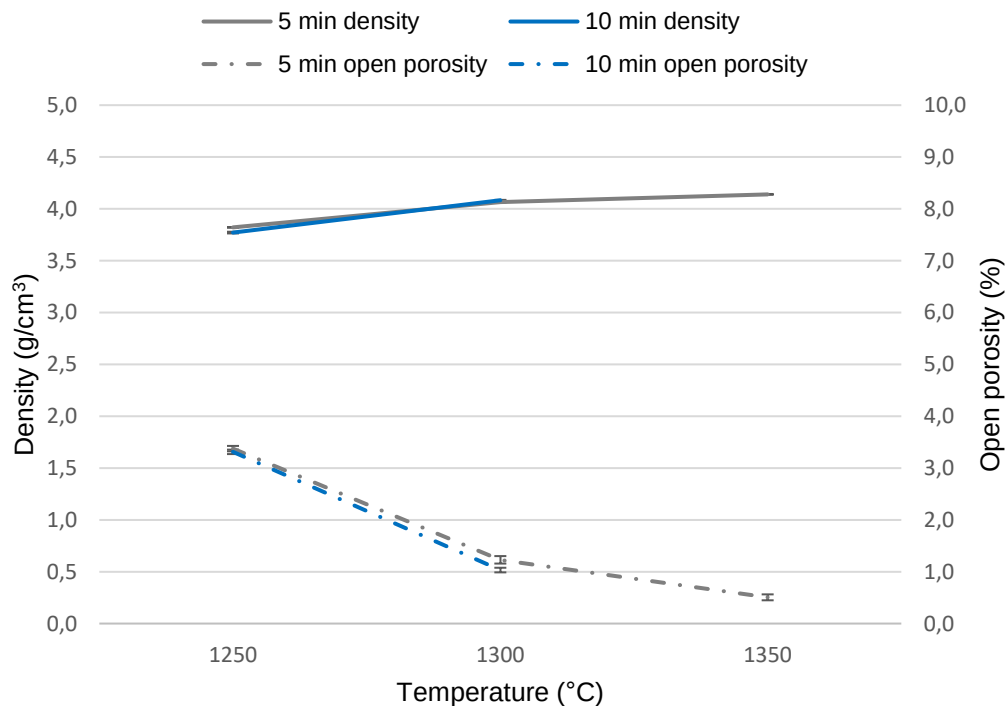


Figure 4.69: Densities and open porosities of $\text{Ti}_3\text{SiC}_2\text{-cBN}$ (40 vol.%, 100 μm) samples sintered at different temperatures for different dwell time.

Figure 4.70 shows the SEM (BSE) images of the $\text{Ti}_3\text{SiC}_2\text{-cBN}$ samples sintered for 5 and 10 minutes. And Figure 4.71 shows the EDX analysis of the samples sintered at 1350°C for 5 minutes as the samples sintered at 1250°C and 1300°C displayed similar morphology as the samples presented in Section 4.3.3.

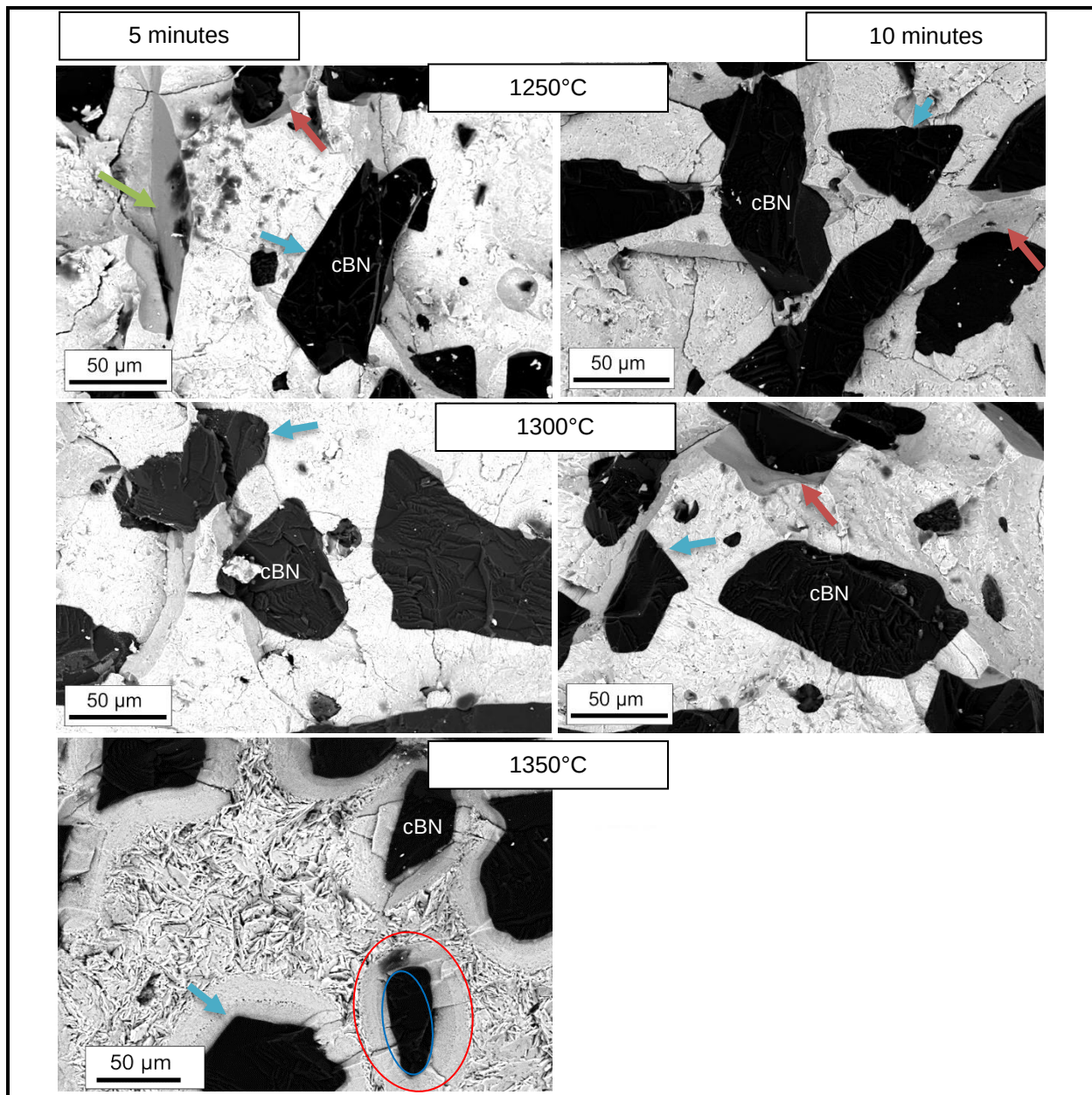
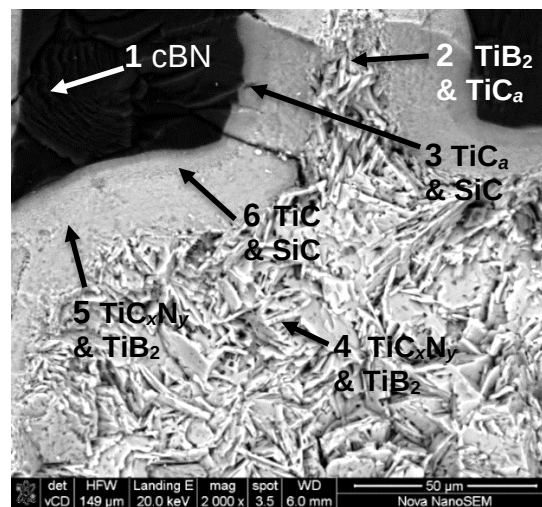


Figure 4.70: SEM (BSE) images of Ti_3SiC_2 -cBN (40 vol.%, 100 μm) samples sintered at different temperatures for 5 minutes (left) and 10 minutes (right).

The sample sintered at 1350°C showed a reaction area (between red and blue circles) which was approximately 30 μm thick. It was observed that in all samples, there were instances where the crack propagated through the cBN (blue arrows) indicating that the bond between the cBN and the matrix was strong. Samples below 1350°C showed evidence of the crack propagating between the cBN and the matrix (red arrows), with the exception of the sample

sintered 1300°C for 5 minutes, this indicated that the bond between the cBN and the matrix was not strong in these samples. The sample sintered at 1250°C for 5 minutes also displayed possible cBN pull-out, green arrow. This indicated that samples sintered below 1350°C may have had a combination of weak and strong bonds between the cBN and the matrix. The sample sintered at 1350° would have only strong bonds of cBN to the matrix, this could be attributed to the reaction area.



		B	C	N	Al	Si	Ti	Total
		atomic %						
site 1	average	44,7	11,0	44,1	0,0	0,0	0,1	100
	std dev	3,7	5,0	2,6	0,0	0,0	0,1	
site 2	average	21,6	51,1	0,0	0,0	0,0	27,2	100
	std dev	0,9	1,4	0,0	0,0	0,0	1,6	
site 3	average	30,6	25,9	30,9	0,0	0,3	12,3	100
	std dev	4,7	2,9	2,5	0,0	0,0	2,6	
site 4	average	23,5	53,0	2,3	0,0	0,1	21,1	100
	std dev	1,2	6,8	4,6	0,0	0,0	2,9	
site 5	average	30,8	40,8	5,3	0,0	0,1	23,0	100
	std dev	2,1	3,7	4,4	0,0	0,1	0,9	
site 6	average	35,9	12,7	38,7	0,0	0,2	12,4	100
	std dev	2,3	0,5	0,6	0,0	0,0	1,2	

Figure 4.71: SEM (BSE) and EDX analysis of Ti_3SiC_2 -cBN (40 vol.%, 100 μm) samples sintered at 30 MPa, 1300°C for 5 minutes.

In Figure 4.71, the EDX analysis of the sample showed that in Site 1 there was a BN phase. Site 2 showed some TiB_2 and TiC_a , demonstrating that these phases were found distributed in the matrix. Site 3 showed TiC_a , a little SiC and BN phases, this section of the reaction area contained TiC_a , and the BN detected could have been because the site of analysis was very close to the cBN. Sites 4 showed evidence that this was TiC_xN_y and TiB_2 could be found. Site 5 also showed evidence of the phases seen in site 4, however, from the at.% of Site 5 suggests that in Site 5 had different proportions of TiB_2 and TiC_xN_y than Site 4. This demonstrated that these phases could be found distributed in the matrix and in the reaction area. Site 6 shows some evidence of BN phase as B and N occurred in almost equal proportions. TiC could also be within this site with Ti and C in almost equal proportions as well, there was also a little Si, which could be SiC. Evidence of TiC_xN_y and TiB_2 were further away from the cBN within the reaction area (Site 5) and more also found in the matrix (Site 4). No evidence of Ti_3SiC_2 was found, this could be because, as seen in Figure 4.66, there was very little Ti_3SiC_2 in the sample.

4.5 Evaluating of the mechanical properties of the MAX-cBN composites

From the study in the previous sections of reaction/optimisation temperatures of different MAX phases and cBN at different volume fraction and size of cBN, the samples that were considered successful are shaded green (Figures 4.72, 4.73 and 4.74). The successful samples for mechanical testing were selected as follows:

For the Ti_2AlC -cBN composites, the 1250°C sintering temperature samples were chosen for all three variations of volume fraction and size of cBN (Figure 4.72). These contained both the MAX phase and the cBN as the major phase, but also no hBN present. However, for the composite samples containing 40 vol.% of the 100 μm cBN all samples sintered at 1250°C and the sample sintered at 1300°C for 5 minutes, could also be considered successful under the same criteria.

For the Ti_3AlC_2 -cBN composites, the 1300°C 10 minutes sintering condition was chosen for sintering the 20 vol.% of $100\mu\text{m}$ cBN samples for mechanical testing. The 1350°C for 5 minutes sintering condition was chosen for sintering 40 vol.%, $100\mu\text{m}$ cBN composites for mechanical testing (Figure 4.73). The latter contained both the MAX phase and the cBN as the major phase with no hBN present. However, the former had other phases as the major phases, but contained an acceptable amount of the MAX phase and cBN in addition to containing only the Ti_3AlC_2 instead of the Ti_2AlC in the composite. The 20 vol.% samples were not considered because they contained both very little amounts of the MAX phase and high amounts of hBN.

For the Ti_3SiC_2 -cBN composites, the 1250°C for 5 minutes sintering conditions were chosen for sintering the 20 vol.% of $100\mu\text{m}$ cBN samples for mechanical testing as the samples sintered at these conditions contained both Ti_3SiC_2 phase and cBN as the major phase with no hBN. The 1300°C for 5 minutes sintering conditions were chosen for sintering 40 vol.%, $100\mu\text{m}$ cBN composites for mechanical testing (Figure 4.74) as the samples sintered at these conditions contained both Ti_3SiC_2 and cBN, however other phases were the major phases. The 20 vol.% samples were not considered because they contained both very little amounts of the MAX phase and high amounts of hBN.

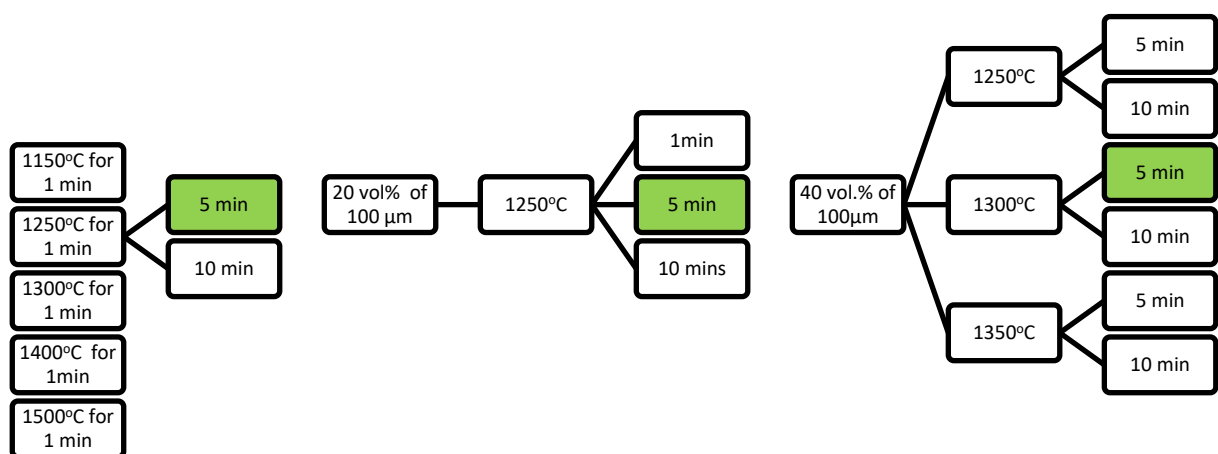


Figure 4.72: A chart showing decision making for the temperatures to use to synthesise Ti_2AlC -cBN composites. Selected optimal conditions from previous sections are highlighted in green.

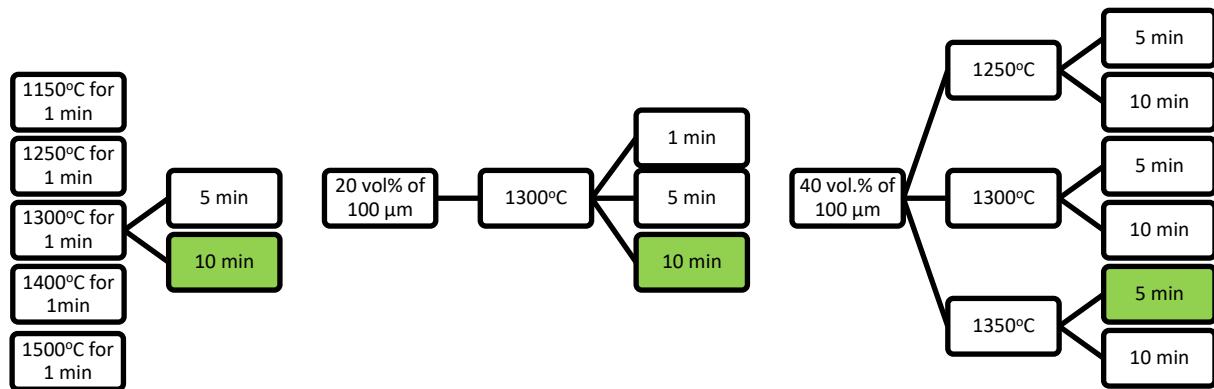


Figure 4.73: A chart showing decision making for the temperatures to use to synthesise $\text{Ti}_3\text{AlC}_2\text{-CBN}$ composites. Selected optimal conditions from previous sections are highlighted in green.

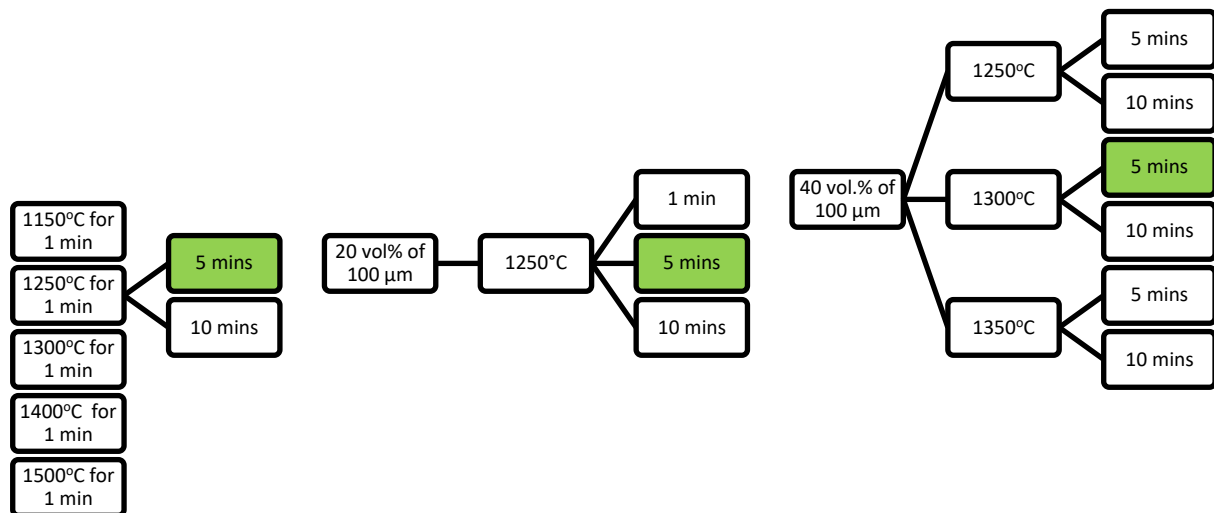


Figure 4.74: A chart showing decision making for the temperatures to use to synthesise $\text{Ti}_3\text{SiC}_2\text{-CBN}$ composites. Selected optimal conditions from previous sections are highlighted in green.

4.5.1 Vickers hardness

This section shows the hardness results of the selected samples as shown in Figures 4.72, 4.73 and 4.74. There were large errors observed with the results in this section. This large error variance can be due to the diamond tip indenting different phases in the composites. Hence, when the hardness was taken, spanning different phases in the composites there was a large variance recorded in the hardness of the composites.

Figure 4.75 shows the microhardness results for the composites that were determined to be the optimum in Sections 4.2, 4.3, and 4.4. The Vickers microhardness tests as well as bulk hardness tests (Figure 4.76) were done on the samples and compared. The microhardness of the Ti_2AlC - and Ti_3AlC_2 - cBN composites did not change with the change of cBN average size from 10 to 100 μm . The bulk hardness of the Ti_2AlC -cBN composites also showed the same result as the microhardness, whereas Ti_3AlC_2 -cBN composites displayed an increase in both bulk and microhardness. The bulk hardness of the Ti_3SiC_2 - cBN both showed an increase in the hardness of the composites when the average particle size of the cBN was increased from 10 to 100 μm . whereas the microhardness showed that there was not much change in the hardness of the composites with increased particle size. The bulk and microhardness results showed that the hardness of the samples stayed the same when the volume fraction of the cBN increased from 20 to 40 vol. %.

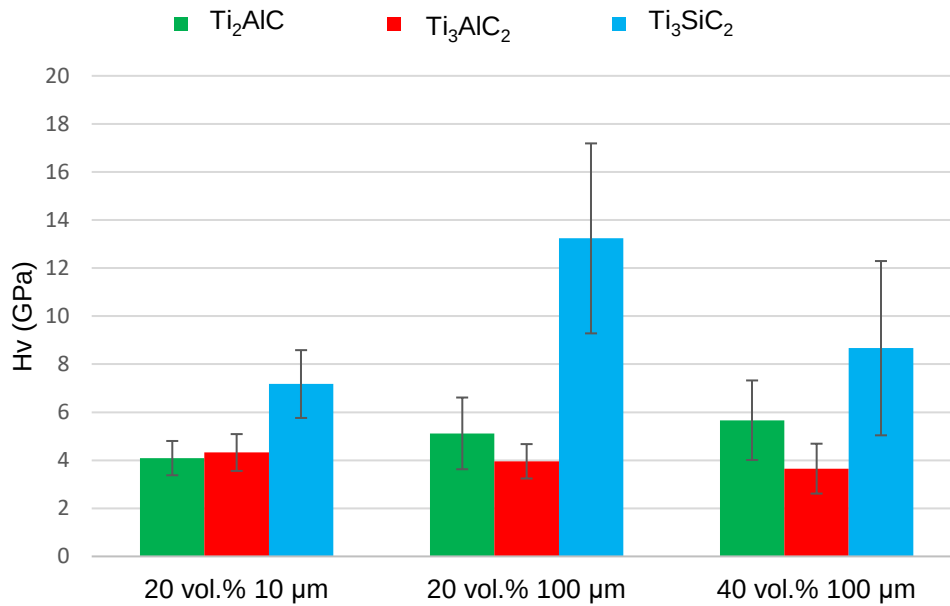


Figure 4.75: Vickers microhardness results for the selected samples.

The microhardness ranking of the composites was $\text{Ti}_3\text{SiC}_2 > \text{Ti}_3\text{AlC}_2 \approx \text{Ti}_2\text{AlC}$ for all the different size and fraction of cBN, Figure 4.75. The bulk hardness ranking of the composites was $\text{Ti}_3\text{SiC}_2 \approx \text{Ti}_3\text{AlC}_2 \approx \text{Ti}_2\text{AlC}$ for the composites with 20 vol.% of the 10 μm cBN, $\text{Ti}_3\text{SiC}_2 \approx \text{Ti}_3\text{AlC}_2 \approx$

Ti_2AlC for the composites with 20 vol.% of the 100 μm cBN and $\text{Ti}_3\text{SiC}_2 > \text{Ti}_3\text{AlC}_2 > \text{Ti}_2\text{AlC}$ for the composites with 40 vol.% of the 100 μm cBN, Figure 4.76.

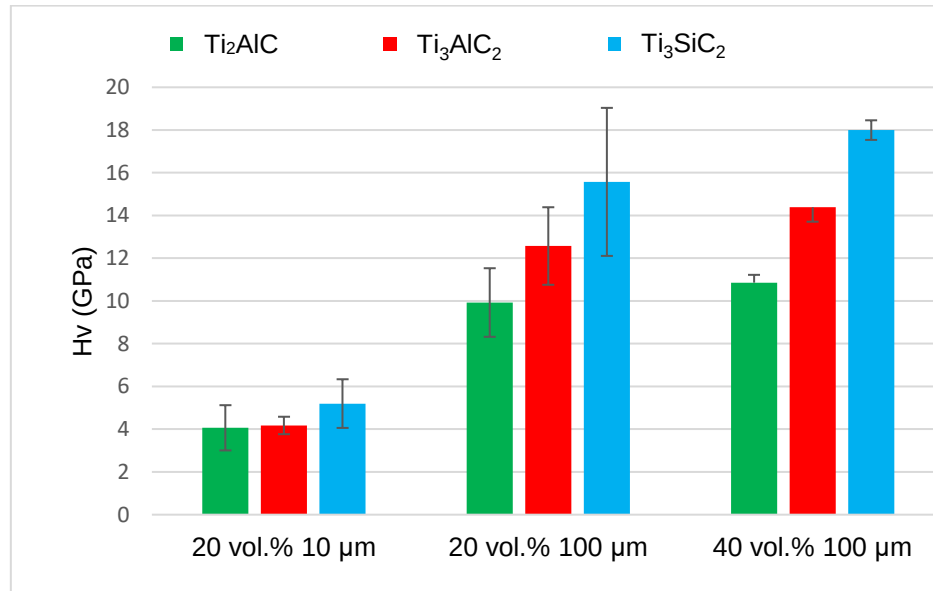


Figure 4.76: Vickers bulk hardness results for the selected samples.

4.5.2 Wear results

This section shows the wear results of the samples as shown in Figures 4.72, 4.73 and 4.74. In this section, only one sample was tested for each composite, thus a variance was not shown.

Figures 4.77 and 4.78 show the wear test results for the composites that were determined to be the optimum from Sections 4.2, 4.3, and 4.4. Both the linear wear and wear rate of the Ti_2AlC -cBN composites, between the 10 μm and 100 μm size of the 20 vol.% cBN decreased, then remained the same when the volume fraction of the cBN was doubled.

Both the linear wear and wear rate of the Ti_3AlC_2 -cBN composites decreased when the size of the cBN increased and when the volume fraction of the cBN was doubled. The linear wear and of all MAX-cBN composites decreased with increase in cBN fraction and size. The Wear rate of all MAX-cBN composites displayed the same trend as their linear wear. The ranking of

both the linear wear and wear rate of the composites was $\text{Ti}_3\text{SiC}_2 < \text{Ti}_2\text{AlC} < \text{Ti}_3\text{AlC}_2$ for the composites with 20 vol.% of the 10 μm cBN, $\text{Ti}_3\text{SiC}_2 = \text{Ti}_2\text{AlC} = \text{Ti}_3\text{AlC}_2$ for the composites with 20 vol.% of the 100 μm cBN and $\text{Ti}_2\text{AlC} > \text{Ti}_3\text{AlC}_2 > \text{Ti}_3\text{SiC}_2$ for the composites with 40 vol.% of the 100 μm cBN, Figures 4.77 and 4.78.

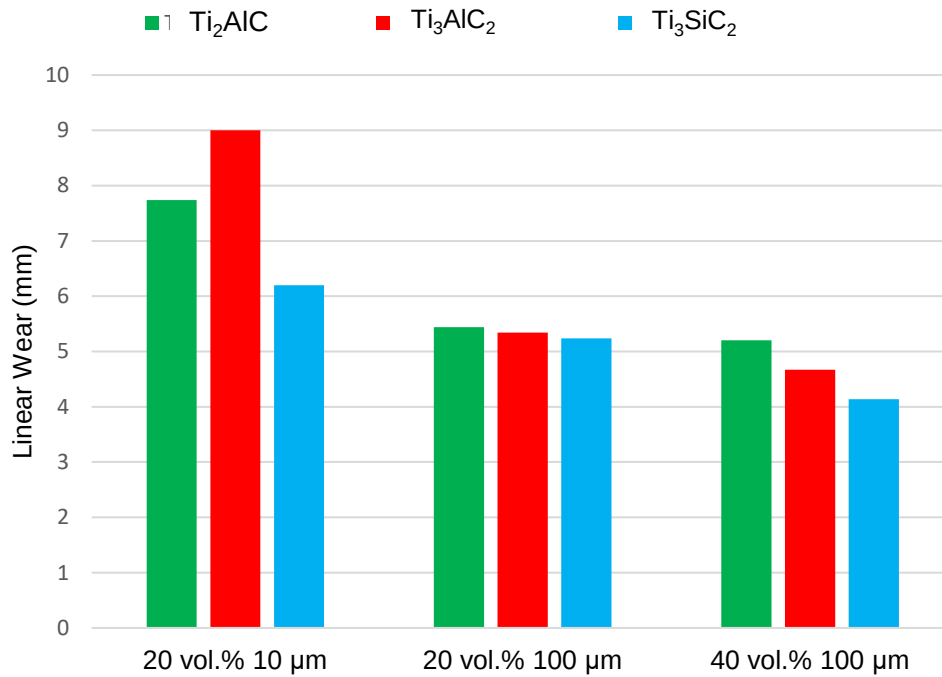


Figure 4.77: Linear wear results for the selected samples, pin-on-belt wear tests.

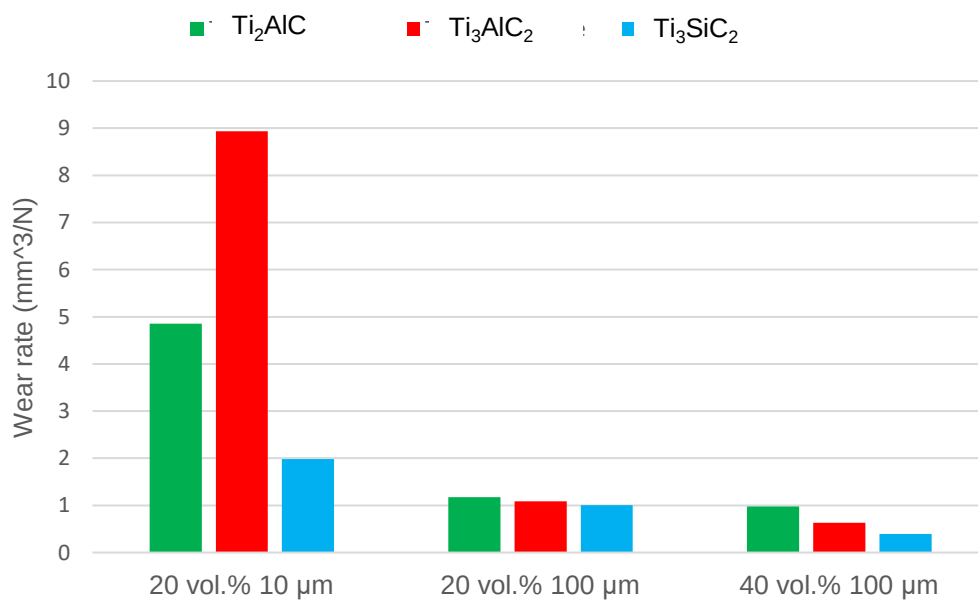


Figure 4.78: Wear rate results for the selected samples, pin-on-belt wear tests

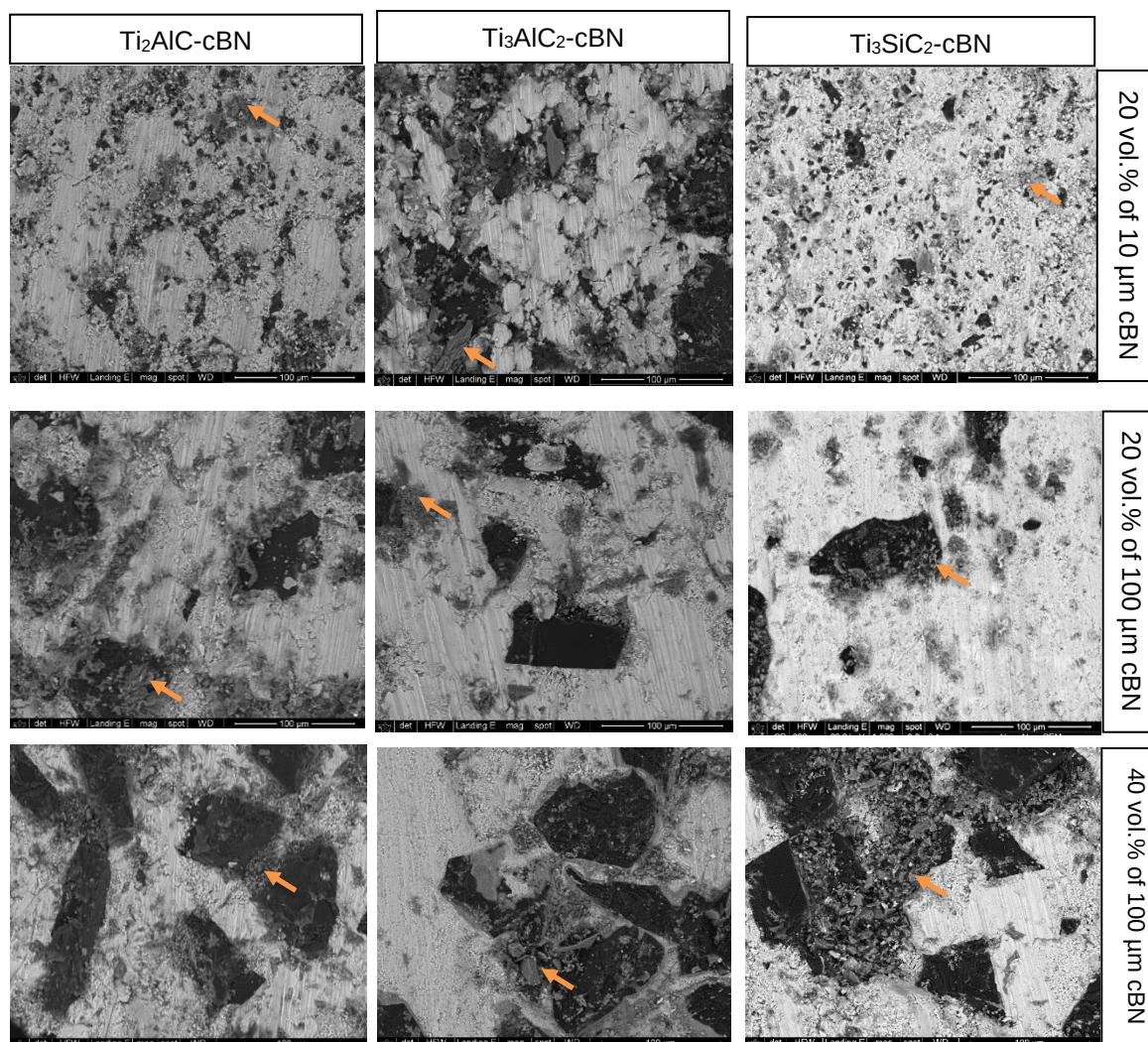


Figure 4.79: SEM (BSE) images of wear scars for the selected samples, pin-on-belt wear tests. Orange arrows show the SiC particles worn from SiC counterphase by the composites.

CHAPTER FIVE: DISCUSSION

5.1 Introduction

This chapter discusses the results for the synthesis, physical and mechanical testing results for the MAX-cBN composites and their potential for grinding wheel applications. There was a delicate balance between the decomposition of the MAX phase (generally $< 1600^{\circ}\text{C}$, **Barsoum and Hough, 1993**) and the hexagonalisation of the cBN (starts at 798.5°C under 30MPa, Equation 5.1; **Vel et al., 1991**). Since hBN is much softer and less strong than the cBN, this presents a problem, especially if the cBN converts to hBN, because the abrasive will not be able to perform as intended when it is in the hBN form. Thus, in this study, the aim was to have no hBN, or only limited amounts that would not promote cBN pull-out. It was shown by **Wolfrum et al. (2018)** that the hexagonalisation of the cBN occurred on the surface of the cBN during sintering, thus the bond between the cBN and the matrix would be compromised and there would be a high likelihood of the abrasive being pulled out of the matrix during application if hBN was present.

In this study, a constant pressure of 30 MPa was maintained during sintering for all samples. This was done for several reasons. Firstly, work done by **Rampai et al., (2013)** and **Li et al., (2014)** showed that at certain low pressures and temperatures investigated, there were some conditions that yielded no hBN in the sample, although at times this was associated with a lack of the MAX phase in the sample. Secondly, the novelty of this work was to have moderate pressure synthesis of the composites, as **Li et al. (2014)** claimed that at lower pressures, the synthesis of the MAX phase in the composites was near to impossible. According to Equation 2.7 by **Vel et al. (1991)**, at temperatures of about 1100°C , the pressure required to avoid conversion to hBN was about 5 GPa. **Li et al. (2014)** also demonstrated that even at these

pressures, some compositions of synthesizing the cBN-MAX composites still yielded hBN in the sample, and this aspect of the problem was examined further in this research.

The SPS method of sintering was used in this work, the field assisted technology of this method results in the applied temperature concentrated on the sample and the die rather than heating up the whole chamber of the furnace. Therefore, heating up to reaction temperatures and cooling down to room temperature is done in a matter of minutes, as seen in the SPS sintering profiles in Section 4.1.1. This relative short exposure to high temperatures means that grain growth can be avoided, thus, the grains of the resulting reaction phases would generally be small. A homogeneous distribution of small grains may be would be an advantage to improving the properties of the composites, such as the fracture toughness.

The XRD diffractograms of some samples showed peaks that had multiple phases within them, thus these peaks showed a shoulder to the largest peak or peak splitting. For example, in Figure 4.27 the diffractogram at 1250°C for 1 minute, the peaks between 46° and 47° 2 θ would belong to Ti₂AlC and Ti₂AlN which have the same hexagonal structure and composition, the only difference in this case would be the presence of C or N in the phases. The occurrence can be seen clearer in Figure A6 where, if the Ti₂AlN is present in the sample, the peak between 46° 2 θ and 47° 2 θ is broad and has a shoulder on the right. The Ti₂AlC has a major peak at 46,3° 2 θ (Table B1) and the major peak for Ti₂AlN is at 46,9° 2 θ (Table B2). Thus, if Ti₂AlC occurs at higher proportion than Ti₂AlN, the shoulder is on the right, Figure A6, (smaller Ti₂AlN peak), and if Ti₂AlN is at higher proportion, the shoulder would be on the left, Figure A9, (smaller Ti₂AlC peak). If Ti₂AlN phase is absent, Figure A34, the peak is thinner and sharp as the peak at 46,3° 2 θ would be the only one existing. These two phases have the same peaks at lower angles (15,1° 2 θ for both phases, Table B1, B2 and Figure A6), and the peaks start to differ slightly at higher angles (46,3 & 62,8° 2 θ for Ti₂AlC and 46,9 & 63,3° 2 θ for Ti₂AlN), Tables B1 and B2.

The other occurrence is when there is Ti_2AlC , Ti_2AlN and Ti_3AlC_2 peaks between 45° and 47° 2θ , Figure 4.28 sample sintered for 10 minutes, which have the similar hexagonal structures and composition, the difference in this case would be the presence of C or N in the phases or the Ti:C ratios. This results in peak splitting, in addition to the shoulders, indicating a phase transformation from Ti_2AlC to Ti_3AlC_2 . The occurrence can be clearly seen in Figure A10 where, if the Ti_3AlC_2 is also present in the sample, the peak between 45° 2θ and 47° 2θ is split. Ti_3AlC_2 has a major peak at $45,7^\circ$ 2θ (Table B3), Ti_2AlC at $46,3^\circ$ 2θ (Table B1) and the major peak for Ti_2AlN is at $46,9^\circ$ 2θ (Table B2), this results in a broad split peak. The distinction between the present M_2AX phases and Ti_3AlC_2 is that the peaks at higher and lower angles would be different and easily distinguishable, Figure A10.

Another occurrence of shared peaks causing peak splitting and shoulders in this work was observed for TiC_a , TiN_b and TiC_xN_y . There were XRD scans that displayed peaks with shoulders between 41° and 43° 2θ also the peaks between 46° and $47,5^\circ$ 2θ , for example, samples sintered for 1 and 5 minutes in Figure 4.28, and peak splitting for the sample sintered for 10 minutes (Figure 4.28). In these peaks, a few things may happen; if a and b in TiC_a and TiN_b are both equal to 1 (Figure A3), then there is a clear differentiation between the two phases and the two largest peaks are at $42,1^\circ/49,2^\circ$ 2θ and $43,0^\circ/49,9^\circ$ 2θ respectively (Tables B11 and B12). The one occurrence that makes it difficult to differentiate the phases within this region occurs when TiC_xN_y is present. Depending on the values of x and y , the peaks of these phases can either be closer to the TiC_a , peaks for $x > y$ (Figure A6 and Table B12 and B13), or closer to TiN_b , peaks for $x < y$ (Figure A19 and Table B11 and 13) or in between the TiN_b and TiC_a peaks, for $x = y$ (Figure A18, Table B11, B12 and 13). Therefore, when the respective peaks look more like broad peaks with shoulders rather than peak splitting, this indicated the presence of TiC_xN_y in the sample. There were cases where there was a presence of TiC_xN_y with TiN_b (Figure A22) where the shoulder was on the right, and TiC_xN_y with TiC_a (Figure A24) where the shoulder was on the left.

In all cases of peak splitting or formation of shoulders, the present phases in those peaks was confirmed by Rietveld. All the XRD peaks given for the phases in the respective figures can also be found in Appendix B where the peak lists for the phases that were found in the samples in this study are given.

Several EDS analyses were also undertaken in this study, the difficulty in this method was analysing the phases in the samples. These phases were mostly smaller than 2 μm in the samples containing nominally 10 μm cBN particles, making analysis challenging as the beam size is also about 2 μm in size. The small sizes of the phases was a consequence of the sintering method, as outlined in the literature review Section 2.1.3.1, using the SPS method suppresses grain growth as the heat is delivered to the sample and sample holder thus heating up and cooling down takes a matter of minutes. This resulted in high errors in the at.% averages reported in Chapter 4 and Appendix E. To try and account for these potential errors 5 scans per phase were completed, Appendix F, when calculating the averages, Appendix E. The high errors in this case are due to the limitations of this method, in that when analysing a phase that is less than 2 μm , the likelihood would be that the detector also picks up the x-rays from the neighbouring phase or phases. Since there are at times as many as 8 phases in the sample (Figure 4.7) any of these phases could be close to any of the 5 to 10 chosen phases of the same contrast, therefore a high variability in the at.% of the elements was seen in some sites in the EDX analysis figures. The exception generally is with cBN, as the average particle sizes of the cBN added was larger than 2 μm . Thus, depending on whether the cBN had a rough surface or some cBN particles were smaller than 2 μm or that the x-rays of the phases beneath the cBN phase could also be detected. This would also result in high errors in the at.% of the elements present or the B:N ratio not making sense, Figure 4.16 for example.

The occurrence of high errors was also observed in samples containing 100 μm cBN. Since the EDX analysis of these samples was done on fracture surfaces rather than polished surfaces, the errors here were also due to the rough surface. EDX analysis of rough surfaces

also produces high errors in the at.% of the respective elements as the x-rays are randomly diffracted by the uneven surface.

These results would be deemed not useful as they often resulted in high errors. However, since in this study it was also important to understand the interaction of the respective MAX phases and cBN, these results were used as a guide to evaluate the elements present in the general matrix versus those found in the reaction areas. This would give some important information of the migration of Al, Si, Ti, B and N as cBN reacts with MAX phases. The phases assigned on the respective SEM-BSE images were based on the XRD results of the respective samples and the principles of how SEM-BSE resulting contrasts of different phases is based on the atomic number of the elements making up the phases seen in the XRD.

In addition to the limits of the equipment, there were errors associated with human interaction. These errors arise as the choosing of the different contrasts, representing different phases, were dependent on human judgement. This judgment would be subjective for most samples in this work, as the samples contained as many as 8 phases (Figure 4.7), with the contrasts ranging from cBN to the MAX phases which contained Ti. Many phases found in the same sample would be very similar in contrast, such as TiN_b and TiC_a or Ti_2AlC and Ti_2AlN . Therefore, even if the XRD showed a certain number of phases (8 for example) the SEM-BSE images would seem to display less than that to the naked eye. Therefore, in some cases analysing the contrast for Ti_2AlC could show similar results to the phase analysis of Ti_2AlN and is similar in the 5 analysed phase contrasts where N would be seen and more C in other cases. This resulted in larger errors that were observed for some phase contrasts.

These results, and the intended application for the composites required this study to assess the making of the composites in two different ways: the thermodynamics of the phase interactions and the engineering which comprised the feasibility of the production of the

composites under the given conditions. The four novel aspects of this work are described below.

Firstly, the reactivity of the MAX phases with the cBN was assessed at the chosen pressure (30 MPa) and different temperatures to establish whether this pressure was appropriate for the formation of the composites. **Li et al. (2014)** mentioned that the presence of the cBN inhibits the synthesis of the MAX phase. **Jaworski et al. (2001)** and **Mu et al. (2011)** demonstrated that diamond, unlike cBN, promoted the reactivity of the MAX phase, although there was hardly any diamond found in the resultant composites they investigated.

Secondly, the phase interactions were assessed by looking at the change, if any, of the interaction of cBN and MAX phases when the surface area of the cBN was changed. **Benko et al. (2004)**, **Li et al. (2012)**, **Yang et al. (2016)**, **Kolabylina et al. (2017)** and **Yue et al. (2018)** worked on cBN-MAX composites and used cBN particle sizes of 1 – 30 μm . In this study, the 10 μm cBN was initially used in order to verify synthesis conditions for the composites. The increase of the particle size from 10 μm to 100 μm was undertaken to assess whether the interaction changed when the surface area of the cBN was reduced. The engineering relevance was that as per Table 2.8 (**Link diamond, 2018**), different sizes of the abrasive particles serve different functions or applications of a grinding wheel.

Thirdly, the phase interactions were assessed to find the volume of the cBN in the composites. A wide range of cBN proportions have been studied (**Benko et al. (2004)**, **Li et al. (2012)**, **Yang et al. (2016)**, **Kolabylina et al. (2017)** and **Yue et al. (2018)**). In this work, only an increase to 40 vol.% was done to evaluate the interaction of cBN and the selected MAX phases in different proportions. The engineering aspect from Table 2.7 (**Link diamond, 2018**) showed the application for both hard bond and soft bond composites for different working conditions. This would further expand the application of the composites should they be proved effective.

According to **McKie et al. (2011)** and **Kolabylina, et al. (2017)**, the increase in the cBN proportion in the composite increased the hardness of the composite, therefore, the composites can be useful in high stock removal from workpieces whether they are used in hard or soft bond application.

Finally, Ti_3AlC_2 and Ti_3SiC_2 MAX phases have been investigated to supplement the research that exists for the cBN composites of these MAX phases (**Benko et al. (2004)**, **Li et al. (2012)**, **Yang et al. (2016)**, **Kolabylina et al. (2017)** and **Yue et al. (2018)**), but the Ti_2AlC MAX phase has not been studied as a composite with cBN. Since the Ti_2AlC MAX phase behaves very differently from the Ti_3AlC_2 and Ti_3SiC_2 MAX phases, it was essential to assess the reactivity of the MAX phase with the cBN when the Ti and C ratios were increased, and also when Al was substituted with Si.

Li et al. (2014) and **Kolabylina et al. (2017)** investigated the composites of MAX phases with cBN using the MAX phase powder. In both investigations, it was noted that when using the MAX phase powder, the decomposition temperature of the MAX phase decreased and also the pressure applied drove the decomposition temperature lower. Also, in previous work (**Rampai et al. 2012**) it was shown that there was a high probability of contamination in the MAX phase powder using the method of making the MAX phase first, then crushing it and mixing with cBN. In this work, “MAX” powders of T, Al, C and Ti, SiC, C were mixed with cBN for each respective MAX phase. The aim was to have a simultaneous synthesis of the MAX phase and reaction with cBN, relying on the research reported in Section 2.1.3 and establishing whether this approach gave improved results. The powder processing methodology outlined for Section 3.1 gave a homogeneous mixture for all MAX phase base powders manufactured. Homogeneity of the cBN in all composites was also evaluated, and it was achieved after modification of the mixing process by including 10 mm Al_2O_3 balls and mixing for 4 hours.

5.2 MAX-cBN composite synthesis

This section focuses on the results from Sections 4.1, 4.2, 4.3 and 4.4. For the purpose of this study, a “successful composite” was taken as a composite that had both the MAX phase and cBN present, with minimal or no hBN. The MAX phase in all samples needed to be one of the major phases.

5.2.1 Ti₂AlC – cBN composites

5.2.1.1 Reaction Temperature evaluation for 20 vol.% of 10 µm cBN powder.

This section discusses the results given in Section 4.1.1. Here, the synthesis of cBN-Ti₂AlC composites was undertaken by using 2Ti:1.2Al:1C powders with cBN.

To establish the most effective temperature for sintering the Ti₂AlC-cBN composites, the dwell time and the pressure were kept constant at 1 minute and 30 MPa respectively, while the temperature was varied up to 1500°C, Figure 4.3. The piston displacement, as well as the displacement's derivative with time curves from the SPS during sintering were shown in Figure 4.3a, and 4.3b respectively. From Figure 4.3a, all sintering temperature profiles showed sample volume change takes place at around 680°C. At this temperature a reaction peak was also observed in the “piston derivative's with time” curve (Figure 4.3b). This was associated with the formation of Ti-Al intermetallic phases such as TiAl₃, Ti₃Al and TiAl₂(Figure 4.5), which can only form subsequent to the melting of the aluminium at 660°C, **Skolakova et al. (2018)**. **Skolakova et al. (2018)** noted the difficulty in determining the resultant Ti-Al phases from the exothermic reaction at ~680°C. The presence of these phases and the unreacted Ti and cBN was determined by XRD in a sample sintered at 700°C (Figure 4.5).

In Figure 4.3a, the samples sintered at 1300°C and above all showed an additional increased densification rate of one and a half millimetres at approximately 1300°C. After this fast densification, no further densification was observed in the samples. In this temperature range, there was a corresponding peak observed in the “piston derivative’s with time” curve (Figure 4.3b). This peak was related to the reaction of the MAX phase with the cBN, because there was no MAX phase found and the cBN content was also significantly reduced in samples sintered at and above 1300°C (Figures 4.6 and 4.7). This exothermic peak can be attributed to the reaction of Ti, Al and C (from Ti_2AlC) with B and N (from cBN) to form TiB_2 , AlN and TiC_xN_y in addition to TiC_a , which results from the degradation of Ti_2AlC (Zhou et al., 2003). The rapid increase of the temperature, due to the heat released, could have driven the degradation reaction of the MAX phase and more hexagonalisation of the cBN, which would promote the formation of these phases. The hBN was only observed in samples sintered at and above the reaction temperature of 1300°C. The exception was the sample sintered at 1500°C (Figure 4.6), and this could have been due to all the hBN possibly reacting completely to further form the reaction products (TiB_2 , AlN and TiC_xN_y).

Yoshida et al. (2010) reported that the solid-liquid angle between the $Al(l)$ and $C(s)$ was more than 100°, therefore, wetting was unfavourable and the reaction between Ti and C could not occur. However, this angle decreases with increasing temperature above 900°C. The solid liquid angle between the $Al(l)$ and $C(s)$ in this case decreased to approximately 60° which promoted the formation of TiC . At temperatures of approximately 1100°C and above the formation of the Ti_2AlC from Ti-Al and TiC occurred. Figure 4.3a shows that the Ti_2AlC densification curve had a small but constant densification from approximately 900°C until 1300°C (shown by the densification curves changing from horizontal to diagonal). This was due to the gradual reaction of the formed Ti-Al intermetallic phases, Ti and C forming the MAX phase. This was likely since the gradual increase indicated that the pistons were moving relative to each other, thus a volume change was occurring. This would happen as the

formation of the MAX phase from TiAl_3 and TiAl_2 would induce a volume change because the MAX phase has a higher density than the intermetallic phases (Table 5.1).

In these composites, two MAX phases were observed, Ti_2AlC and Ti_2AlN , as shown in Figure 4.7 for samples sintered at 1150°C and 1250°C. The presence of Ti_2AlN was possible since hBN present in the samples provided the N source for the formation of this MAX phase. **Chen et al., (2009)** and **Lin et al. (2007)** both noted that the formation of Ti_2AlC and Ti_2AlN occurred through the reaction of Ti-Al intermetallic compounds together with either a C or N source respectively. As noted by **Yoshida et al. (2010)**, the reaction of Ti-Al intermetallic phases with TiC occurs at 1100°C. **Zhou et al., (2005)**, **Mei et al., (2004)** and **Kulkarni et al., (2010)** all indicated the synthesis of Ti_2AlC below 1200°C through the reaction of TiC and the resultant Ti-Al intermetallic compounds. Similarly, **Liu et al. (2017)** noted the formation of Ti_2AlN from TiN and Ti-Al intermetallic phases at temperatures around 700°C. This can occur in this case since the cBN has transformed into hBN, which provides a N-rich environment. **Tomashik and Perrot (2005)** noted that the N solubility was high in Ti, and that the Gibbs free energy of formation of the Ti_2AlN system was -135.5,5 kJ.mol⁻¹ of atoms at 850°C. The formation of Ti_2AlN in this study was limited by the amount of hBN available, thus it was found in lesser amounts than the Ti_2AlC since there was relatively more C added to the sample. The piston displacement curves (Figure 4.3a) of the SPS sintering for the composite samples sintered at 1300°C and above showed a small but constant densification, followed by a rapid and significant increase at 1300°C. The piston displacement curves of the composite samples sintered at 1150°C and 1250°C (Figure 4.3a) do not show this rapid increase, due to the lower maximum temperatures at which these samples sintered.

The major phases (TiC_xN_y , TiB_2) in the samples sintered at 1300°C (Figure 4.6 and Table 5.1) and above were denser than the major phases (Ti_2AlC , TiAl_2 and cBN) in the samples sintered at 1150°C and 1250°C (Figure 4.7 and Table 5.1). Thus, this shows the formation of phases that are denser forming at 1300°C, which was corroborated with the measured densities of the

samples, Figure 4.4. It was observed in Figure 4.4 that the densities of the samples increased at 1300°C and were generally constant above this temperature as the phases generally remained the same (Figure 4.6). The samples sintered at 1300°C and above showed no further densification during heating (Figure 4.3a). This was indicated by the pistons of the SPS sinter press no longer moving relative to each other, and thus the samples were assumed to have reached full densification.

The SEM image, Figure 4.8, corroborated the XRD results that showed the cBN proportions decreased with increased temperature. Also, this image shows that for samples sintered at 1300°C and above there was a clear reaction area (between the red and blue circles in Figure 4.8). This further shows that the exothermic reaction at 1300°C promoted the hexagonalisation of the cBN, which then reacted with the MAX phases to form the reaction products found in the reaction area, TiB_2 and AlN (Figure 4.9).

Table 5.1: Density of phases found in the sintered samples (Springer, 2018).

Phase	Density (g/cm ³)	Phase	Density (g/cm ³)
TiN	5.39	Ti₃Al	4.26
TiB₂	4.53	TiAl₂	3.51
TiC	4.09	TiAl₃	3.36
		TiC_{0.3}N_{0.7}	5.25
Ti₂AlN	4.30	AlN	3.26
Ti₃AlC₂	4.25	cBN	3.49
Ti₂AlC	4.07	hBN	2.26

Wolfrum et al. (2018) noted that the hexagonalisation of the cBN started at the surface of the cBN and moved inwards; this was seen in these samples where the outer dimensions of the reaction area (red circle, Figure 4.8) was constant at ~10 µm (average cBN size) for all the samples. In addition, it was also noted by **Li et al. (2012)** that, in a Ti-Al-C-BN system, cBN

would hexagonilise at temperatures as low as 1150°C if it was in contact with a suitable reagent. In this case the reagent was Ti as N is significantly soluble in Ti (**Tomashik and Perrot (2005)**). This was further supported by the calculation using Equation 5.1, that under 30 MPa pressure, the cBN would hexagonilise at temperatures as low as 800°C. This consequently leads to the likely reaction of the cBN to the MAX phase by $\text{cBN} \rightarrow \text{hBN}$, the hBN would then react with Ti (from Ti_2AlC) as hBN was more likely to participate in diffusion processes under these conditions than cBN. The actual outline of the BN phase seen was some distance from the original outline (blue circle, Figure 4.8) in samples sintered at 1300°C. The reaction product TiB_2 was found both in the reaction area and the matrix. The proportions found in the matrix could have been formed as the MAX phases were formed, and those in the reaction area could more likely be the product of the exothermic reaction at 1300°C. The AlN phase was found around the original outline of the BN phase (near the red circle in Figure 4.8 and 4.9) in composites sintered at 1300°C and above. **Cui et al., (2011)** from their study noted that the loosely bound Al in the Ti_2AlC layered structure was the first to leave the Al plane to react with O_2 . The Ti would only react thereafter when the Ti_2AlC structure had critically low quantities of Al. Thus, it was assumed in this study that there was a migration of the loosely bound Al in the MAX phase (**Zhou et al. 2003**) towards the cBN high reaction site. Hence AlN was found in the reaction area surrounding the cBN particles (Figures 4.8 and 4.9). This triggered B in the BN to migrate into the MAX matrix and react with the Al deficient MAX phase to form TiB_2 and $\text{TiC}_a/\text{TiC}_x\text{N}_y$, which were mostly observed in the matrix (Figure 4.9), and were also confirmed to be present in the samples by the XRD results (Figure 4.6).

The hypothesised reaction of Ti_2AlC or Ti_2AlN with cBN in this work was that the cBN first hexagonalises, where after this hexagonalisation was simultaneously accompanied by the hBN reacting with Ti_2AlC . This can occur, since the hBN was much more susceptible to diffusion processes and reactions than cBN at these temperatures owing to the bonds in the hBN being less strong than those in cBN (**Monteiro et al., 2013**). This was also noted by **Li et al. (2012)** that, in a Ti-Al-C-cBN system, the cBN would hexagonalise. This could happen only

in small amounts on the surface of the cBN under these conditions. At the conditions used in these reaction studies for samples sintered below 1300°C, the simultaneous hexagonalisation of the cBN and the reaction of the hBN with Ti_2AlC was most likely to occur in a complementary manner, leaving no unreacted hBN on the surface of the cBN, Figure 4.7. However, as sintering temperatures reached 1300°C and above the exothermic reaction would induce greater cBN hexagonalisation, thus creating excess hBN which had not reacted (Figure 4.6). This unreacted cBN would reduce with temperature as it reacts further to increase phases such as TiB_2 , AlN and TiC_xN_y until it is depleted at 1500°C (Figure 4.6).

$$P \text{ (kbar)} = 0.030 T(\text{K}) - 10.3, (1 \text{ kbar} = 0.1 \text{ GPa})$$

Equation 5.1 (Vel et al., 1991)

The reaction mechanism hypothesised from these results (Figures 4.5, 4.6 and 4.7) is shown in Equations 5.2 to 5.5, with the formation of TiC in Equation 5.3 from **Chen et al., (2009)** and reflects what was seen in this study for samples sintered between 700°C and 1300°C (Figures 4.5, 4.6 and 4.7).



Since the sample sintered at 1250°C contained the most Ti_2AlC , it was decided to use this temperature and vary the dwell time, Figure 4.23. This was done in order to optimise the proportion of Ti_2AlC and minimise the Ti-Al intermetallic phases, without compromising the presence of the cBN. For all composites, Ti_2AlC , Ti_2AlN and cBN were present with no hBN in any samples. However, the composite sintered for 10 minutes also contained Ti_3AlC_2 . The presence of TiAl_3 , Ti_2Al_5 , TiN_b , TiC_a , TiB_2 and Ti_2Al secondary phases were observed in all of the composites, with the Ti-Al phases decreasing with increased dwell time (Figure 4.24).

Thus, the optimum sintering time at 1250°C was 5 minutes, which gave the highest amounts of M_2AX without compromising the cBN content, and small amounts of the secondary phases with no Ti_3AlC_2 .

The density of the sample sintered for 1 minute was higher than that for the samples sintered for 5 and 10 minutes, Figure 4.25. This might be due to the fact that there was a higher content of the Ti-Al intermetallic phases in the sample sintered for 1 minute compared to the other two samples which had similar densities (Figure 4.24). The fact that the densities of the samples sintered for 5 and 10 minutes was similar does not indicate that the phase content was the same, but rather that the phases present in the sample sintered for 5 minutes were similar in density to the phases in the samples sintered for 10 minutes. For example, the sample sintered for 5 minute has Ti_3Al and the sample sintered at 10 minutes has Ti_3AlC_2 instead (Figure 4.23), these two Phases have similar densities (Table 5.1). The other reason may be the proportion in which each phase is present in the respective samples that creates samples of similar densities.

The SEM images of the samples sintered at 1250°C and different times, Figure 4.26, show that there was a reaction area in samples sintered for 5 and 10 minutes only (between red and blue circles). In the sample sintered for 1 minute, the fracture propagated around the cBN particles (red arrow in Figure 4.26), which implied that there was not a strong bond between the cBN and the matrix, as the crack would travel a path of least resistance. The polished surface of the same sample also confirms this, because unlike the other two samples, there was no reaction area in this sample. The samples sintered for 5 minutes and 10 minutes had reaction areas with strong bonds to both Ti_2AlC and cBN, and thus the cracks would propagate through the cBN and the reaction area (blues arrows in Figure 4.26) as this would be the path of least resistance in these cases.

In the sample sintered for 5 minutes, the reaction area was approximately 1 μm thick, and in the sample sintered for 10 minutes the reaction area was on average 2,3 μm thick (Figure 4.26). These samples did not have the dark ring around the outer surface of the reaction area because they did not contain AlN (Figure 4.23) as in the samples sintered at 1300°C and above (Figures 4.6 and 4.8). They did, however, have the same phase distribution of the Ti-Al phases and TiC_a , TiN_b or (TiC_xN_y) and TiB_2 in the matrix, with the matrix mostly consisting of Ti_2AlC and Ti_2AlN in this case (Figures 4.7 and 4.23). The samples sintered for 10 minutes displayed a large amount of a layered Ti_2AlC phase in the matrix (Figure 4.26). The sample sintered for 10 minutes also showed a more evident porous structure (Figure 4.26), this could be due to the formation of Ti_3AlC_2 from the Ti_2AlC grains leaving the matrix more porous since the Ti_2AlC is less dense than Ti_3AlC_2 .

From the sample sintered at 1250°C for 5 minutes, it was concluded from XRD and SEM/EDX data that the MAX phase and cBN were present, but also Ti_2AlC -cBN interface had a reaction area as required.

5.2.1.2 Increased particle size (10 to 100 μm) and volume fraction of the 100 μm cBN (20 to 40 vol.%)

The 1250°C, 5 minutes sintering condition was used to sinter samples with 20 vol.% of 100 μm cBN as recommended in Section 5.2.1. In addition, samples were also sintered at 1300°C and 1150°C in order to evaluate the interaction reaction of Ti_2AlC and cBN for a decrease in surface area of the cBN.

Decreasing the surface area of the cBN, by increasing the cBN particle size, did not have a significant effect on the phases present in the samples sintered at 1250°C for 5 minutes, Figures 4.23 and 4.37. The first notable difference was the complete lack of Ti_2Al_5 and the presence of TiC_xN_y in the sample with 100 μm cBN particles (Figure 5.1). This could have been

due to the low availability of surface area of the cBN, leading to less hBN forming on the surface. Thus, the Ti-Al phases had a higher likelihood to react with the TiC_a to form more Ti_2AlC , instead of reacting with hBN to form TiN_b and more TiB_2 as shown in Figure 4.23. The second notable difference was the presence of hBN in the samples sintered at 1250°C for 10 minutes in the $100\text{ }\mu\text{m}$ cBN samples (Figure 4.37). Figure 4.39 shows that the proportion of the cBN in the sample apparently increased in the sample sintered for 10 minutes. This would not be feasible in this situation; the likely reason is that the proportion reported in vol.% and the phases formed in the sample sintered for 10 minutes had a higher density than cBN (Figure 4.37 and Table 5.1). Thus, the cBN, having lower density, would likely occupy more volume in the sample, but the actual content of cBN reduced.

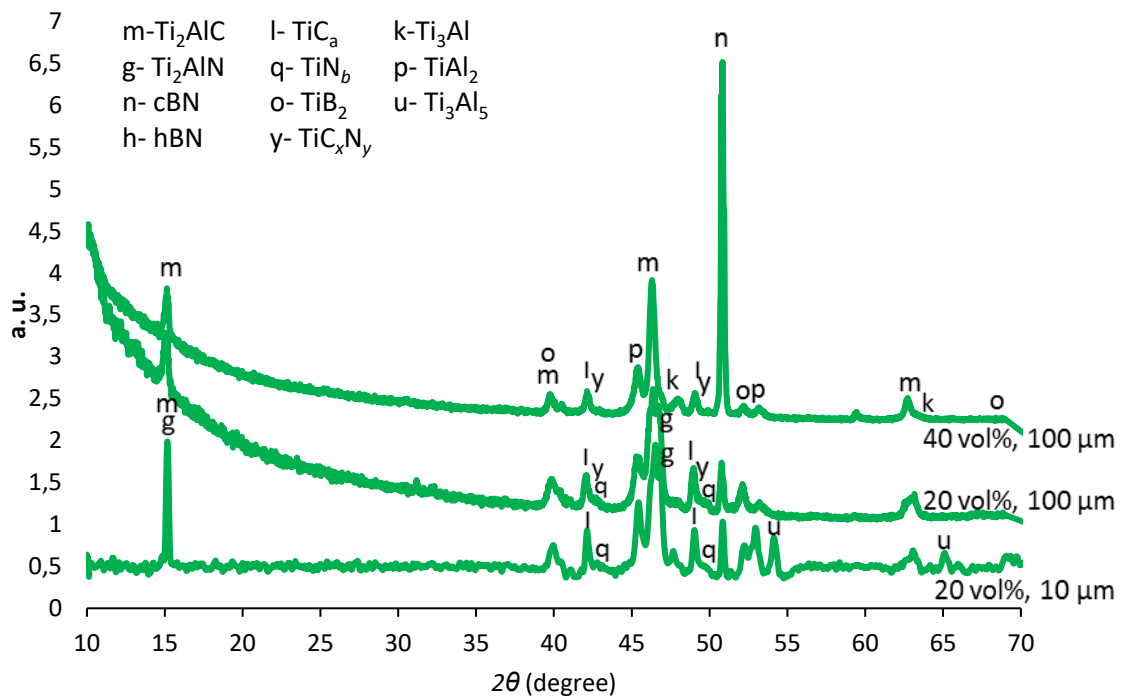


Figure 5.1: XRD traces of Ti_2AlC -cBN samples sintered at 1250°C for 5 minutes, showing different volume fraction (20 or 40 vol.%) and different size (10 and 100 μm) cBN. The XRD traces are taken from Figure 4.23, 4.37 and 4.54.

Another notable difference in decreasing the surface area was that the exothermic reaction observed at 1300°C in Figure 4.3b occurred at a higher temperature than 1300°C. This reaction related to the complete decomposition of Ti_2AlC and Ti_2AlN , Figure 4.7, but in this case Ti_2AlC and Ti_2AlN were found in the samples sintered at 1300°C (Figure 4.38). This suggests that the high surface area of the cBN promoted the exothermic reaction to occur at 1300°C, and the low surface area suppressed the exothermic reaction at the same temperature and shifted it to a higher temperature. It was observed, however, that there was also excess hBN found in the samples sintered at 1300°C for samples with both high and low surface area of cBN (Figures 4.5 and 4.38). This, as discussed before, may have been due to the increase in temperature at 30 MPa promoting the hexagonalisation of cBN (calculated from Equation 5.1).

Decreasing the surface area of the cBN altered the reactivity of the cBN with the MAX phases. In this case, as shown in Figures 4.26 and 4.41, there was no clear reaction area observed in the samples containing 100 μm of 20 vol.% cBN. Also, the present phases (Figure 5.1) with the exception of absence of Ti_3Al_5 in the composites containing 20 vol.% of 100 μm cBN. When considering the composites containing 20 vol.% of 100 μm cBN, there was no significant difference in the microstructure in the samples sintered at 1250°C and 1300°C (Figure 4.41).

These results indicated that for samples sintered with 20 vol.% of 100 μm cBN, the optimum condition for sintering the Ti_2AlC -cBN composites was also 1250°C for 5 minutes. Thus, the sintering conditions of 1250°C for 5 minutes were also used to sinter samples with 40 vol.% of 100 μm cBN. In addition, samples were also sintered for 10 minutes at 1300°C and 1350°C in order to evaluate the interaction reaction of Ti_2AlC and cBN with an increased in the amount of cBN.

The first notable difference in increasing the cBN proportion was that TiN_b was not formed in the samples containing 100 μm of 40 vol.% cBN as shown in Figures 5.1 which reflects what

was observed in all the samples in this respect, Figures 4.54 and 4.55. Also, in the sample sintered at 1250°C for 10 minutes (Figure 4.55), the 40 vol.% of 100 µm cBN samples did not contain the Ti_3AlC_2 phase. This phase was only observed in the samples sintered at 1350°C for 5 minutes, Figure 4.54. Also, the transition from Ti_2AlC to Ti_3AlC_2 was more defined than in the samples with 20 vol.% of cBN, Figures 4.23 and 4.37. This was because in the samples with 40 vol.% cBN, Ti_2AlC and Ti_3AlC_2 were not found in the same sample (Figure 4.54). In addition, increasing the proportion of the cBN in the samples further promoted the Ti_2AlC as the only M_2AX phase in the relevant samples which could have resulted from the decreased hexagonalisation of cBN, thus N source was limited to the TiN_b from which the Ti_2AlN could have formed, Figures 4.37, 4.38, 4.54 and 4.55. In the samples sintered at 1250°C and 1300°C, cBN remained the major phase and was surpassed by TiB_2 , TiN_b and TiC_xN_y in the samples sintered at 1350°C (Figures 4.54, 4.55, 4.56). This change in major phase was also reflected in the density changes in the samples (Figure 4.57), where the density of the samples sintered at 1250°C and 1300°C was approximately 3.5 g/cm³. But the density increased for samples sintered at 1350°C (approximately 3.8 g/cm³) as the major phases present have a higher density than cBN (Table 5.1, Figures 4.54 and 4.55). The Ti_2AlC decomposition temperature was also observed to be above 1300°C (~1350°C) for samples containing 40 vol.% cBN (Figures 4.54 and 4.55).

There was no hBN in the samples sintered at 1250°C, but there was for all samples sintered at 1350°C (Figures 4.54 and 4.55). However, for samples sintered at 1300°C for 5 minutes there was no hBN present (Figure 4.54), but there was hBN in the samples sintered for 10 minutes (Figure 4.55). Thus, increasing the volume fraction of the cBN in the samples further suppressed the formation of hBN in the samples sintered using these conditions. The samples sintered at 1300°C for 5 minutes, there was hBN found in the sample containing 20 vol.% of 100 µm cBN but not in the sample containing 40 vol.% of 100 µm cBN (Figures 4.38 and 4.54).

The matrix of the sample sintered at 1350°C displayed a layered structure (Figure 4.58), but also a large number of pores that could be due to the weight loss of Al at high temperature (Zhou et al. 2003) as the Al vaporised. This shows that for samples sintered with 40 vol.% of 100 µm cBN, the optimum conditions for sintering the Ti₂AlC-cBN composites was 1300°C for 5 minutes. Even though the sample sintered at 1250°C for 5 minutes had a good proportion of Ti₂AlC and cBN, with no hBN, the sample sintered at 1300°C had a much lower proportion of the secondary phases with the highest content of T₂AlC (Figure 4.56). However, samples sintered at 1250°C for both 5 and 10 minutes also proved successful for this work's intended grinding wheel purposes.

5.2.2 Ti₃AlC₂ – cBN composites

5.2.2.1 Reaction Temperature evaluation for 20 vol.% of 10 µm cBN powder

The second most researched MAX-cBN composites of the chosen MAX phases for this study was Ti₃AlC₂-cBN.

Zhou et al. (2003a) and Yang et al. (2009) showed that the Ti₃AlC₂ can be synthesised at temperatures as low as 1050°C to 1250°C at pressures as low as 35 and 22 MPa. However, they noted that these conditions needed to be coupled with, either mechanical alloying of the starting powders, or first synthesising Al₄C₃ and then reacting it with Ti and C. In this work, the synthesis of cBN-Ti₃AlC₂ composites was developed using 3Ti:1.2Al:2C powders with cBN. The reactivity of these powders with cBN showed very similar behaviour to the reactivity of the 2Ti:1.2Al:1C powders with cBN. This similarity was observed in four ways, and therefore, the discussions in Section 5.2.1.1 also apply in these cases.

Firstly, the density fluctuation in the two systems was similar, below the large exothermic reaction (Figures 4.3 and 4.10), and then increased after this exothermic reaction. This was accompanied by the decrease in the open porosity in both systems (Figures 4.4 and 4.11).

Secondly, the microstructures of the samples in the two systems were similar in the respective samples. The difference seen in this respect was that the reaction area in the Ti_2AlC -cBN composites was seen in samples sintered at 1300°C (Figure 4.8) and above, whereas in the Ti_3AlC_2 -cBN composites the reaction area was only seen in samples sintered at 1400°C (Figure and 4.15). This was also due to the large exothermic reaction occurring at higher temperatures (1350°C) for the Ti_3AlC_2 -cBN composites (Figure 4.10).

Thirdly, the phase distribution in the samples were similar (Figures 4.9 and 4.16, also the respective Figures in Appendix D). Since the phase distribution assessed in Figures 4.9 and 4.15 were for samples sintered at 1600°C for both systems, the phase distributions here were the same, regardless of the large exothermic reaction occurring at different temperatures. The only exception was the presence of TiC_a in the Ti_3AlC_2 -cBN, this could have resulted in the higher Ti:C ratio in these composites, creating excess TiC_a in the composites. This was also noted by **Bandyopadhyay et al. (2000)**, as the ratio of Ti and C increases the present phases (Ti_2AlC and TiC) would remain in the system beyond 1300°C .

And finally, the reactivity and reaction products of the MAX powders and cBN were similar in both composites. The reaction of the Ti with Al at 680°C to form the Ti-Al intermetallic phases was seen to be the same even with the resultant intermetallic phases (Figures 4.3 with 4.5, and 4.10 with 4.12). The difference in the case of the Ti_3AlC_2 composites was that there was more unreacted Ti than in the Ti_2AlC , and this was expected since there was more Ti in the starting powders of the Ti_3AlC_2 . **Bandyopadhyay et al. (2000)** noted in their phase diagram, that at molar ratios of 2:1 Ti:Al, the Ti_3Al phase was observed to remain until 1100°C , whereas in the molar ratio of 3:1 of Ti:Al, the resultant TiAl_3 would degrade at 990°C . The same

formation mechanisms of the MAX phases were observed in this work as discussed in Section 2.1.1, only in these composites an excess of TiC was observed since the phase formed was Ti_2AlC not Ti_3AlC_2 as expected from the starting powder ratio. Then, there was a second, more significant exothermic reaction that occurred, at $\sim 1350^\circ\text{C}$ in Ti_3AlC_2 -cBN composites, that results in the decomposition of the MAX phase and significant hexagonalisation of the cBN (Figures 4.3 with 4.5, and 4.10 with 4.12). The difference in this case was that this exothermic reaction occurred approximately 50°C higher in the in these composites compared to the Ti_2AlC -cBN composites (Figures 4.3 and 4.10). This meant that at 1300°C , the Ti_2AlC -cBN composites showed complete decomposition of Ti_2AlC and little cBN, whereas this was only seen at 1360°C in the Ti_3AlC_2 -cBN composites. Also, the reaction products for the two systems were very similar at all temperatures (Figures 4.5/4.6/4.7 and 4.12/4.13/4.14 respectively). The difference here was the sample sintered at 1300°C , in the Ti_2AlC -cBN composites, there was no MAX phase found and cBN had hexagonalised, whereas in the Ti_3AlC_2 composites, the MAX phase was still present with a significant proportion of cBN (Figures 4.7 and 4.14). This was because the exothermic reaction in the Ti_3AlC_2 composites only occurred at approximately 1350°C (not 1300°C), Figure 4.10, thus the MAX phase and the cBN would be present in large quantities in this case (Figure 4.14). In addition, the MAX phase formed in both cases was Ti_2AlC with Ti_2AlN also present, instead of Ti_3AlC_2 for the Ti_3AlC_2 -cBN composites, even though these were synthesised with $3\text{Ti}:1.2\text{Al}:2\text{C}$. In addition, the Ti_3AlC_2 -cBN composites contained TiC_a in samples sintered at 1400°C and above, whereas the Ti_2AlC -cBN composited did not.

The likely reaction path for the formation of the composite Ti_3AlC_2 was, therefore, similar to that seen in the Ti_2AlC composite (Equations 5.2 to 5.5). The difference would be that the reaction in Equation 5.5 only occurred at 1350°C . The likely reason for the large exothermic reaction occurring approximately 50°C higher in the Ti_3AlC_2 -cBN system is that there was excess Ti and C in this system. This presence of the excess TiC might serve as a

thermodynamic competitor for the formation of the TiB_2 and TiC_xN_y , but only to a small extent as this occurs only approximately 50°C higher in the Ti_3AlC_2 -cBN system (Figure 4.10).

In the Ti_3AlC_2 -cBN composites the formation of Ti_2AlC rather than Ti_3AlC_2 was observed even though the Ti:Al:C ratios were 3:1,2:2 rather than 2:1,2:1. **Zhou et al. (2003b)** noted that the synthesis of Ti_3AlC_2 was more dependent on kinetics rather than thermodynamics and that Ti_2AlC was easier to form, from a kinetic point of view, under these conditions. **Zhou et al. (2003b)** also mentioned that the synthesis of Ti_3AlC_2 could occur in two different reaction paths depending on the temperatures used. Higher temperatures ($\sim 1600^\circ\text{C}$) could lead to the formation of Ti_3AlC_2 directly from TiC (Equation 2.4). Conversely, lower temperatures ($\sim 1300^\circ\text{C}$), such as those used in this study, would lead to the formation of Ti_3AlC_2 from the Ti_2AlC phase (Equation 2.3).

Weibing et al. (2009) showed that a composite of Ti_3AlC_2 and TiB_2 can be synthesised with the conditions chosen for this study (at 30 MPa and 1250°C for 8 minutes). **Li et al. (2012)**, **Yang et al. (2016)** and **Yue et al. (2018)** attempted to synthesise Ti_3AlC_2 -cBN composites, however, only **Li et al. (2012)** had demonstrated a presence of Ti_3AlC_2 and cBN in the sample without significant hexagonalisation of the cBN. **Yang et al. (2016)** and **Yue et al. (2018)** sintered samples at 5.5 GPa at 1350°C for 12 minutes with 60-95 wt% of $1\text{ }\mu\text{m}$ cBN. All the powder combinations they worked with yielded no evidence of MAX phase in the samples from their reported XRD data. This can be attributed to the reasoning given above about the exothermic reaction at 1350°C around 30 MPa pressure yielding a decomposition of the MAX phase and a significant hexagonalisation of the cBN. In the case of **Yang et al. (2016)** and **Yue et al. (2018)** the cBN was not as significantly hexagonalised, and this was likely due to the high pressures used in their work stabilising the cBN.

Similar to the Ti_3SiC_2 -cBN composites discussed in Section 5.1.3.1, **Li et al. (2012)** sintered samples at 4.5 GPa for 10 minutes with different starting powder combinations and

temperatures for the Ti_3AlC_2 -cBN (50 vol.% of 20-30 μm) composites. They found that all powder combinations, including 2Ti:1.2Al:TiC:cBN and 3Ti:1.2Al:TiC:cBN produced successful samples from 1050°C. An increase of hBN was observed as the sintering temperature was increased. The optimum sintering temperature for the powder combination of 3Ti:1.2Al:2Ti:cBN was 1250°C. However, **Li et al. (2012)**, did note that having a higher fraction of free Ti promoted the formation of TiC, which was an exothermic reaction, thus promoting the hexagonalisation of cBN and, in this work, the decomposition of the MAX phase. The dwell time used by **Li et al. (2012)** was in excess of 10 minutes for both powder combinations. It was then decided to use similar dwell times in this work, as was done by **Li et al. (2012)** in order to promote the formation of Ti_3AlC_2 .

It was, therefore, decided to optimise the sintering conditions of Ti_3AlC_2 -cBN samples at temperatures below 1350°C to preserve both MAX phase and cBN but above the 1150°C so that there would be fewer Ti-Al intermetallic phases in the samples. Thus, the selected temperatures were 1250°C and 1300°C. The results of this method for samples sintered at 1250°C yielded no Ti_3AlC_2 in the composites, only Ti_2AlC as seen in Figure 4.27. However, increasing the dwell time to 10 minutes for the samples sintered at 1300°C yielded the Ti_3AlC_2 in the samples, which was in addition to the Ti_2AlC and Ti_2AlN (Figure 4.28). The Ti_3AlC_2 MAX phase was the major phase found in this sample (Figure 4.29). This showed that the reaction path in Equation 2.3 by **Zhou et al. (2003b)** was the one followed by the system investigated in this work, also that the results in this work was similar to the work by **Li et al. (2012)**. The input parameters such as the pressure used and the volume fraction of cBN were different, therefore some resultant phases were different from the current work. For example, at 1250°C for 10 minutes, the resultant phases shown by **Li et al. (2012)** were Ti_3AlC_2 , TiC, TiAl, TiN and excess hBN; whereas in the current work the resultant phases were Ti_2AlC , Ti_2AlN , TiC, TiAl₂, Ti₃Al, TiN, TiB₂ and excess hBN. However, increasing the temperature to 1300°C in the current work led to similar phases such as Ti_3AlC_2 and TiN; and more different phases such as Ti_2AlC , Ti_2AlN , TiC_xN_y , TiB₂ and hBN (Figure 4.28).

The impact of higher cBN content in the composites was discussed in Section 5.2.2.2. Also, as noted by Li et al. (2012), for both the 2:1,2:1 and 3:1,2:2 molar ratios of Ti:Al:C, there was Ti_3AlC_2 found in the samples sintered for 10 minutes (Figures 4.23 and 4.28). The only difference was that for the 3:1,2:2 ratio, the Ti_3AlC_2 phase was seen in the sample sintered at 1300°C, and only seen in the sample sintered at 1250°C for the 2:1,2:1 ratio (Figures 4.23 and 4.28). The reason for this would be the same as discussed in the reactivity study, that the presence of the extra TiC in the 3:1,2:2 ratio would promote reaction to happen ~50°C higher than in the 2:1,2:1 ratio.

The microstructure and phase distributions for the Ti_3AlC_2 -cBN composites sintered at 1300°C at different dwell times were very similar to the composites of Ti_2AlC -cBN sintered at 1250°C at different dwell times (Figures 4.26 and 4.31). The noticeable difference was the fact that for the sample sintered for 5 minutes in the Ti_2AlC -cBN composites there was a reaction area around the cBN (Figure 4.26), unlike in the Ti_3AlC_2 composite sintered for 5 minutes (Figure 4.31).

It was concluded from the XRD, Rietveld and SEM/EDX data that the optimal sintering condition for the sample sintered with 3:1,2:2 molar ratio of Ti:Al:C powders were 1300°C for 10 minutes. This was due to Ti_3AlC_2 -cBN and cBN were present as required, however, this was coupled with the presence of Ti_2AlC and Ti_2AlN , but the Ti_3AlC_2 was the major phase (Figure 4.29). Also, that the MAX-cBN interface had a reaction area as required, Figure 4.31.

5.2.2.2 Increased in particle size (10 to 100 μm) and volume fraction of the 100 μm cBN (20 to 40 vol.%)

The 1300°C, sintering condition temperature was used to sinter samples containing 20 vol.% of 100 μm cBN as recommended in Section 5.2.2.1. The dwell time was varied from 1 to 10

minutes to investigate the best dwell time to achieve Ti_3AlC_2 in the samples with the larger cBN as the formation of Ti_3AlC_2 is dependent on kinetics (**Zhou et al. (2003b)**). Decreasing the surface area of the cBN had an effect on the formed phases and their distributions in the sample in several ways as discussed below.

The first difference observed was the proportion of MAX phases present in the resultant composite samples. For samples sintered with 10 μm cBN the combined Ti_2AlC and Ti_2AlN phases proportion decreased from 42,9 to 38,2 vol.% when the dwell time was increased from 1 to 5 minutes (Figure 4.29). These MAX phases were then further decreased to 11,9 vol.% when the dwell time was further increased to 10 minutes, and this was coupled with the presence of Ti_3AlC_2 as the major phase in the sample (Figure 4.29).

The observed trend in the samples containing 100 μm cBN was that the combined Ti_2AlC and Ti_2AlN in the samples increased from 47,1 to 50 vol% when the time was increased from 1 to 5 minutes (Figure 4.44). These MAX phases were then depleted when the dwell time further increased to 10 minutes, leaving Ti_3AlC_2 as the major MAX phase in the sample, with only ~3 vol.% Ti_2AlC and no Ti_2AlN . The Ti_3AlC_2 proportion in the sample containing 100 μm cBN was 10 vol.% less than in the sample containing 10 μm cBN (Figures 4.29 and 4.44). The higher proportion of Ti_2AlC and Ti_2AlN in the samples sintered for 1 and 5 minutes (Figure 4.43) could have been due the smaller surface area of cBN available to hexagonalise, thus less formation of the Ti-B/N based reaction products. This would lead to more Ti available to form the MAX phases. This was also supported by the fact that there was a lower proportion of Ti-Al intermetallic compounds observed in the samples sintered with 100 μm cBN (Figure 4.43) than in the samples sintered with 10 μm cBN (Figure 4.28).

The second observed difference was the excess hBN in the samples sintered at 1300°C. The excess hBN found in the sample sintered for 5 minutes was less in the 100 μm cBN composites (Figure 4.43) than in the 10 μm composite (Figure 4.28). This could be due to the smaller

available surface area of the cBN, leading to less hBN forming on the surface. Also, in the samples containing 100 μm cBN sintered for 10 minutes, there was hBN observed, unlike in the sample containing 10 μm cBN (Figure 5.2). This could have been due to the same reasoning given above, there was less available Ti to react with the excess hBN to form the reaction products, and a small amount of hBN was present in the sample.

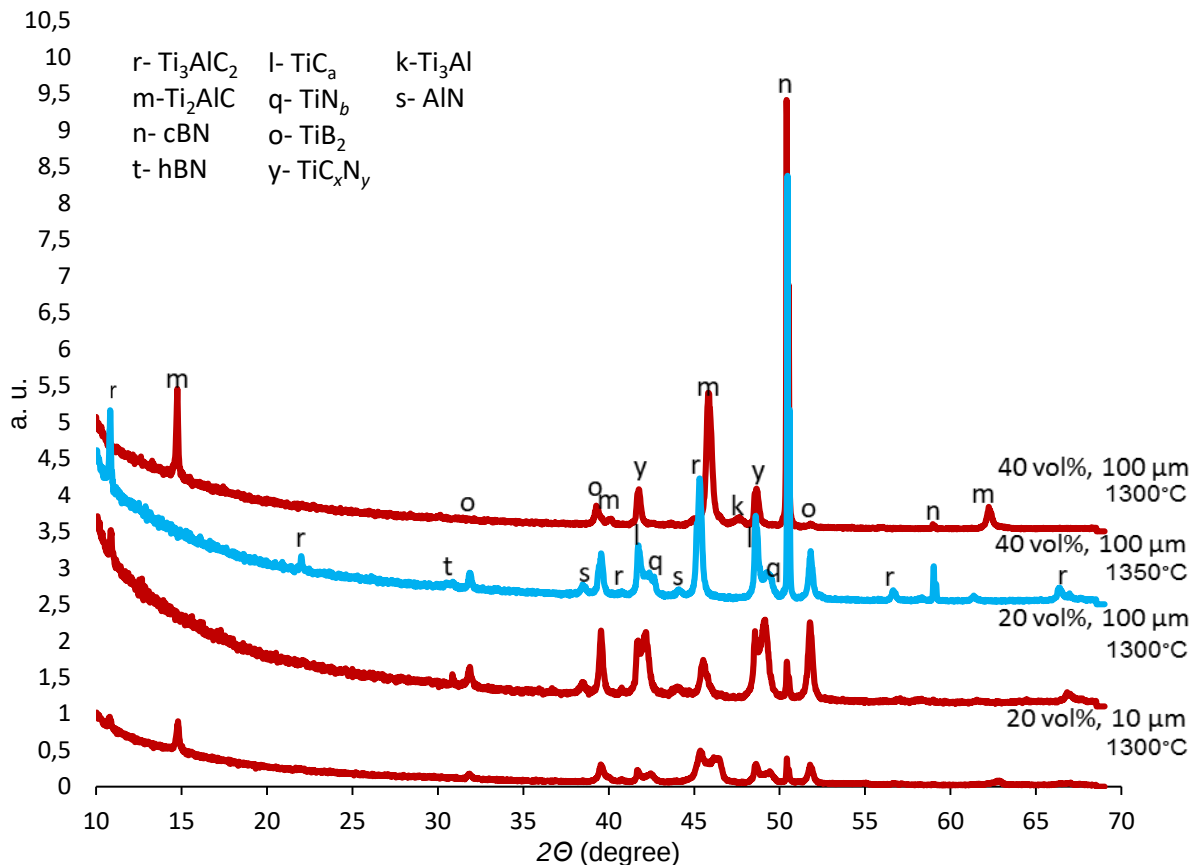


Figure 5.2: XRD traces of Ti_3AlC_2 -cBN samples sintered at 1300°C for 10 minutes, showing different volume fraction (20 or 40 vol.%) and different size (10 and 100 μm) cBN, also included was the successful sample at the 40 vol.% cBN sample sintered at 1350°C for 5 minutes.

The third observed difference was in the resultant reaction products for samples sintered at 1300°C. The one noted above was the presence of Ti_3AlC_2 as the only MAX phase in the sample containing 100 μm cBN sintered for 10 minutes (Figure 5.2). The TiC in the sample containing 100 μm cBN was also observed in this case in contrast to the sample containing 10

μm cBN (Figure 5.2). The presence of AlN in all samples containing 100 μm cBN was also different from the samples containing the 10 μm cBN (Figures 4.28 and 4.43).

The density and open porosity trends (Figures 4.30 and 4.45), microstructural evolution (Figures 4.31 and 4.46) and the phase distributions (Figures 4.16 and 4.47) were all observed to be similar in the samples containing 10 and 100 μm cBN. Thus, the sintering conditions of 1300°C for 10 minutes was used to sinter samples with 40 vol.% of 100 μm cBN. In addition, samples were also sintered for 5 minutes and 1250°C and 1350°C in order to evaluate the interaction reaction of Ti_3AlC_2 and cBN with an increased cBN amount.

Increasing the volume fraction of the low surface area cBN (100 μm) had a significant effect on the phases, Figure 5.2. The samples with 40 vol.% cBN sintered at different temperatures for 5 minutes had no excess hBN, Figures 4.60 and those sintered for 10 minutes showed little hBN, Figure 4.61. Also, the sample containing 40 vol.% cBN sintered at 1300°C for 10 minutes had Ti_2AlC as the only MAX phase (Figure 4.61). This was not the case for the samples containing 20 vol.% of 100 μm cBN and 20 vol.% of the 10 μm cBN under the same conditions (Figures 4.28 and 4.43). The former contained Ti_3AlC_2 as the only MAX phase (Figures 4.43), while the latter contained Ti_2AlC , Ti_2AlN and Ti_3AlC_2 (Figure 4.28). Increasing the temperature to 1350°C for the samples containing 40 vol.% cBN resulted in the formation of the desired Ti_3AlC_2 as the only MAX phase (Figure 5.2), but also a more significant decrease of the cBN in the sample (Figure 4.62). In the samples sintered containing 40 vol.% of 100 μm cBN there was no Ti_2AlN (Figures 4.60 and 4.61) unlike in the samples containing 20 vol.% of 100 μm (Figure 4.43) and 20 vol.% 10 μm cBN (Figures 4.27 and 4.28). This shows evidence that the increased volume fraction of cBN further reduced the extent of hexagonalisation of the cBN, as the Ti_2AlN phase formation was dependent on the presence of N rich source; in this case hBN.

Therefore, increasing the volume fraction of cBN suppressed the decomposition of the Ti_3AlC_2 and the hexagonalisation of the cBN and further promoted the formation of Ti_3AlC_2 as the only MAX phase in the composites. The density and open porosity trends observed for the samples containing 40 vol.% cBN were different from those containing 20 vol.% cBN. The densities of all samples with 40 vol.% were similar for all samples (Figure 4.63), whereas for the 20 vol.% samples showed an increase followed by a decrease with increased dwell time for samples sintered at 1300°C but were similar in samples sintered at 1250°C (Figures 4.30 and 4.45). This was because for the samples containing 40 vol.% cBN there was no major phase change for sintering temperatures of 1250°C and 1300°C or dwell times of 5 and 10 minutes (Figures 4.60 and 4.61).

The samples containing 20 vol.% of cBN, however, showed phase changes especially for samples sintered at 1300°C 10 minutes (Figures 4.28 and 4.43) with the phases such as $\text{TiC}_a/\text{TiN}_b$, TiB_2 and TiC_xN_y increasing significantly. However, there was no significant difference observed in the microstructure between the samples containing 20 and 40 vol.% of cBN (Figures 4.46 and 4.64), or the phase distribution (Figures 4.47 and D18 in Appendix D), apart from this difference the samples sintered at 1350°C showed a clear reaction area unlike the samples sintered below this temperature (Figures 4.64). This was similar to samples sintered with 20 vol.% of 10 μm cBN above 1300°C (Figures 4.15 and 4.16). This may be evidence that the same exothermic reaction occurs at 1350°C, but does not deplete the MAX phase or cBN due to the lower surface area and higher content of cBN stabilising effect on the two phases.

These results show that for samples sintered with 40 vol.% of 100 μm cBN, the optimum conditions for sintering the Ti_3AlC_2 -cBN composites was 1350°C for 5 and 10 minutes.

5.2.3 Ti_3SiC_2 - cBN composites

5.2.3.1 Reaction Temperature evaluation for 20 vol.% of 10 μm cBN powder

This section of the discussion evaluates the Ti_3SiC_2 MAX phase composite together with cBN. Of the three MAX phases under investigation in this study, Ti_3SiC_2 has been the most extensively researched (**Benko et al., 2004; Rampai et al., 2013; Qin & He, 2013; Li et al., 2014; Kolabylina et al., 2017; Yue et al., 2018**).

Gao et al. (2002) and **Liang et al. (2008)** showed that Ti_3SiC_2 can be synthesised at temperatures as low as 1000°C to 1300°C at pressures as low as 30 to 60 MPa. **Gao et al. (2002)** and **Liang et al. (2008)** noted that these conditions needed to be coupled with either additions of small amounts of Al with mechanically alloyed powders or using base powders that yielded Ti:Si:C in the ratio of 2:1:1. Thus, these temperature ranges were investigated in this system as 30 MPa was the operational pressure, but additions of Al were not included in the current work. The other difference in this study was that SiC was used instead of Si. This was not hypothesised to be a limiting factor for the formation of this phase as **El-Raghy & Barsoum (1999a)** noted that SiC was an intermediate product in the formation of the Ti_3SiC_2 phase. **Bandyopadhyay, (2004)** demonstrated that at the utilised molar ratios of Ti:Si:C, 3:1:2, sintered at 1250°C the resultant phases should be Ti_3SiC_2 and $\text{Ti}_5\text{Si}_3\text{C}_{1-x}$, which was observed in this study.

For the synthesis of Ti_3SiC_2 -cBN composites, the SPS data were first considered in order to evaluate the reactivity of the starting powders with increased temperature, these data were supported by XRD, density and SEM/EDX analyses. Figure 4.17a shows that for the piston displacement curves, at 1400°C the relative piston position increased by approximately 1 mm. This was indicative of the formation of products (TiC_a , TiC_xN_y and TiB_2) with a higher density that became more significant phases in the samples sintered above this temperature (Figures

4.18, 4.20 and Table 5.2). **Naka et al. (1997)** showed that in the reaction path between Ti and SiC, Ti_3SiC_2 would form at approximately 1400°C at 1-minute dwell time. This was not observed in this study. The likely reason was due to the hexagonalisation of cBN, there was a N-rich environment within the sample, as shown in Figures 4.19 and 4.20, where there was an excess hBN found in all samples. **Tomashik & Perrot (2005)** noted that the solubility of N in Ti was significant and the excess Ti would react with the N and C to form the TiC_xN_y , as shown in Figure 4.19, where this phase was present in significant amounts from 1150°C . This may form a deficiency of Ti to form the Ti_3SiC_2 . Since the Ti_2SiC phase does not exist, only a small amount of the Ti_3SiC_2 was found (1150°C) which further diminishes with increases in temperature.

Table 5.2: Density of the secondary phases, listed in descending order, found in the sintered samples, as well as cBN, hBN, and Ti_3SiC_2 phases under the triple border for comparison (**Springer, 2018**).

Phase	Density (g/cm^3)	Phase	Density (g/cm^3)
TiN	5.39	Ti_5Si_3	4.41
$\text{TiC}_{0.3}\text{N}_{0.7}$	5.25	TiSi	4.25
TiB_2	4.53	SiC	3.22
TiC	4.09	SiB_4	2.26
Ti_3SiC_2	4.53	cBN	3.49
		hBN	2.26

The samples sintered above 1400°C showed a flat line after this increase, indicating that the sample had reached full density at the given conditions (Figure 4.17a). The samples sintered below 1400°C still showed increasing curves during the dwell time, indicating that a level of densification was reached, but not fully dense. The reason for this densification was assumed to be the exothermic chemical reaction forming the TiC_a , TiC_xN_y and TiB_2 (Figure 4.17b). This assumption was supported by the power “drop” of the SPS equipment, and the change or

increase in some phases such as TiB_2 and TiC_xN_y (Figures 4.19 and 4.20) for samples sintered at or above 1400°C .

The hypothesised reaction of Ti_3SiC_2 with cBN, was the same as in the Al-based MAX phases and most likely occurred by the cBN first hexagonalising, followed by a simultaneous reaction of the hBN with Ti_3SiC_2 . As stipulated earlier (Sections 5.2.1.1 and 5.2.2.1), this can occur since the hBN was much more susceptible to diffusion processes and reactions than cBN at these temperatures. Thus, TiN_b and TiB_2 were found in samples sintered at temperatures as low as 1150°C , as these are a result of Ti reacting with hBN (Figure 4.19). This was also noted by **Li et al. (2012)** in the Ti-Al-C-BN system, and calculations using Equation 5.1, it was seen that at these temperatures cBN would hexagonalise. In the Ti_3SiC_2 -cBN system, this occurred to a significant extent since a large amount of TiN_b and excess hBN were found in the sintered samples even at temperatures as low as 1150°C and 1250°C (Figure 4.19). At the conditions used in these reaction studies, there might have been a large amount of hBN formed due to the unreacted Ti from the starting powder which drove the reaction with the hBN to form TiB_2 and TiN_b and TiC_xN_y , rather than forming the counterpart MX phase as was also noted by **Tomashik & Perrot (2005)**. Hence, Ti_3SiC_2 was only seen in very small amounts in the samples sintered at 1150°C and also absent at temperatures above this (Figure 4.19). Tables 4.1 and 4.2 further show that the reaction of Ti with BN was more thermodynamically favourable (Gibbs free energy $< -391\text{kJ}$) than the formation of Ti_3SiC_2 at temperatures ranging from 100°C to 1600°C .

Thus, the likely reactions for forming the small amounts of MAX phase found in the samples during this study were the same as those found by **El-Raghy & Barsoum (1999a)** (Equations 5.6 to 5.10):





This was in opposition to the reaction suggested by by **Li & Zhai (2005)** (Equation 5.11) as SiC was used in this study and the formation of Ti_2Si was not likely:



In addition to Equations 5.6 to 5.10, the following reactions occurred in this system as the temperature was increased:



The reaction of BN with the MAX phase:



The exothermic reaction in Equation 5.12 may provide the heat to drive the endothermic reaction in Equation 5.13 which yielded an unsuccessful composite, because it depleted the MAX phase. This was supported by the XRD results in Figure 4.20 where there was no Ti_3SiC_2 phase in these samples. Thus, for optimisation of the MAX and cBN proportions, temperatures of 1400°C and above were avoided in synthesising the composites.

As the temperature increased was up to 1400°C, the densities of the samples were similar (Figure 4.18), this was because the phases were the same in these samples (Figures 4.19 and 4.20). However, there was an observed increase in density as temperature was increased to

1500°C (Figure 4.18). That was because as temperatures reached 1500°C phases of low density such as cBN and hBN were significantly reduced, forming phases of a much higher density such as TiB_2 and TiC_xN_y (Table 5.2 and Figure 4.19). The microstructure of the sintered samples showed a clear reaction area (between the red and blue circles) in all samples, even samples sintered at 1250°C (Figure 4.21). The EDX analysis of the sample sintered at 1600°C showed that TiC_xN_y and TiB_2 were well distributed in the matrix (Figure 4.22).

From the data collected, it was decided to use sintering conditions less than 1400°C for Ti_3SiC_2 -cBN composites. Also, sintering was done at 1150°C in order to further react the Ti, SiC and the carbon to form more Ti_3SiC_2 . In addition, 1250°C was used, since there was also very little MAX phase formation in the samples compared to samples sintered above 1300°C (Figure 4.19).

An increase in dwell time, from 1 to 10 minutes, gave no Ti_3SiC_2 proportions in the samples sintered at 1150°C or 1250°C (Figures 4.32 and 4.33). All samples also showed very little cBN (Figure 4.34), thus it was deemed that these samples were unsuccessful in achieving the desired result. The samples also displayed very similar phase contents with increased dwell time for all sintering temperatures, however, the phase proportions differed. The densities of all samples investigated displayed very similar values as a result (Figure 4.35). The only difference observed was the fluctuation of hBN in the samples sintered at 1250°C (Figure 4.33). There was a possible presence of Ti_3SiC_2 in the sample sintered at 1250°C for 10 minutes, but only in a very small amount (Figure 4.33).

The microstructure of the samples with dwell times of 1, 5 and 10 minutes revealed that there was no strong bond between the matrix and the cBN (Figure 4.36). This was seen because the cracks in the samples propagated around the cBN particles (red arrow), and a large amount of cBN pull-out was observed (green arrows) for the samples sintered for 1 and 5 minutes. This may be due to the large amount of the hBN in the sample as hBN would be present at the

surface of the cBN (as discussed in Section 5.2.1.1), causing a weak point that the crack could propagate through. All samples displayed a reaction area around the BN phase (Figure 4.36 between red and blue circles).

It was therefore decided that the samples sintered at 1250°C would be considered for the optimisation studies, with the lower surface area cBN particles. However, the optimisation attempts for Ti_3SiC_2 -cBN composites, with 20 vol.% of 10 μm cBN, were not successful since there was little to no Ti_3SiC_2 in all samples and a significant amount of hBN.

5.2.3.2 Increased particle size (10 to 100 μm) and volume fraction of the 100 μm cBN (20 to 40 vol.%)

A sintering temperature of 1250°C was used to sinter samples with 20 vol.% of 100 μm cBN as recommended in Section 5.2.3.1. In addition, samples were also sintered at 1300°C in order to evaluate the interaction reaction of Ti_3SiC_2 and cBN with a decrease in surface area of the cBN.

Decreasing the surface area of the cBN, by increasing the size, had some effect on the phase contents of samples sintered at 1250°C, as shown in Figure 4.48. A significant effect was the much lower proportion of the excess hBN found these samples compared to the samples with 10 μm cBN (Figure 5.3). This could be due to the low available surface area of the cBN, leading to less hBN forming on the surface. Thus, there was a higher likelihood of the available Ti to form Ti_3SiC_2 instead of reacting with hBN to form more TiN_b even though it was still found in small amounts. This was supported by the lower proportions of TiC and TiB_2 reaction products between Ti_3SiC_2 and BN. Samples containing 20 vol.% of 100 μm cBN showed evidence of Ti_3SiC_2 even at sintering temperatures of 1300°C (Figure 4.49). All samples sintered at 1250°C and 1300°C showed very similar phases (Figures 4.48 and 4.49) and thus their densities were also similar but not the same as the proportions of the phases present differed (Figure 4.51).

The only exception was the sample sintered at 1300°C for 10 minute (Figure 4.49) which showed a much higher proportion of TiN_b than the other samples and no evidence of Ti_3SiC_2 . The Ti_3SiC_2 at both sintering temperatures this with increased dwell time. This could have been because as the dwell time increases the amount of hBN increased forming more TiN_b and less Ti_3SiC_2 (Figure 4.50).

The microstructure of the samples sintered with 20 vol.% of 100 μm cBN (Figure 4.52) was similar to that of the samples sintered with 20 vol.% of 10 μm cBN (Figure 4.36). The phase distribution was also similar (Figure 4.53) with only the addition of TiC_a seen in the matrix of the samples containing 100 μm cBN. Thus, it was hypothesised that in the Ti_3SiC_2 -cBN composites, decreasing the surface area of the cBN decreased the hBN content, thus promoting the formation of Ti_3SiC_2 (Figure 4.49).

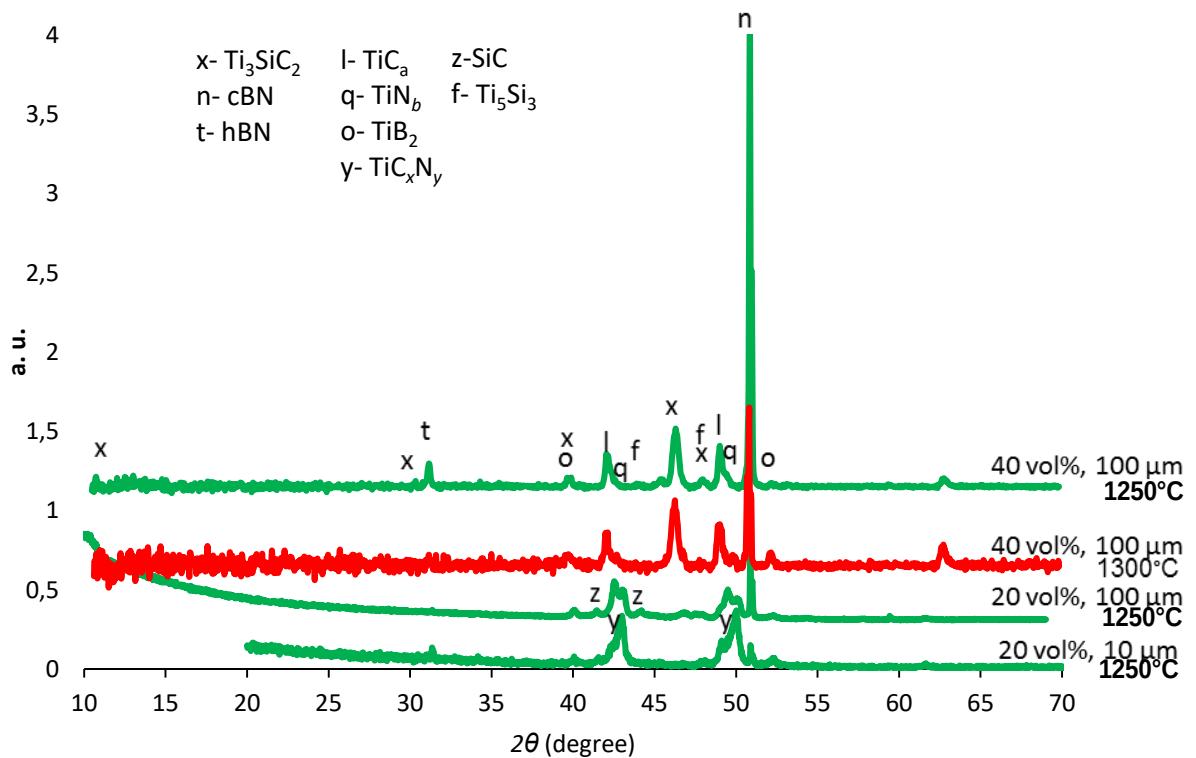


Figure 5.3: XRD traces of Ti_3SiC_2 -cBN samples sintered at 1250°C for 5 minutes, showing different volume fractions (20 or 40 vol.%) and different sized (10 and 100 μm) cBN; also included was the successful sample at the 40 vol.% cBN sample sintered at 1300°C for 5 minutes.

As shown in Figure 5.3, for the 20 vol.% cBN samples, TiB_2 and TiC peaks for the 100 μm were higher than the cBN than in the sample with 10 μm cBN. The second notable difference was the presence of hBN, in the samples sintered at 1250°C for 10 minutes, there was hBN in the samples containing 10 μm cBN (Figure 4.33), but not the 100 μm cBN samples (Figure 4.48). Also, the samples sintered at 1300°C (Figure 4.49) had very little hBN and Ti_3SiC_2 , which showed that for samples containing 100 μm cBN, the optimum sintering temperature was also 1250°C. Thus, the 1250°C sintering temperature was further used to sinter samples with 40 vol.% of 100 μm cBN. In addition, samples were also sintered at 1300°C and 1350°C in order to evaluate the interaction reaction of Ti_3SiC_2 and cBN with an increased amount of the cBN at these different temperatures.

Increasing the volume fraction of the low surface area cBN had a significant effect on the phase proportions as shown in Figures 4.66 and 4.67 for samples sintered at 1250°C and 1300°C. The first notable difference in increasing the cBN proportion was that, instead of TiC_a and TiN_b in the sintered samples at similar conditions but with 20 vol.% of cBN, there was TiC_xN_y , Figure 5.3. Also, in the sample sintered at 1350°C for 5 minutes (Figure 4.66), there was a very small amount of Ti_3SiC_2 present in the sample (Figure 4.68).

Another noted difference was the presence of hBN in the samples sintered at 1250°C and 1300°C (Figure 4.66 and 4.67) compared to the samples containing 20 vol.% of 100 μm cBN only having hBN in samples sintered at 1250°C for 1 minute and at 1300°C for 10 minutes (Figures 4.48 and 4.49). The density of the samples increased with increasing sintering temperature (Figure 4.69). This was attributed to the increase in the phases with higher density (Table 5.2) such as TiC_xN_y , TiB_2 and TiC_a (Figure 4.68) as the temperature increased. The microstructure of the samples containing 40 vol.% cBN sintered at 1250°C and 1300°C was similar to their counterparts in samples containing 20 vol.% cBN. The microstructure of the sample sintered at 1350°C for 5 minutes showed a reaction area around the BN phases (Figure

4.70). The phase distribution in the reaction area (between red and blue circles in Figure 4.70) revealed that there was mainly TiC_a , TiB_2 and SiC in the reaction area and TiB_2 and TiC_xN_y were found more in the matrix (Figure 4.71).

Generally, in this system, increasing the volume fraction of the cBN in this system increases the formation of excess hBN (Figure 4.66). The matrix of the samples displayed some pores (Figure 4.70). Thus, for the 40 vol.% of 100 μm cBN composites, the optimum conditions for sintering Ti_3SiC_2 -cBN composites was 1250°C for 5 minutes as this has the highest content of cBN and Ti_3SiC_2 with minimal hBN.

5.2.4 Overall MAX cBN composites reactivity

Figure 5.4 shows the cBN hexagonalisation and MAX phase proportion in the samples that were selected for mechanical properties testing. The hexagonalisation of the cBN was estimated by taking the gradient of the cBN graph in each respective Rietveld analysis results shown in Chapter 4.

Generally, each cBN graph showed a reduction in cBN with increase in dwell time or sintering temperature. **Garrett et al. (2015)** also used 10 and 100 μm cBN at 30 MPa to make composites with Sialon; they found that hexagonalisation decreased with sintering temperature, whereas this work agreed more with work done by **Sachdev et al. (1997)** where they demonstrated that the hexagonalisation increased with increase in temperature. The units for the rate of hexagonalisation of samples with 20 vol.% cBN were vol.%/min, and for the samples with 40 vol.% cBN the units were vol./°C. This was because the graphs with 20 vol.% cBN showed a phase content increase with dwell time and those with 40 vol.% showed this increase with increasing sintering temperature (Figures 4.34, 4.50 and 4.68). The phase proportions in Figure 5.4 were reported as shown in the respective Rietveld analysis graphs in

Chapter 4. The M_2AX proportion reported is the sum of Ti_2AlC and Ti_2AlN as they were both found in the samples and have similar structure and properties.

It was observed that the rate of hexagonalisation of cBN in the Ti_3SiC_2 based composites was higher than in the Al based composites at 20 vol.% cBN. The rate of hexagonalisation for the two Al based composites was the same in samples containing 10 μm sample with the rate of hexagonalisation for Ti_3SiC_2 -cBN composites slightly higher (Figure 5.4). In the Ti_2AlC -cBN and Ti_3SiC_2 -cBN composites the rate of cBN hexagonalisation increased with increased cBN size whereas a decrease in rate of cBN hexagonalisation was observed in Ti_3AlC_2 -cBN composites. The rate of hexagonalisation for all composites decreased when the proportion of the cBN powder increased. This, however, was not a viable comparison because the rate for the samples containing 40 vol.% cBN was controlled by temperature not time, and these samples were sintered at different temperatures to the other samples. It was observed that the rate was the same for the two 3:1:2 MAX phases and was lower than the rate for Ti_2AlC based composite. In general, the hexagonalisation rate in the small cBN was more dependent on the species of the A group (Al or Si) in the MAX phases, and dependant on the Ti:C ratios in higher sizes and proportions of cBN.

The MAX phase proportions in the samples showed an increase with vol.% and proportion of cBN for the Ti_3SiC_2 based composites. For the Ti_3AlC_2 based composites the opposite was observed and Ti_2AlC based composites showed an increase then a decrease of the MAX phase. The decrease in the MAX phase proportion in the Al based MAX phase composites with samples containing 40 vol.% was probably due to the doubling in the cBN content rather than the absolute decrease of the MAX phase. Ti_3SiC_2 showed the opposite, and this was probably because very little Ti_3SiC_2 was found in the samples containing 20 vol.% of cBN. Therefore, the Ti_3SiC_2 composite sample containing 40 vol.% would show an increase, due to the stabilisation effect of the cBN, even though the cBN was doubled.

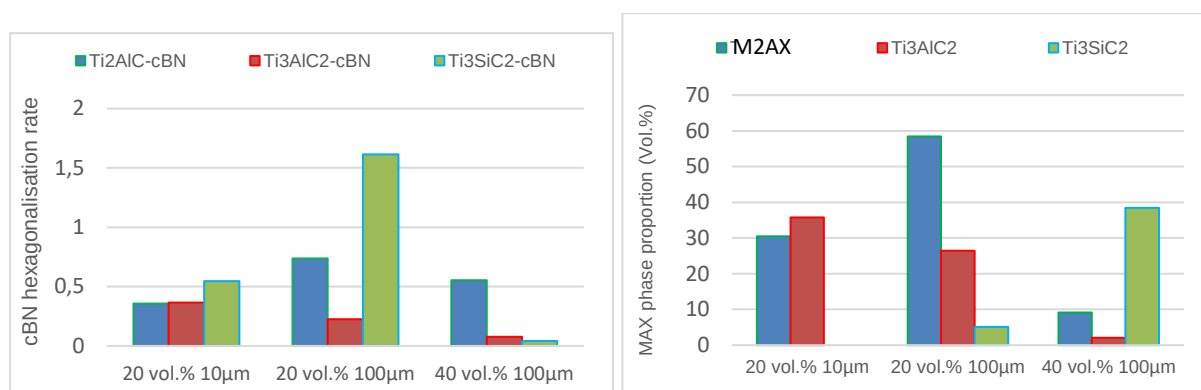


Figure 5.4: Graphs showing the rate of cBN hexagonalisation (left) and proportion of MAX phases formed (right) in all successful composites selected for mechanical tests.

In general, having Al as the A phase in the MAX phase reduces the hexagonalisation of cBN with small cBN particles. Having a higher Ti:C proportion also suppressed the hexagonalisation of the cBN with large and high content cBN particles. The reaction dynamics were also different depending on the proportion of Ti:C in the MAX phase, and also having either Al or Si as the A-group (Sections 5.2.1.1, 5.2.2.1 and 5.2.3.1). The composites containing 3:1:2 ratios of M:A:X proved more challenging to fabricate, and that was due to the energy of formation of the Ti₂AlC being much less compared to the other MAX phases.

The Ti₂AlC composites could be fabricated using two methods. The first was using the 2:1:1 MAX powder combination at 1250°C for 5 minutes for all cBN sizes and proportions (with an additional 1250°C for 10 minutes and 1300°C for 1 minute for samples containing 40 vol.% cBN). The second method was using the molar ratio 3:1:2 of the MAX phase powders. The appropriate conditions were 1300°C for 1 minute for samples containing 20 vol.% cBN, 1250°C (5 and 10 minutes) and 1300°C (5 and 10 minutes) for samples containing 40 vol.% cBN. Similarly, the Ti₃AlC₂ based composites could be synthesised in two different ways. The first with 2:1:1 molar ratios of MAX powders. With this method, the sintering conditions were 1250°C for 20 minutes for the samples containing 20 vol.% cBN. This, however, led to the coexistence of Ti₂AlC and Ti₂AlN in the resultant samples, and no successful composite of the samples containing 40 vol.% cBN.

The second method was using the molar ratio of 3:1:2 for the MAX powders. This was coupled with the use of 1300°C sintering temperature for 10 minutes in samples containing 20 vol.% cBN. This yielded the coexistence of Ti_2AlC and Ti_2AlN in the resultant composite for samples containing 10 μm cBN particles. The optimum sintering conditions for samples containing 40 vol.% were 1350°C for 5 and 10 minutes. Ti_3SiC_2 based composites were only successful in samples containing 100 μm cBN using. The optimum conditions for the sample containing 20 vol.% cBN were 1250°C for 5 minutes, and for the sample containing 40 vol.% cBN was 1300°C for 5 and 10 minutes.

5.3 Mechanical properties of the successful MAX-cBN composites

This section discusses results in Section 4.5, testing of the successful samples as shown in Figures 4.72, 4.73 and 4.74.

The microhardness of the MAX-cBN composites (Figure 4.75) seemed to be closer to the hardness of the MAX phases (Table 2.2), rather than the cBN (Table 2.5). Also, for all samples there did not seem to be much change in the microhardness of the respective samples with increase in particle size and proportion of the cBN. The likely reason for this would be that for the microhardness tests the indenter probably penetrated the matrix which was mostly the respective MAX phase. This would account for the microhardness being more like the respective MAX phase hardness and why it does not increase with increase in cBN size and/or proportion. Therefore, for the purpose of assessing the effect of cBN size and proportion on the hardness of the composites, the bulk hardness of the composites was considered (Figure 4.76).

For all MAX-cBN composites, it was observed that increasing the size of the cBN increased the bulk hardness of the respective composites and increasing the proportion of the cBN did

not cause a change in the hardness. The bulk hardness of the all MAX composites with cBN containing 20 vol.%, 10 μm were the same, also for the MAX composites containing 20 vol.% of 100 μm cBN. However, in the sample containing 40 vol.% of 100 μm cBN the bulk hardness range was $\text{Ti}_3\text{SiC}_2 > \text{Ti}_3\text{AlC}_2 > \text{Ti}_2\text{AlC}$. Also, the hardness of Ti_3SiC_2 -cBN composites investigated by **Benko et al. (2004)** for 25 and 50 vol.% were 16 and 28 GPa respectively. This was higher than the values reported in this work of 15,6 and 18 GPa. This might have been due to a few factors, first that sizes of the cBN particles were different. Also there was more MAX phase in the current work than in **Benko et al. (2004)**, therefore the hardness values in the current work would be lower because the hardness of the MAX phases are lower than of the hardness's of the reaction phases, TiC, SiC and TiB_2 , found in the samples sintered by **Benko et al. (2004)** (Table 2.2).

In combination with the highest hardness, the wear resistance of the Ti_3SiC_2 based composite with 40 vol.% of 100 μm cBN was also the highest (Figures 4.77 and 4.78), followed by the Ti_3AlC_2 -cBN (40 vol.%, 100 μm), then the Ti_2AlC -cBN (40 vol.%, 100 μm). Generally, the wear resistance of the MAX-cBN composites increased significantly with the increased in size of the cBN from 10 μm to 100 μm , then slightly more with the increased of the volume fraction of the same size cBN from 20 to 40 vol.%.

The mass loss reported by **Li et al. (2012)** for a Ti_3AlC_2 -cBN with 50 % cBN was 0,10 mg, whereas in this work it was 6,8 mg for a sample containing 40 vol.% cBN. This difference could account for the fact that the counterphase used for the two wear tests were different. In this work SiC was used, whereas **Li et al. (2012)** used Si_3N_4 which has half the hardness of SiC, thus the SiC would wear the samples more rapidly. The SEM images of the wear scars of the selected samples (Figure 4.79) from this work showed that the Ti_3SiC_2 -cBN composites displayed a lesser extent of wear scars that the other composites for all vol.% and proportions of cBN. Also, it was observed that the sample containing 40 vol.% of 100 μm cBN retained a

larger portion of the counterphase (Figure 4.79), further demonstrating that they were more wear resistant.

These results suggested that the wear of these composites depended more on the size of the cBN rather than the volume fraction, whereas the hardness depended more on the volume fraction (Figure 5.5) rather than the size of the cBN. Also, the general relationship between the bulk hardness and wear rate indicated that the higher the hardness of the sample, the lower the wear rate (high wear resistance) as shown in Figure 5.5.

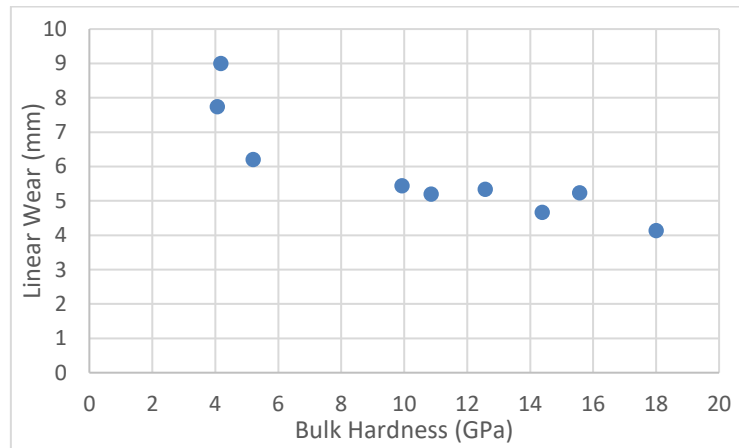


Figure 5.5: Relationship between the Vickers hardness and linear wear of all MAX-cBN composites synthesised.

5.4 Suitability of the successful MAX-cBN composites for grinding wheels

From the reactivity studies and SEM images shown and mechanical tests performed in this work the following was determined. Provided the optimised manufacturing parameters were used, the successful Ti_2AlC -cBN (20 vol.%, 10 μm) composite under investigation here would be a viable alternative for cBN based grinding wheels. The high proportion of Ti_2AlC in the matrix, a significant proportion of cBN and the absence of hBN gave the most suitable composition to manufacture a grinding wheel with a good combination of properties. According to Tables 2.6 and 2.8, this composition would be better suited for fine, precision grinding and

polishing. Since the composite was considered relatively “soft”, according to Tables 2.7 and 2.8, the operational conditions would be suitable for a wide range of grinding coatings, special processes, large contact areas, workpieces sensitive to heat and for dry grinding, more so since MAX phases are known to be self-lubricating (**Barsoum & Radovic, 2004**).

Figure 4.26 shows that the reaction area is strongly bonded to both the cBN and the Ti_2AlC . This indicated that during grinding there would most likely be no cBN pull-out during service, probably leading to an extended and effective service life. Both the 312 MAX phase based composites were marginally successful in this case. This was due to the Ti_3SiC_2 -cBN composites lacking Ti_3SiC_2 in the resultant samples containing 20 vol.% cBN (Figures 4.33 and 4.48). Also, the Ti_3AlC_2 -cBN due to having both Ti_2AlC and Ti_2AlN additional MAX phases in the resultant samples containing 10 μm cBN (Figure 4.28). However, because Ti_3AlC_2 was the major phase in the sample, this composite can also be a viable option for grinding wheel manufacture. Since the Ti_3AlC_2 -cBN composite had similar properties as the Ti_2AlC -cBN composites, the same classification and operational conditions apply in this system as well.

Also, from the reactivity studies, SEM images and mechanical tests performed in this work, it was concluded that the selected successful samples were a suitable alternative for grinding wheel applications, provided the optimised manufacturing parameters were used. The successful Ti_2AlC -cBN and Ti_3AlC_2 -cBN (20 vol.%, 100 μm) composites would both be viable alternatives to cBN based grinding wheels. These composites had a high proportion of Ti_2AlC and Ti_3AlC_2 in the matrix of the respective samples, a significant proportion of cBN abrasives and no hBN. According to Tables 2.6 and 2.8, these composites would be better suited for finish and surface grinding. Since these composites were considered relatively “soft”, according to Tables 2.7 and 2.8, the operational conditions would be suitable for a wide range of grinding coatings, larger coatings width, workpieces sensitive to heat and for dry grinding. The respective SEM images (Figures 4.41 and 4.46) of these composites also showed some evidence that the reaction area had a strong bond to both the cBN and the matrix. This

indicated that during grinding there would most likely be no cBN pull-out, leading to an extended and effective service life using these composites too. The Ti_3SiC_2 -cBN composites were not suitable, since they do not contain sufficient Ti_3SiC_2 in the resultant samples.

Similarly, reactivity studies, SEM images (Figures 4.58, 4.64 and 4.70) and mechanical tests (Figure 4.76 and 4.77) performed in this work were considered. From these, it was determined that the successful Ti_2AlC , Ti_3AlC_2 and Ti_3SiC_2 composites with cBN (40 vol.%, 100 μm) would all be viable alternatives for cBN based grinding wheels provided the optimised manufacturing parameters were used. With a high proportion of each MAX phase in the respective composite matrix, a significant amount of cBN and no hBN, suitable conditions to manufacture grinding wheels with a good combination of properties were found.

During wear tests the MAX-cBN composites wore out the SiC counterphase, these SiC particles worn out from the counterphase were mostly concentrated around the cBN particles in the composites, which suggests that cBN was the abrasive in this case, thus the composites are suitable for grinding wheel applications. Using Tables 2.6 and 2.8, as in the previous case, these composites would be better suited for use in grinding wheels where finish grinding, profile grinding, form holding and slitting were required. But, unlike the previous case, the operational conditions would be suitable for a wide range of grinding coatings, higher coating widths, workpieces sensitive to heat and for dry grinding. The SEM images of these composites (Figures 4.26, 4.31, 4.41, 4.46, 4.52, 4.58, 4.64 and 4.70) also showed that the bond of the MAX phases and cBN to the reaction area was good which indicated that during grinding there would most likely be no cBN pull-out, leading to an extended effective service life in this case as well. However, out of the three composites the Ti_3SiC_2 based composite would appear to be the best suited since it had the highest wear resistance to the Al-based co

CHAPTER SIX: CONCLUSIONS AND RECOMMENDATIONS

The following conclusions were made from this work:

- Elevated temperatures and moderate pressures can be used to fabricate Ti_2AlC -cBN composites, by a controlled method of simultaneous hexagonalisation and reaction of the cBN with Ti_2AlC .
- The Ti_2AlC -cBN (20 vol.% of 10 μm) composite can be successfully synthesised with the cBN and Ti_2AlC as major phases with an additional Ti_2AlN MAX phase observed. The optimum conditions were 1250°C, at 30 MPa pressure, for 5 minutes. These conditions produced clearly visible reaction zones and the composite also comprised TiC_a , TiAl_2 , Ti_3Al_5 , TiN_b , Ti_3Al and TiB_2 .
- The Ti_2AlC -cBN (20 vol.% of 100 μm) composite was successfully synthesised with mainly the cBN and the MAX phase present. Using the optimum conditions from the Ti_2AlC -cBN (20 vol.% of 10 μm) studies, it was correctly predicted that the conditions that would be optimum for the Ti_2AlC -cBN (20 vol.% of 100 μm) composite were 1250°C, at 30 MPa pressure, for 5 minutes. These conditions gave reaction zones between the cBN and Ti_2AlC and the composite also comprised limited amounts of TiC_a , TiC_xN_y , TiAl_2 , TiN_b , Ti_3Al and TiB_2 .
- The Ti_2AlC -cBN (40 vol.% of 100 μm) composite was successfully synthesised with the cBN and the MAX phase present as major phases. Using the predicted results from the Ti_2AlC -cBN (20 vol.% of 100 μm) studies, it was correctly anticipated that the conditions would be appropriate for producing these samples were 1300°C, at 30 MPa pressure, for 5 minutes. These conditions gave reaction zones between the cBN and Ti_2AlC and the composite also contained small amounts of TiC , TiAl_2 , TiN , Ti_3Al and TiB_2 .
- Elevated temperatures and moderate pressures were used to fabricate Ti_3AlC_2 -cBN composites, by a controlled method of simultaneous hexagonalisation and reaction of the cBN with Ti_3AlC_2 .

- Ti_3AlC_2 -cBN (20 vol.% of 10 μm) composites proved to be difficult to make with the Ti_3AlC_2 as the only MAX phase the samples. However, Ti_3AlC_2 -cBN (20 vol.% of 10 μm) composites were successfully fabricated at 30 MPa, 1300°C for 10 minutes with cBN and Ti_3AlC_2 as the major phases, but this was in combination with the presence of Ti_2AlN and Ti_2AlC . At these conditions other phases found in the sample were TiB_2 , TiC_xN_y and TiN_b .
- Ti_3AlC_2 -cBN (20 vol.% of 100 μm) was synthesised successfully with Ti_3AlC_2 and cBN as the major phases, this was achieved with 30MPa, 1300°C for 10 minutes. These composites also had phases such as TiB_2 , AlN, TiC_a , TiC_xN_y and small amount of hBN.
- The Ti_3AlC_2 -cBN (40 vol.% of 100 μm) composite was successfully synthesised with the cBN and the MAX phase significantly present. Using the predicted results from the Ti_3AlC_2 -cBN (20 vol.% of 100 μm) studies, it was accurately forecast that the conditions appropriate for these samples manufacture were 1350°C, at 30 MPa pressure, for 5 minutes. These conditions gave reaction zones between the cBN and Ti_3AlC_2 and the composite also had small amounts of TiC, TiN, AlN and TiB_2 .
- Elevated temperatures and moderate pressures were used to fabricate Ti_3SiC_2 -cBN composites, by a controlled method of simultaneous hexagonalisation and reaction of the cBN with Ti_3SiC_2 .
- Ti_3SiC_2 -cBN (20 vol.% of 10 μm) composites also proved to be difficult to make with the Ti_3SiC_2 as a major phase in the composite. The same conclusions were noted with the Ti_3SiC_2 -cBN (20 vol.% of 100 μm). The optimum sintering conditions in both cases were 1250°C, with 30 MPa pressure, for 5 minutes. No MAX phase was found in the samples sintered at the conditions, however, hBN, cBN, TiB_2 , TiC_a , TiC_xN_y , TiN_b , SiC and Ti_5Si_3 .
- The Ti_3SiC_2 -cBN (40 vol.% of 100 μm) composite was successfully synthesised with the cBN and the MAX phase significantly present. Using the predicted results from the Ti_3SiC_2 -cBN (20 vol.% of 100 μm) studies, it was accurately predicted that the

conditions required for manufacturing these samples were 1300°C, at 30 MPa pressure, for 5 minutes. These conditions gave reaction zones between the cBN and Ti_3SiC_2 and the composite also comprised small amounts of TiC, TiN, SiC and TiB_2 .

- Increasing in the size of the cBN decreases the extent of hexagonalisation of the cBN. This is because the exposed surface area of the cBN is reduced and thus less cBN is available to hexagonilise.
- Increasing the fraction of the cBN in the MAX – cBN composites promotes the formation of all MAX phases. This is because as more cBN is present in the samples the less heat the MAX phase is exposed to and thus cBN provides thermal shielding.
- Increasing the volume fraction of the cBN particles promoted the formation of the MAX phase, by reducing the hexagonalisation of cBN, thus keeping the secondary phase amounts low and supressing the formation of hBN at lower temperatures.
- The SEM micrographs of the wear sites and fracture surfaces of the optimum composites selected showed good potential for the composites for cBN based grinding wheels by demonstrating that pull-out of the cBN in the composites was highly unlikely due to the strong bond of the reaction area to both the cBN and respective MAX phase.
- The mechanical properties of the optimum composites selected showed good potential for the MAX phases to be an alternate vitrified bond for cBN in cBN based grinding wheels.

In addition, the following conclusions with regard to the novelty of this work were drawn:

- Successfully demonstrating that using the simultaneous hexagonalisation of cBN and reaction of the hBN with other phases to form secondary phases yields composites with strong bonds between the cBN and the MAX phases. Researches who investigate these systems rather focus on stabilising the cBN to avoid hexagonalisation by using higher pressures and temperatures, most time this results in decomposition of the MAX

phase. Therefore, using moderate pressures and elevated temperatures yields energy saving, presence of cBN and MAX phases in the composites, and secondary phases formed that have a strong bond to both the cBN and MAX phases to form stronger composites.

- Using moderate pressures and elevated temperatures can successfully yield MAX-cBN composites where both the MAX phases and cBN are present.
- Successfully fabricating of Ti_2AlC – cBN composites with different size and volume fraction of the cBN were archived. Investigation of the Ti_2AlC – cBN composites have never been investigated before.
- Successfully fabricating composites where Ti_3AlC_2 and cBN were present in the samples at all volume fractions and sizes of cBN, this had not been demonstrated by other researchers who investigated the same system.
- Successfully fabricating Ti_3SiC_2 cBN samples with 40 vol.% of 100 μm which has never been shown by any other researchers.
- Quantification of the rate of hexagonilisation rate of the cBN with different MAX phases, at different sizes of the cBN and different volume fractions of the cBN.
- Using physical and mechanical properties of the composites to show that that MAX phases are a new viable alternative to be carrier phases for cBN in cBN based grinding wheels.

The following recommendations were made for future work:

- To investigate slightly higher pressures for stabilising the cBN in the some of the composites that displayed large amounts of excess hBN.
- To investigate whether small additive additions could help stabilise the Ti_3SiC_2 in the Ti_3SiC_2 composites of smaller and lower fraction of cBN.
- To investigate whether larger sizes of cBN particles, more than 100 μm , could stabilise the fraction of the MAX phases and supress the formation of hBN further.

- To investigate lower temperatures ($<1150^{\circ}\text{C}$) for the synthesis of the Ti_3SiC_2 composites.
- To investigate different starting powders for the two 312 MAX phases in order to assess better ways of forming the two MAX phases with lower volume fractions of cBN.

REFERENCES

- Anselmi-Tamburini, U., Gennari, S., Garay, J.E. & Munir, Z.A. 2005. Fundamental investigations on the spark plasma sintering/synthesis process II. Modelling of current and temperature distributions. *Materials Science and Engineering, A* 394:139–148.
- ASTM E92. 1997. *Annual book of ASTM standards*. Copyright ASTM.
- Barsoum, M.W. & El-Raghy, T. 2001. The MAX Phases: Unique New Carbide and Nitride Materials. *American Scientist*, 89: 334-343.
- Bandyopadhyay, D. 2004. The Ti-Si-C System (Titanium-Silicon-Carbon). *Basic and Applied Research: Section I*, 25:415-420.
- Bandyopadhyay, D., Sharma, R.C. & Chakraborti, N. 2000. Phase Diagram Evaluations: Section II: The Ti- Al- C System (Titanium - Aluminum - Carbon). *Journal of Phase Equilibria*, 21: 195-198.
- Barsoum, M.W., El-Raghy, T., Rawn, C.J., Porter, W.D., Wang, H., Payzant, E.A., & Hubbard, C.R. 1999. Thermal properties of Ti_3SiC_2 . *Journal of Physics and Chemistry of Solids*, 60: 429-439.
- Barsoum, M.W., Farber, L. & El-Raghy, T. 1999. Dislocations, kink bands, and room-temperature plasticity of Ti_3SiC_2 . *Metallurgical and Materials Transactions*, 30A: 1727-1738.
- Barsoum, M.W. and Houg, B. 1993. Transient plastic phase processing of Ti-B-C composites. *Journal of American Ceramics Society*, 76, 1445–1446.
- Barsoum, M.W. & Radovic M. 2004. In *Encyclopaedia of Materials: Science and Technology*, ed. K.H. Jürgen Buschow, R.W. Cahn, M.C. Flemings, B. Ilschner, E.J. Kramer, S. Mahajan & P. Veyssi re, Elsevier, Oxford, 1-16.
- Barsoum, M.W. & Radovic, M. 2011. Elastic and Mechanical Properties of the MAX Phases. *Annual Review Materials Research* 41:195–227.
- Barsoum, M.W., Salama, I., El-Raghy, T., Golczewski, J., Porter, W.D., Wang, H., Seifert, H.J. & Aldinger, F. 2002. Thermal and electrical properties of Nb_2AlC , $(\text{Ti}, \text{Nb})_2\text{AlC}$ and Ti_2AlC . *Metallurgical and Materials Transactions A*, 33: 2775-2779.
- Barsoum, M.W., Zhen, T., Kalidindi, S.R., Radovic, M., & Murugaiah, A. 2003. Fully reversible, dislocation-based compressive deformation of Ti_3SiC_2 to 1 GPa. *Nature Materials*, 2: 107-111.
- Benko, E., Klimczyk, P., Mackiewicz, S., Barr, T.L., Piskorska, E. 2004. cBN- Ti_3SiC_2 composites. *Diamond and Related Materials*, 13: 521-525.
- Brown, W.P. Part 6. Cubic and hexagonal boron nitride, 2000-2011. (<http://www.docbrown.info/page03/nanochem06.htm>) [ACCESSED: 06 September 2019].
- Chanthapan S., Rape, A., Gephart, S., Kulkarni, A. K., Singh, J. 2011. Industrial Scale Field Assisted Sintering Is an Emerging Disruptive Manufacturing Technology. *Advanced Materials and Processes*. 169: 21-26
- Chen, Y.L., Yan, M., Sun, Y.M., Mei, B.C., Zhu, J.Q. 2009. The phase transformation and microstructure of $\text{TiAl/Ti}_2\text{AlC}$ composites caused by hot pressing. *Ceramics International*, 35: 1807–1812.

- Cui, B., Jayaseelan, D.D., Lee, W. E. 2011. Microstructural evolution during high-temperature oxidation of Ti_2AlC ceramics. *Acta Materialia*, 59: 4116-4125.
- Element Six, *The Properties of Cubic Boron Nitride*, Element Six, 2008. <https://www.e6.com/> [ACCESSED: 06 September 2019]
- El-Raghy, T. & Barsoum, M.W. 1999(a). Processing and Mechanical Properties of Ti_3SiC_2 : I, Reaction Path and Microstructure Evolution. *Journal of American Ceramics society*, 82: 2849-2854.
- El-Raghy, T. & Barsoum, M.W. 1999(b). Processing and Mechanical Properties of Ti_3SiC_2 :II, Effect of Grain Size and Deformation Temperature. *Journal of American Ceramics Society*, 82: 2855- 2860.
- Farber, L. 1999. Transmission electron microscopy study of a low-angle boundary in plastically deformed Ti_3SiC_2 . *Philosophical Magazine Letters*, 79: 163-170.
- Farber, L., Barsoum, M.W., Zavaliangos, A., El-Raghy, T. & Levin, I. 1998. Dislocations and Stacking Faults in Ti_3SiC_2 . *Journal of American Ceramics Society*, 81: 1677-1681.
- Gao, J.T., Li, D. Zhang, Y. Miyamoto. 2002. Rapid synthesis of dense Ti_3SiC_2 by spark plasma sintering. *Journal of the European Ceramic Society*, 22: 2365–2370.
- Garrett, J.C., Sigalas, I., Wolfrum, A.K. & Herrmann., M. 2015. Effect of cubic boron nitride grain size in the reinforcing of α -Sialon ceramics sintered via SPS. *Journal of the European Ceramic Society*, 35: 451–462.
- Gordon England. 2018. <https://www.gordonengland.co.uk/hardness/hvconv.htm> [ACCESS: 06 September 2019].
- Hess, J.B. & Barrett, C.S. 1949. Structure and nature of kink-bands in zinc. *Transactions AIME*, 185: 599-605.
- Jaworska, L., Szutkowska, M., Morgiel, J., Tobierski, L. & Lis, J. 2001. Ti_3SiC_2 as a bonding phase in diamond composites. *Journal of Materials Science Letters*, 20: 1783-1786.
- Jeitschko, W. & Nowotny, H. 1967. The crystal structure of Ti_3SiC_2 - a new complex carbide type. *Chemical Monthly*, 98: 329-337.
- Kolabylina, T., Bushlya, V., Petrusha, I., Johansson, D., Ståhl, J.E. & Turkevich, V. 2017. Super-hard pcBN tool materials with Ti_3SiC_2 MAX-phase binder: Structure, properties, application. *Journal of Super-hard Materials*, 39: 155-165.
- Kooi, B.J., Poppen, R.J., Carvalho, N.J.M., De Hosson, J.T.M. & Barsoum, M.W. 2003. Ti_3SiC_2 : A Damage Tolerant Ceramic Studied with Nano-Indentations and Transmission Electron Microscopy. *Acta Materia*, 51: 2859-2872.
- Kulkarni, S. & Datye, A. 2010. Synthesis of Ti_2AlC by spark plasma sintering of TiAl –carbon nanotube powder mixture. *Journal of Alloys and Compounds*, 490: 155-159.
- Kuroda Y., Low I.M., Barsoum M.W. & El-Raghy T. 2001. Indentation responses, wear and damage characteristics of hot-isostatically-pressed Ti_3SiC_2 . *Journal of the Australian Ceramic Society*, 37: 95-102.

- Li, S., Xie, J., Zhao, J. & Zhang, L. 2002. Mechanical properties and mechanism of damage tolerance for Ti_3SiC_2 . *Materials Letters*, 57: 119-123.
- Li, S. & Zhai, H. 2005. Synthesis and reaction mechanism of Ti_3SiC_2 by mechanical alloying of elemental Ti, Si, and C Powders. *Journal of American Society*, 88: 2092-2098.
- Li, L., Zhou, A., Wang, L., Li, S., Wu, D. & Yan, C. 2012. In situ synthesis of cBN– Ti_3AlC_2 composites by high-pressure and high-temperature technology. *Diamond & Related Materials*, 29: 8-12.
- Li, Z., Zhou, A., Li, L., Wang, L., Hu, M., Li, S. & Gupta, S. 2014. Synthesis and characterization of novel Ti_3SiC_2 -cBN composites. *Diamond and related materials*, 43: 29-33.
- Liang, B.Y., Jin, S.Z., Wang, M.Z. 2008. Low-temperature fabrication of high purity Ti_3SiC_2 . *Journal of Alloys and Compounds*, 460: 440-443.
- Lin, Z.J., Zhuo, M.J., Zhou, Y.C., Li, S. M. & Wang, J. Y. 2006. Microstructural characterization of layered ternary Ti_2AlC . *Acta Materialia*, 54: 1009-1015.
- Lin, Z.J., Zhuo, M.J., Zhou, Y.C., Li, S. & Wang, J. Y. 2006(a). Microstructures and Theoretical Bulk Modulus of Layered Ternary Tantalum Aluminium Carbides. *Journal of the American Ceramic Society*, 89: 3765-3769.
- Lin, Z.J., Zhuo, M.J., Li, M.S., Wang, J.Y. & Zhou, Y.C. 2007. Synthesis and microstructure of layered-ternary Ti_2AlN ceramic. *Scripta Materialia*. 56 :1115-1118
- Link diamond. 2018. <http://linkdiamondtools.com/Pages/Technical-Info.asp> [ACCESSED: 18 November 2018]
- Liu, Y., Li, Y., Li, F., Cui, H., Zhang, L. & Guo, S. 2017. Synthesis and microstructure of Ti_2AlN ceramic by thermal explosion. *Ceramics International*. 43: 13618-13621.
- Magnuson, M. & Mattesini. 2017. Chemical bonding and electronic structure in MAX phases as viewed by X-ray spectroscopy and density functional theory. *Thin Solid Films*, 621: 108-130.
- McKie, A., Winzer, J., Sigalas, I., Herrmann, M., Weiler, L., Rödel, J. & Can, N. 2011. Mechanical properties of cBN–Al composite materials. *Ceramics International*, 37: 2011, 1-8.
- Mei, B. & Miyamoto, Y. 2002. Investigation of $\text{TiAl}/\text{Ti}_2\text{AlC}$ composites prepared by spark plasma sintering. *Materials Chemistry and Physics*, 75: 291-295.
- Mei, B., Zhou, W., Zhu, J. & Hong, X. 2004. Synthesis of Ti_2AlC by hot pressing and its mechanical and electrical properties. *Journal of Materials Science*, 39: 1471-1472.
- Monteiro, S.N., Skury, A.L., de Azevedo, M.G. & Bobrovnitchii, G.S. 2013. Cubic boron nitride competing with diamond as a super-hard engineering material – an overview. *Journal of Materials Research and Technology*, 2: 68-74.
- Mu, Y., Guo, J., Liang, B. & Wang, Q. 2011. Rapid fabrication of the Ti_3SiC_2 bonded diamond composite by spark plasma sintering. *International Journal of Refractory Metals and Hard Materials*, 29: 397-400.
- Naka, M. Feng, J.C. and Schuster, J.C. 1997. Phase Reaction and Diffusion Path of the SiC/Ti System. *Metallurgical and Materials Transactions A*: 28A: 1385-1390.

- Okamoto, H. & Massalski, T. B. 1991. Thermodynamically Improbable Phase Diagrams. *Journal of Phase Equilibria*, 12: 148-168.
- Pampuch, R., Lis, J., Stobierski, L. & Tymkiewicz, M. 1989. Solid combustion synthesis of Ti_3SiC_2 . *Journal of the European Ceramic Society*, 5: 283-287.
- Palmquist, J. P., Li, S., Persson, P.O.A., Emmerlich, J., Wilhelmsson, O., Hogberg, H., Katsnelson, M.I., Johansson, B., Ahuja, R., Eriksson, O., Hultman, L. & Jansson, U. 2004. $\text{M}_{n+1}\text{AX}_n$ phases in the Ti-Si-C system studied by thin-film synthesis and ab initio calculations. *Physical Review B*, 70: 165401-13.
- Qin, J. & He, D. 2013. Phase stability of Ti_3SiC_2 at high pressure and high temperature. *Ceramics International*, 39: 9361–9367.
- Rampai, T. & Lang, C. I. 2011. Synthesis of Ti_2AlC , Ti_3AlC_2 and Ti_3SiC_2 MAX phase ceramics; and their composites with c-BN. *University of Cape Town*.
- Rampai, T., Lang, C. I. & Sigalas, I. 2013. Investigation of MAX phase/c-BN composites. *Ceramics International*, 39: 4739–4748.
- Rong, X., Tsurumi, T., Fukunaga, O. & Yano, T. 2002. High-Pressure Sintering of cBN–TiN–Al Composite for Cutting Tool Application. *Diamond and Related Materials*, 11: 280-286.
- Sachdev, H., Haubner, R., Noth, H. & Lux, B. 1997. Investigation of the c-BN/h-BN phase transformation at normal pressure. *Diamond Related Materials*, 6: 286-292.
- Školáková, A., Salvetr, P., Novák, P. & Vojtěch, D. 2018. Formation of Ti–Al Phases during SHS Process. *Acta Physica Polonica A*, 134 743 – 747.
- Springer. 2016. https://materials.springer.com/isp/crystallographic/docs/sd_1013340 [ACCESSED 1 December 2018].
- Tomashik, V. & Perrot, P. 2005. Aluminium-Nitrogen-Titanium. *Springer London. Landolt-Bornstein*. 11A3: 322-333.
- Vel, L., Demazeau, G. & Etourneau, J. 1991. Cubic boron nitride: synthesis, physicochemical properties and applications. *Materials Science and Engineering B*, 10: 149-164.
- Wang, P., Li, H., Qi, L., Zheng, X. & Zhou, H. 2011. Synthesis of Al–TiAl₃ compound by reactive deposition of molten Al droplets and Ti powders. *Progress in Natural Science: Materials International*, 21: 153-158.
- Wang, P., Mei, B., Hong, X. & Zhou, W. 2007. Synthesis of Ti_2AlC by hot pressing and its mechanical and electrical properties. *Transactions of Nonferrous Metals Society of China*, 17: 1001-1004.
- Wang, X.H. & Zhou, Y.C. 2002a. Microstructure and properties of Ti_3AlC_2 prepared by the solid–liquid reaction synthesis and simultaneous in-situ hot pressing process. *Acta Materialia*, 50: 3143-3151.
- Wang, X.H. & Zhou, Y.C. 2002b. Solid–liquid reaction synthesis of layered machinable Ti_3AlC_2 ceramic. *Journal of Materials Chemistry*, 12: 455-460.

- Wang, X.H. & Zhou, Y.C., 2010a. Layered Machinable and Electrically Conductive Ti_2AlC and Ti_3AlC_2 Ceramics: A Review. *Journal of materials science and technology*, 26, 385-416
- Wang, J., Y. Zhou, T., Liao, J., Zhanga & Lina, Z. 2008. A first-principles investigation of the phase stability of Ti_2AlC with Al vacancies. *Scripta Materialia*, 58: 227–230.
- Weibing, Z., Bingchu, M. & Jiaoqun, Z. 2009. Rapid synthesis of $\text{Ti}_3\text{AlC}_2/\text{TiB}_2$ composites by the spark plasma sintering (SPS) technique. *Ceramics International*, 35: 3507–3510.
- Wolfrum, A., Matthey, B., Michaelis, A., & Herrmann, M. 2018. On the Stability of c-BN-Reinforcing Particles in Ceramic Matrix Materials, *Materials*, 11:255-242.
- Yang, C., Jin, S.Z., Liang, B.Y., Jia, S.S. 2009. Low-temperature synthesis of high-purity Ti_3AlC_2 by MA-SPS technique. *Journal of European Ceramic Society*, 29: 181-185.
- Yang, L., Gong, J., Yue, Z. & Chu, X. 2016. Preparation and characterization of cBN-based composites from cBN- Ti_3AlC_2 mixtures. *Diamond & related Materials*, 66: 183-187.
- Yang, C., Wang, F., Ai, T. & Zhu, J. 2014. Microstructure and mechanical properties of in situ $\text{TiAl}/\text{Ti}_2\text{AlC}$ composites prepared by reactive hot pressing. *Ceramics international*, 40: 8165-8171.
- Yoshida, M., Hoshima, Y., Ommyoji, J. & Yamagichi, A. 2010. Reaction mechanism for the synthesis of Ti_3AlC_2 through an intermediate carbide of Ti_2AlC from elemental Ti, Al and C powder mixture. *Journal of the Ceramic Society of Japan*, 118: 37-42.
- Yu, R., Zhang, Q., He, L.L., Zhou, Y.C. & Ye, H.Q. 2003. Stacking faults and grain boundaries of Ti_3SiC_2 . *Philosophical Magazine Letters*, 83: 325-331.
- Yue, Z., Yang, L., Gong, J. & Gao, J. 2018. Synthesis and Comparison of Two cBN Composites with Starting Ternary Carbide Binders. *Journal of Materials Engineering and Performance*, 27(5): 2124-2130.
- Zhang, H.B., Zhou, Y.C., Bao, Y.W. & Li, S. 2004. Improving the oxidation resistance of Ti_3SiC_2 by forming a $\text{Ti}_3\text{Si}_{0.9}\text{Al}_{0.1}\text{C}_2$ solid solution. *Acta Materialia*, 52: 3631–3637.
- Zhou, A., Wang, C. & Huang, Y. 2003a Synthesis and mechanical properties of Ti_3AlC_2 by spark plasma sintering. *Journal of Materials Science*, 38: 3111-3115.
- Zhou, A., Wang, C., Huang, Y. 2003b. A possible mechanism on synthesis of Ti_3AlC_2 . *Materials Science and Engineering: A*, 352: 333-339.
- Zhou, W.B., Mei, B.C., Zhu, J.Q. & Hong, X.L. 2005. Rapid synthesis of Ti_2AlC by spark plasma sintering technique. *Materials Letters*, 59: 131-134.
- Zhou, Y.C., Sun, Z.M. & Yu, B.H. 2000. Microstructure of Ti_3SiC_2 prepared by the in-situ hot pressing/solid-liquid reaction process. *Zeitschrift fuer Metallkunde.*, 91: 937-941.

APPENDICES

Appendix A: Supplementary individual XRD data for sintered samples

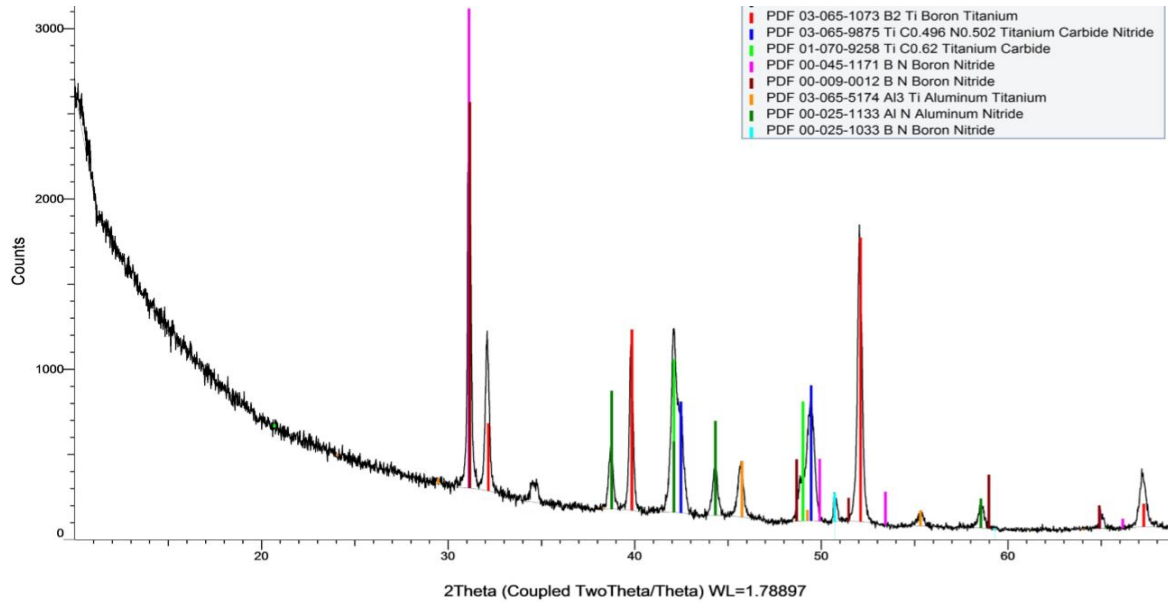


Figure A 1: XRD analysis, of Ti_2AlC -cBN (20 vol.%, 10 μm) samples sintered at 1300°C for 1 minute.

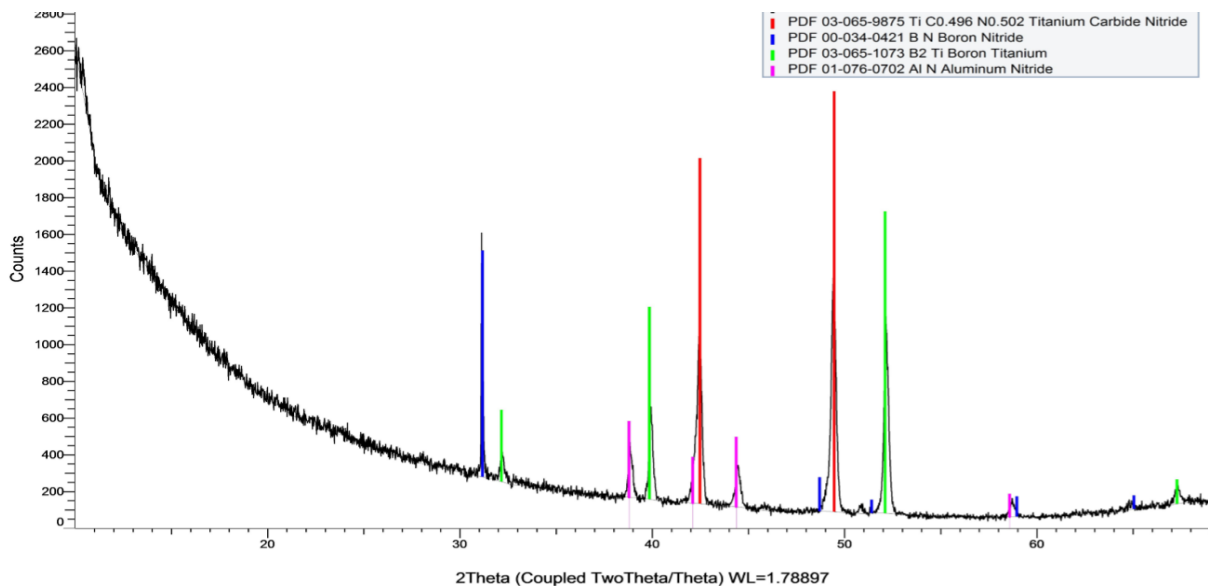


Figure A2: XRD analysis, of Ti_2AlC -cBN (20 vol.%, 100 μm) samples sintered at 1500°C for 1 minute.

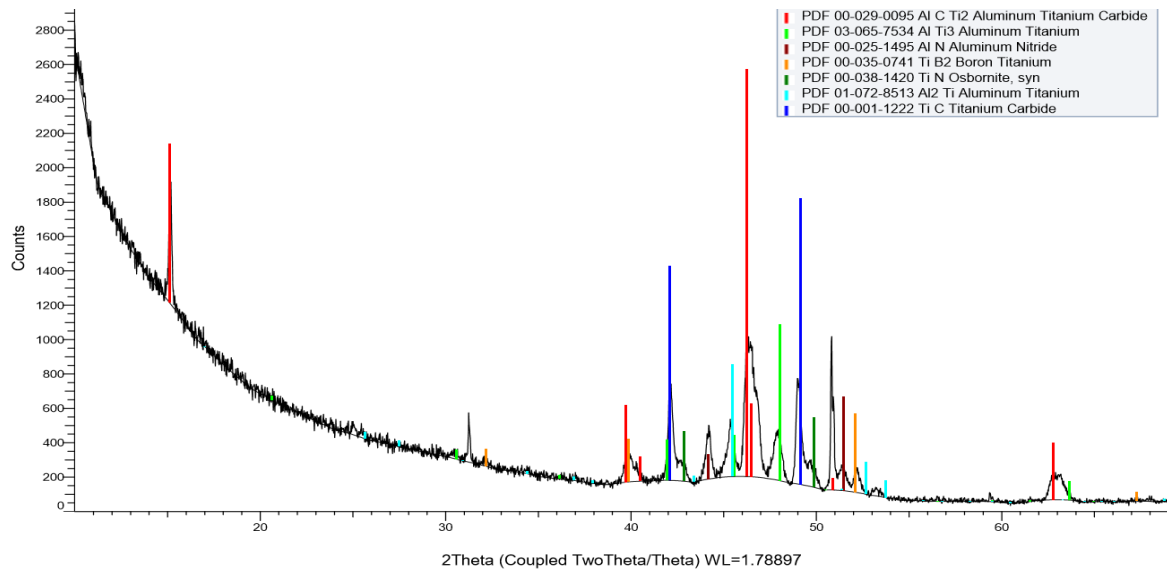


Figure A3: XRD analysis, of Ti_2AlC -cBN (20 vol.%, 10 μm) samples sintered at 1250°C for 1 minute.

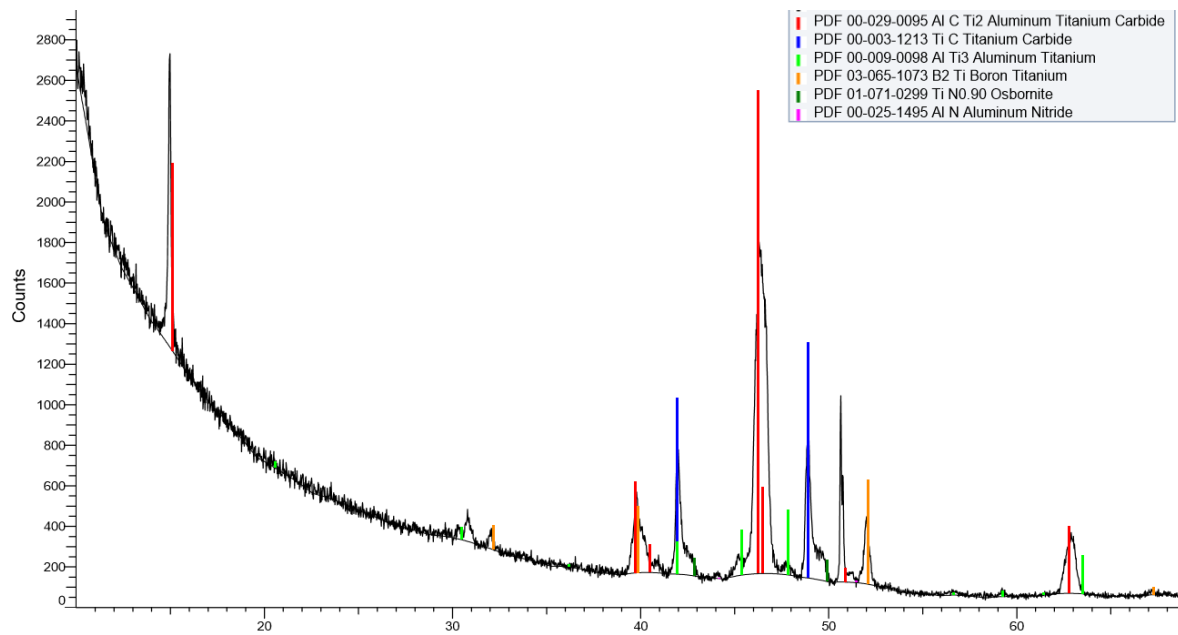


Figure A4: XRD analysis, of Ti_2AlC -cBN (20 vol.%, 10 μm) samples sintered at 1250°C for 5 minutes.

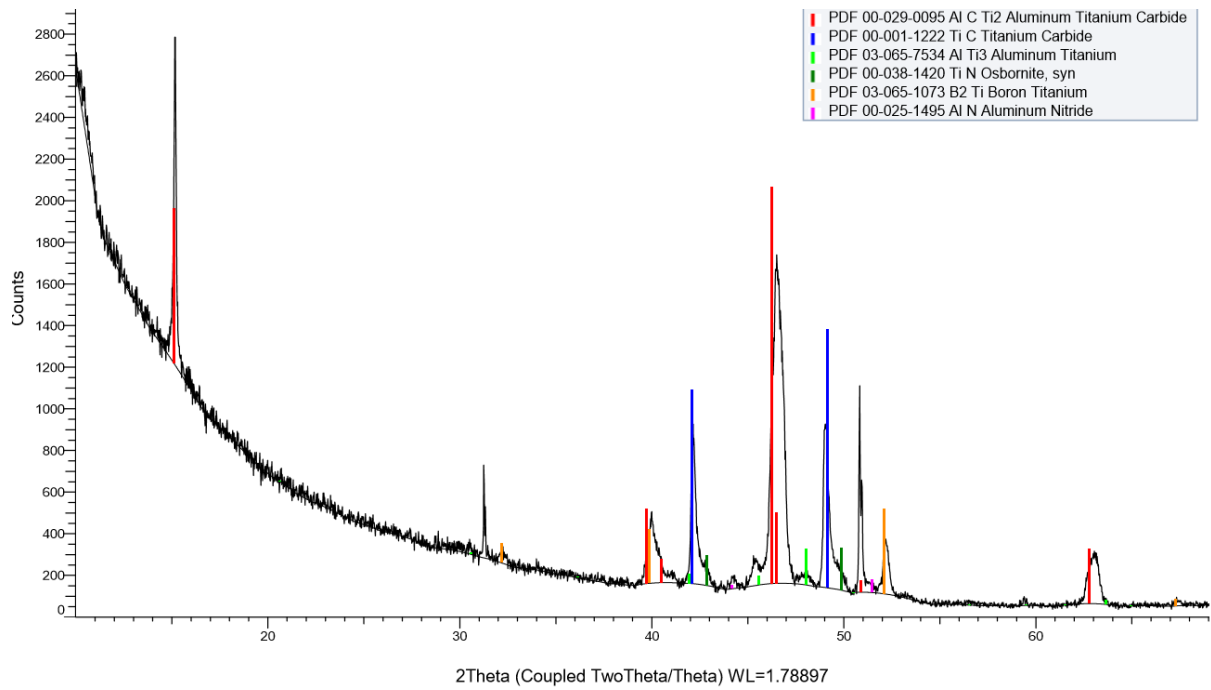


Figure A5: XRD analysis, of Ti_2AlC -cBN (20 vol.%, 10 μm) samples sintered at 1250°C for 10 minutes.

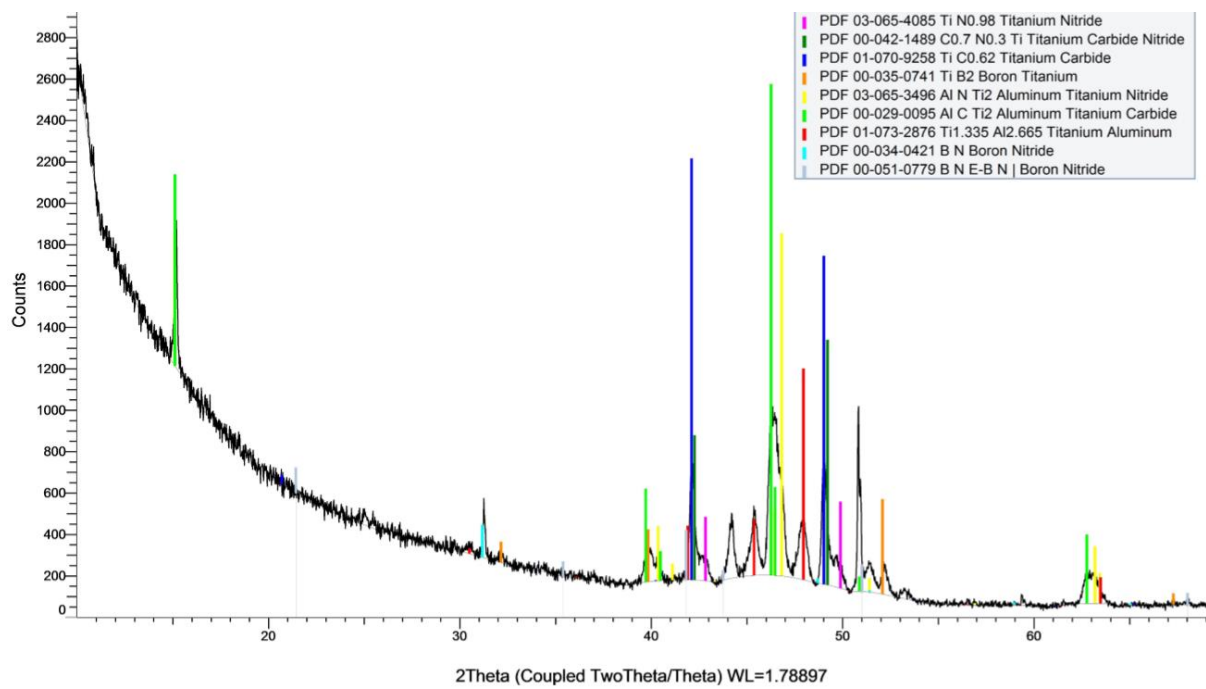


Figure A6: XRD analysis, of Ti_3AlC_2 -cBN (20 vol.%, 10 μm) samples sintered at 1250°C for 1 minute.

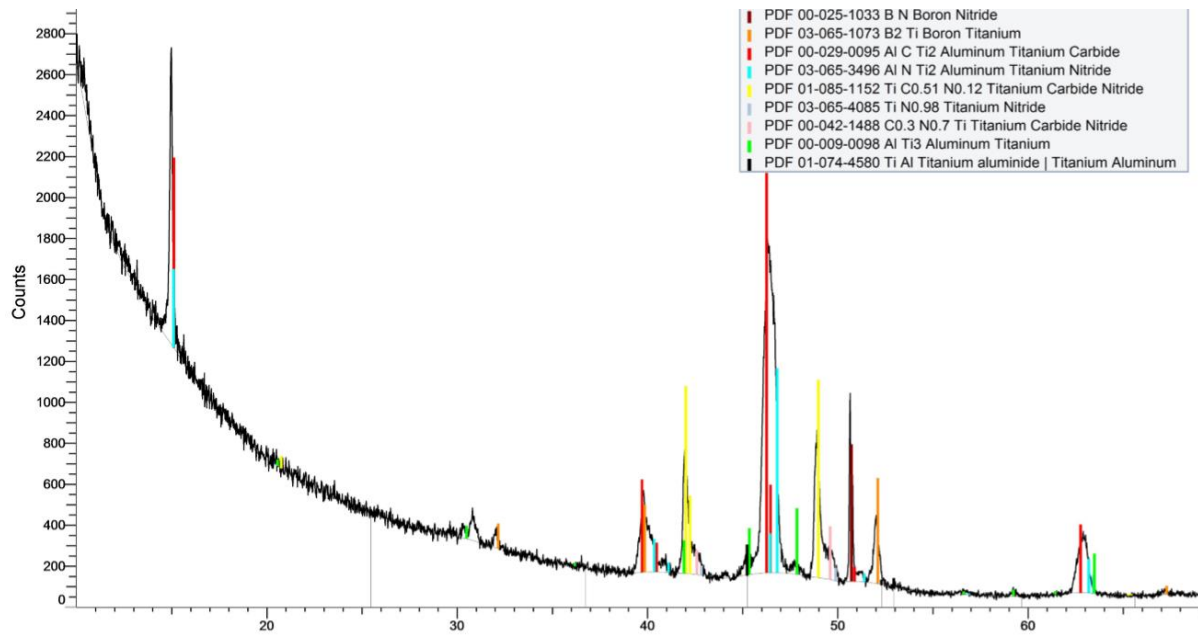


Figure A7: XRD analysis, of $\text{Ti}_3\text{AlC}_2\text{-cBN}$ (20 vol.%, 10 μm) samples sintered at 1250°C for 5 minutes.

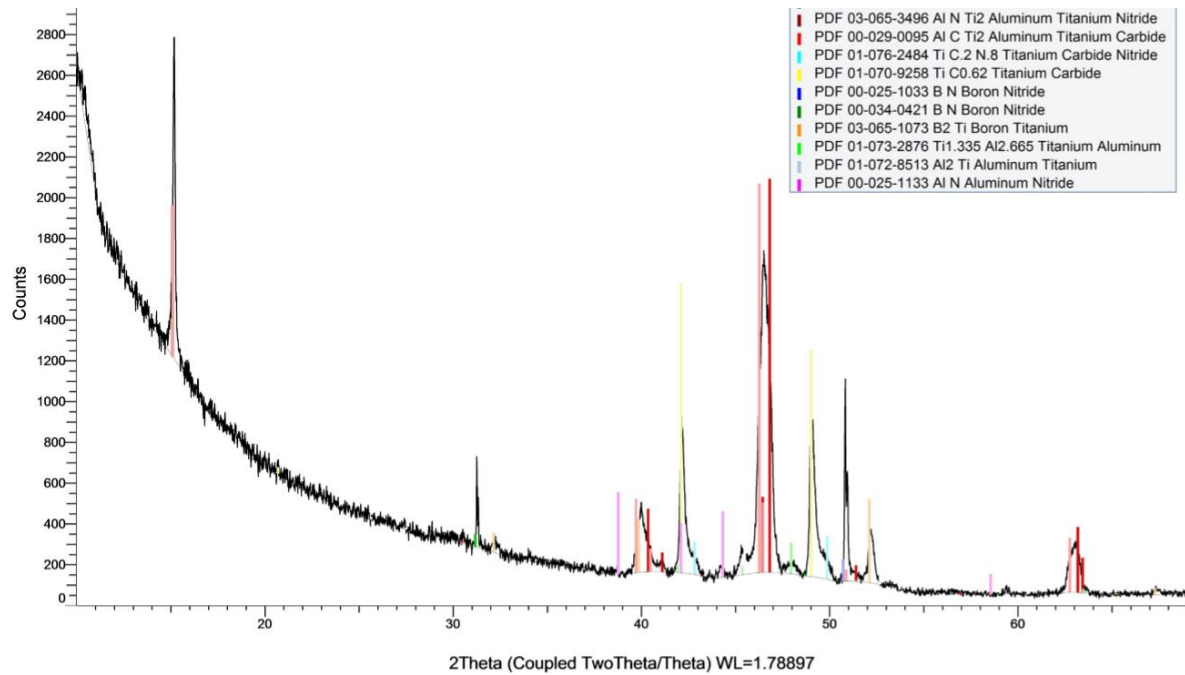


Figure A8: XRD analysis, of $\text{Ti}_3\text{AlC}_2\text{-cBN}$ (20 vol.%, 10 μm) samples sintered at 1250°C for 10 minutes.

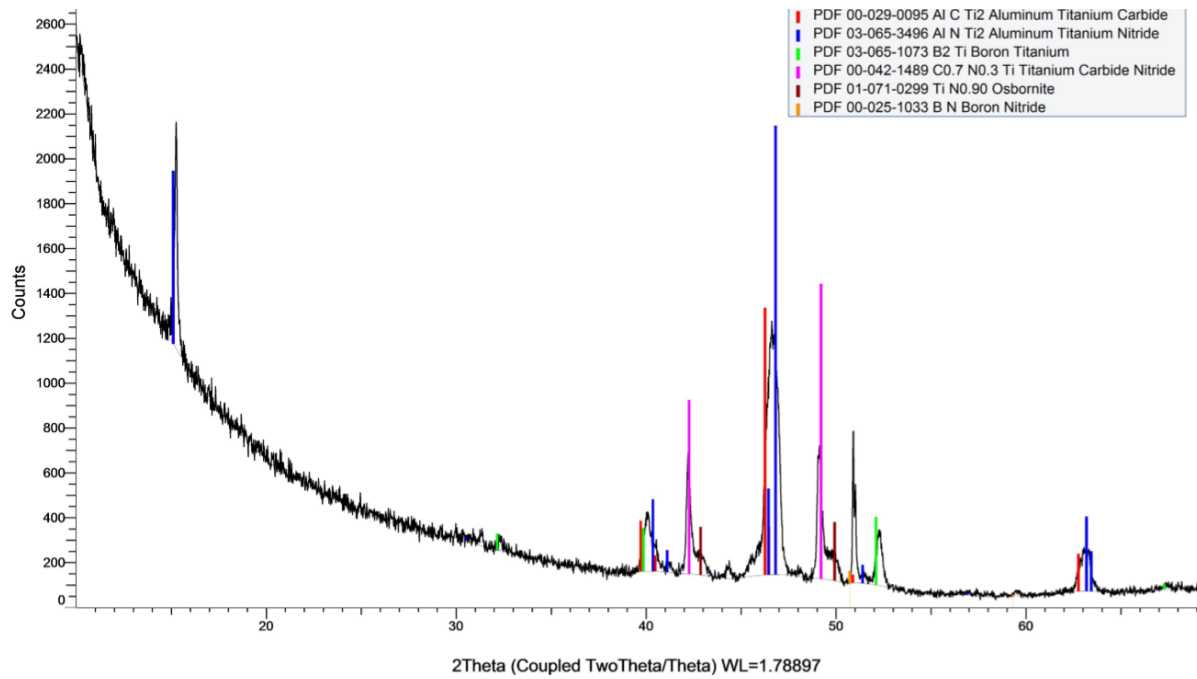


Figure A9: XRD analysis, of Ti_3AlC_2 -cBN (20 vol.%, 10 μm) samples sintered at 1300°C for 1 minute.

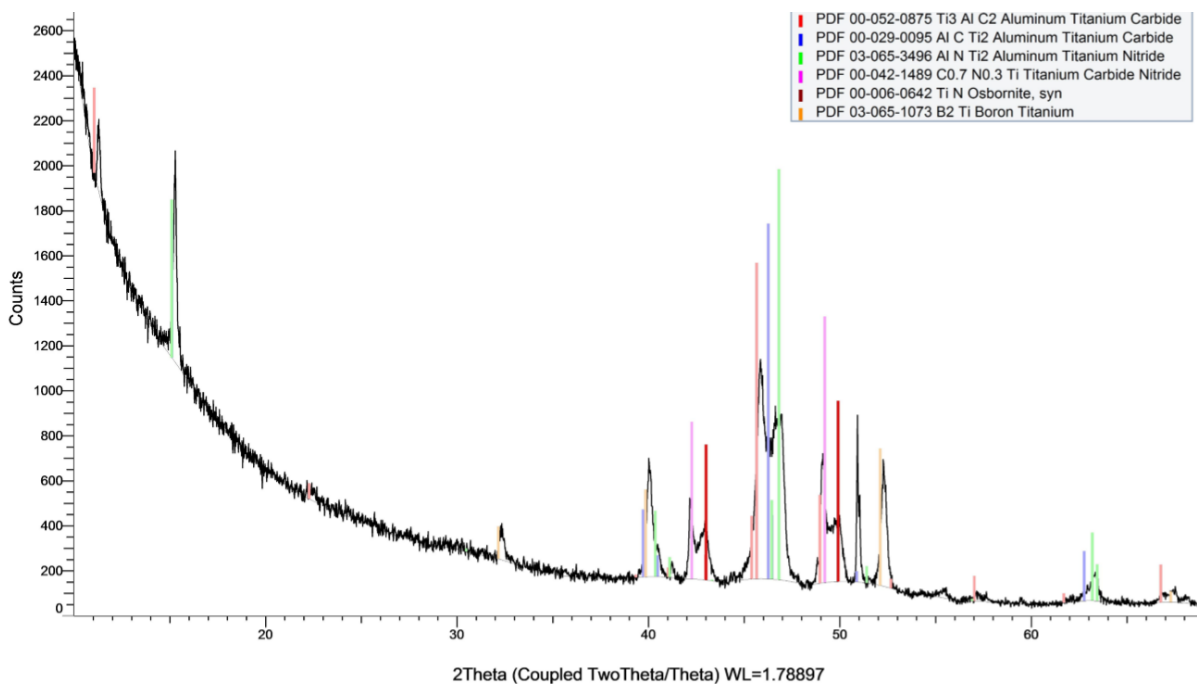


Figure A10: XRD analysis, of Ti_3AlC_2 -cBN (20 vol.%, 10 μm) samples sintered at 1300°C for 10 minutes.

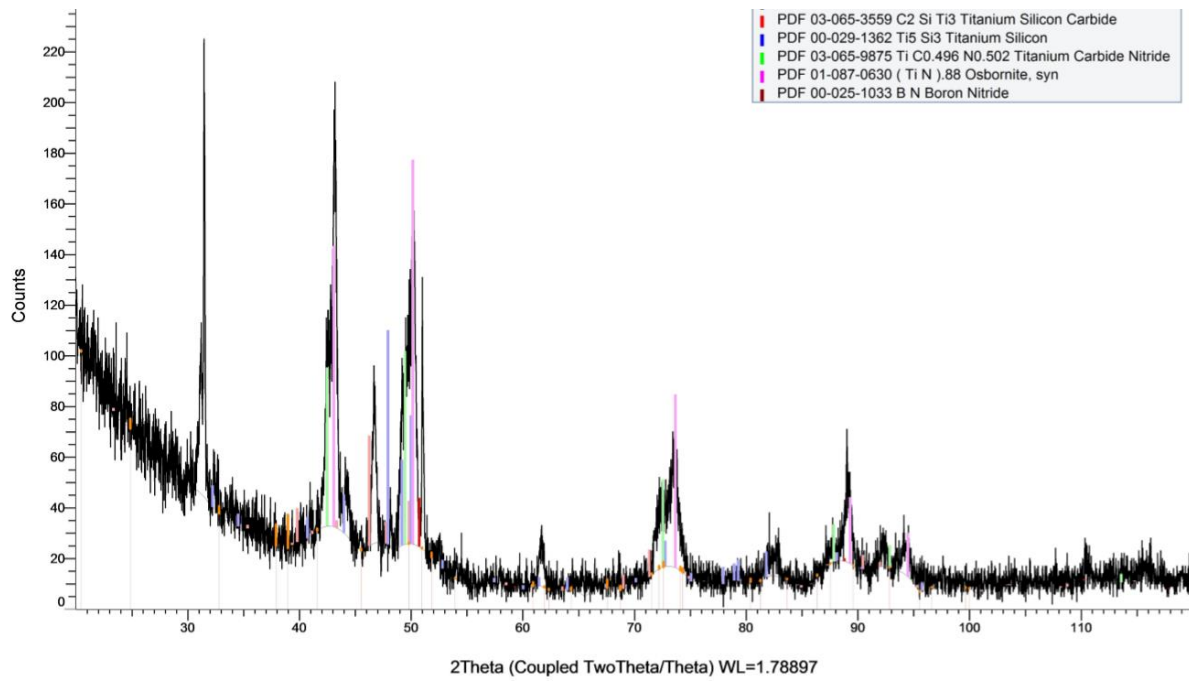


Figure A11: XRD analysis, of $\text{Ti}_3\text{SiC}_2\text{-cBN}$ (20 vol.%, 10 μm) samples sintered at 1150°C for 1 minute.

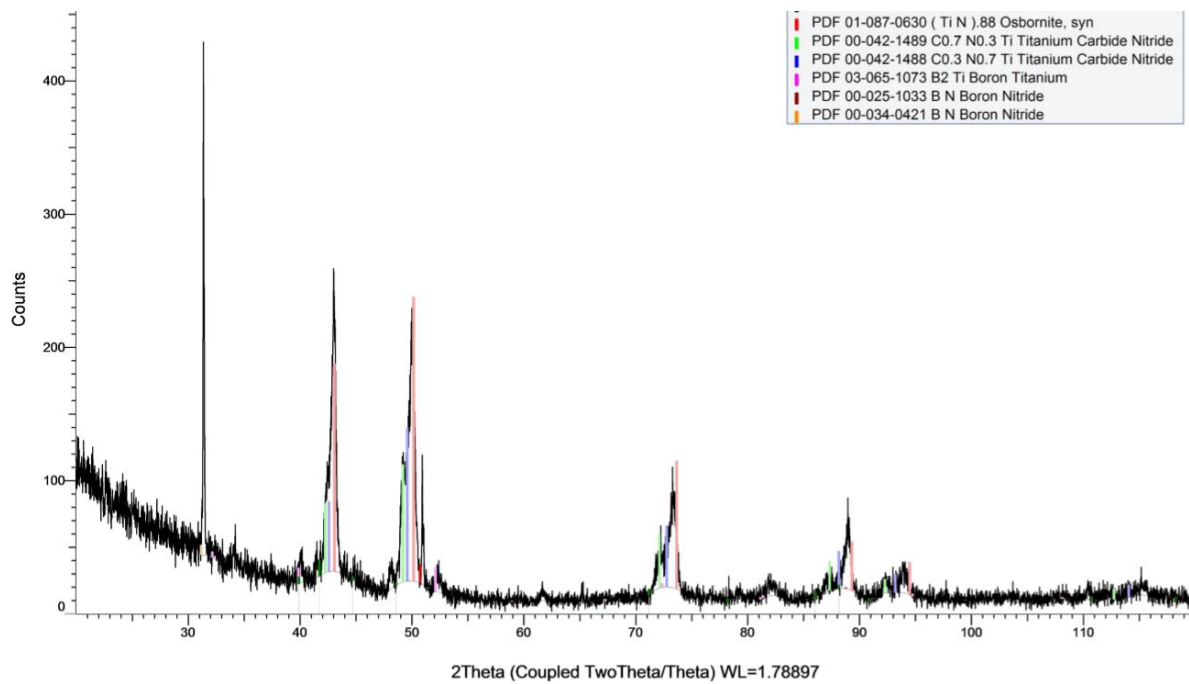


Figure A12: XRD analysis, of $\text{Ti}_3\text{SiC}_2\text{-cBN}$ (20 vol.%, 10 μm) samples sintered at 1250°C for 1 minute.

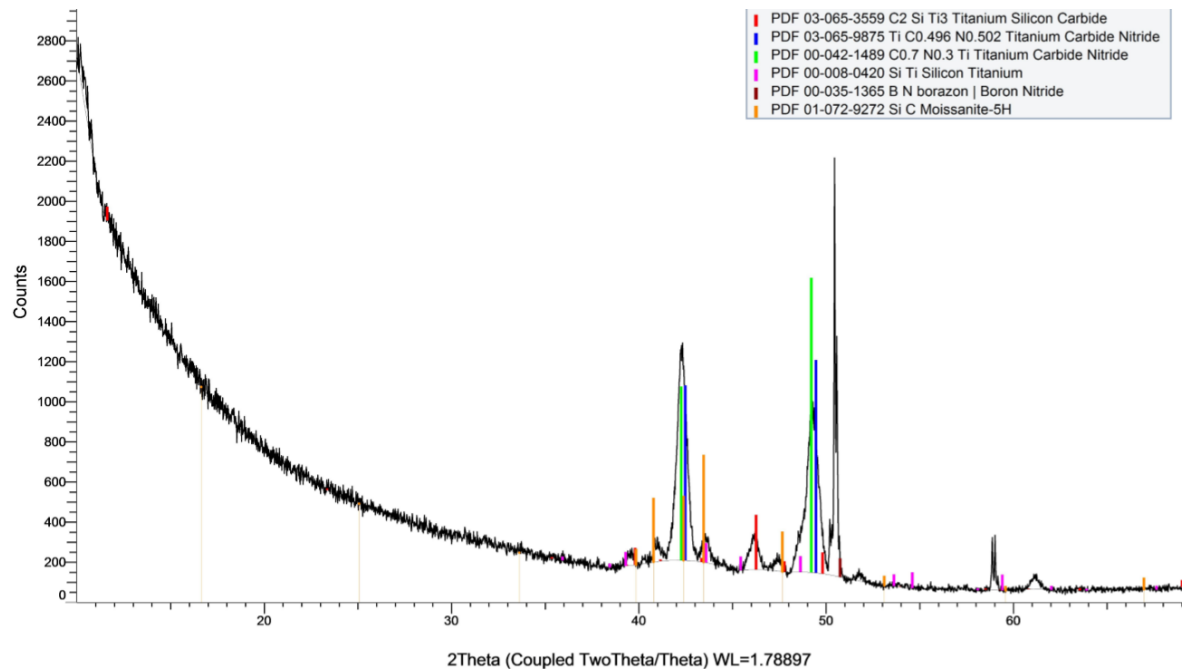


Figure A13: XRD analysis, of Ti_3SiC_2 -cBN (20 vol.%, 10 μm) samples sintered at 1300°C for 1 minute.

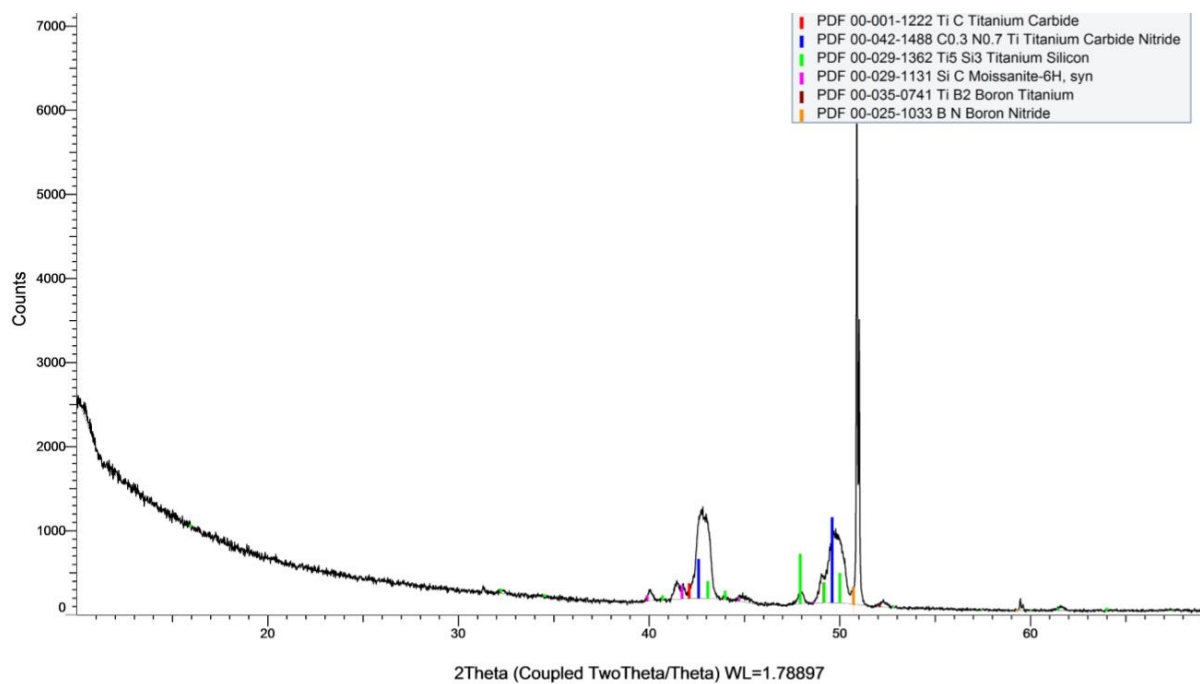


Figure A14: XRD analysis, of Ti_3SiC_2 -cBN (20 vol.%, 10 μm) samples sintered at 1300°C for 3 minutes.

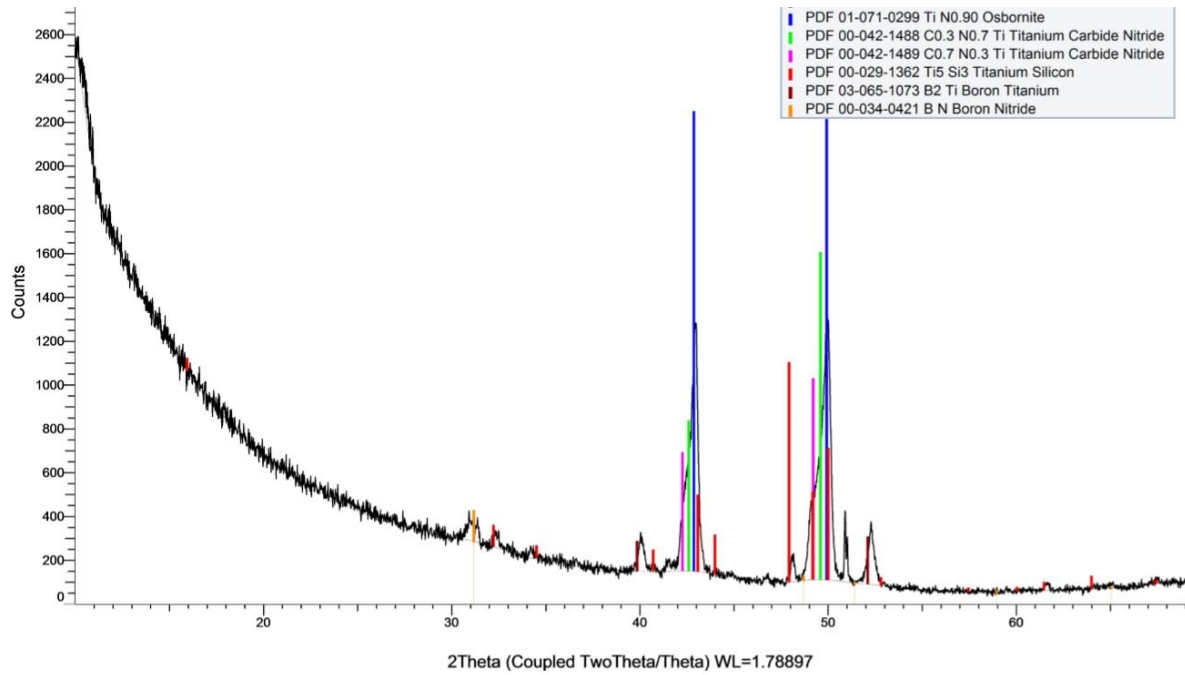


Figure A15: XRD analysis, of $\text{Ti}_3\text{SiC}_2\text{-cBN}$ (20 vol.%, 10 μm) samples sintered at 1300°C for 10 minutes.

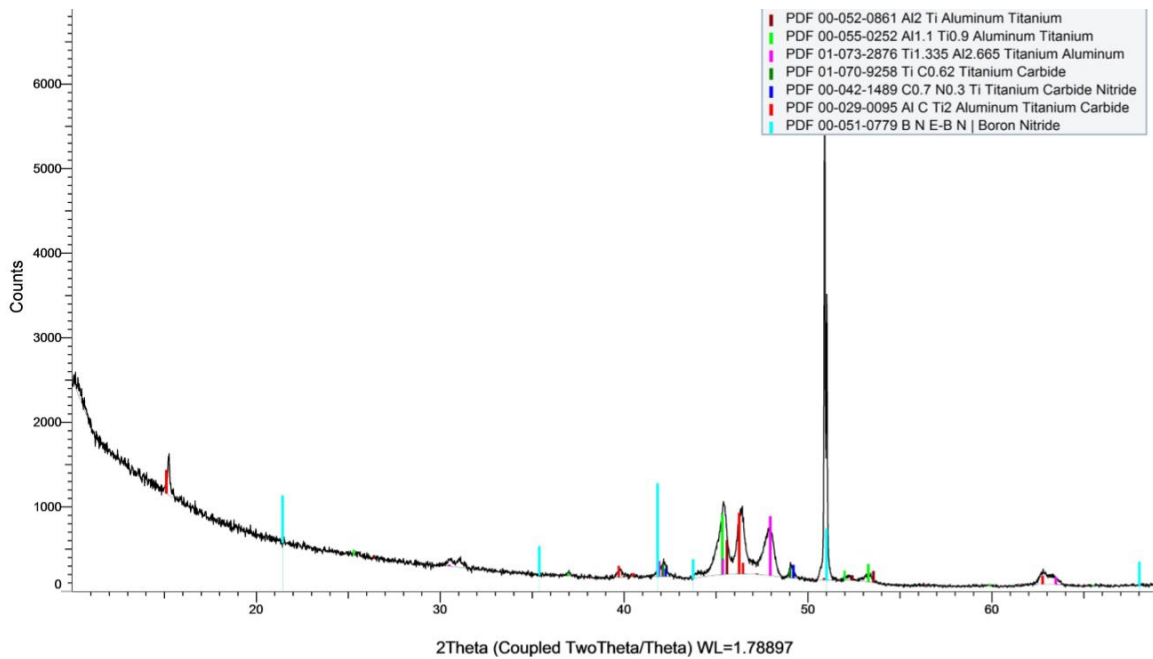


Figure A16: XRD analysis, of $\text{Ti}_2\text{AlC-cBN}$ (20 vol.%, 100 μm) samples sintered at 1150°C for 1 minute.

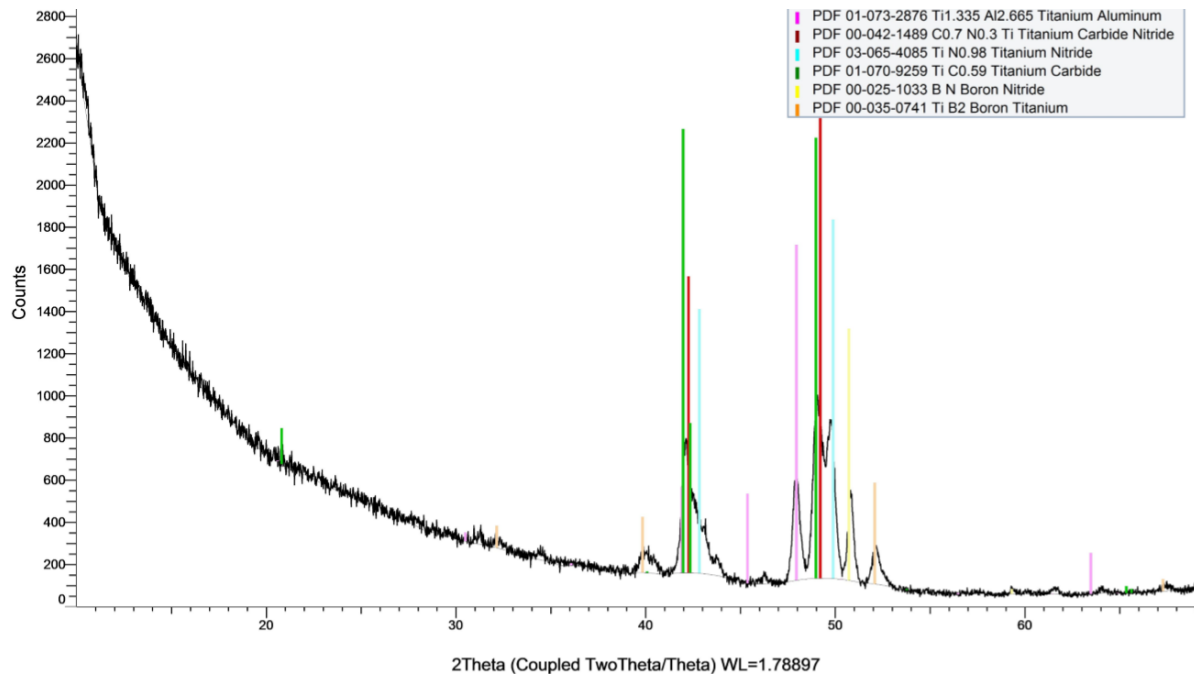


Figure A17: XRD analysis, of Ti_2AlC -cBN (20 vol.%, 100 μm) samples sintered at 1250°C for 1 minute.

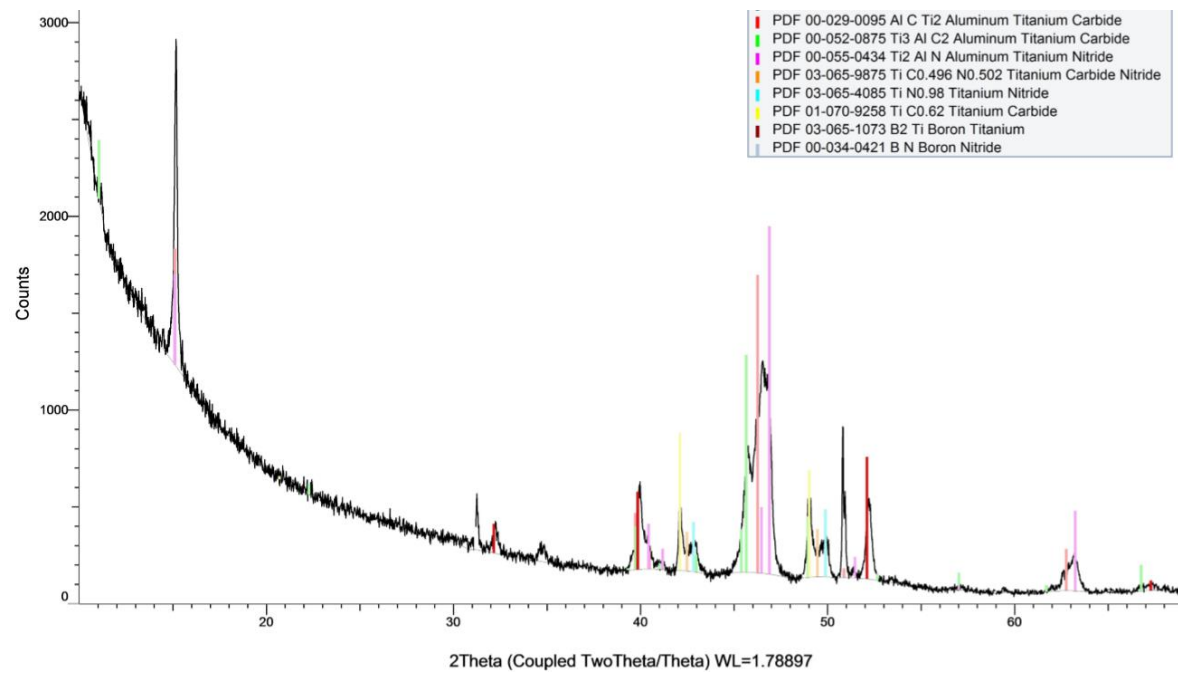


Figure A18: XRD analysis, of Ti_2AlC -cBN (20 vol.%, 100 μm) samples sintered at 1250°C for 5 minutes.

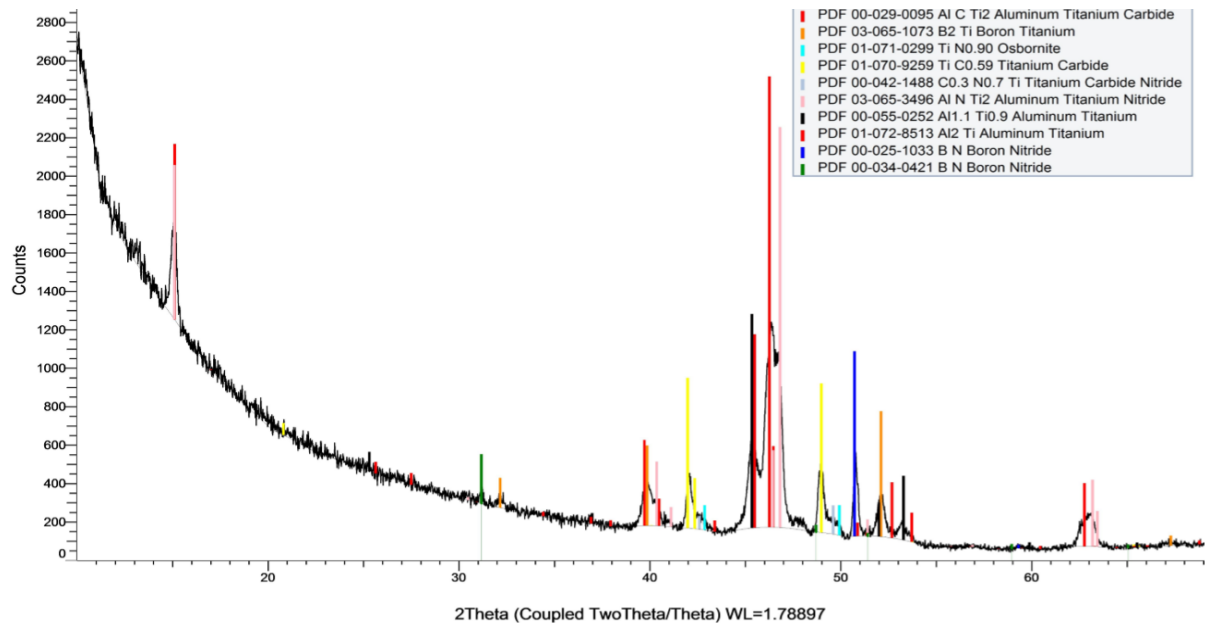


Figure A19: XRD analysis, of Ti_2AlC -cBN (20 vol.%, 100 μm) samples sintered at 1250°C for 10 minute.

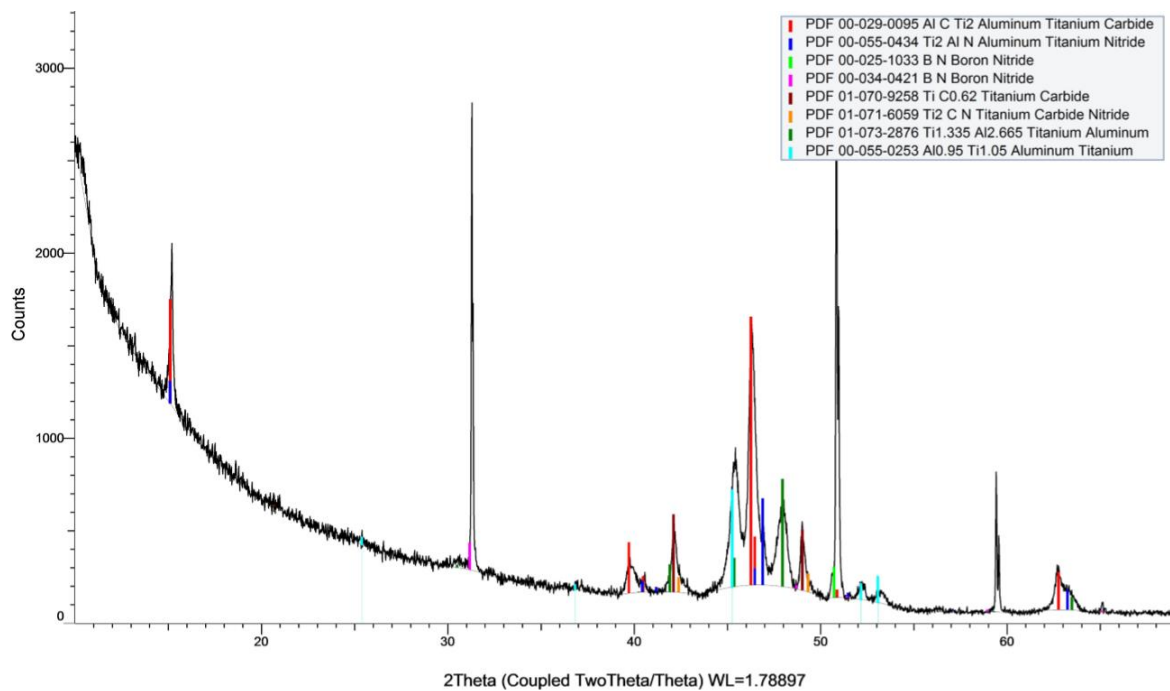


Figure A20: XRD analysis, of Ti_2AlC -cBN (20 vol.%, 100 μm) samples sintered at 1300°C for 1 minute.

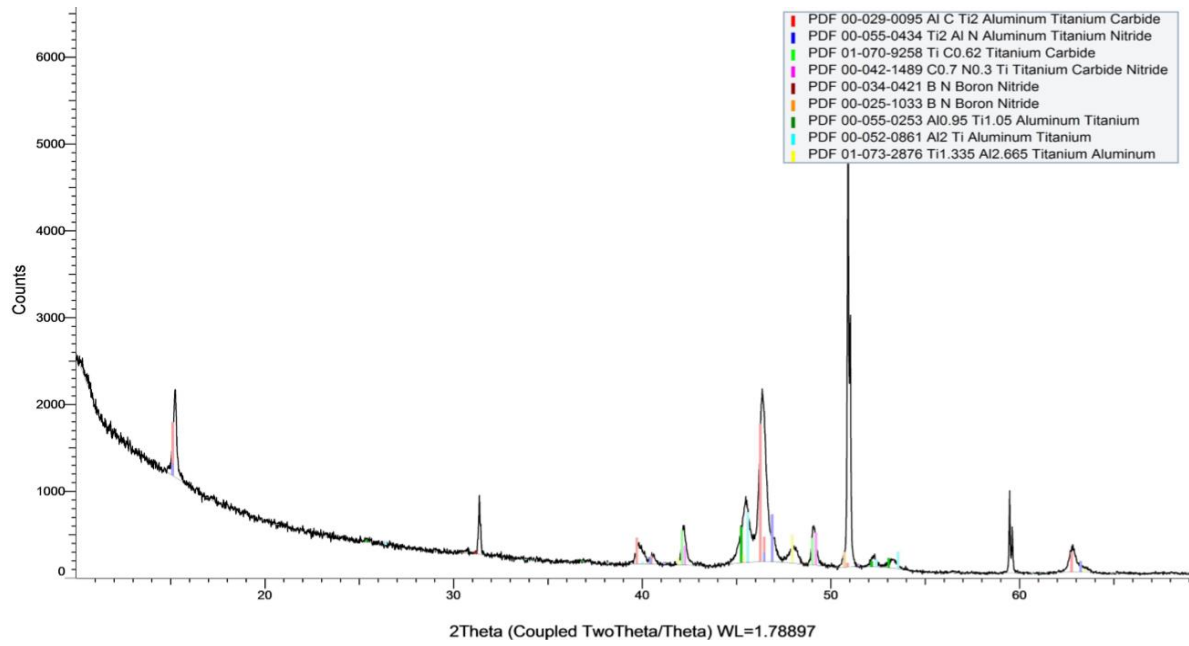


Figure A21: XRD analysis, of Ti_2AlC -cBN (20 vol.%, 100 μm) samples sintered at 1300°C for 5 minutes.

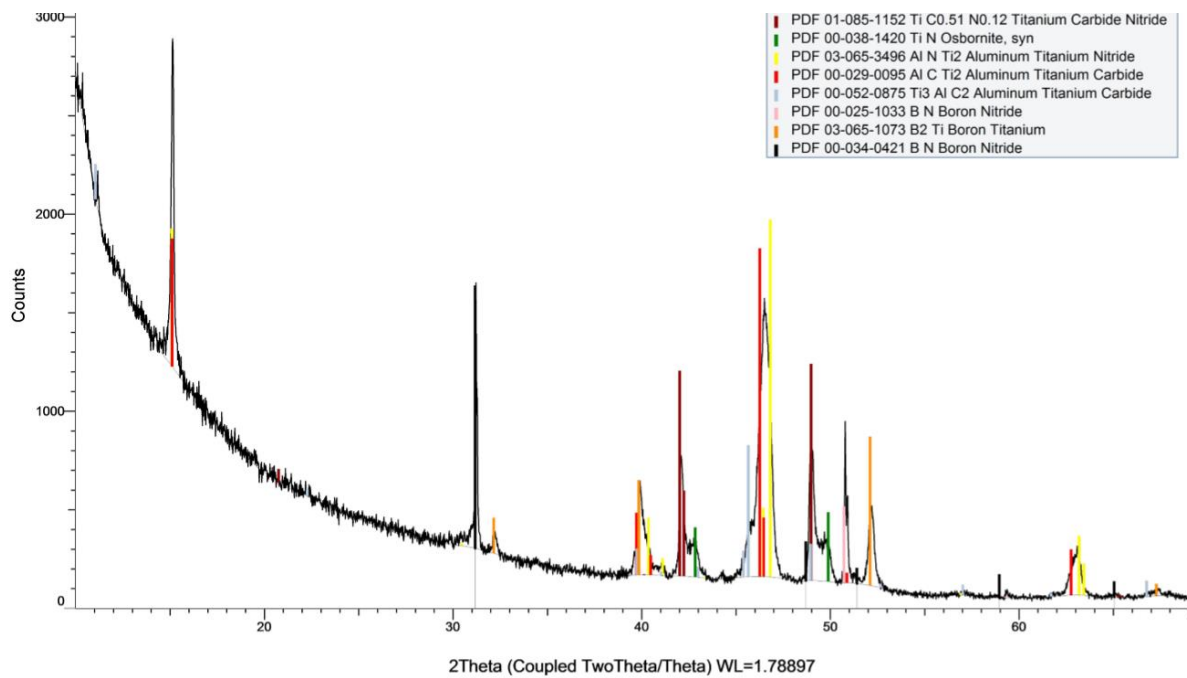


Figure A22: XRD analysis, of Ti_3AlC_2 -cBN (20 vol.%, 100 μm) samples sintered at 1300°C for 1 minute.

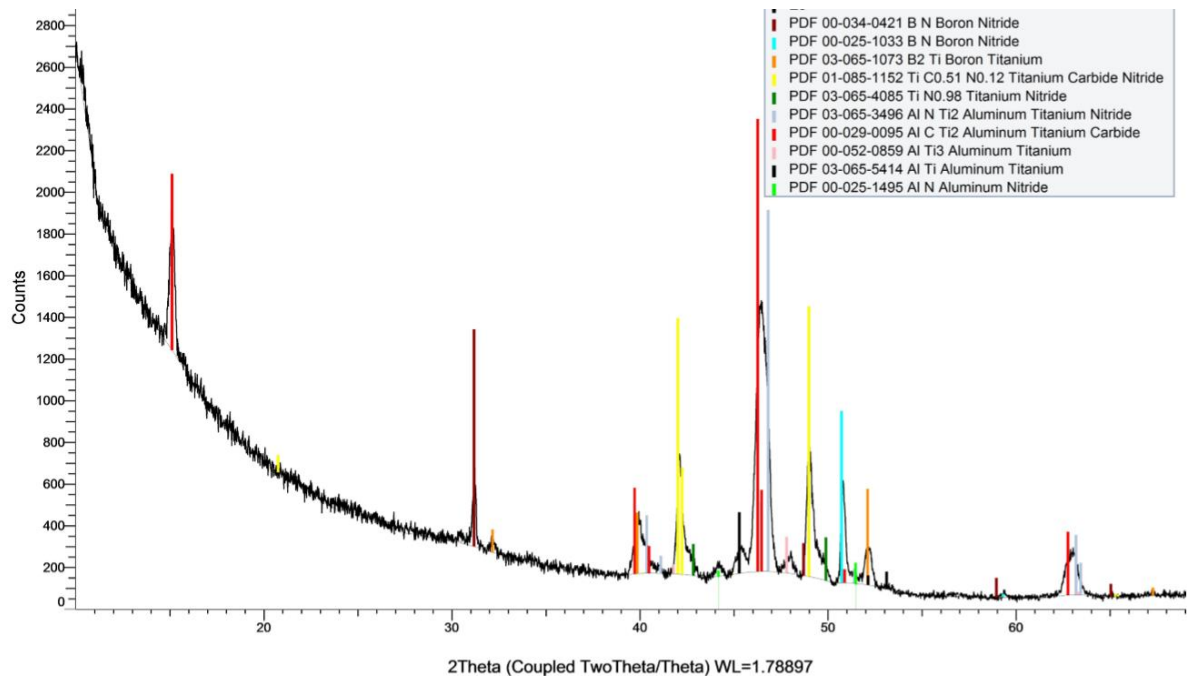


Figure A23: XRD analysis, of Ti_3AlC_2 -cBN (20 vol.%, 100 μm) samples sintered at 1300°C for 5 minutes.

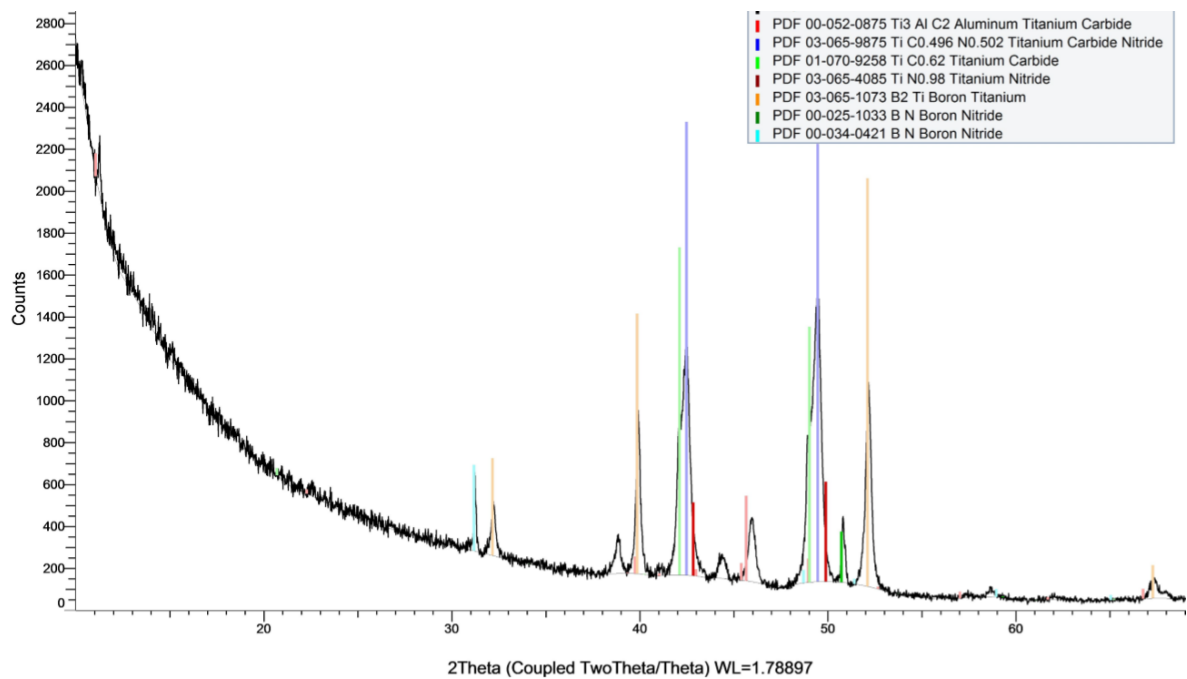


Figure A24: XRD analysis, of Ti_3AlC_2 -cBN (20 vol.%, 100 μm) samples sintered at 1300°C for 10 minutes.

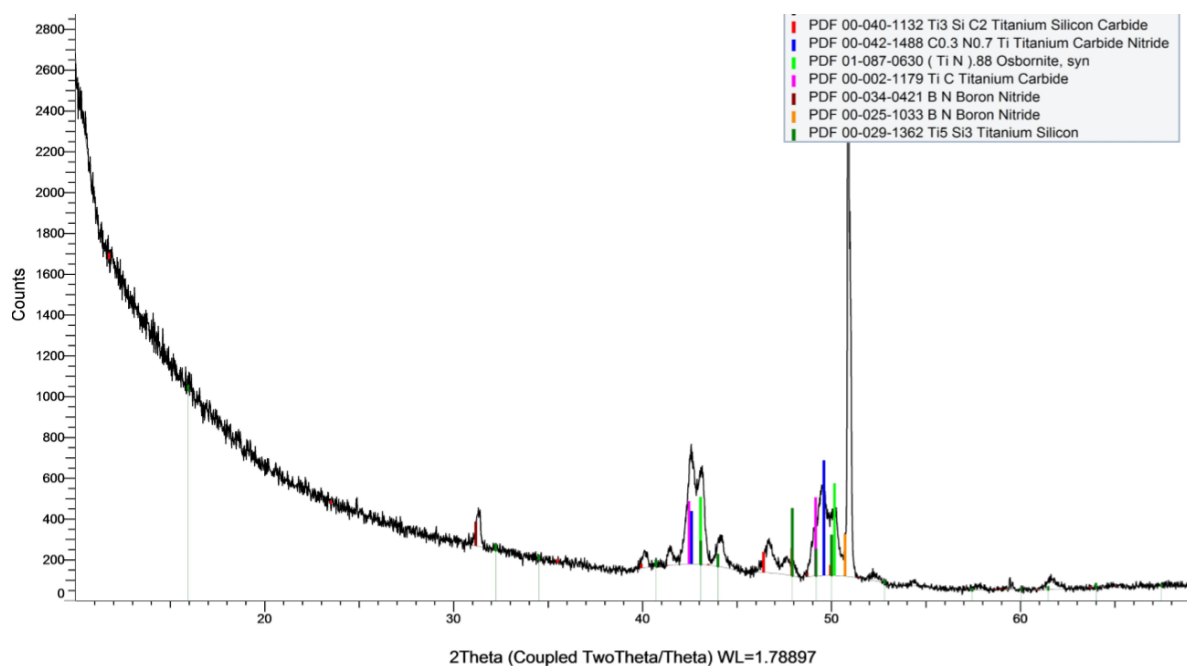


Figure A25: XRD analysis, of Ti_3SiC_2 -cBN (20 vol.%,100 μm) samples sintered at 1250°C for 1 minute.

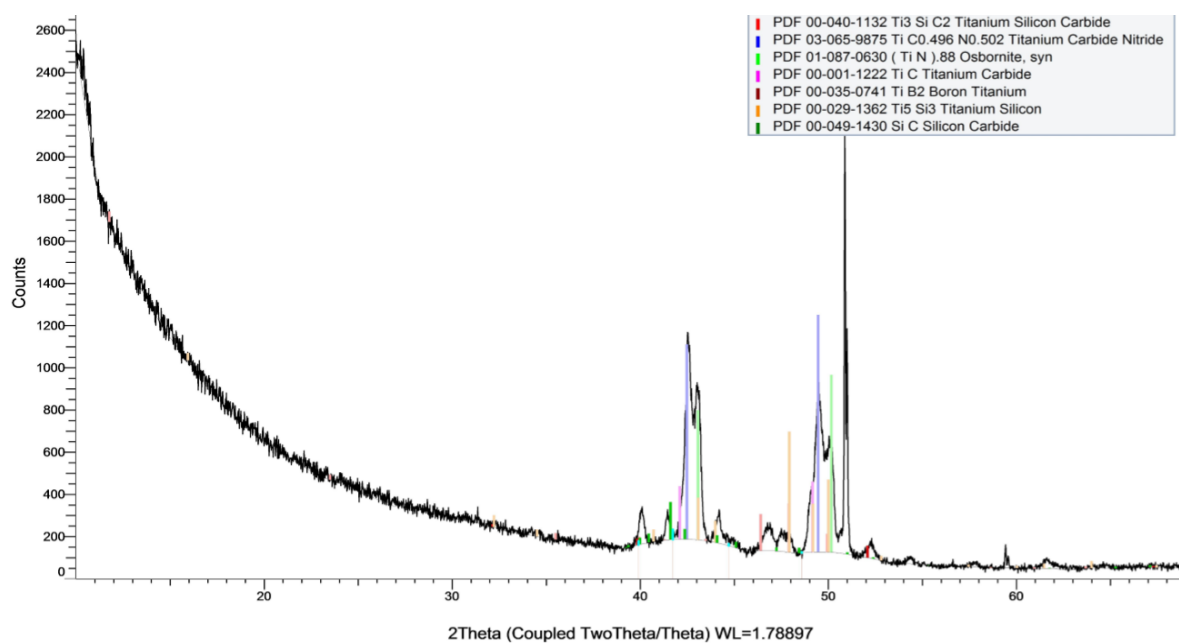


Figure A26: XRD analysis, of Ti_3SiC_2 -cBN (20 vol.%,100 μm) samples sintered at 1250°C for 5 minutes.

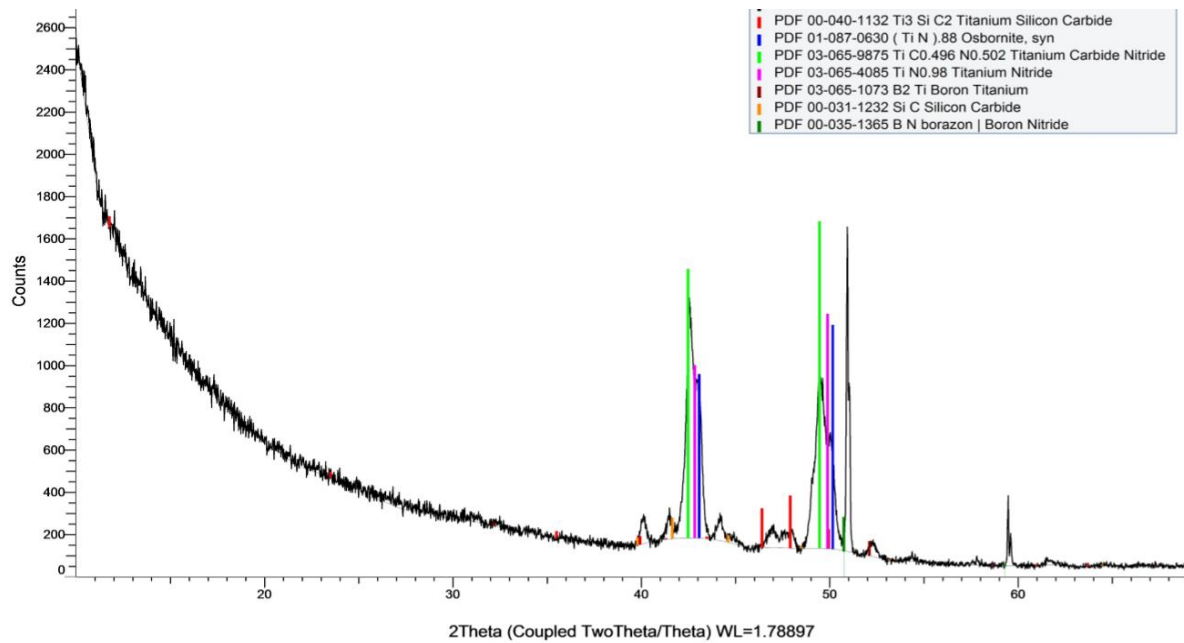


Figure A27: XRD analysis, of Ti_3SiC_2 -cBN (20 vol.%, 100 μm) samples sintered at 1250°C for 10 minutes.

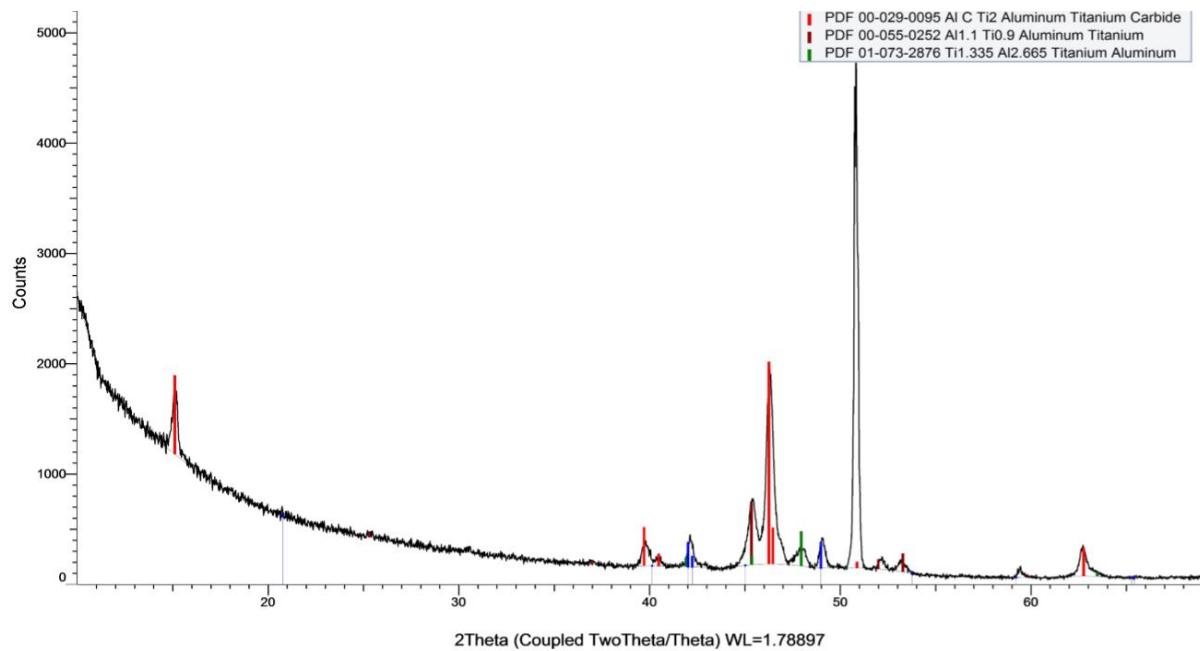


Figure A28: XRD analysis, of Ti_2AlC -cBN (40 vol.%, 100 μm) samples sintered at 1250°C for 5 minutes.

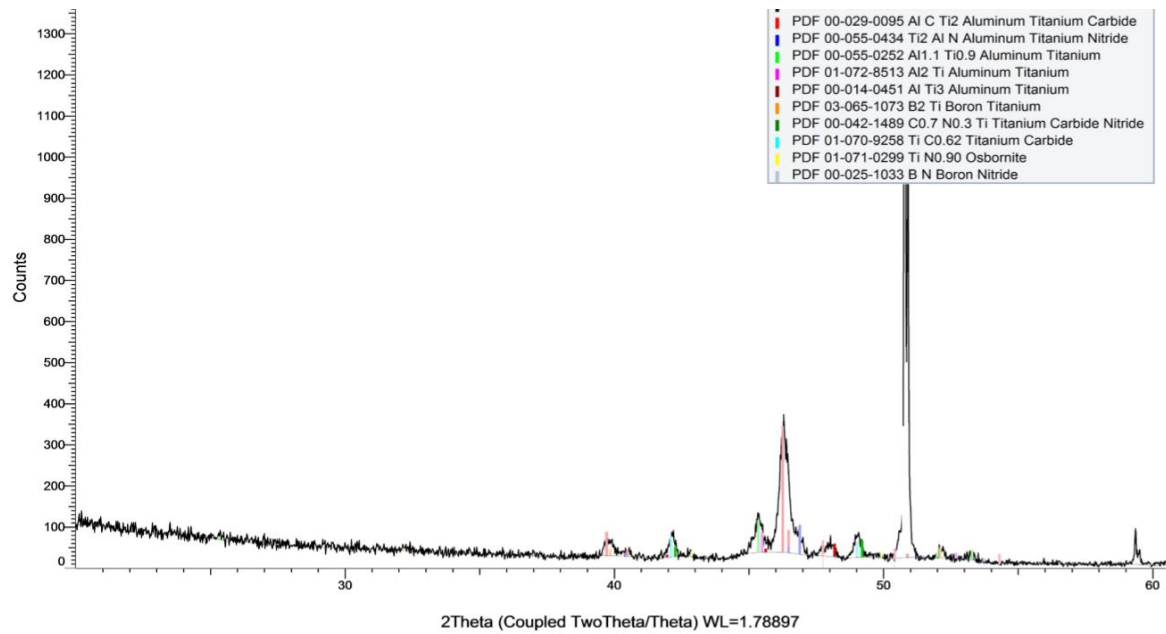


Figure A29: XRD analysis, of Ti_2AlC -cBN (40 vol.%, 100 μm) samples sintered at 1250°C for 10 minutes.

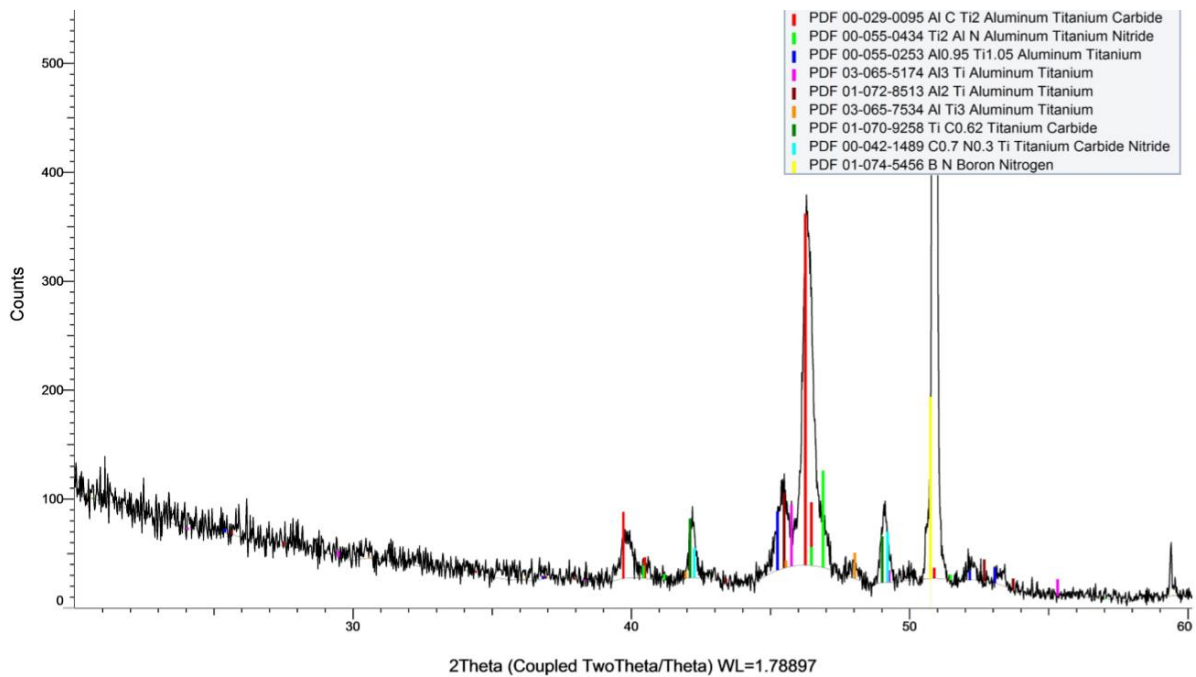


Figure A30: XRD analysis, of Ti_2AlC -cBN (40 vol.%, 100 μm) samples sintered at 1300°C for 5 minutes.

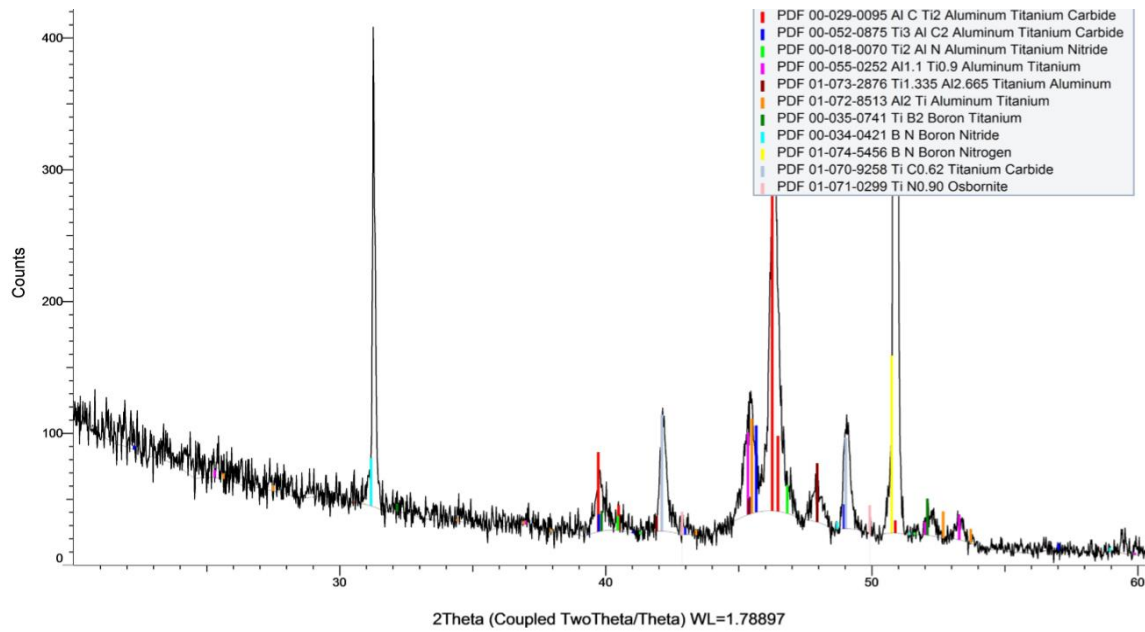


Figure A31: XRD analysis, of Ti_2AlC -cBN (40 vol.%, 100 μm) samples sintered at 1300°C for 10 minutes.

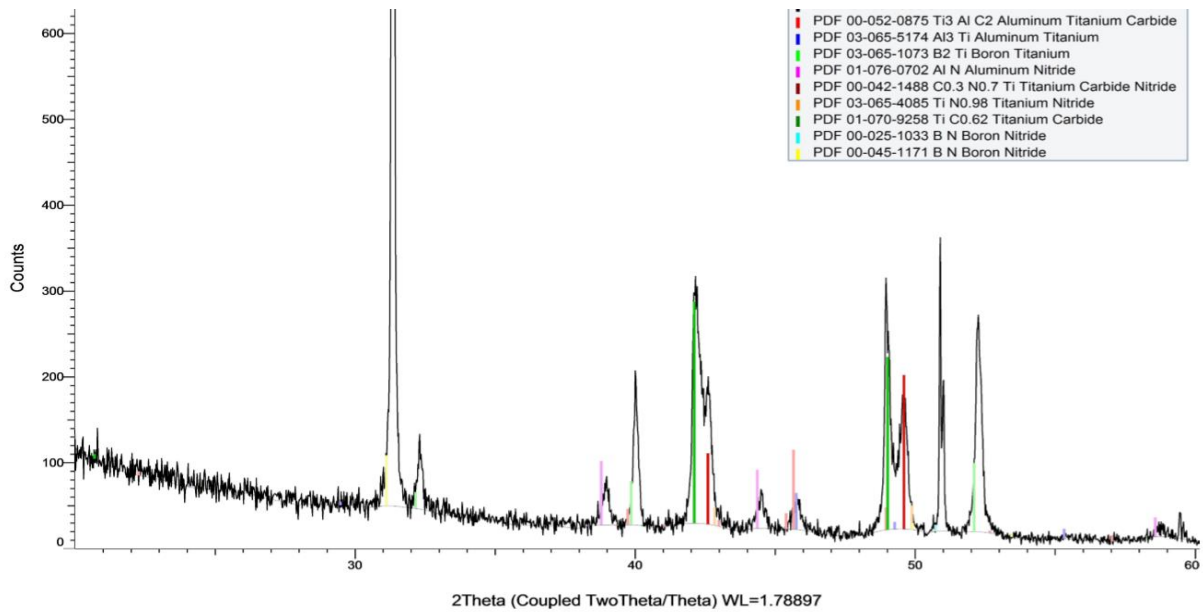


Figure A32: XRD analysis, of Ti_2AlC -cBN (40 vol.%, 100 μm) samples sintered at 1350°C for 5 minutes.

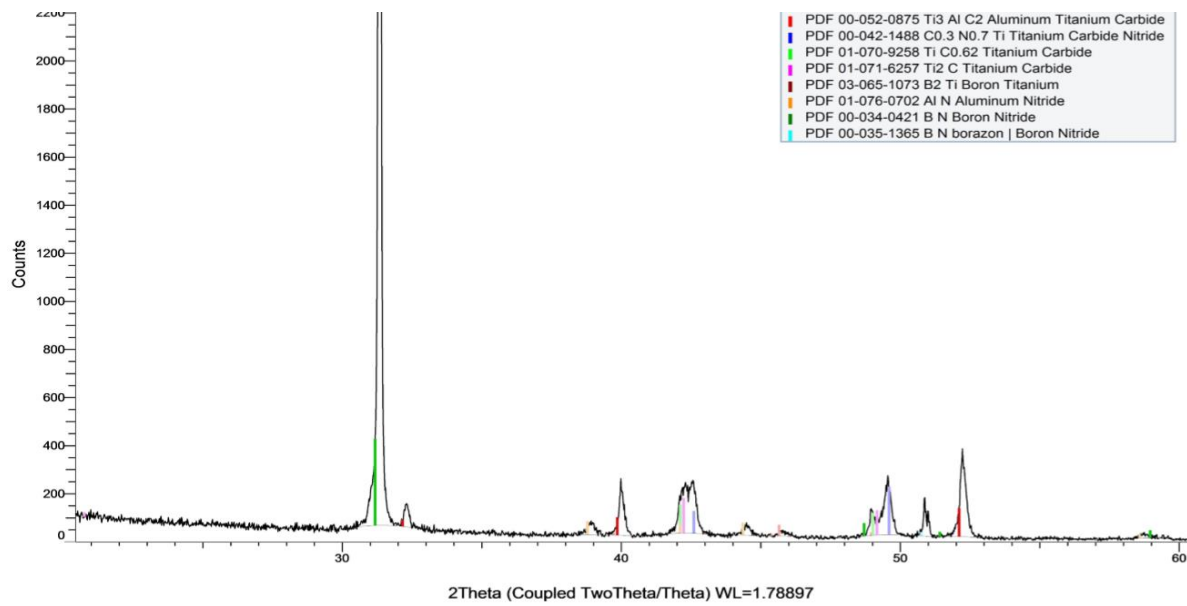


Figure A33: XRD analysis, of Ti_2AlC -cBN (40 vol.%, 100 μm) samples sintered at 1350°C for 10 minutes.

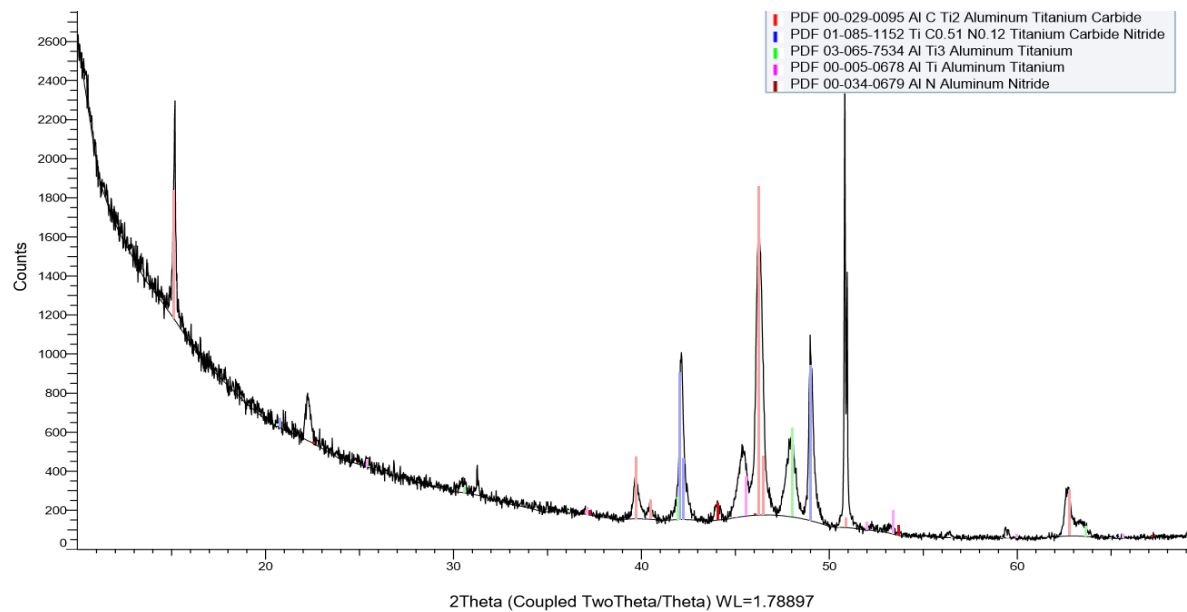


Figure A34: XRD analysis, of Ti_3AlC_2 -cBN (40 vol.%, 100 μm) samples sintered at 1250°C for 5 minutes.

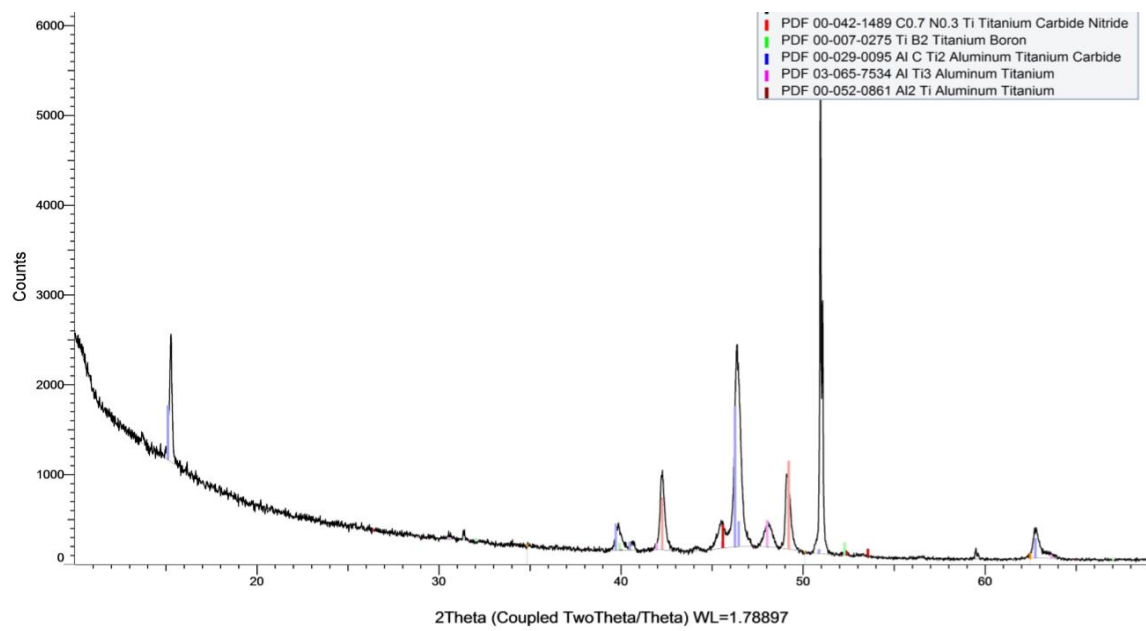


Figure A35: XRD analysis, of $\text{Ti}_3\text{AlC}_2\text{-cBN}$ (40 vol.%, 100 μm) samples sintered at 1250°C for 10 minutes.

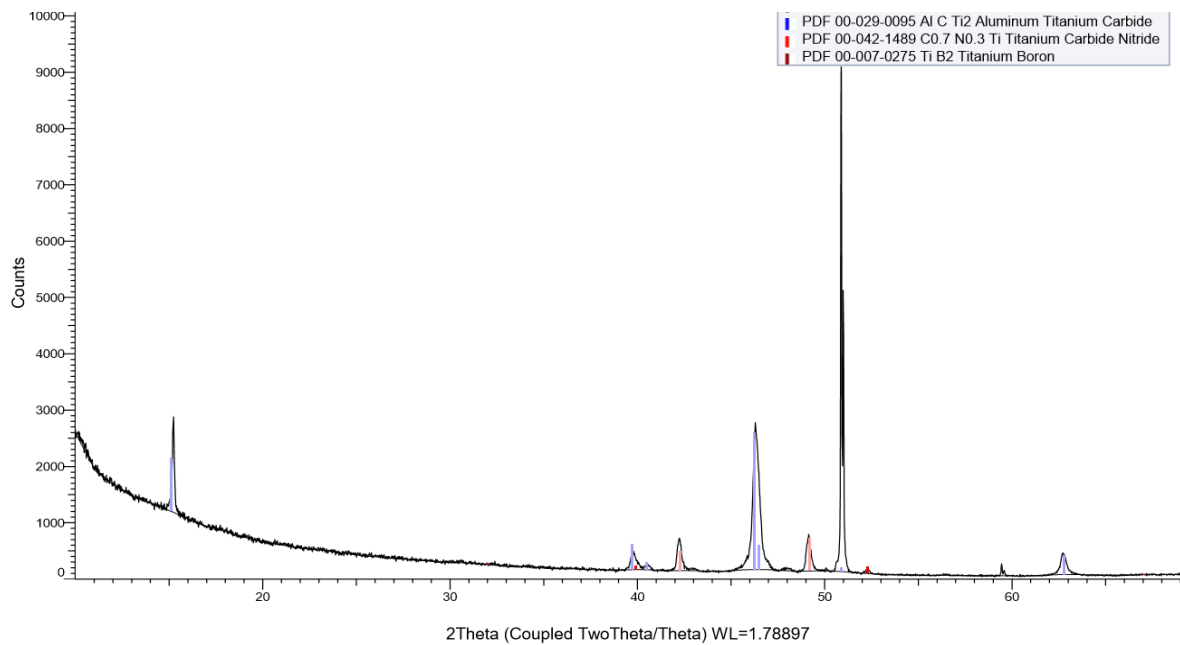


Figure A36: XRD analysis, of $\text{Ti}_3\text{AlC}_2\text{-cBN}$ (40 vol.%, 100 μm) samples sintered at 1300°C for 5 minutes.

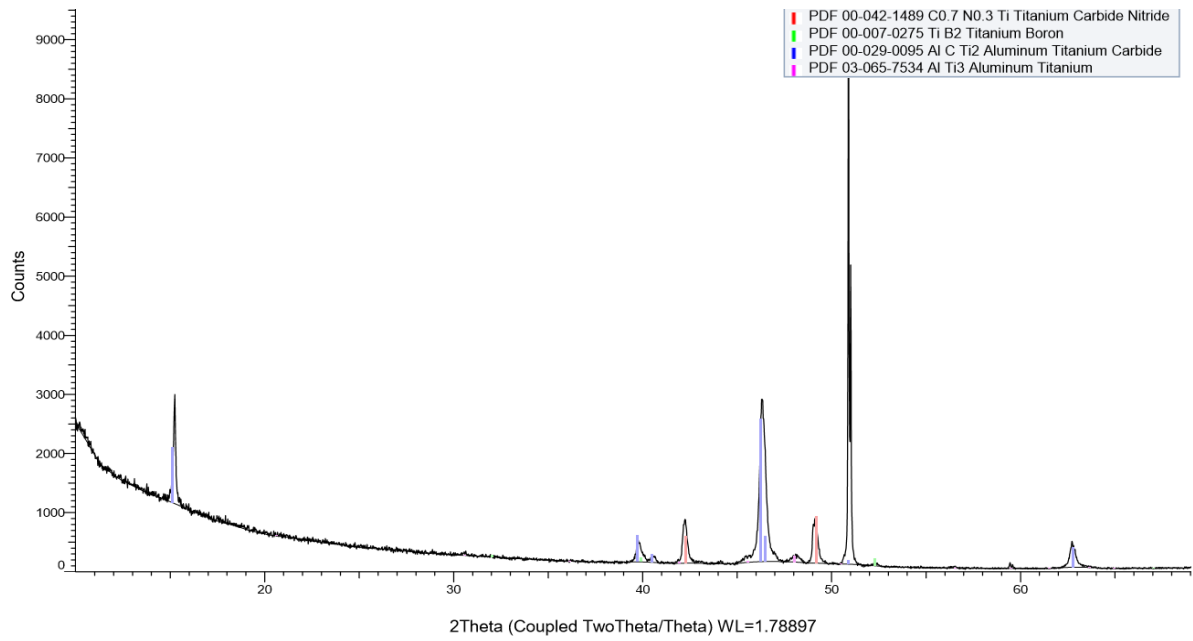


Figure A37: XRD analysis, of Ti_3AlC_2 -cBN (40 vol.%,100 μm) samples sintered at 1300°C for 10 minutes.

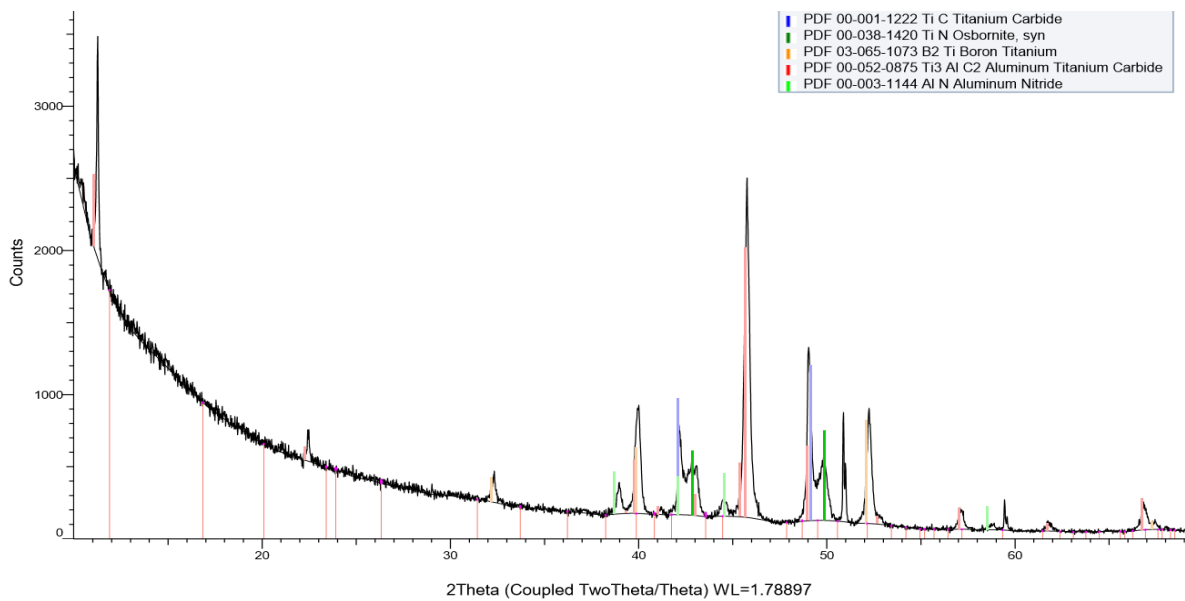


Figure A38: XRD analysis, of Ti_3AlC_2 -cBN (40 vol.%,100 μm) samples sintered at 1350°C for 5 minutes.

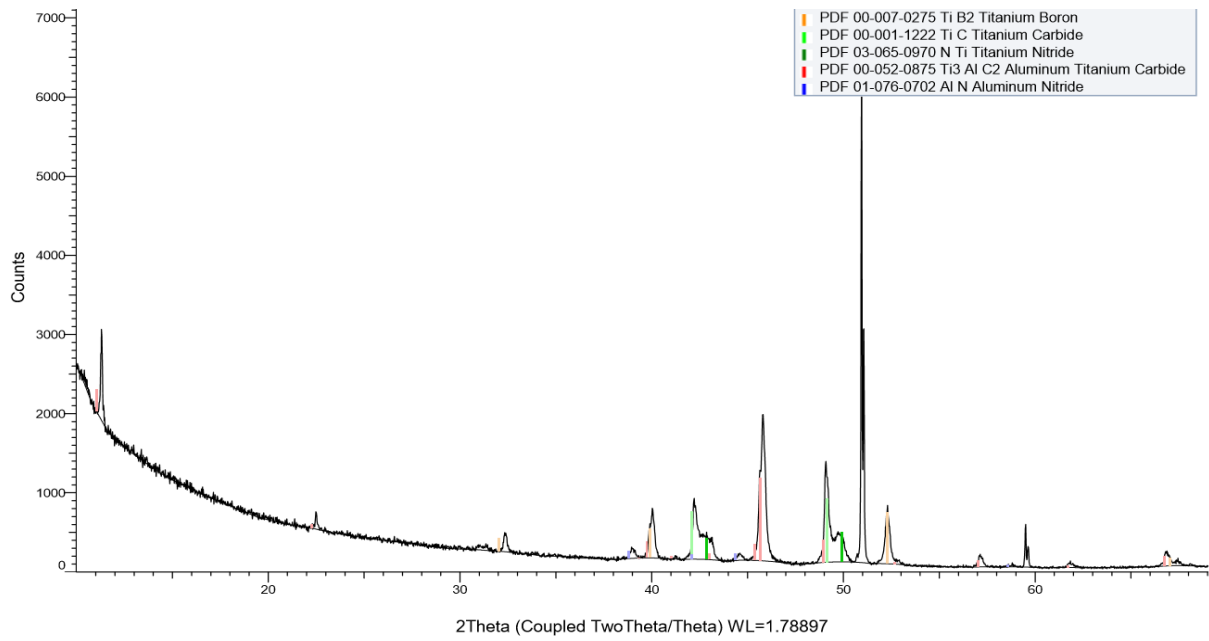


Figure A39: XRD analysis, of $\text{Ti}_3\text{AlC}_2\text{-cBN}$ (40 vol.%, 100 μm) samples sintered at 1350°C for 10 minutes.

Appendix B: Supplementary phase peak lists for peaks assigned in the XRD analysis.

Table B 1: Peak lists for Ti_2AlC . Top are the calculated peak lists for the Co detector used in this work, bottom is the peak lists for the Mo detector as given by the PDF's sourced from the XRD program from the XRD machine used. Bold peaks are the primary peaks.

AlTi2C-00-029-0095

(θ)-rad	(2θ) deg	d (Å)	I
0,131927	15,11775	6,8	39
0,346628	39,72066	2,633	19
0,353344	40,49019	2,585	6
0,403722	46,26311	2,277	100
0,405607	46,47913	2,267	18
0,444091	50,8891	2,082	3
0,547738	62,76614	1,7177	14
0,62919	72,09987	1,52	14
0,747093	85,6105	1,3164	2
0,751199	86,08108	1,3106	9
0,787477	90,23817	1,2624	11
0,703363	80,59943	1,383	2

d-spacings (16) - Al C Ti2 - 00-029-0095 (Stick, Fixed Slit Intensity) - Mo Ka1 0.70930 Å

2θ (°)	d (Å)	I	h	k	l	*	2θ (°)	d (Å)	I	h	k	l	*	2θ (°)	d (Å)	I	h	k	l
5.979	6.8000	39	0	0	2		23.831	1.7177	14	1	0	6		41.868	0.9926	2	2	0	9
15.482	2.6330	19	1	0	0		26.986	1.5200	14	1	1	0		42.803	0.9719	3	2	1	3
15.771	2.5850	6	1	0	1		31.258	1.3164	2	2	0	0		45.950	0.9086	2	1	1	12
17.921	2.2770	100	1	0	3		31.400	1.3106	9	1	0	9		50.520	0.8311	2	2	1	9
18.001	2.2670	18	0	0	6		32.632	1.2624	11	1	1	6							
19.615	2.0820	3	1	0	4		36.307	1.1383	2	2	0	6							

Table B 2: Peak lists for Ti_2AlN . Top are the calculated peak lists for the Co detector used in this work, bottom is the peak lists for the Mo detector as given by the PDF's sourced from the XRD program from the XRD machine used. Bold peaks are the primary peaks.

(θ)-rad	(2 θ) deg	d (Å)	I
0,131791	15,10211	6,807	26
0,352916	40,4412	2,588	13
0,359442	41,18901	2,543	6
0,405607	46,47913	2,267	9
0,409239	46,89536	2,248	19
0,449179	51,47207	2,06	100
0,497607	57,02153	1,874	6
0,551927	63,24614	1,706	1
0,613355	70,28536	1,554	23
0,641417	73,50093	1,495	2
0,65944	75,5663	1,46	17
0,715873	82,03304	1,363	1

d-spacings (18) - Ti2 Al N - 00-055-0434 (Stick, Fixed Slit Intensity) - Mo Kα1 0.70930 Å

2θ (°)	d (Å)	I	h	k	l	*	2θ (°)	d (Å)	I	h	k	l	*	2θ (°)	d (Å)	I	h	k	l	*
5.973	6.807	26	0	0	2		21.818	1.874	1	1	0	5		31.514	1.306	18	1	1	0	9
15.753	2.588	13	1	0	0		23.997	1.706	23	1	0	6		31.814	1.294	1	2	0	0	
16.033	2.543	6	1	0	1		26.384	1.554	2	1	0	7		33.019	1.248	16	1	1	6	
18.001	2.267	19	0	0	6		27.446	1.495	17	1	1	0		33.183	1.242	16	2	0	3	
18.154	2.248	100	1	0	3		28.117	1.460	2	1	1	2		36.416	1.135	3	0	0	12	
19.827	2.060	6	1	0	4		30.164	1.363	1	0	0	10		36.751	1.125	4	2	0	6	

(θ)-rad	(2 θ) deg	d (Å)	I
0,13183	15,10657	6,805	324
0,266023	30,48399	3,4025	8
0,352223	40,36177	2,59288	159
0,358842	41,12021	2,54707	49
0,378125	43,32994	2,42296	3
0,405355	46,45028	2,26833	190
0,408634	46,82604	2,25114	1000
0,448639	51,41021	2,06231	41
0,496615	56,90784	1,87743	6
0,55148	63,1949	1,70724	163
0,612659	70,20552	1,55554	12
0,640419	73,38665	1,497	156
0,658359	75,4424	1,46204	11
0,680094	77,93299	1,42241	3

d-spacings (56) - Ti₃AlN - 04-001-6325 (Stick, Fixed Slit Intensity) - Mo K α 1 0.70930 Å

2θ (°)	d (Å)	I	h	k	l	*	2θ (°)	d (Å)	I	h	k	l	*
5.975	6.805000	324	0	0	2		30.001	1.370240	2	1	1	4	
11.966	3.402500	8	0	0	4		30.209	1.361000	3	0	0	10	
15.723	2.592880	159	1	0	0		31.506	1.306290	104	1	0	9	
16.008	2.547070	49	1	0	1		31.752	1.296440	12	2	0	0	
16.833	2.422960	3	1	0	2		31.900	1.290600	3	2	0	1	
17.990	2.268330	190	0	0	6		32.339	1.273530	1	2	0	2	
18.129	2.251140	1000	1	0	3		32.980	1.249440	98	1	1	6	
19.804	2.062310	41	1	0	4		33.059	1.246540	89	2	0	3	
21.777	1.877430	6	1	0	5		34.044	1.211480	3	2	0	4	
23.979	1.707240	163	1	0	6		34.231	1.205080	1	1	0	10	
26.358	1.555540	12	1	0	7		35.276	1.170460	1	2	0	5	
27.408	1.497000	156	1	1	0		36.444	1.134170	14	0	0	12	
28.077	1.462040	11	1	1	2		36.732	1.125570	24	2	0	6	
28.876	1.422410	3	1	0	8		37.036	1.116650	1	1	0	11	

© 2020 International Centre for Diffraction Data. All rights reserved

Table B 3: Peak lists for Ti₃AlC₂. Top are the calculated peak lists for the Co detector used in this work, bottom is the peak lists for the Mo detector as given by the PDF's sourced from the XRD program from the XRD machine used. Bold peaks are the primary peaks.

Ti₃AlC₂-00-052-0875

(θ)-rad	(2θ) deg	d (Å)	I
0,096487	11,05664	9,28509	27
0,194432	22,28022	4,62973	5
0,343444	39,35579	2,65643	1
0,346841	39,74504	2,63145	20
0,358067	41,03148	2,55234	3
0,375193	42,9939	2,44099	8
0,39618	45,39886	2,31799	20
0,398458	45,65991	2,30544	100
0,427295	48,96439	2,1585	28
0,459687	52,67626	2,01616	3

d-spacings (30) - Ti₃AlC₂ - 00-052-0875 (Stick, Fixed Slit Intensity) - Mo K α 1 0.70930 Å

2θ (°)	d (Å)	I	h	k	l	*	2θ (°)	d (Å)	I	h	k	l	*	2θ (°)	d (Å)	I	h	k	l	*
4.378	9.28509	27	0	0	2		21.821	1.87369	8	1	0	7		32.215	1.27830	18	1	1	8	
8.787	4.62973	5	0	0	4		23.463	1.74421	3	1	0	8		32.360	1.27272	9	2	0	4	
15.345	2.65643	1	1	0	0		25.204	1.62554	12	1	0	9		32.842	1.25453	2	1	0	13	
15.491	2.63145	20	1	0	1		26.724	1.53461	24	1	1	0		32.933	1.25117	4	2	0	5	
15.974	2.55234	3	1	0	2		27.030	1.51755	3	1	1	2		34.757	1.18737	2m	1	0	14	
16.708	2.44099	8	1	0	3		28.914	1.42059	5	1	0	11		34.757	1.18737	2m	2	0	7	
17.602	2.31799	20	0	0	8		30.846	1.33357	11m	1	0	12		35.713	1.15658	2	0	0	16	
17.698	2.30544	100	1	0	4		30.846	1.33357	11m	2	0	0		35.810	1.15355	1	2	0	8	
18.914	2.15850	28	1	0	5		31.098	1.32300	4m	0	0	14		37.019	1.11715	7	2	0	9	
20.263	2.01616	3	1	0	6		31.098	1.32300	4m	2	0	1		39.747	1.04327	3	2	0	11	

Table B 4: Peak lists for Ti_3SiC_2 . Top are the calculated peak lists for the Co detector used in this work, bottom is the peak lists for the Mo detector as given by the PDF's sourced from the XRD program from the XRD machine used. Bold peaks are the primary peaks.

Ti_3SiC_2 -00-040-1132

(θ)-rad	(2θ) deg	d (Å)	I
0,102723	11,77117	8,72328	22
0,20515	23,50848	4,39098	11
0,309846	35,50574	2,93365	13
0,348642	39,95138	2,61841	16
0,360542	41,31504	2,53558	2
0,379531	43,49099	2,41442	4
0,404983	46,40762	2,2703	75
0,418102	47,91095	2,20307	100
0,435925	49,95332	2,11843	37

d-spacings (21) - Ti_3SiC_2 - 00-040-1132 (Stick, Fixed Slit Intensity) - Mo $\text{K}\alpha_1$ 0.70930 Å

2θ (°)	d (Å)	I	h	k	l	*	2θ (°)	d (Å)	I	h	k	l	*	2θ (°)	d (Å)	I	h	k	l	*
4.660	8.72328	22	0	0	2		15.569	2.61841	16	1	0	1		17.974	2.27030	75	1	0	4	
9.265	4.39098	11	0	0	4		16.081	2.53558	2	1	0	2		18.528	2.20307	100	0	0	8	
13.887	2.93365	13	0	0	6		16.893	2.41442	4	1	0	3		19.275	2.11843	37	1	0	5	

© 2020 International Centre for Diffraction Data. All rights reserved.

Page :

Ti_3SiC_2 -04-001-6420

(θ)-rad	(2θ) deg	d (Å)	I
0,101425	11,62247	8,8345	171
0,203913	23,3667	4,41725	28
0,308631	35,36648	2,94483	33
0,343371	39,34746	2,65697	20
0,347394	39,80842	2,62743	304
0,359237	41,16549	2,54439	33
0,378294	43,3493	2,42193	64
0,403756	46,26698	2,27682	1000
0,416984	47,78281	2,20863	188
0,434778	49,8219	2,12366	385
0,470623	53,92947	1,9727	3

d-spacings (79) - Ti_3SiC_2 - 04-001-6420 (Stick, Fixed Slit Intensity) - Mo $\text{K}\alpha_1$ 0.70930 Å

2θ (°)	d (Å)	I	h	k	l	*	2θ (°)	d (Å)	I	h	k	l	*
4.601	8.834500	171	0	0	2		15.515	2.627430	304	1	0	1	
9.210	4.417250	28	0	0	4		16.025	2.544390	33	1	0	2	
13.834	2.944830	33	0	0	6		16.841	2.421930	64	1	0	3	
15.341	2.656970	20	1	0	0		17.922	2.276820	1000	1	0	4	

Table B 5: Peak lists for cBN. Top are the calculated peak lists for the Co detector used in this work, bottom is the peak lists for the Mo detector as given by the PDF's sourced from the XRD program from the XRD machine used. Bold peaks are the primary peaks.

BN-00-025-1033

(θ)-rad	(2θ) deg	d (Å)	I
0,442724	50,73248	2,088	100
0,517545	59,30631	1,808	2
0,77491	88,79817	1,2785	6
0,96241	110,2841	1,0901	3
1,028565	117,8649	1,0443	1
1,424977	163,2904	0,9041	1

d-spacings (7) - B N - 00-025-1033 (Stick, Fixed Slit Intensity) - Mo Ka1 0.70930 Å

2θ (°)	d (Å)	I	h	k	l	*	2θ (°)	d (Å)	I	h	k	l	*	2θ (°)	d (Å)	I	h	k	l	*
19.558	2.0880	100	1	1	1		37.972	1.0901	3	3	1	1		50.611	0.8297	3	3	3	1	
22.625	1.8080	2	2	0	0		39.706	1.0443	1	2	2	2								
32.210	1.2785	6	2	2	0		46.191	0.9041	1	4	0	0								

Table B 6: Peak lists for hBN. Top are the calculated peak lists for the Co detector used in this work, bottom is the peak lists for the Mo detector as given by the PDF's sourced from the XRD program from the XRD machine used. Bold peaks are the primary peaks.

BN-00-009-0012

(θ)-rad	(2 θ) deg	d (Å)	I
0,27196	31,16434	3,33	100
0,424883	48,68802	2,17	16
0,449179	51,47207	2,06	6
0,514728	58,98344	1,817	14
0,566398	64,90438	1,667	6
0,614263	70,38934	1,552	2
0,743176	85,16173	1,322	4

d-spacings (19) - B N - 00-009-0012 (Stick, Fixed Slit Intensity) - Mo Ka1 0.70930 Å

2 θ (°)	d (Å)	I	h	k	l	*	2 θ (°)	d (Å)	I	h	k	l	*	2 θ (°)	d (Å)	I	h	k	l	*
12.227	3.330	100	0	0	2		32.884	1.253	6	1	1	0		41.501	1.001	6	1	1	4	
18.812	2.170	16	1	0	0		35.197	1.173	8	1	1	2		42.028	0.989	2	1	0	6	
19.827	2.060	6	1	0	1		36.317	1.138	<1	1	0	5		42.753	0.973	<1	2	0	3	
22.511	1.817	14	1	0	2		37.231	1.111	2	0	0	6		45.875	0.910	2	2	0	4	
24.567	1.667	6	0	0	4		38.121	1.086	2	2	0	0		50.591	0.830	6	1	1	6	
26.419	1.552	2	1	0	3		38.676	1.071	<1	2	0	1								
31.122	1.322	4	1	0	4		40.199	1.032	2	2	0	2								

BN-00-034-0421

(θ)-rad		(2θ) deg		d (Å)		I						
0,272117		31,1823		3,32813		100						
0,425029		48,70475		2,1693		15						
0,448734		51,42118		2,0619		6						
0,514547		58,96276		1,81758		9						
0,56769		65,05249		1,66362		6						
0,614763		70,44667		1,5509		<1						

0,744674	85,33338	1,31985	2
----------	----------	---------	---

d-spacings (20) - B N - 00-034-0421 (Stick, Fixed Slit Intensity) - Mo Ka1 0.70930 Å

2 θ (°)	d (Å)	I	h	k	l	*	2 θ (°)	d (Å)	I	h	k	l	*	2 θ (°)	d (Å)	I	h	k	l	*
12.234	3.328130	100	0	0	2		32.908	1.252100	5	1	1	0		42.086	0.987702	<1	1	0	6	
18.819	2.169300	15	1	0	0		35.226	1.172050	5	1	1	2		45.949	0.908612	<1	2	0	4	
19.808	2.061900	6	1	0	1		36.430	1.134570	<1	1	0	5		50.471	0.831851	<1	0	0	8	
22.504	1.817580	9	1	0	2		37.285	1.109460	<1	0	0	6		50.568	0.830356	1	1	1	6	
24.618	1.663620	6	0	0	4		38.182	1.084320	<1	2	0	0		51.271	0.819727	<1	2	1	0	
26.438	1.550900	<1	1	0	3		40.234	1.031150	1	2	0	2		52.917	0.795985	<1	2	1	2	
31.174	1.319850	2	1	0	4		41.521	1.000520	3	1	1	4								

Table B 7: Peak lists for Ti₃Al. Top are the calculated peak lists for the Co detector used in this work, bottom is the peak lists for the Mo detector as given by the PDF's sourced from the XRD program from the XRD machine used. Bold peaks are the primary peaks.

AlTi3-00-009-0098

(θ)-rad	(2 θ) deg	d (Å)	I
0,179506	20,56992	5,01	10
0,266223	30,50695	3,4	20
0,315816	36,18982	2,88	5
0,365913	41,93054	2,5	50
0,395817	45,35733	2,32	70
0,417713	47,86639	2,205	100
0,494154	56,62585	1,886	5
0,516916	59,23424	1,81	10
0,536178	61,44144	1,751	5
0,554101	63,49535	1,7	60

d-spacings (30) - Al Ti3 - 00-009-0098 (Stick, Fixed Slit Intensity) - Mo Ka1 0.70930 Å

2 θ (°)	d (Å)	I	h	k	l	*	2 θ (°)	d (Å)	I	h	k	l	*	2 θ (°)	d (Å)	I	h	k	l	*
8.119	5.010	10	1	0	0		27.844	1.474	5	1	0	3		42.753	0.973	30	4	0	3	
11.975	3.400	20	1	0	1		28.455	1.443	50	2	2	0		44.085	0.945	10	4	2	0	
14.147	2.880	5	1	1	0		30.438	1.351	5	3	0	2		44.987	0.927	40	4	2	1	
16.311	2.500	50	2	0	0		31.292	1.315	60	2	0	3		46.143	0.905	40	2	2	4	
17.586	2.320	70	0	0	2		32.938	1.251	10	4	0	0		47.764	0.876	10	4	2	2	
18.511	2.205	100	2	0	1		33.601	1.227	40	2	2	2		48.114	0.870	40	2	0	5	
21.677	1.886	5	2	1	0		34.145	1.208	30	4	0	1		49.320	0.850	10	4	0	4	
22.599	1.810	10	1	1	2		35.605	1.160	20	0	0	4		50.332	0.834	20	6	0	0	
23.371	1.751	5	2	1	1		37.547	1.102	20	4	0	2		52.209	0.806	50	4	2	3	
24.083	1.700	60	2	0	2		39.481	1.050	20	2	0	4		53.790	0.784	40	6	0	2	

Table B 8: Peak lists for TiAl₃. Top are the calculated peak lists for the Co detector used in this work, bottom is the peak lists for the Mo detector as given by the PDF's sourced from the XRD program from the XRD machine used. Bold peaks are the primary peaks.

Ti1.335Al2.665-01-073-2876

(θ)-rad	(2 θ) deg	d (Å)	I
0,179822	20,60609	5,0013	1
0,266163	30,50006	3,40075	25
0,314967	36,09258	2,8875	7
0,365813	41,91913	2,50065	254
0,395998	45,37798	2,319	266

0,4185	47,95652	2,2011	1000
0,439158	50,32377	2,10384	1
0,492926	56,48514	1,89031	4
0,51752	59,30343	1,80808	3
0,536347	61,46089	1,7505	1
0,553963	63,4795	1,70038	125
0,566359	64,90001	1,6671	1
0,606717	69,52462	1,56883	2
0,650528	74,54499	1,47704	1
0,656692	75,25137	1,4652	3
0,668195	76,56956	1,44375	126
0,700853	80,31179	1,38711	1
0,721917	82,72554	1,35362	1
0,738381	84,61224	1,32895	1
0,748086	85,72435	1,31499	124
0,797226	91,3554	1,25032	16
0,818077	93,74476	1,22563	120

d-spacings (65) - Ti1.335 Al2.665 - 01-073-2876 (Stick, Fixed Slit Intensity) - Mo K α 1 0.70930 Å

2θ (°)	d (Å)	I	h	k	l	*	2θ (°)	d (Å)	I	h	k	l	*	2θ (°)	d (Å)	I	h	k	l	*
8.133	5.001300	1	1	0	0		34.168	1.207230	84	4	0	1		45.032	0.926122	57	4	2	1	
11.972	3.400750	25	1	0	1		34.477	1.196730	1	2	1	3		45.278	0.921357	1	3	2	3	
14.110	2.887500	7	1	1	0		34.666	1.190410	1	3	1	2		45.428	0.918463	1	5	0	2	
16.307	2.500650	254	2	0	0		35.620	1.159500	16	0	0	4		45.766	0.912045	1	1	0	5	
17.594	2.319000	266	0	0	2		36.009	1.147380	1	3	2	0		46.195	0.904041	36	2	2	4	
18.544	2.201100	1000	2	0	1		36.463	1.133580	1	3	0	3		46.509	0.898259	1	5	1	0	
19.410	2.103840	1	1	0	2		36.598	1.129540	1	1	0	4		46.878	0.891595	1	4	1	3	
21.627	1.890310	4	2	1	0		37.134	1.113800	1	3	2	1		47.024	0.888971	1	3	3	2	
22.624	1.808080	3	1	1	2		37.598	1.100550	18	4	0	2		47.426	0.881872	1	5	1	1	
23.378	1.750500	1	2	1	1		37.926	1.091370	1	4	1	0		47.807	0.875252	17	4	2	2	
24.077	1.700380	125	2	0	2		38.489	1.075990	1	1	1	4		48.132	0.869693	25	2	0	5	
24.565	1.667100	1	3	0	0		39.003	1.062360	1	4	1	1		49.309	0.850188	8	4	0	4	
26.130	1.568830	2	3	0	1		39.406	1.051920	15	2	0	4		49.959	0.839811	1	5	0	3	
27.786	1.477040	1	1	0	3		40.181	1.032450	1	3	1	3		50.099	0.837617	1	5	1	2	
28.015	1.465200	3	2	1	2		40.346	1.028390	1	3	2	2		50.361	0.833549	15	6	0	0	
28.440	1.443750	126	2	2	0		41.533	1.000260	1	5	0	0		51.105	0.822208	1	4	3	0	
29.627	1.387110	1	3	1	0		42.056	0.988376	1	2	1	4		51.226	0.820405	1	6	0	1	
30.378	1.353620	1	3	0	2		42.096	0.987481	1	4	1	2		51.551	0.815570	1	3	2	4	
30.956	1.328950	1	3	1	1		42.791	0.972177	34	4	0	3		51.893	0.810572	1	3	0	5	
31.293	1.314990	124	2	0	3		43.242	0.962500	1	3	3	0		52.182	0.806397	43	4	2	3	
32.956	1.250320	16	4	0	0		43.749	0.951899	1	3	0	4		52.571	0.800848	1	5	2	0	
33.639	1.225630	120	2	2	2		44.077	0.945156	10	4	2	0								

TiAl3-04-007-1546

(θ)-rad	(2θ) deg	d (Å)	I
0,209954	24,05892	4,29195	31
0,257263	29,48015	3,51566	91
0,334462	38,32653	2,72498	22
0,399366	45,76394	2,30048	1000m
0,399366	45,76394	2,30048	1000m
0,429953	49,269	2,14598	196
0,482767	55,32103	1,92685	272

d-spacings (52) - Ti Al3 - 04-007-1546 (Stick, Fixed Slit Intensity) - Mo K α 1 0.70930 Å

2θ (°)	d (Å)	I	h	k	l	*	2θ (°)	d (Å)	I	h	k	l	*
9.480	4.291950	37	0	0	2		17.737	2.300480	1000m	1	0	3	
11.579	3.515660	91	1	0	1		17.737	2.300480	1000m	1	1	2	
14.956	2.724980	22	1	1	0		19.025	2.145980	196	0	0	4	

© 2020 International Centre for Diffraction Data. All rights reserved.

04-007-1546

2θ (°)	d (Å)	I	h	k	l	*	2θ (°)	d (Å)	I	h	k	l	*
21.212	1.926850	272	2	0	0		41.581	0.999158	2m	2	1	7	
23.279	1.757830	9	2	0	2		42.133	0.986642	1	2	2	6	
24.232	1.689710	16	2	1	1		43.199	0.963425	18	4	0	0	
24.287	1.685940	8	1	1	4		44.330	0.940033	1	4	0	2	
26.141	1.568210	6	1	0	5		44.459	0.937440	32	2	0	8	
27.800	1.476310	9	2	1	3		44.951	0.927704	64	3	1	6	
28.643	1.433720	170	2	0	4		45.964	0.908326	1	3	3	0	
30.175	1.362490	69	2	2	0		46.017	0.907349	2	3	2	5	
31.697	1.298620	2	2	2	2		47.043	0.888643	32m	3	3	2	
32.420	1.270420	5	3	0	1		47.043	0.888643	32m	4	1	3	
32.518	1.266690	100	1	1	6		47.135	0.886998	2	3	0	7	
33.838	1.218650	2	3	1	0		47.595	0.878915	29	4	0	4	
33.906	1.216290	4	2	1	5		48.606	0.861714	29	4	2	0	
35.218	1.172310	148m	3	0	3		48.807	0.858390	1	0	0	10	
35.218	1.172310	148m	3	1	2		49.641	0.844854	2	4	2	2	
35.336	1.168540	4	1	0	7		49.759	0.842970	27	2	2	8	
35.917	1.150240	68	2	2	4		50.172	0.836480	1	3	3	4	
38.601	1.072990	12	0	0	8		50.299	0.834500	2	2	1	9	
39.069	1.060630	2	3	2	1		51.193	0.820888	2	4	1	5	
39.105	1.059700	2	3	1	4		51.338	0.818729	25	1	1	10	
40.341	1.028520	1	3	0	5		52.228	0.805726	2m	3	1	8	
41.490	1.001250	2	3	2	3		52.228	0.805726	2m	3	2	7	
41.581	0.999158	2m	1	1	8		52.655	0.799653	53	4	2	4	

Table B 9: Peak lists for TiAl₂. Top are the calculated peak lists for the Co detector used in this work, bottom is the peak lists for the Mo detector as given by the PDF's sourced from the XRD program from the XRD machine used. Bold peaks are the primary peaks.

TiAl₂-04-003-1677

(θ)-rad	(2 θ) deg	d (Å)	I
0,148465	17,01287	6,0472	3
0,223741	25,63883	4,0315	55
0,240032	27,50567	3,76263	57
0,269932	30,93196	3,3544	1
0,300336	34,41595	3,0236	23
0,322215	36,92309	2,82474	33
0,331211	37,95396	2,75073	31
0,378794	43,40654	2,41889	59
0,397012	45,49418	2,31339	1000
0,448217	51,36184	2,06412	16
0,459788	52,68779	2,01575	290m
0,459788	52,68779	2,01575	290m
0,468864	53,72782	1,97955	153
0,486756	55,77818	1,91231	1
0,495494	56,77948	1,88132	1
0,50849	58,26861	1,8373	4
0,519147	59,48985	1,80293	3
0,527561	60,45404	1,77683	17m

Table B 10: Peak lists for Ti_5Si_3 . Top are the calculated peak lists for the Co detector used in this work, bottom is the peak lists for the Mo detector as given by the PDF's sourced from the XRD program from the XRD machine used. Bold peaks are the primary peaks.

(θ)-rad	(2θ) deg	d (Å)	I
0,139131	15,94328	6,45	6
0,28123	32,22664	3,223	10
0,301219	34,5172	3,015	6
0,355353	40,72042	2,571	10
0,375999	43,08637	2,436	35
0,383947	43,99713	2,388	18
0,418318	47,93569	2,202	100
0,429309	49,19517	2,149	40
0,43646	50,01463	2,116	60
0,460958	52,82186	2,011	4

d-spacings (2 θ) - Ti5 Si3 - 00-029-1362 (Stick, Fixed Slit Intensity) - Mo K α 0.70930 Å																				
2 θ (°)	d (Å)	I	h	k	l	*	2 θ (°)	d (Å)	I	h	k	l	*	2 θ (°)	d (Å)	I	h	k	l	*
6.304	6.450	6	1	0	0		21.972	1.861	2	2	2	0		29.199	1.407	8	4	1	0	
12.635	3.223	10	2	0	0		22.881	1.788	2	3	1	0		29.305	1.402	10	2	1	3	
13.511	3.015	6	1	1	1		23.385	1.750	4	2	2	1		30.096	1.366	12	4	0	2	
15.858	2.571	10	0	0	2		24.257	1.688	6	3	1	1		32.017	1.286	4	0	0	4	
16.743	2.436	35	2	1	0		25.435	1.611	2	4	0	0		32.669	1.261	<1	1	0	4	
17.082	2.388	18	1	0	2		26.333	1.557	2	1	1	3		33.405	1.234	2	4	1	2	
18.537	2.202	100	2	1	1		27.204	1.508	12	2	2	2		33.857	1.218	4	4	2	0	
18.998	2.149	40	3	0	0		27.748	1.479	2	3	2	0		34.204	1.206	4	3	3	1	
19.297	2.116	60	1	1	2		27.960	1.468	4	3	1	2								
20.315	2.011	4	2	0	2		28.884	1.422	8	3	2	1								

Table B 11: Peak lists for TiN_b. Top are the calculated peak lists for the Co detector used in this work, bottom is the peak lists for the Mo detector as given by the PDF's sourced from the XRD program from the XRD machine used. Bold peaks are the primary peaks.

TiN-00-006-00642

(θ)-rad	(2 θ) deg	d (Å)	I
0,375352	43,01222	2,44	75
0,43558	49,91379	2,12	100
0,640918	73,44374	1,496	55
0,776061	88,93005	1,277	25
0,820376	94,00816	1,223	16
1,005947	115,2731	1,059	8
1,168777	133,9319	0,972	12
1,233252	141,3202	0,948	20

d-spacings (10) - Ti N - 00-006-0642 (Stick, Fixed Slit Intensity) - Mo Ka1 0.70930 Å

2 θ (°)	d (Å)	I	h	k	l	*	2 θ (°)	d (Å)	I	h	k	l	*	2 θ (°)	d (Å)	I	h	k	l	*
16.715	2.440	75	1	1	1		33.714	1.223	16	2	2	2		48.410	0.865	20	4	2	2	
19.260	2.120	100	2	0	0		39.132	1.059	8	4	0	0		51.522	0.816	1	5	1	1	
27.427	1.496	55	2	2	0		42.799	0.972	12	3	3	1								
32.248	1.277	25	3	1	1		43.938	0.948	20	4	2	0								

TiN-00-038-1420

(θ)-rad	(2 θ) deg	d (Å)	I
0,373878	42,84321	2,44917	72
0,435424	49,89594	2,12071	100
0,639093	73,23469	1,49967	45
0,774589	88,76133	1,27892	19
0,819072	93,85872	1,22449	12
1,003838	115,0314	1,06042	5
1,166249	133,6423	0,973049	6
1,23181	141,155	0,948481	14

d-spacings (10) - Ti N - 00-038-1420 (Stick, Fixed Slit Intensity) - Mo Ka1 0.70930 Å

2 θ (°)	d (Å)	I	h	k	l	*	2 θ (°)	d (Å)	I	h	k	l	*	2 θ (°)	d (Å)	I	h	k	l	*
16.652	2.449170	72	1	1	1		33.672	1.224490	12	2	2	2		48.364	0.865770	12	4	2	2	
19.254	2.120710	100	2	0	0		39.077	1.060420	5	4	0	0		51.497	0.816367	7	5	1	1	
27.358	1.499670	45	2	2	0		42.750	0.973049	6	3	3	1								
32.199	1.278920	19	3	1	1		43.914	0.948481	14	4	2	0								

TiN0.9-04-004-2917

(θ)-rad	(2 θ) deg	d (Å)	I
0,374163	42,87591	2,44739	807
4,22E-07	4,84E-05	2119500	1000
0,639569	73,28925	1,49871	457
0,775209	88,83242	1,27811	192
0,819771	93,93889	1,22369	115
1,004832	115,1452	1,05975	45
1,167586	133,7955	0,972493	62
1,233646	141,3654	0,947869	119

d-spacings (10) - Ti N0.9 - 04-004-2917 (Stick, Fixed Slit Intensity) - Mo Ka1 0.70930 Å

2 θ (°)	d (Å)	I	h	k	l	*	2 θ (°)	d (Å)	I	h	k	l	*	2 θ (°)	d (Å)	I	h	k	l	*
16.664	2.447390	807	1	1	1		33.694	1.223690	115	2	2	2		48.393	0.865282	97	4	2	2	
19.265	2.119500	1000	2	0	0		39.103	1.059750	45	4	0	0		51.536	0.815796	57	5	1	1	
27.376	1.498710	457	2	2	0		42.776	0.972493	62	3	3	1								
32.220	1.278110	192	3	1	1		43.944	0.947869	119	4	2	0								

TiN0.98-03-065-4085

(θ)-rad	(2 θ) deg	d (Å)	I
0,373895	42,84523	2,44906	735
0,435372	49,88991	2,12095	1000
0,639059	73,23072	1,49974	451
0,774543	88,75607	1,27898	176
0,819037	93,85471	1,22453	114
1,003764	115,0229	1,06047	44
1,165985	133,612	0,973159	57
1,231699	141,1423	0,948518	118

d-spacings (10) - Ti N0.98 - 03-065-4085 (Stick, Fixed Slit Intensity) - Mo Ka1 0.70930 Å

2 θ (°)	d (Å)	I	h	k	l	*	2 θ (°)	d (Å)	I	h	k	l	*	2 θ (°)	d (Å)	I	h	k	l	*
16.653	2.449060	735	1	1	1		33.671	1.224530	114	2	2	2		48.358	0.865874	96	4	2	2	
19.252	2.120950	1000	2	0	0		39.075	1.060470	44	4	0	0		51.498	0.816354	53	5	1	1	
27.357	1.499740	451	2	2	0		42.745	0.973159	57	3	3	1								
32.197	1.278980	176	3	1	1		43.913	0.948518	118	4	2	0								

Table B 12: Peak lists for TiC_a. Top are the calculated peak lists for the Co detector used in this work, bottom is the peak lists for the Mo detector as given by the PDF's sourced from the XRD program from the XRD machine used. Bold peaks are the primary peaks.

TiC-00-001-1222

(θ)-rad	(2 θ) deg	d (Å)	I
0,367452	42,10693	2,49	75
0,429096	49,17077	2,15	100
0,62919	72,09987	1,52	50
0,758841	86,95675	1,3	25
0,797488	91,38544	1,25	10
0,975969	111,8378	1,08	3
1,127961	129,2548	0,99	5
1,173654	134,4909	0,97	9

d-spacings (10) - Ti C - 00-001-1222 (Stick, Fixed Slit Intensity) - Mo Ka1 0.70930 Å

2 θ (°)	d (Å)	I	h	k	l	*	2 θ (°)	d (Å)	I	h	k	l	*	2 θ (°)	d (Å)	I	h	k	l	*
16.38	2.49	75					32.96	1.25	10					47.53	0.88	5				
18.99	2.15	100					38.34	1.08	3					50.59	0.83	2				
26.99	1.52	50					41.98	0.99	5											
31.66	1.30	25					42.89	0.97	9											

TiC0.62-04-017-1603

(θ)-rad	(2 θ) deg	d (Å)	I
0,180634	20,6991	4,97907	19
0,297753	34,11996	3,04904	1
0,351184	40,24274	2,60023	2

0,367525	42,11526	2,48953	1000
0,427823	49,02491	2,156	789
0,469138	53,75922	1,97848	1
0,533018	61,07932	1,76037	1
0,569201	65,22561	1,65969	4

d-spacings (35) - Ti C0.62 - 04-017-1603 (Stick, Fixed Slit Intensity) - Mo K α 1 0.70930 Å

2 θ (°)	d (Å)	I	h	k	l	*	2 θ (°)	d (Å)	I	h	k	l	*
8.169	4.979070	19	1	1	1		26.904	1.524520	396	4	4	0	
13.359	3.049040	1	2	2	0		28.162	1.457720	1	5	3	1	
15.678	2.600230	2	3	1	1		28.570	1.437330	1	4	4	2	
16.380	2.489530	1000	2	2	2		30.151	1.363570	1	6	2	0	
18.936	2.156000	789	4	0	0		31.660	1.300120	244	6	2	2	
20.653	1.978480	1	3	3	1		33.107	1.244770	107	4	4	4	
23.245	1.760370	1	4	2	2		34.157	1.207600	2	5	5	1	
24.677	1.659690	4	5	1	1		35.846	1.152430	1	6	4	2	

Table B 13: Peak lists for TiC_xN_y. Top are the calculated peak lists for the Co detector used in this work, bottom is the peak lists for the Mo detector as given by the PDF's sourced from the XRD program from the XRD machine used. Bold peaks are the primary peaks.

TiNO.3CO.7-00-042-1489

(θ)-rad	(2 θ) deg	d (Å)	I
0,368896	42,27234	2,4807	59
0,429458	49,21226	2,1483	100
0,629525	72,13831	1,5193	46
0,76214	87,33479	1,2955	25
0,805366	92,28814	1,2405	12
0,983857	112,7418	1,0743	9
1,136813	130,2691	0,9859	10
1,196878	137,1521	0,9609	23

d-spacings (10) - C0.7 N0.3 Ti - 00-042-1489 (Stick, Fixed Slit Intensity) - Mo K α 1 0.70930 Å

2 θ (°)	d (Å)	I	h	k	l	*	2 θ (°)	d (Å)	I	h	k	l	*	2 θ (°)	d (Å)	I	h	k	l	*
16.439	2.4807	59	1	1	1		33.224	1.2405	12	2	2	2		47.694	0.8772	22	4	2	2	
19.004	2.1483	100	2	0	0		38.552	1.0743	9	4	0	0		50.788	0.8270	19	5	1	1	
26.998	1.5193	46	2	2	0		42.166	0.9859	10	3	3	1								
31.776	1.2955	25	3	1	1		43.318	0.9609	23	4	2	0								

TiNO.3CO.7-00-042-1488

(θ)-rad	(2 θ) deg	d (Å)	I
0,371786	42,60357	2,4623	46
0,432875	49,60387	2,1324	100
0,635092	72,77621	1,5078	40
0,769441	88,17145	1,2857	24
0,813346	93,20256	1,2311	12
0,995524	114,0786	1,0661	8
1,15366	132,1997	0,9784	9
1,2169	139,4465	0,9536	21

d-spacings (10) - C0.3 N0.7 Ti - 00-042-1488 (Stick, Fixed Slit Intensity) - Mo K α 1 0.70930 Å

2θ (°)	d (Å)	I	h	k	l	*	2θ (°)	d (Å)	I	h	k	l	*	2θ (°)	d (Å)	I	h	k	l	*
16.562	2.4623	46	1	1	1		33.486	1.2311	12	2	2	2		48.084	0.8705	20	4	2	2	
19.147	2.1324	100	2	0	0		38.861	1.0661	8	4	0	0		51.206	0.8207	14	5	1	1	
27.208	1.5078	40	2	2	0		42.505	0.9784	9	3	3	1								
32.024	1.2857	24	3	1	1		43.666	0.9536	21	4	2	0								

TiC0.2N0.8-01-076-2484

(θ)-rad	(2θ) deg	d (Å)	I
0,373793	42,83348	2,4497	741
0,435251	49,87609	2,1215	1000
0,638865	73,20858	1,50013	457
0,77429	88,72714	1,27931	183
0,818757	93,8227	1,22485	117
1,003349	114,9754	1,06075	45
1,165381	133,5428	0,973411	59
1,230965	141,0582	0,948764	123

d-spacings (10) - Ti C0.2 N0.8 - 01-076-2484 (Stick, Fixed Slit Intensity) - Mo K α 1 0.70930 Å

2θ (°)	d (Å)	I	h	k	l	*	2θ (°)	d (Å)	I	h	k	l	*	2θ (°)	d (Å)	I	h	k	l	*
16.648	2.449700	741	1	1	1		33.662	1.224850	117	2	2	2		48.344	0.866099	100	4	2	2	
19.247	2.121500	1000	2	0	0		39.065	1.060750	45	4	0	0		51.484	0.816566	55	5	1	1	
27.350	1.500130	457	2	2	0		42.734	0.973411	59	3	3	1								
32.189	1.279310	183	3	1	1		43.901	0.948764	123	4	2	0								

TiC0.51N0.12-01-085-1152

(θ)-rad	(2θ) deg	d (Å)	I
0,181151	20,75841	4,965	55
0,35029	40,14032	2,60659	3
0,366755	42,02701	2,49452	934
0,368615	42,24022	2,4825	330
0,392941	45,02772	2,33609	1
0,427464	48,98374	2,1577	1000
0,469028	53,74659	1,97891	2
0,516634	59,20187	1,8109	1
0,569641	65,27602	1,65855	11
0,571015	65,43351	1,655	3
0,625148	71,63672	1,5285	246
0,627776	71,93785	1,52296	237
0,658995	75,51523	1,46084	4
0,684908	78,48465	1,41401	1
0,691128	79,19746	1,40335	1
0,717832	82,2575	1,35994	1
0,745604	85,43997	1,31852	1

d-spacings (53) - Ti C0.51 N0.12 - 01-085-1152 (Stick, Fixed Slit Intensity) - Mo K α 1 0.70930 Å

2 θ (°)	d (Å)	I	h	k	l	*	2 θ (°)	d (Å)	I	h	k	l	*
8.192	4.965000	55	0	0	3		31.581	1.303290	89	0	2	2	
15.640	2.606590	3	0	1	1		31.624	1.301570	150	1	1	6	
16.347	2.494520	934	1	0	2		31.709	1.298150	72	0	1	10	
16.427	2.482500	330	0	0	6		33.039	1.247260	93	2	0	4	
17.464	2.336090	1	0	1	3		33.204	1.241250	29m	0	0	12	
18.921	2.157700	1000	0	1	4		33.204	1.241250	29m	1	1	7	
20.648	1.978910	2	1	0	5		34.097	1.209670	1	0	2	5	
22.588	1.810900	1	1	0	6		34.217	1.205550	5	1	0	11	
24.694	1.658550	11	0	1	7		35.351	1.168040	1	0	2	6	
24.748	1.655000	3	0	0	9		36.786	1.123980	2m	1	0	12	
26.833	1.528500	246	1	1	0		36.786	1.123980	2m	2	0	7	
26.932	1.522960	237	1	0	8		36.823	1.122870	2	1	1	9	
28.100	1.460840	4	1	1	3		38.383	1.078850	47	0	2	8	
29.051	1.414010	1	1	1	4		39.422	1.051520	2	0	1	13	
29.277	1.403350	1	0	1	9		41.614	0.998388	1	1	2	1	
30.233	1.359940	1	1	1	5		41.907	0.991727	45	2	1	2	
31.207	1.318520	1	2	0	1		42.008	0.989453	22	2	0	10	

TiC0.496N0.502-03-065-9875

(θ)-rad	(2 θ) deg	d (Å)	I
0,370768	42,48686	2,46875	821
0,431665	49,46521	2,138	1000
0,633149	72,55349	1,51179	453
0,76677	87,86536	1,28926	193
0,810548	92,88201	1,23437	116
0,991354	113,6008	1,069	45
1,14776	131,5236	0,980982	60
1,20977	138,6294	0,956143	120

d-spacings (10) - Ti C0.496 N0.502 - 03-065-9875 (Stick, Fixed Slit Intensity) - Mo K α 1 0.70930 Å

2 θ (°)	d (Å)	I	h	k	l	*	2 θ (°)	d (Å)	I	h	k	l	*	2 θ (°)	d (Å)	I	h	k	l	*
16.519	2.468750	821	1	1	1		33.394	1.234370	116	2	2	2		47.948	0.872835	97	4	2	2	
19.097	2.138000	1000	2	0	0		38.751	1.069000	45	4	0	0		51.058	0.822917	55	5	1	1	
27.135	1.511790	453	2	2	0		42.388	0.980982	60	3	3	1								
31.934	1.289260	193	3	1	1		43.544	0.956143	120	4	2	0								

Table B 14: Peak lists for SiC. Top are the calculated peak lists for the Co detector used in this work, bottom is the peak lists for the Mo detector as given by the PDF's sourced from the XRD program from the XRD machine used. Bold peaks are the primary peaks.

SiC-00-029-1131

(θ)-rad	(2 θ) deg	d (Å)	I
0,348282	39,91023	2,621	40
0,364235	41,73825	2,511	100
0,390139	44,70661	2,352	20
0,424051	48,59264	2,174	10
0,621163	71,18001	1,537	35
0,682612	78,22153	1,418	15
0,750914	86,04843	1,311	40
0,769215	88,14556	1,286	15
0,792607	90,82603	1,256	7
0,966517	110,7547	1,087	15
1,03224	118,286	1,042	7
1,099414	125,9835	1,004	15

d-spacings (17) - Si C - 00-029-1131 (Stick, Fixed Slit Intensity) - Mo K α 1 0.70930 Å

2θ (°)	d (Å)	I	h	k	l	*	2θ (°)	d (Å)	I	h	k	l	*	2θ (°)	d (Å)	I	h	k	l	*
15.553	2.6210	40	1	0	1		31.390	1.3110	40	1	1	6		42.766	0.9727	15	1	1	12	
16.239	2.5110	100	1	0	2		32.017	1.2860	15	2	0	3		47.101	0.8876	15	2	1	8	
17.345	2.3520	20	1	0	3		32.803	1.2560	7	0	0	12		48.565	0.8624	7	2	1	9	
18.778	2.1740	10	1	0	4		38.084	1.0870	15	2	0	8		50.139	0.8370	9	2	1	10	
26.681	1.5370	35	1	1	0		39.797	1.0420	7	2	0	9		52.483	0.8021	9	2	0	15	
28.968	1.4180	15	1	0	9		41.371	1.0040	15	2	1	1								

SiC-00-031-1232

(θ)-rad	(2θ) deg	d (Å)	I
0,347315	39,79942	2,628	35
0,363477	41,65145	2,516	100
0,389267	44,60666	2,357	35
0,423015	48,47397	2,179	14
0,463866	53,15515	1,9993	5
0,562573	64,46608	1,6771	6
0,619445	70,98319	1,5407	45m
0,619445	70,98319	1,5407	45m
0,681581	78,10347	1,4198	12
0,738278	84,60047	1,3291	2

d-spacings (28) - Si C - 00-031-1232 (Stick, Fixed Slit Intensity) - Mo K α 1 0.70930 Å

2θ (°)	d (Å)	I	h	k	l	*	2θ (°)	d (Å)	I	h	k	l	*	2θ (°)	d (Å)	I	h	k	l	*
15.512	2.6280	35	1	0	1		31.319	1.3139	28m	1	1	6		42.693	0.9743	3	1	1	12	
16.207	2.5160	100	1	0	2		31.319	1.3139	28m	2	0	2		42.693	0.9743	3	2	1	4	
17.308	2.3570	35	1	0	3		31.922	1.2897	4	2	0	3		44.262	0.9414	2	1	0	15	
18.734	2.1790	14	1	0	4		32.749	1.2580	3m	0	0	12		46.995	0.8895	6m	2	1	8	
20.435	1.9993	5	1	0	5		32.749	1.2580	3m	2	0	4		46.995	0.8895	6m	3	0	0	
24.417	1.6771	6	1	0	7		37.997	1.0894	3	2	0	8		48.451	0.8643	3	2	1	9	
26.616	1.5407	45m	1	0	8		39.714	1.0441	3	2	0	9		50.037	0.8386	5m	2	1	10	
26.616	1.5407	45m	1	1	0		41.553	0.9998	5m	2	0	10		50.037	0.8386	5m	3	0	6	
28.930	1.4198	12	1	0	9		41.553	0.9998	5m	2	1	2								
30.952	1.3291	2	2	0	1		42.028	0.9890	2	2	1	3								

SiC-01-072-9272

(θ)-rad	(2θ) deg	d (Å)	I
0,072376	8,293635	12,37	1
0,145134	16,63112	6,185	1
0,218676	25,05844	4,12333	1
0,293443	33,6261	3,0925	1
0,347859	39,86171	2,62406	145
0,35594	40,78769	2,56694	588
0,369943	42,39234	2,474	600
0,379329	43,46791	2,41564	1000
0,415951	47,66453	2,21379	375
0,463484	53,11132	2,00083	92
0,520049	59,59319	1,80009	45
0,584487	66,97731	1,62115	114
0,631594	72,37539	1,515	435
0,656403	75,21823	1,46575	277
0,708656	81,20603	1,37444	1

d-spacings (50) - Si C - 01-072-9272 (Stick, Fixed Slit Intensity) - Mo K α 1 0.70930 Å

2θ (°)	d (Å)	I	h	k	l	*	2θ (°)	d (Å)	I	h	k	l	*
3.286	12.370000	1	0	0	1		30.879	1.332170	142	1	0	8	
6.574	6.185000	1	0	0	2		31.365	1.312030	10	2	0	0	
9.868	4.123330	1	0	0	3		31.546	1.304710	42	2	0	1	
13.170	3.092500	1	0	0	4		31.864	1.292000	289	1	1	5	
15.535	2.624060	145	1	0	0		32.082	1.283470	90	2	0	2	
15.883	2.566940	588	0	1	1		32.958	1.250260	50	0	2	3	
16.484	2.474000	600	0	0	5		33.321	1.237000	20	0	0	10	
16.885	2.415640	1000	0	1	2		33.870	1.217540	17	1	0	9	
18.437	2.213790	375	1	0	3		34.151	1.207820	14	0	2	4	
20.419	2.000830	92	1	0	4		35.632	1.159120	7	2	0	5	
22.725	1.800090	45	0	1	5		36.958	1.118910	3	0	1	10	
25.273	1.621150	114	0	1	6		37.375	1.106890	22	2	0	6	
27.076	1.515000	435	1	1	0		39.348	1.053420	67	2	0	7	
28.004	1.465750	277	0	1	7		40.133	1.033630	9	0	1	11	
29.907	1.374440	1	0	0	9		41.526	1.000410	44	0	2	8	

Table B 15: Peak lists for TiB₂. Top are the calculated peak lists for the Co detector used in this work, bottom is the peak lists for the Mo detector as given by the PDF's sourced from the XRD program from the XRD machine used. Bold peaks are the primary peaks.

TiB₂-00-035-0741

(θ)-rad	(2 θ) deg	d (Å)	I
0,280646	32,15961	3,22954	22
0,347772	39,85174	2,62469	55
0,454621	52,09577	2,03703	100
0,587194	67,28751	1,61455	12
0,63143	72,35658	1,51534	27
0,70822	81,15603	1,37514	16
0,71037	81,40238	1,3717	8

d-spacings (21) - Ti B2 - 00-035-0741 (Stick, Fixed Slit Intensity) - Mo Ka1 0.70930 Å

2 θ (°)	d (Å)	I	h	k	l	*	2 θ (°)	d (Å)	I	h	k	l	*	2 θ (°)	d (Å)	I	h	k	l	*
12.609	3.229540	22	0	0	1		31.362	1.312170	7	2	0	0		43.927	0.948214	13	2	1	1	
15.531	2.624690	55	1	0	0		33.925	1.215630	16	2	0	1		47.675	0.877530	3	1	1	3	
20.053	2.037030	100	1	0	1		37.444	1.104900	14	1	1	2		47.838	0.874717	5	3	0	0	
25.378	1.614550	12	0	0	2		38.467	1.076600	<1	0	0	3		49.618	0.845226	7	2	1	2	
27.070	1.515340	27	1	1	0		40.763	1.018330	5	2	0	2		49.671	0.844369	3	3	0	1	
29.891	1.375140	16	1	0	2		41.723	0.995894	8	1	0	3		50.442	0.832293	5	2	0	3	
29.968	1.371700	18	1	1	1		41.898	0.991926	6	2	1	0		52.113	0.807390	1	0	0	4	

TiB₂-03-065-1073

(θ)-rad	(2 θ) deg	d (Å)	I
0,280694	32,16513	3,229	238
0,347859	39,86171	2,62406	637
0,45477	52,11282	2,03641	1000
0,587215	67,28987	1,6145	81
0,631594	72,37539	1,515	183
0,708264	81,16103	1,37507	104
0,71047	81,41388	1,37154	120

d-spacings (21) - B2 Ti - 03-065-1073 (Stick, Fixed Slit Intensity) - Mo Ka1 0.70930 Å

2 θ (°)	d (Å)	I	h	k	l	*	2 θ (°)	d (Å)	I	h	k	l	*	2 θ (°)	d (Å)	I	h	k	l	*
12.611	3.229000	238	0	0	1		31.365	1.312030	40	2	0	0		43.934	0.948085	77	2	1	1	
15.535	2.624060	637	1	0	0		33.928	1.215520	104	2	0	1		47.681	0.877437	11	1	1	3	
20.059	2.036410	1000	1	0	1		37.449	1.104770	87	1	1	2		47.840	0.874686	22	3	0	0	
25.379	1.614500	81	0	0	2		38.477	1.076330	4	0	0	3		49.627	0.845081	32	2	1	2	
27.076	1.515000	183	1	1	0		40.768	1.018210	26	2	0	2		49.678	0.844259	13	3	0	1	
29.893	1.375070	104	1	0	2		41.727	0.995817	45	1	0	3		50.452	0.832148	30	2	0	3	
29.971	1.371540	120	1	1	1		41.904	0.991800	25	2	1	0		52.122	0.807250	6	0	0	4	

Table B 16: Peak lists for AlN. Top are the calculated peak lists for the Co detector used in this work, bottom is the peak lists for the Mo detector as given by the PDF's sourced from the XRD program from the XRD machine used. Bold peaks are the primary peaks.

AlN-00-0250-1133

(θ)-rad	(2 θ) deg	d (Å)	I
0,338331	38,76983	2,695	100
0,367452	42,10693	2,49	60
0,386846	44,32925	2,371	80
0,511021	58,55866	1,829	25
0,6111	70,02686	1,559	40
0,685318	78,53168	1,4133	30
0,725922	83,18458	1,3475	5
0,744989	85,36941	1,3194	25
0,758331	86,89829	1,3007	10

d-spacings (26) - Al N - 00-025-1133 (Stick, Fixed Slit Intensity) - Mo Ka1 0.70930 Å

2 θ (°)	d (Å)	I	h	k	l	*	2 θ (°)	d (Å)	I	h	k	l	*	2 θ (°)	d (Å)	I	h	k	l	*
15.124	2.6950	100	1	0	0		33.101	1.2450	1	0	0	4		45.652	0.9142	<1	2	0	4	
16.377	2.4900	60	0	0	2		34.829	1.1850	4	2	0	2		46.513	0.8982	4	3	0	0	
17.205	2.3710	80	1	0	1		36.579	1.1301	1	1	0	4		48.232	0.8680	10	2	1	3	
22.361	1.8290	25	1	0	2		39.634	1.0461	9	2	0	3		49.644	0.8448	5	3	0	2	
26.352	1.5559	40	1	1	0		40.760	1.0184	3	2	1	0		50.604	0.8298	1	0	0	6	
29.066	1.4133	30	1	0	3		41.640	0.9978	7	2	1	1		52.574	0.8008	5	2	0	5	
30.519	1.3475	5	2	0	0		42.799	0.9720	2	1	1	4		53.124	0.7931	1	1	0	6	
31.185	1.3194	25	1	1	2		44.208	0.9425	3	2	1	2		53.481	0.7882	<1	2	1	4	
31.645	1.3007	10	2	0	1		44.632	0.9340	6	1	0	5								

AlN-00-003-5900

(θ)-rad	(2 θ) deg	d (Å)	I
0,338547	38,79468	2,69334	1000
0,367452	42,10693	2,49	617
0,387179	44,36748	2,36906	934
0,511217	58,58115	1,82836	314
0,612903	70,2335	1,555	538
0,685405	78,54163	1,41315	452
0,72647	83,24729	1,34667	73
0,745317	85,40708	1,31893	345

04-003-5900

d-spacings (24) - Al N - 04-003-5900 (Stick, Fixed Slit Intensity) - Mo Ka1 0.70930 Å

2 θ (°)	d (Å)	I	h	k	l	*	2 θ (°)	d (Å)	I	h	k	l	*	2 θ (°)	d (Å)	I	h	k	l	*
15.133	2.693340	1000	1	0	0		31.663	1.299980	124	2	0	1		44.219	0.942280	50	2	1	2	
16.377	2.490000	617	0	0	2		33.101	1.245000	17	0	0	4		44.623	0.934171	104	1	0	5	
17.219	2.369060	934	1	0	1		34.843	1.184530	56	2	0	2		45.653	0.914180	9	2	0	4	
22.369	1.828360	314	1	0	2		36.579	1.130100	17	1	0	4		46.536	0.897780	69	3	0	0	
26.367	1.555000	538	1	1	0		39.646	1.045810	132	2	0	3		48.243	0.867804	165	2	1	3	
29.069	1.413150	452	1	0	3		40.777	1.017990	47	2	1	0		49.659	0.844560	82	3	0	2	
30.538	1.346670	73	2	0	0		41.659	0.997362	94	2	1	1		50.591	0.830000	10	0	0	6	
31.197	1.318930	345	1	1	2		42.804	0.971877	42	1	1	4		52.576	0.800779	84	2	0	5	

Aug 17, 2020 2:06 PM (new

Table B 17: Peak lists for TiAl. Top are the calculated peak lists for the Co detector used in this work, bottom is the peak lists for the Mo detector as given by the PDF's sourced from the XRD program from the XRD machine used. Bold peaks are the primary peaks.

Al1.1Ti0.9-00-055-0252			
(θ)-rad	(2 θ) deg	d (Å)	I
0,22088	25,31093	4,08286	9
0,322732	36,98237	2,82037	5
0,39578	45,353	2,32021	100
0,453807	52,00246	2,04043	16
0,465091	53,29546	1,99442	30
0,522671	59,89369	1,79189	3
0,571793	65,5226	1,653	2
0,677929	77,68496	1,42623	24
0,68714	78,74043	1,41016	10
0,717588	82,22955	1,36032	<1
0,735714	84,30667	1,33286	1
0,788321	90,33491	1,26134	1
0,818443	93,78671	1,22521	14
0,83651	95,85702	1,20503	28

d-spacings (14) - Al1.1 Ti0.9 - 00-055-0252 (Stick, Fixed Slit Intensity) - Mo K α 1 0.70930 Å

2 θ (°)	d (Å)	I	h	k	l	*	2 θ (°)	d (Å)	I	h	k	l	*	2 θ (°)	d (Å)	I	h	k	l	*
9.966	4.08286	9	0	0	1		22.831	1.79189	3	2	0	1		30.863	1.33286	1	2	2	1	
14.448	2.82037	5	1	1	0		24.778	1.65300	2	1	1	2		32.660	1.26134	1	3	1	0	
17.585	2.32021	100	1	1	1		28.797	1.42623	24	2	0	2		33.651	1.22521	14	1	1	3	
20.019	2.04043	16	0	0	2		29.132	1.41016	10	2	2	0		34.232	1.20503	28	3	1	1	
20.486	1.99442	30	2	0	0		30.224	1.36032	<1	0	0	3								

TiAl-01-074-4580

(θ)-rad	(2 θ) deg	d (Å)	I
0,222194	25,46156	4,0591	97
0,320737	36,75378	2,8373	71
0,394829	45,2441	2,3255	1000
0,456424	52,30228	2,02955	156
0,462129	52,95608	2,00627	295
0,520533	59,64865	1,79857	27
0,572686	65,62493	1,65071	18
0,677602	77,64746	1,42681	147
0,682239	78,17885	1,41865	72
0,722301	82,76954	1,35303	2
0,73143	83,81575	1,33921	6
0,782424	89,65922	1,2688	5

d-spacings (34) - Ti Al - 01-074-4580 (Stick, Fixed Slit Intensity) - Mo K α 1 0.70930 Å

2 θ (°)	d (Å)	I	h	k	l	*	2 θ (°)	d (Å)	I	h	k	l	*	2 θ (°)	d (Å)	I	h	k	l	*
10.025	4.059100	97	0	0	1		33.763	1.221280	72	1	0	3		45.291	0.921095	24	3	0	1	
14.361	2.837300	71	1	0	0		34.056	1.211080	138	2	1	1		46.114	0.905531	23	1	1	4	
17.544	2.325500	1000	1	0	1		35.517	1.162750	57	2	0	2		46.453	0.899286	23	2	2	2	
20.127	2.029550	156	0	0	2		36.861	1.121770	3	1	1	3		46.566	0.897233	22	3	1	0	
20.363	2.006270	295	1	1	0		38.492	1.075910	5	2	1	2		47.759	0.876086	3	3	1	1	
22.745	1.798570	27	1	1	1		40.912	1.014780	8	0	0	4		48.875	0.857257	1	3	0	2	
24.813	1.650710	18	1	0	2		41.408	1.003140	15	2	2	0		50.896	0.825356	19	2	0	4	
28.785	1.426810	147	1	1	2		42.473	0.979114	2	2	0	3		51.211	0.820619	37	3	1	2	
28.954	1.418650	72	2	0	0		42.714	0.973839	2	2	2	1		51.807	0.811820	1	0	0	5	
30.391	1.353030	2	0	0	3		43.575	0.955501	2	1	0	4		52.222	0.805824	1	2	2	3	
30.713	1.339210	6	2	0	1		44.047	0.945767	1	3	0	0								
32.461	1.268880	5	2	1	0		45.061	0.925554	47	2	1	3								

Appendix C: Supplementary Density data

Table C 1: Densities and open porosities of Ti₂AlC-cBN (20 vol.%,10 µm) samples sintered at different temperatures and dwell times.

1 minute dwell time		
Temperature (°C)	Density (g/cm ³)	open porosity (%)
1150	3,86±0,00	0,09 ±0,05
1250	3,99±0,00	1,52±0,05
1300	4,21±0,00	0,16±0,07
1400	4,18±0,01	0,76±0,08
1500	4,25±0,01	0,79±0,33
1250°C sintering temperature		
Time (minute)	Density (g/cm ³)	open porosity (%)
1	3,99±0,00	1,52±0,05
5	3,46±0,03	4,74±0,85
10	3,49±0,00	2,84±0,38

Table C 2: Densities and open porosities of Ti_3AlC_2 -cBN (20 vol.%, 10 μm) samples sintered at different temperatures and dwell times.

Temperature (°C)	Density (g/cm ³)	open porosity (%)
1150	3,21±0,17	12,13±0,63
1250	3,21±0,17	12,13±0,63
1300	3,21±0,17	12,13±0,63
1400	4,12±0,17	1,40±0,06
1500	4,07±0,10	1,32±0,42

Temperature (°C)	1250		1300	
Time (min)	Density (g/cm ³)	open porosity (%)	Density (g/cm ³)	open porosity (%)
1	3,21±0,17	12,13±0,63	3,21±0,17	12,13±0,63
5	3,22±0,01	12,03±0,05	3,22±0,01	12,03±0,05
10	3,24±0,10	11,91±0,49	3,24±0,10	11,91±0,49

Table C 3: Densities and open porosities of Ti_3SiC_2 -cBN (20 vol.%, 10 μm) samples sintered at different temperatures and dwell times.

Temperature (°C)	1150		1250		1300	
Time (min)	Density (g/cm ³)	open porosity (%)	Density (g/cm ³)	open porosity (%)	Density (g/cm ³)	open porosity (%)
1	3,49±0,06	8,57±1,00	3,73±0,09	2,10±0,87	3,41±0,04	11,73±1,36
5	3,65±0,07	6,44±0,57	3,80±0,12	2,60±0,77	3,41±0,00	0,14±0,04
10	3,62±0,02	7,92±1,03	3,78±0,02	2,66±0,36	3,70±0,00	0,10±0,08
15	3,58±0,03	3,52±0,82				

Temperature (°C)	Density (g/cm ³)	open porosity (%)
1150	3,49±0,06	8,57±1,00
1250	3,73±0,09	2,10±0,87
1300	3,41±0,04	11,7±1,36
1400	3,58±0,13	4,15±1,19
1500	4,03±0,10	0,96±0,33
1600	3,73±0,12	1,65±0,73
1700	4,10±0,18	±1,75±0,08

Table C 4: Densities and open porosities of Ti_2AlC -cBN (20 vol.%, 100 μm) samples sintered at different temperatures and dwell times.

Temperature (°C)	1300		1250		1150	
Dwell time (min)	Density (g/cm ³)	open porosity (%)	Density (g/cm ³)	open porosity (%)	Density (g/cm ³)	open porosity (%)
1	3,61±0,07	2,81±0,72	3,55±0,01	2,22±0,32	3,34±0,10	6,91±0,39
5	3,64±0,01	2,64±0,46	3,54±0,03	4,25±0,53	3,47±0,05	5,48±0,73
10	3,66±0,02	1,83±0,32	3,60±0,01	2,32±0,45		

Table C 5: Densities and open porosities of Ti_3AlC_2 -cBN (20 vol.%, 100 μm) samples sintered at different temperatures and dwell times.

Temperature (°C)	1300		1250	
Dwell time (min)	Density (g/cm ³)	open porosity (%)	Density (g/cm ³)	open porosity (%)
1	3,61±0,07	2,81±0,72	3,55±0,01	2,22±0,32
5	3,64±0,01	2,64±0,46	3,54±0,03	4,25±0,53
10	3,66±0,02	1,83±0,32	3,60±0,01	2,32±0,45

Table C 6: Densities and open porosities of Ti_3SiC_2 -cBN (20 vol.%, 100 μm) samples sintered at different temperatures and dwell times.

Temperature (°C)	1300		1250	
Dwell time (min)	Density (g/cm ³)	open porosity (%)	Density (g/cm ³)	open porosity (%)
1	4,04±0,13	1,87±0,39	4,30±0,46	1,55±0,17
5	4,35±0,41	1,54±0,14	4,04±0,21	1,08±0,28
10	3,36±0,07	5,75±1,50	3,94±0,09	1,71±0,52

Table C 7: Densities and open porosities of Ti₂AlC-cBN (40 vol.%,100 µm) samples sintered at different temperatures and dwell times.

Dwell time (min)	5 min		10 min	
Temperature (°C)	Density (g/cm ³)	open porosity (%)	Density (g/cm ³)	open porosity (%)
1250	3,48±0,04	4,39±0,62	3,48±0,03	5,22±0,51
1300	3,50±0,01	3,40±0,72	3,47±0,02	4,62±0,51
1350	3,82±0,02	2,06±0,47	3,87±0,02	1,66±0,44

Table C 8: Densities and open porosities of Ti₃AlC₂-cBN (40 vol.%,100 µm) samples sintered at different temperatures and dwell times.

Dwell time (min)	5 min		10 min	
Temperature (°C)	Density (g/cm ³)	open porosity (%)	Density (g/cm ³)	open porosity (%)
1250	3,58±0,04	2,35±0,98	3,56±0,03	7,38±0,40
1300	3,77±0,31	5,57±1,14	3,65±0,10	5,36±1,36
1350	3,80±0,05	1,88±0,62	3,73±0,14	2,03±0,67

Table C 9: Densities and open porosities of Ti₃SiC₂-cBN (40 vol.%, 100 µm) samples sintered at different temperatures and dwell times.

Dwell time (min)	5 min		10 min	
Temperature (°C)	Density (g/cm ³)	open porosity (%)	Density (g/cm ³)	open porosity (%)
1250		3,37±0,05	3,77±0,01	3,31±0,04
1300	4,07±0,01	1,23±0,07	4,08±0,00	1,03±0,04
1350	4,14±0,00	0,51±0,06	4,04±0,01	0,95±0,13

Appendix D: Supplementary data for Rietveld analysis of samples

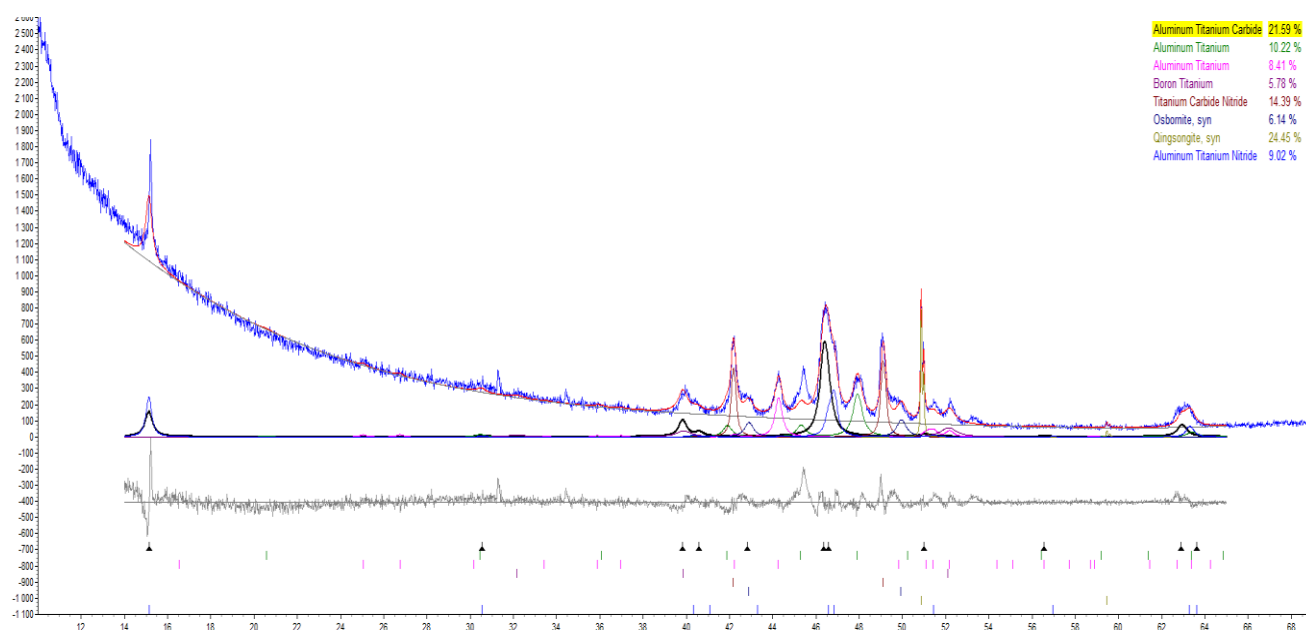


Figure D1: Rietveld analysis, of Ti_2AlC -cBN (20 vol.%, 10 μm) samples sintered at 1250°C for 1 minute.

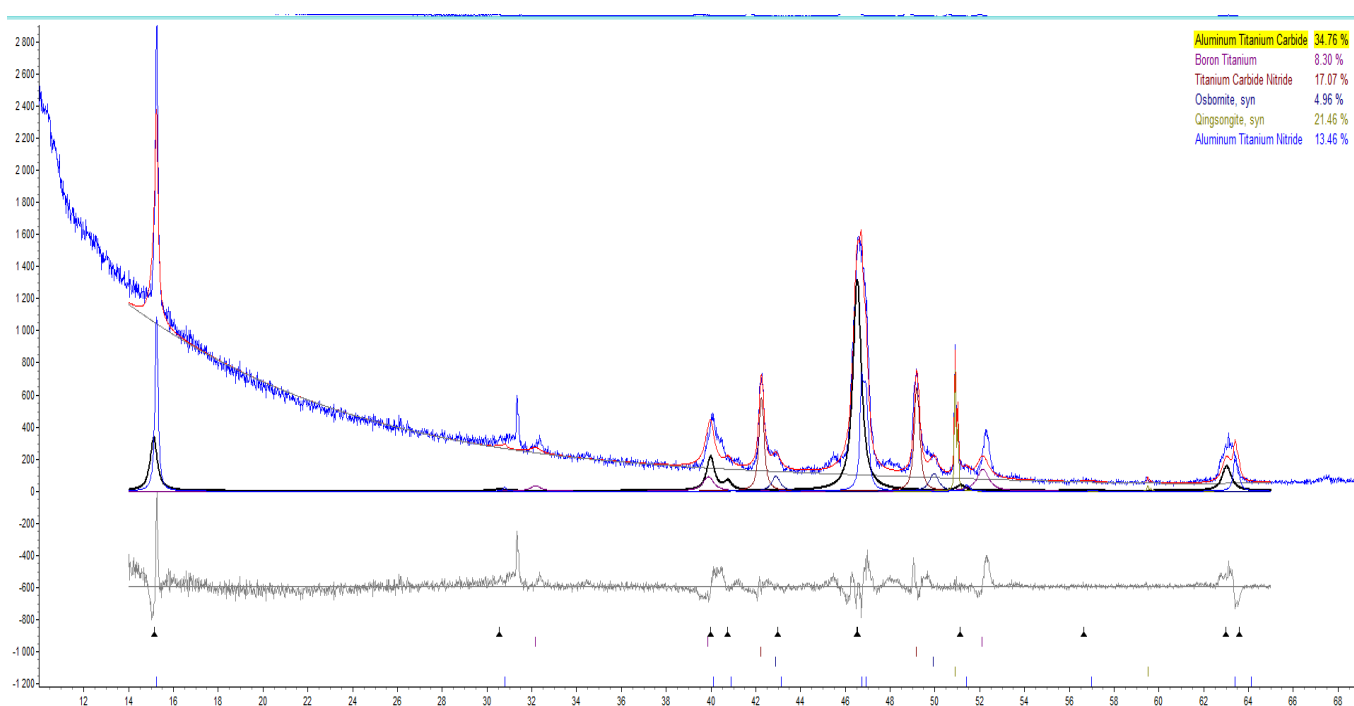


Figure D2: Rietveld analysis, of Ti_2AlC -cBN (20 vol.%, 10 μm) samples sintered at 1250°C for 5 minutes.

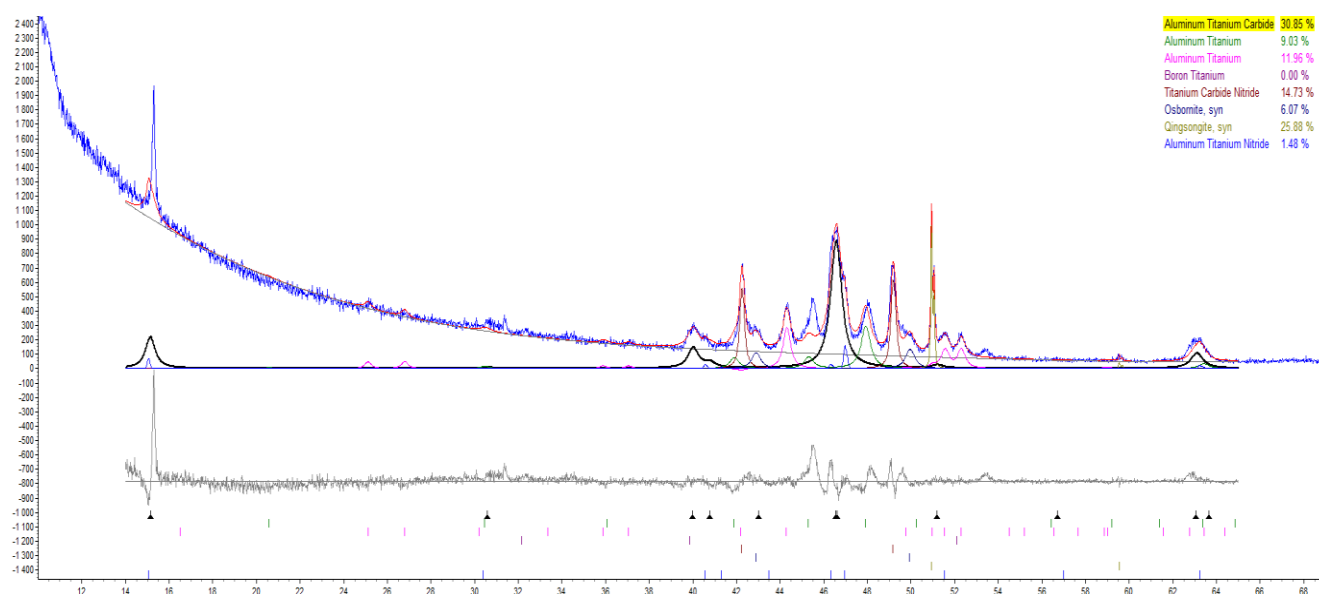


Figure D3: Rietveld analysis, of Ti_2AlC -cBN (20 vol.%, 10 μm) samples sintered at 1250°C for 10 minutes.

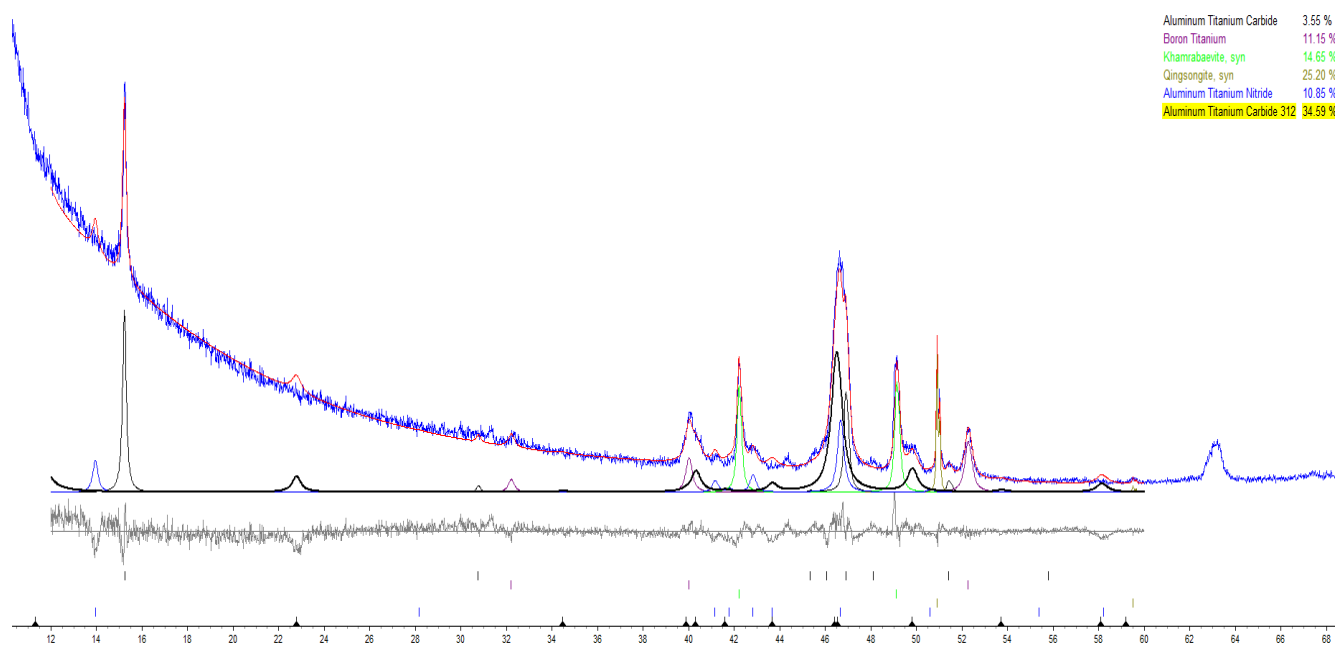


Figure D4: Rietveld analysis, of Ti_3AlC_2 -cBN (20 vol.%, 10 μm) samples sintered at 1300°C for 1 minute.

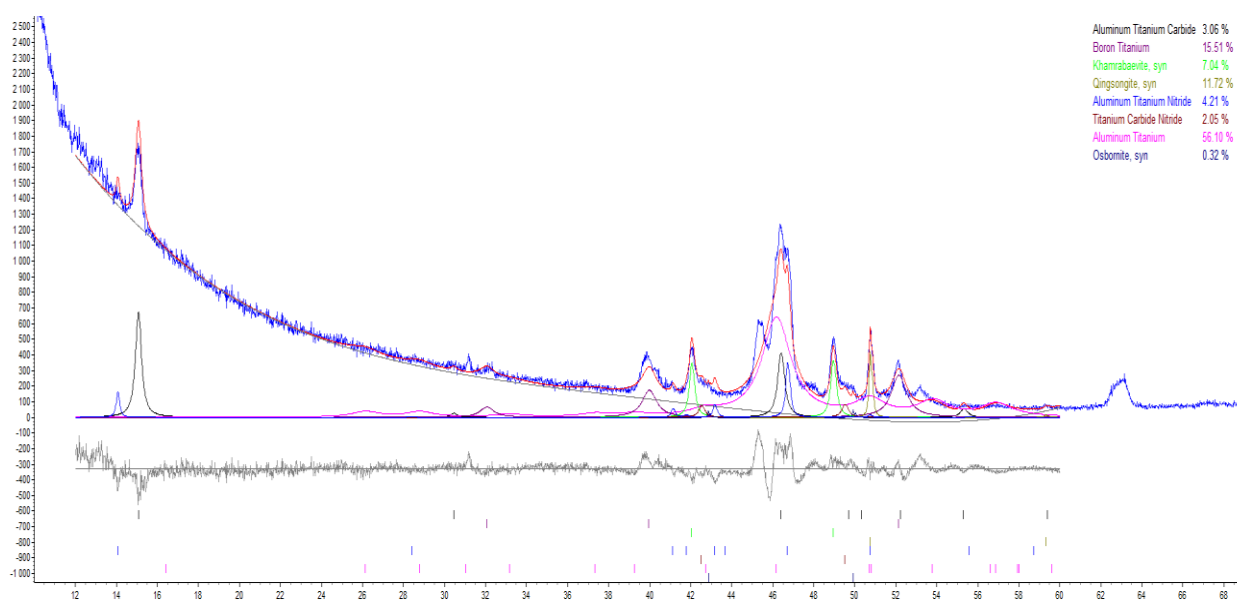


Figure D5: Rietveld analysis, of Ti_3AlC_2 -cBN (20 vol.%, 10 μm) samples sintered at 1300°C for 5 minutes

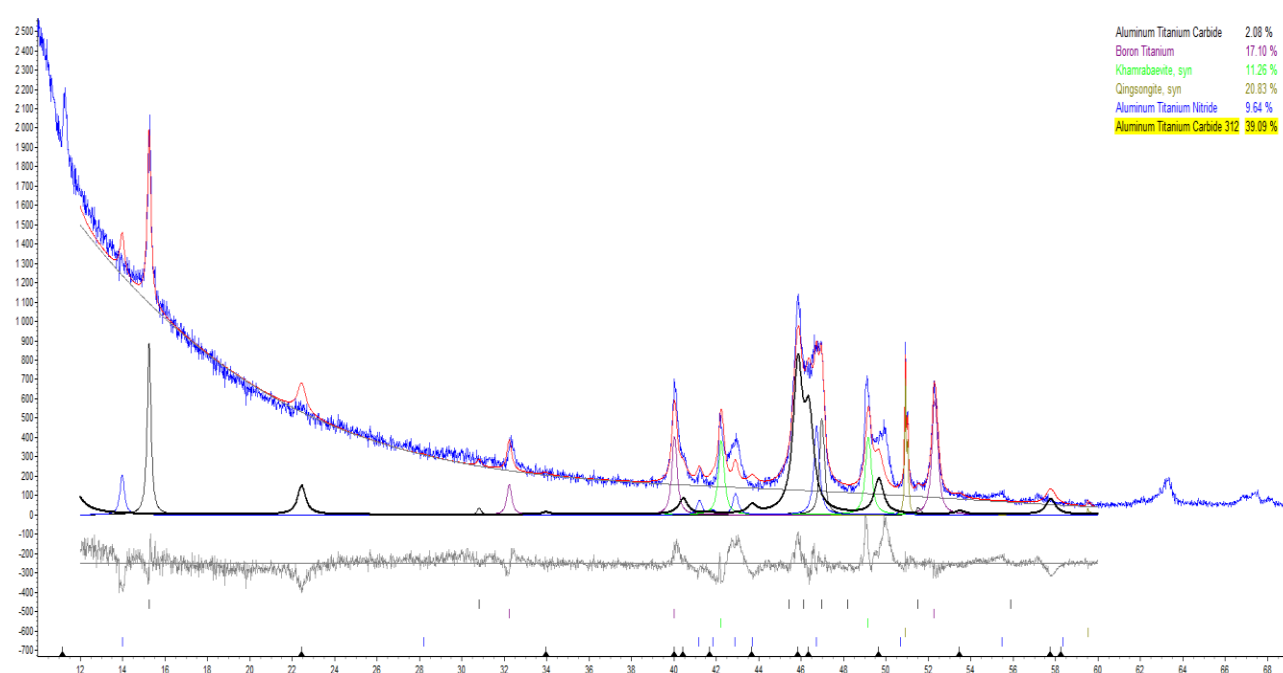


Figure D6: Rietveld analysis, of Ti_3AlC_2 -cBN (20 vol.%, 10 μm) samples sintered at 1300°C for 10 minutes.

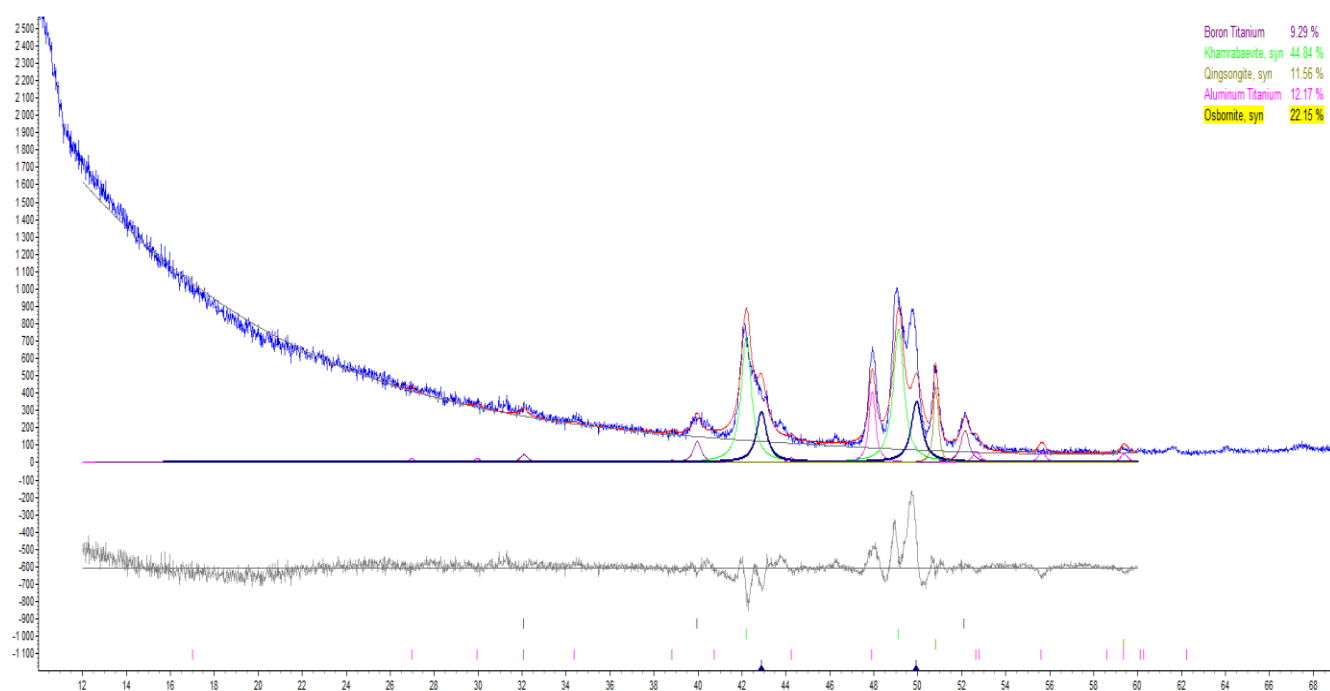


Figure D7: Rietveld analysis, of Ti_2AlC -cBN (20 vol.%, 100 μm) samples sintered at 1250°C for 1 minute.

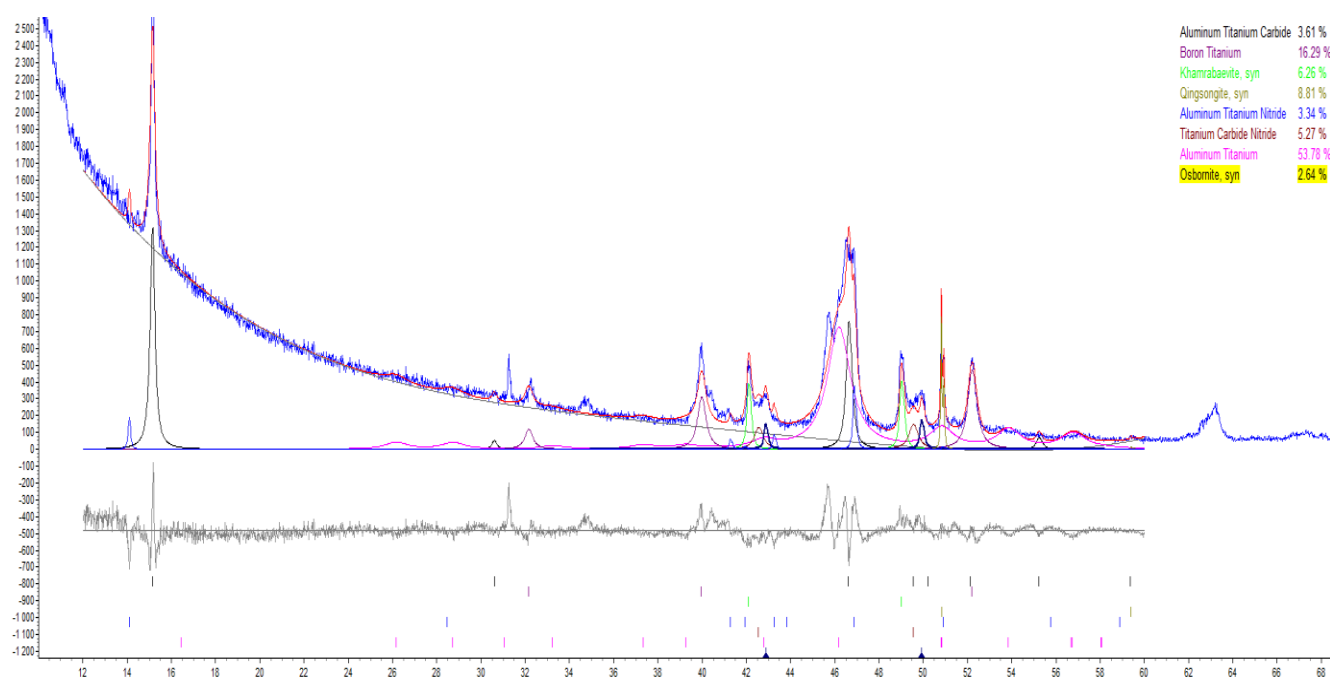


Figure D8: Rietveld analysis, of Ti_2AlC -cBN (20 vol.%, 100 μm) samples sintered at 1250°C for 5 minutes.

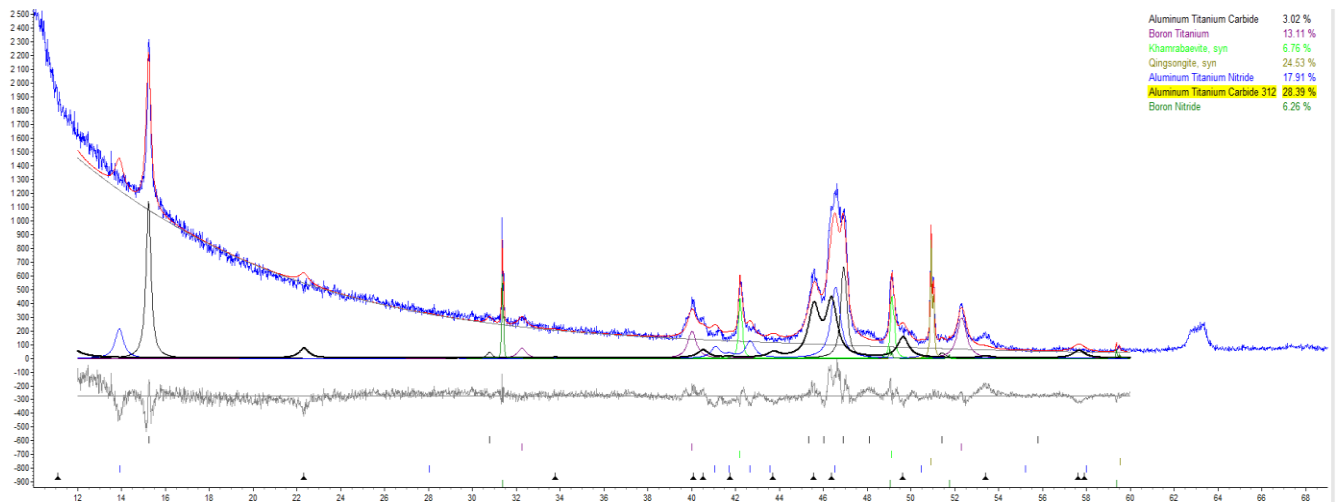


Figure D9: Rietveld analysis, of Ti_2AlC -cBN (20 vol.%, 100 μm) samples sintered at 1250°C for 10 minutes.

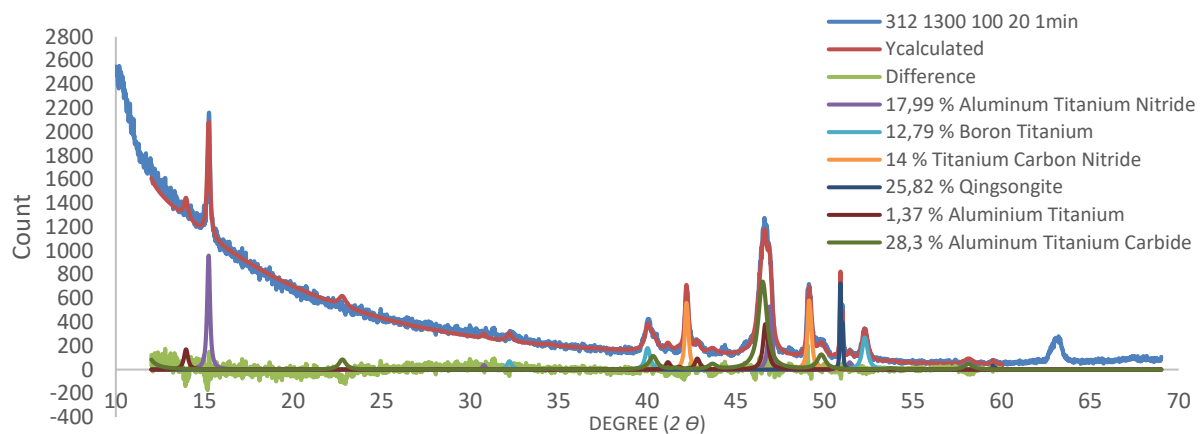


Figure D10: Rietveld analysis, of Ti_3AlC_2 -cBN (20 vol.%, 100 μm) samples sintered at 1300°C for 1 minute.

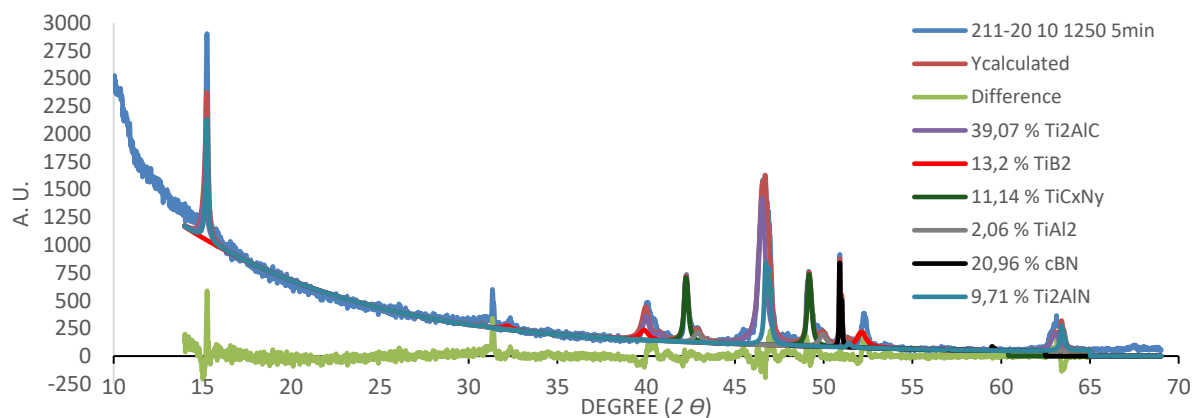


Figure D11: Rietveld analysis, of Ti_3AlC_2 -cBN (20 vol.%,100 μm) samples sintered at 1300°C for 5 minutes.

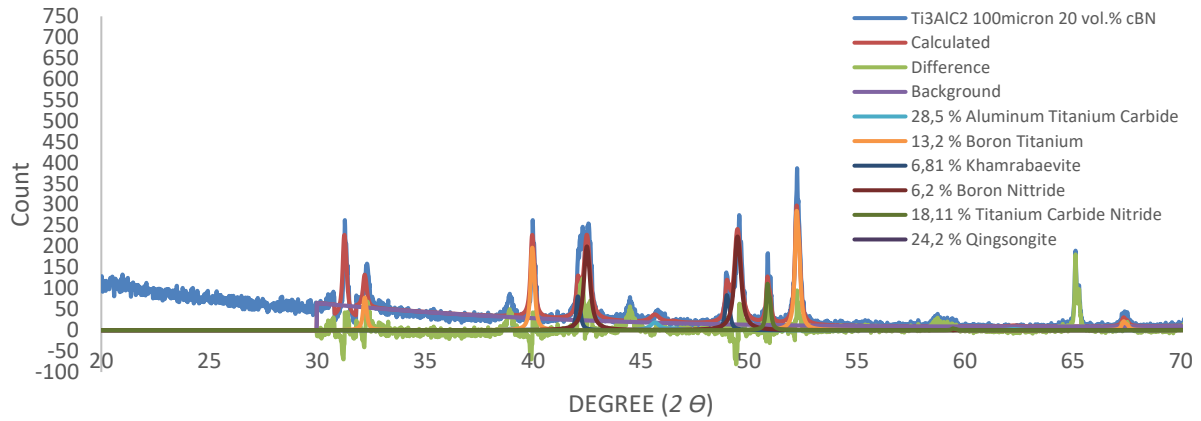


Figure D12: Rietveld analysis, of Ti_3AlC_2 -cBN (20 vol.%,100 μm) samples sintered at 1300°C for 10 minutes.

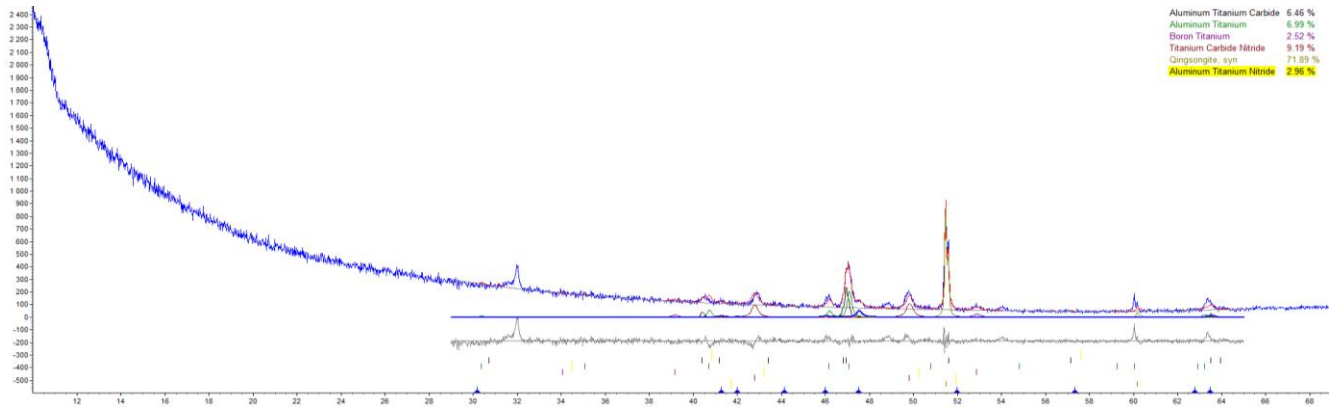


Figure D13: Rietveld analysis, of Ti_2AlC -cBN (40 vol.%,100 μm) samples sintered at 1250°C for 5 minutes.

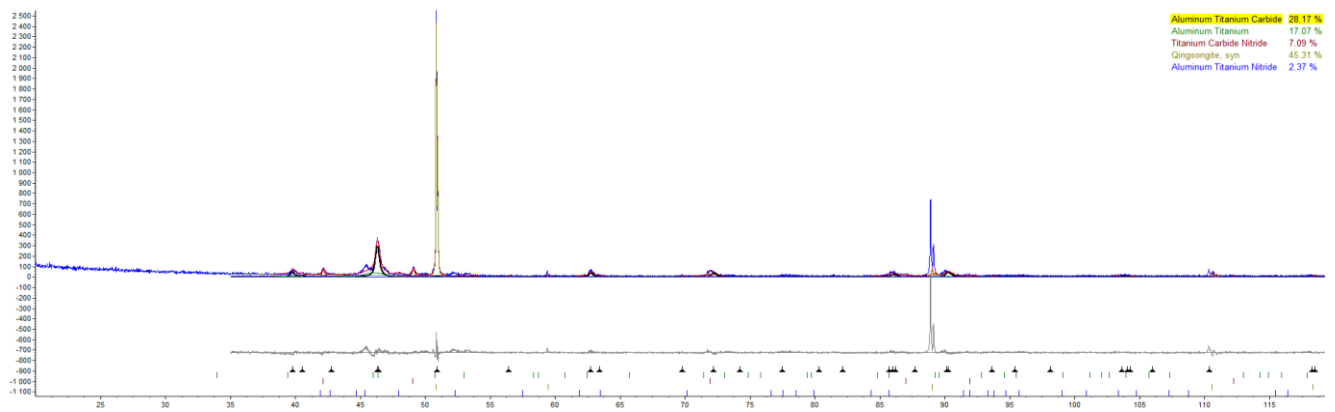


Figure D14: Rietveld analysis, of Ti_2AlC -cBN (40 vol.%,100 μm) samples sintered at 1300°C for 5 minutes.

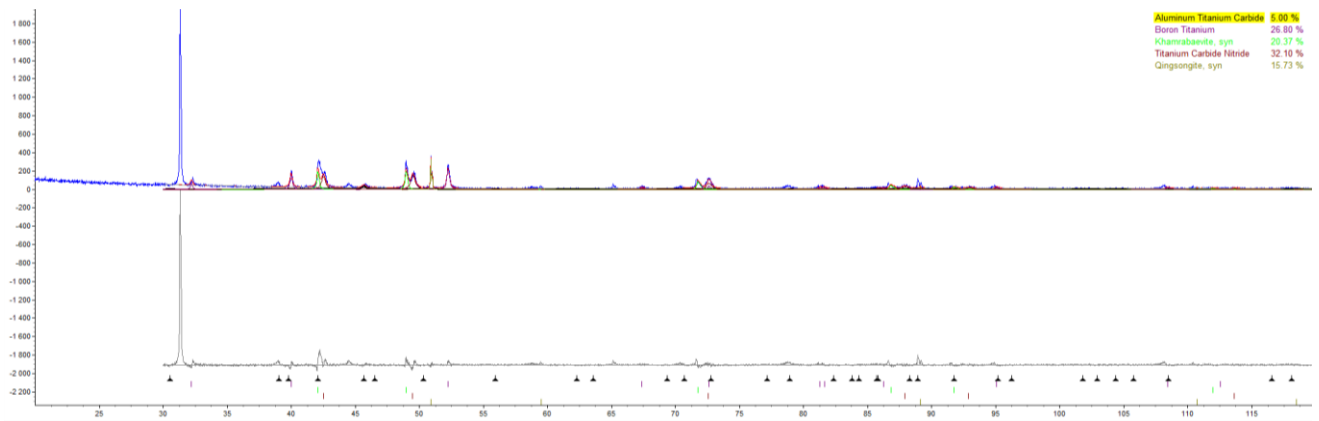


Figure D15: Rietveld analysis, of Ti_2AlC -cBN (40 vol.%,100 μm) samples sintered at 1350°C for 5 minutes.

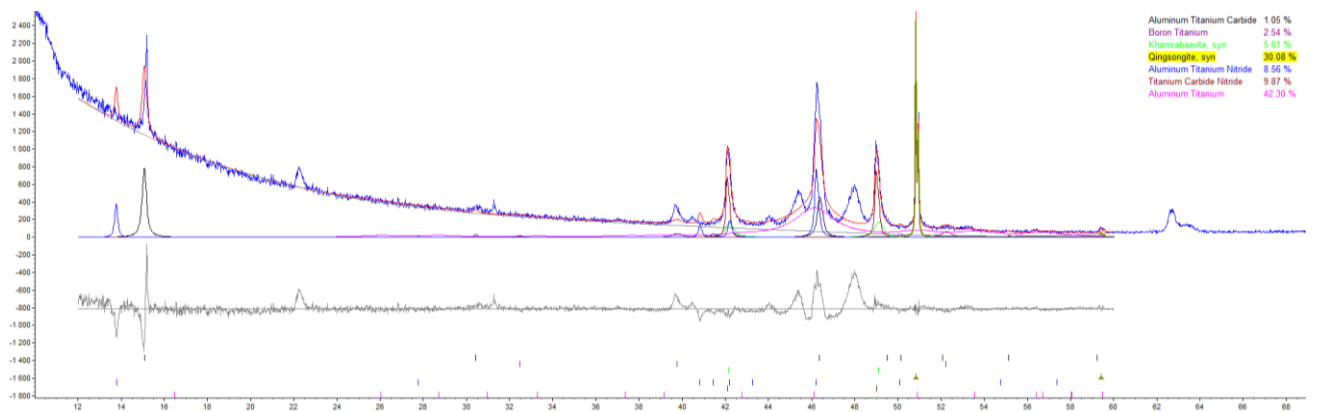


Figure D16: Rietveld analysis, of Ti_3AlC_2 -cBN (40 vol.%,100 μm) samples sintered at 1250°C for 5 minutes.

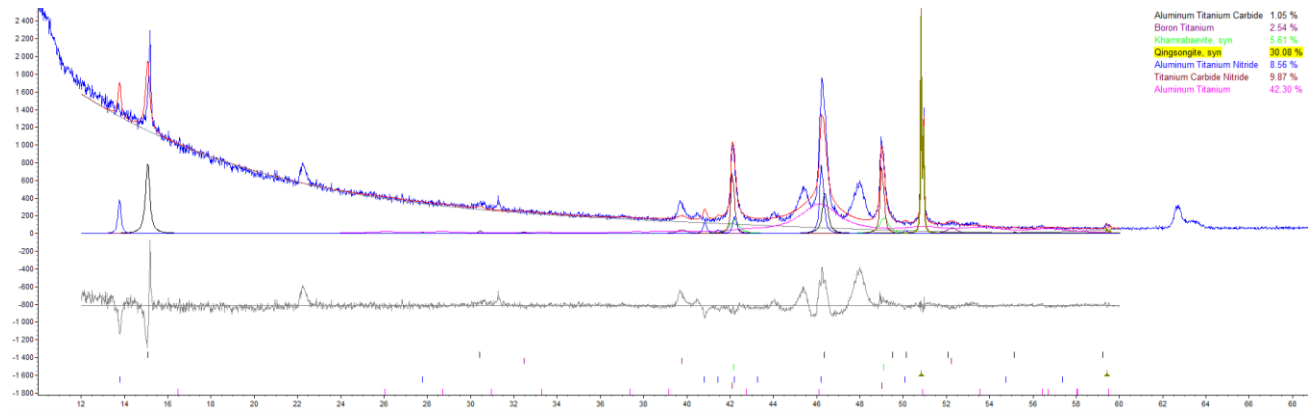


Figure D17: Rietveld analysis, of Ti_3AlC_2 -cBN (40 vol.%,100 μm) samples sintered at 1300°C for 5 minutes.

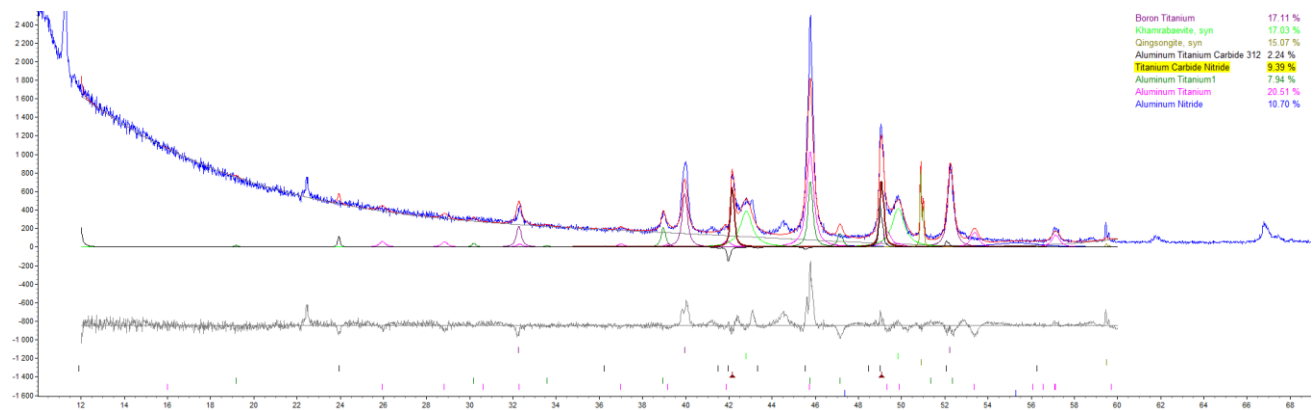


Figure D18: Rietveld analysis, of Ti_3AlC_2 -cBN (40 vol.%,100 μm) samples sintered at 1350°C for 5 minutes.

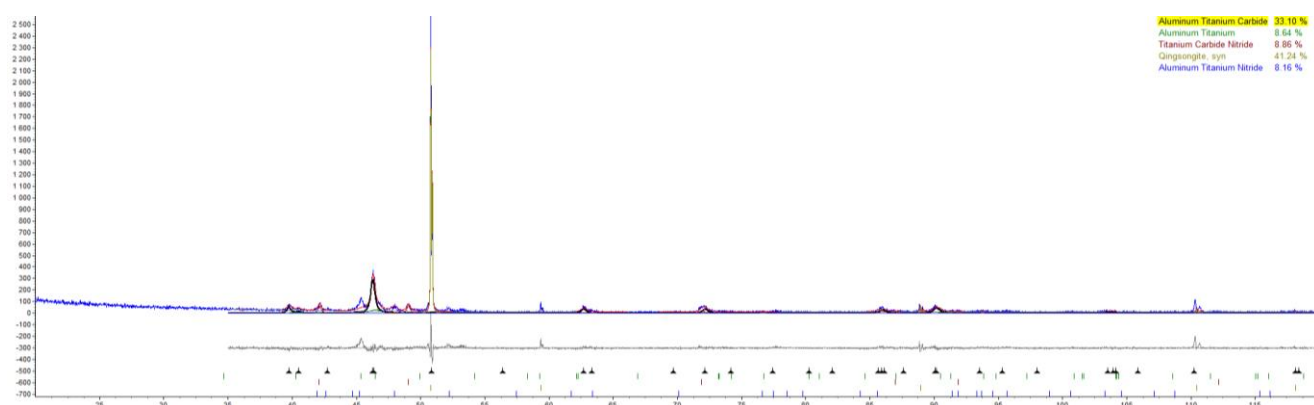


Figure D19: Rietveld analysis, of Ti_3SiC_2 -cBN (40 vol.%,100 μm) samples sintered at 1250°C for 5 minutes.

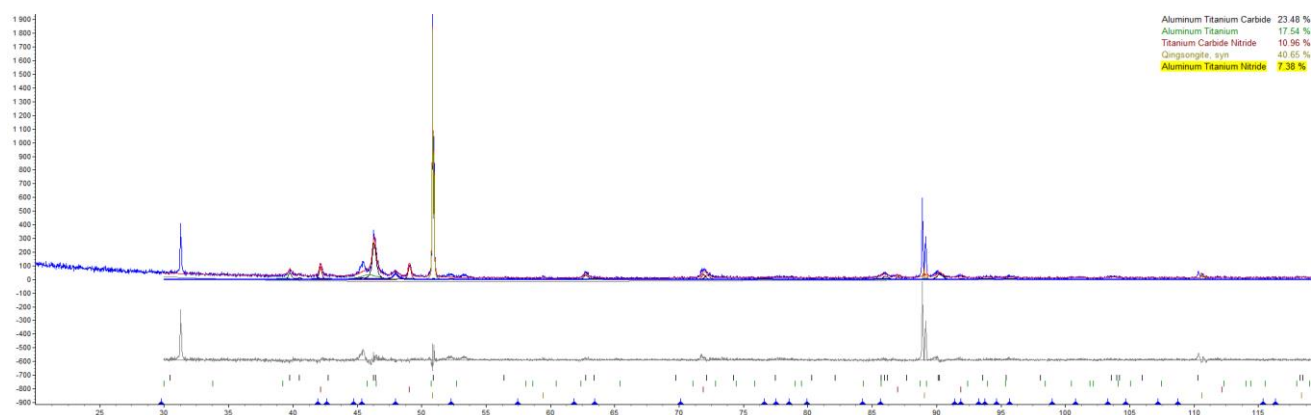


Figure D20: Rietveld analysis, of Ti_3SiC_2 -cBN (40 vol.%,100 μm) samples sintered at 1300°C for 5 minutes.

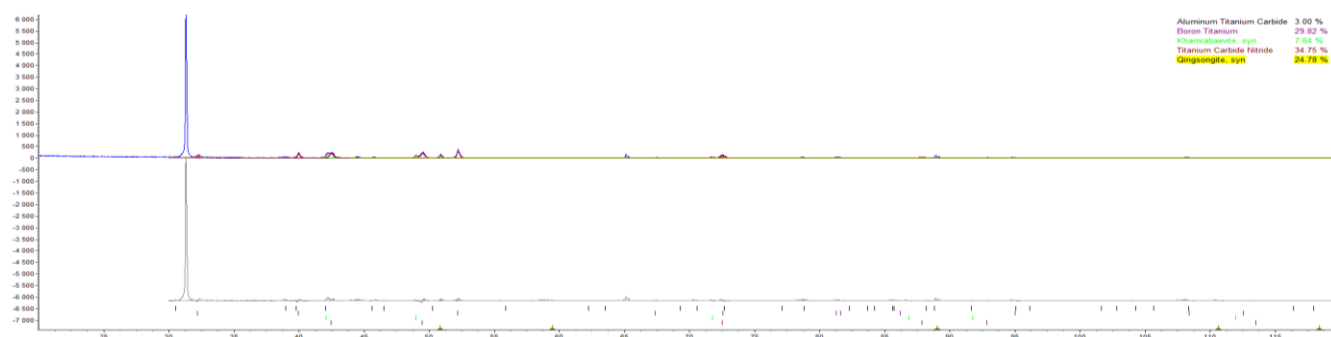
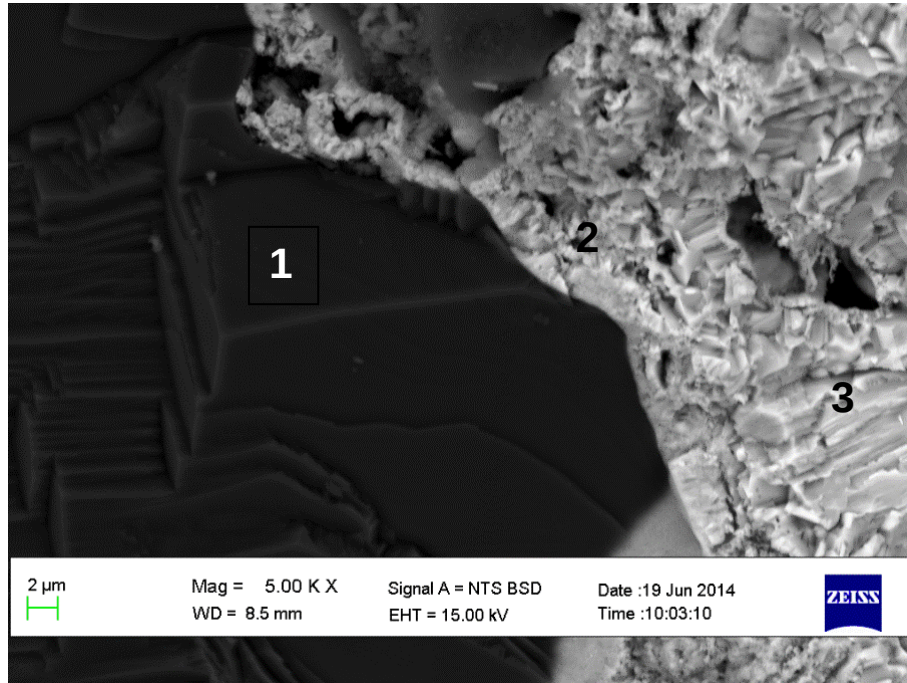


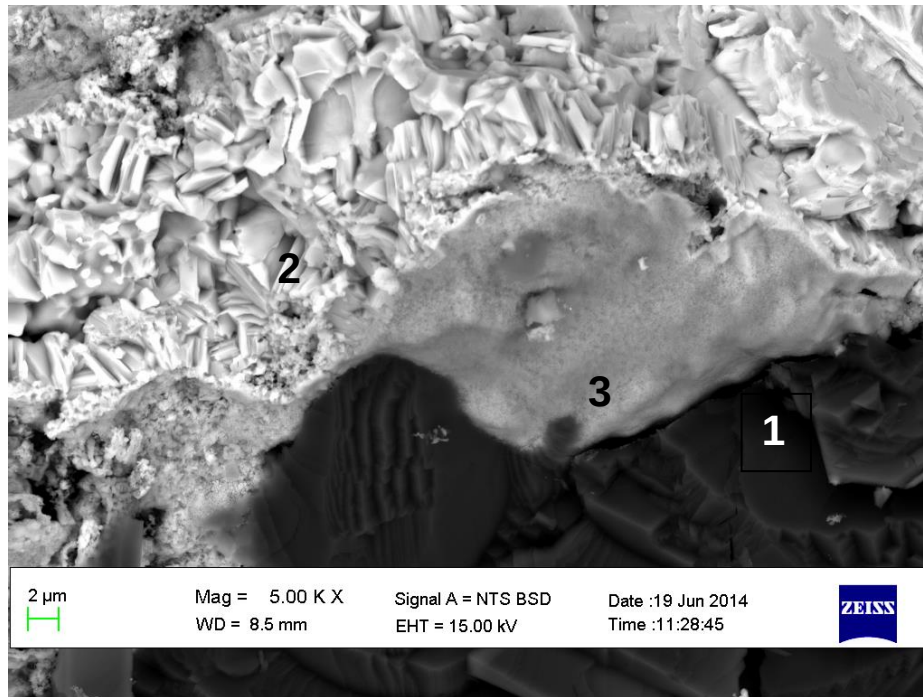
Figure D 21: Rietveld analysis, of Ti_3SiC_2 -cBN (40 vol.%,100 μm) samples sintered at 1350°C for 5 minutes.

Appendix E: Supplementary SEM/EDX analysis of samples



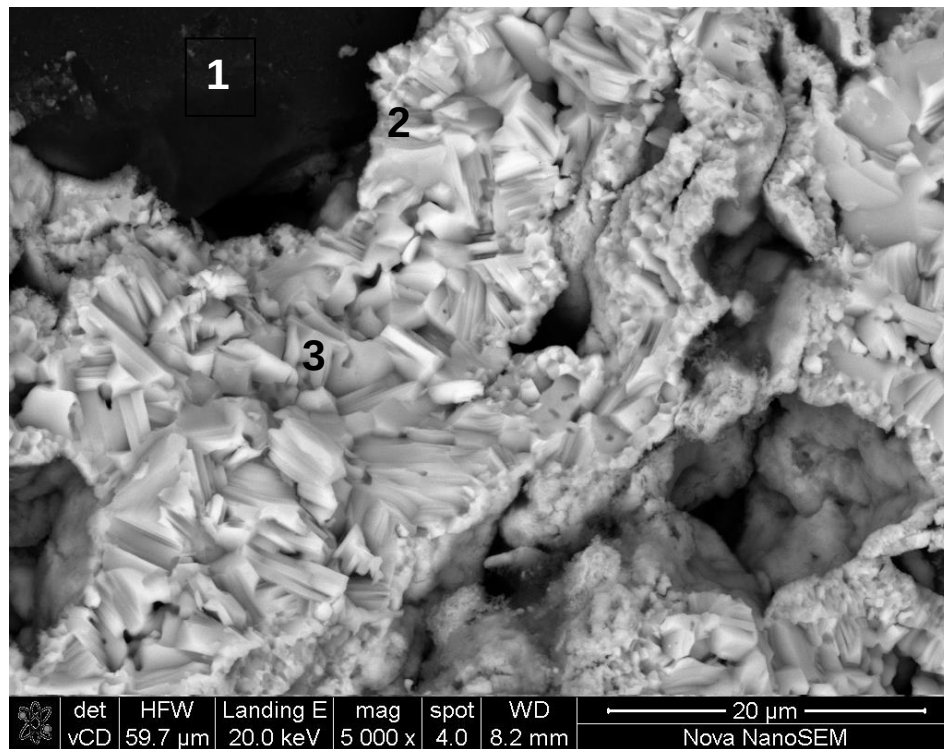
		<i>B</i>	<i>C</i>	<i>N</i>	<i>Si</i>	<i>Ti</i>	<i>Total</i>
		<i>atomic %</i>					
<i>site 1</i>	average	49,5	6,1	44,3	0,0	0,1	100,0
	std deviation	3,3	3,7	1,1	0,0	0,1	
<i>site 2</i>	average	28,6	42,1	12,3	0,0	16,9	100,0
	std deviation	8,4	14,1	9,0	0,1	7,6	
<i>site 3</i>	average	25,0	42,3	0,0	0,7	32,0	100,0
	std deviation	2,3	3,6	0,0	0,5	5,6	

Figure E 1:SEM (BSE) and EDX analysis of Ti_2AlC -(20 vol.% of 100 μm) cBN samples sintered at 30 MPa, 1250°C for 1 minute.



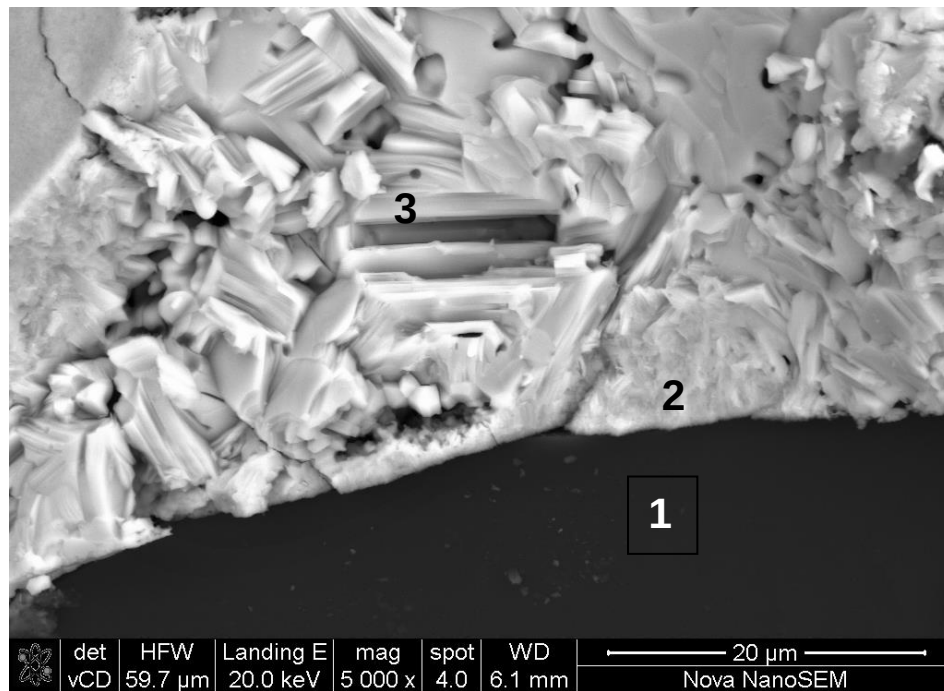
		<i>B</i>	<i>C</i>	<i>N</i>	<i>Al</i>	<i>O</i>	<i>Ti</i>	<i>Total</i>
		atomic %						
<i>site 1</i>	average	48,8	6,4	43,7	0,9	0,1	0,1	100,0
	std dev	1,5	1,8	1,0	0,3	0,1	0,0	
<i>site 2</i>	average	28,2	30,2	0,0	5,5	9,3	26,8	100,0
	std dev	5,9	5,2	0,0	1,2	1,6	8,6	
<i>site 3</i>	average	32,4	34,1	5,9	5,0	4,7	18,0	100,0
	std dev	12,0	17,0	7,4	2,3	3,4	2,5	

Figure E 2: SEM (BSE) and EDX analysis of Ti_2AlC -(20 vol.% of 100 μm) cBN samples sintered at 30 MPa, 1250°C for 10 minutes.



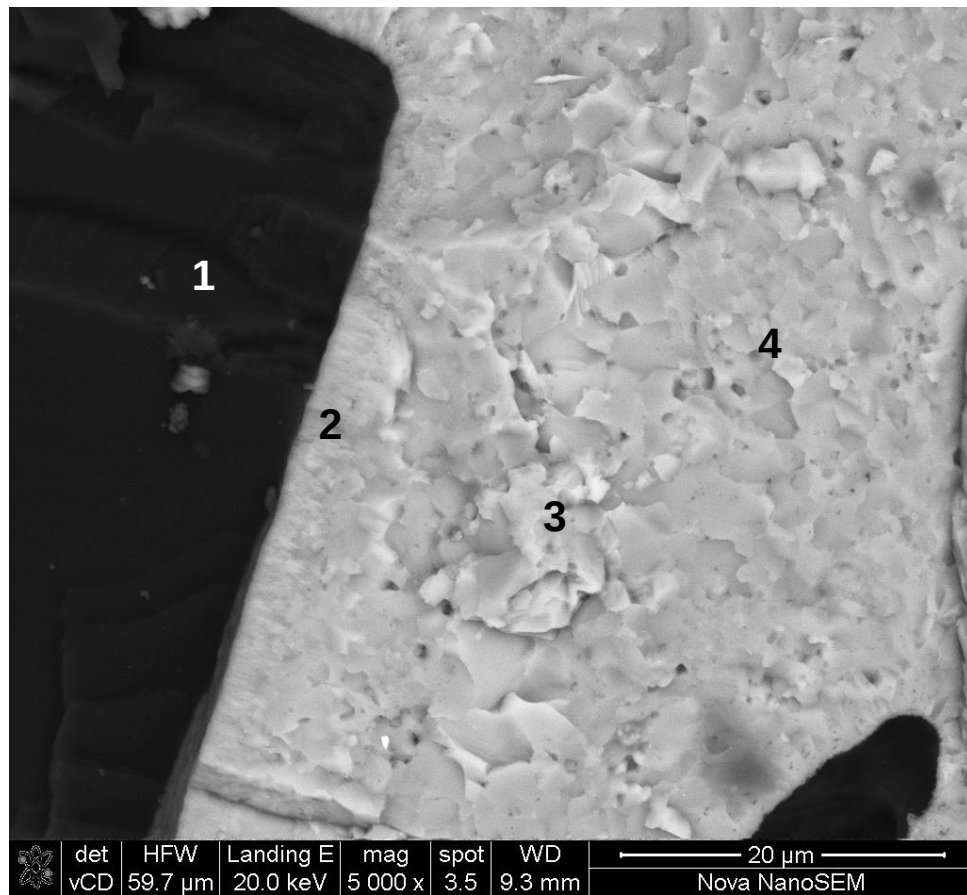
		B	C	N	O	Al	Ti	Total
		<i>atomic %</i>						
site 1	average	54,3	0,0	43,5	3,5	0,0	0,2	101,5
	std dev	1,7	0,0	3,9	2,1	0,0	0,2	
site 2	average	0,0	53,8	0,0	0,0	2,0	44,2	100,0
	std dev	0,0	10,3	0,0	0,0	3,1	10,3	
site 3	average	0,0	30,5	0,0	0,0	22,6	46,9	100,0
	std dev	0,0	6,8	0,0	0,0	4,7	2,9	

Figure E 3: SEM (BSE) and EDX analysis of Ti_3AlC_2 -cBN (20 vol.%, 100 μm) samples sintered at 30 MPa, 1300°C for 1 minute.



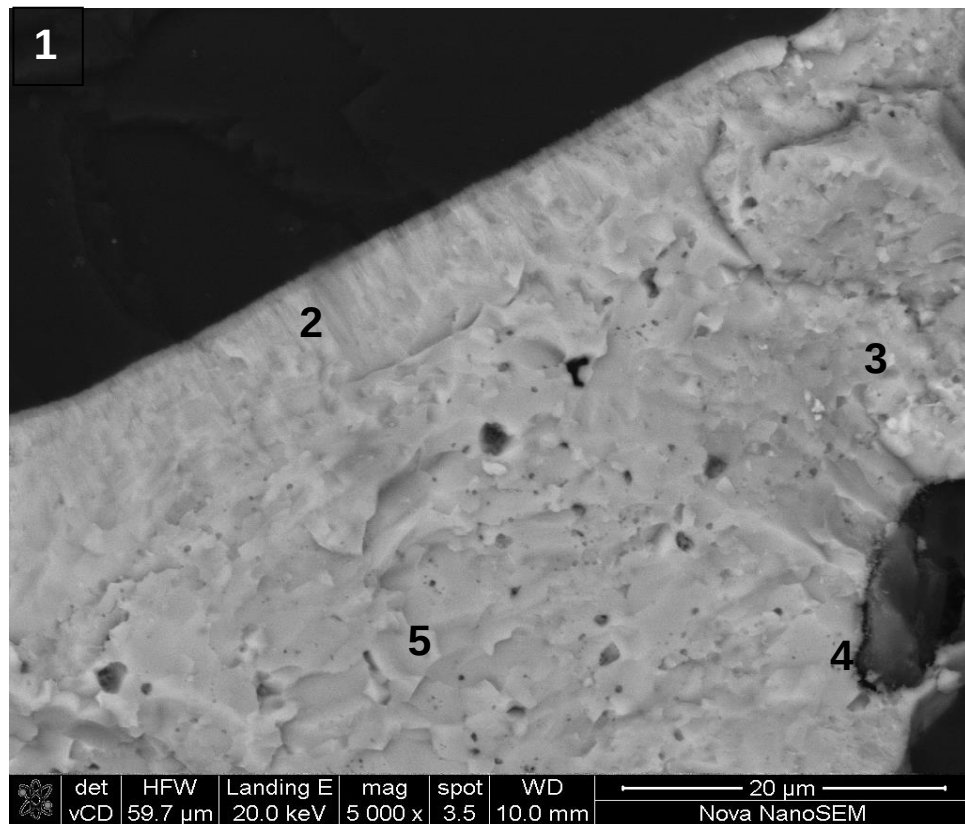
site		B	C	N	Al	O	Ti	Total
atomic %								
Site 1	average	49,7	5,4	44,1	0,7	0,0	0,1	100,0
	std deviation	0,8	1,2	0,4	0,2	0,0	0,0	
Site 2	average	28,7	25,9	0,0	4,6	15,6	25,3	100,0
	std deviation	6,4	8,4	0,0	0,9	7,4	6,9	
Site 3	average	21,7	41,6	0,0	14,6	2,5	19,6	100,0
	std deviation	2,9	14,1	0,0	15,8	3,6	9,4	

Figure E4: SEM (BSE) and EDX analysis of Ti_3AlC_2 -cBN (20 vol.%, 100 μm) samples sintered at 30 MPa, 1300°C for 5 minutes.



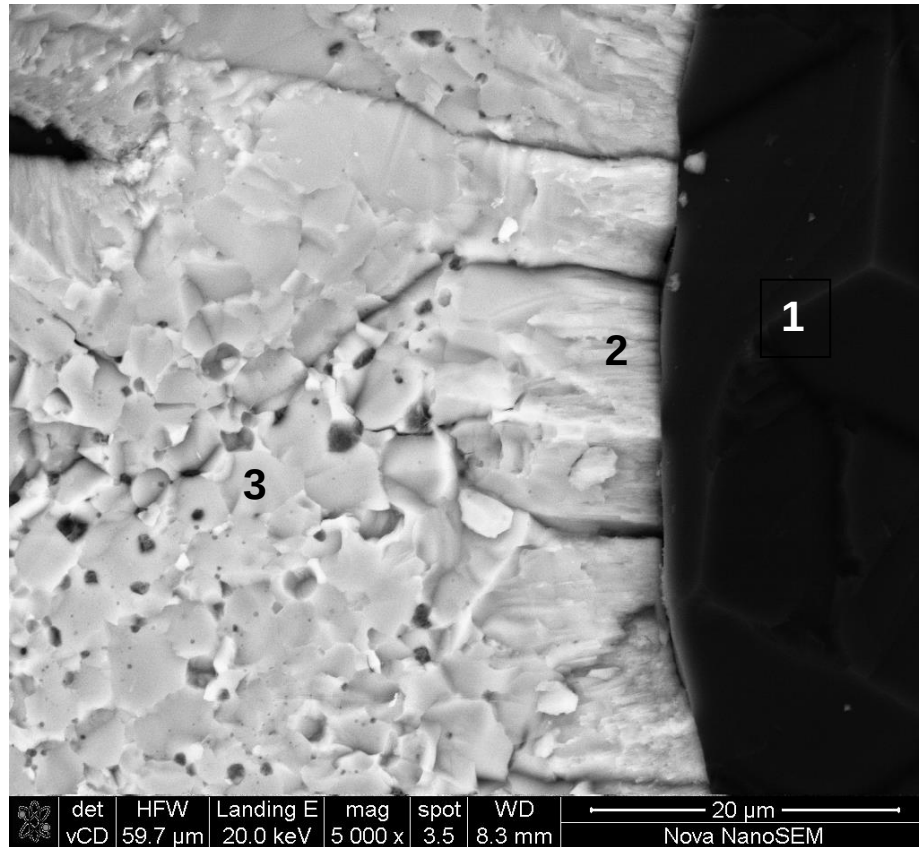
		<i>B</i>	<i>C</i>	<i>N</i>	<i>Si</i>	<i>Ti</i>	<i>Total</i>
		<i>atomic %</i>					
<i>site 1</i>	average	55,7	0,0	44,3	0,0	0,0	100
	std deviation	3,6	0,0	3,6	0,0	0,0	
<i>site 2</i>	average	60,5	22,0	0,0	0,0	17,5	100
	std deviation	5,4	4,6	0,0	0,0	3,0	
<i>site 3</i>	average	55,8	21,4	0,0	4,6	18,2	100
	std deviation	2,0	1,8	0,0	3,3	5,0	
<i>site 4</i>	average	42,5	39,6	0,0	0,4	17,5	100
	std deviation	4,0	6,1	0,0	0,2	3,4	

Figure E5: SEM (BSE) and EDX analysis of $\text{Ti}_3\text{SiC}_2\text{-cBN}$ (20 vol.%, 100 μm) samples sintered at 30 MPa, 1250°C for 1 minute.



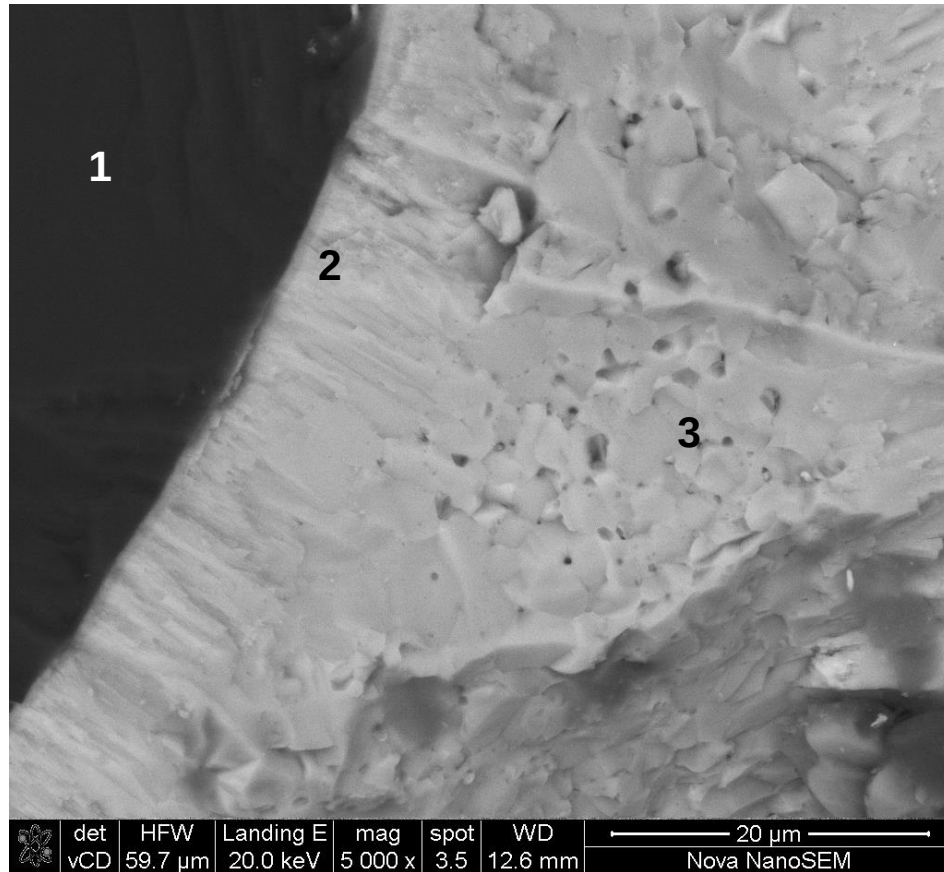
		B	C	N	Si	Ti	Total
		atomic %					
site 1	average	47,8	12,9	39,2	0,0	0,1	100,0
	std deviation	2,4	1,4	1,4	0,0	0,1	
site 2	average	60,6	21,8	0,0	0,0	17,5	100,0
	std deviation	4,8	5,1	0,0	0,0	3,3	
site 3	average	50,4	29,6	0,0	3,3	16,6	100,0
	std deviation	2,0	3,3	0,0	0,7	4,8	
site 4	average	59,6	19,7	0,0	0,0	20,6	100,0
	std deviation	0,9	4,6	0,0	0,0	3,9	
site 5	average	48,8	27,3	0,0	0,8	23,1	100,0
	std deviation	3,4	5,4	0,0	0,4	5,0	

Figure E6: SEM (BSE) and EDX analysis of Ti_3SiC_2 -cBN (20vol.%, 100 μm) samples sintered at 30 MPa, 1250°C for 10 minutes.



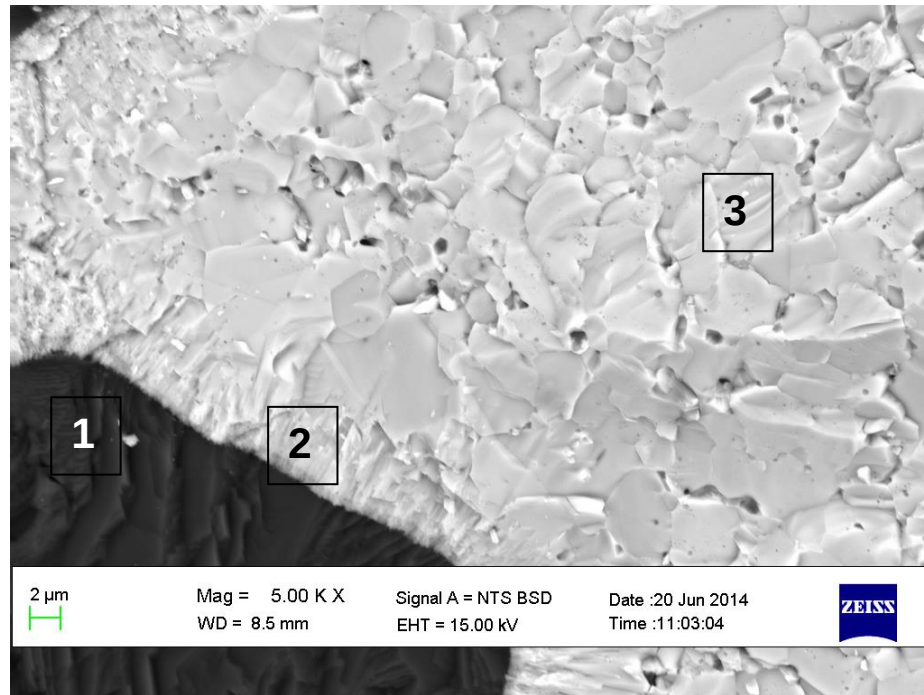
		<i>B</i>	<i>C</i>	<i>N</i>	<i>Al</i>	<i>Si</i>	<i>Ti</i>	<i>Total</i>
		<i>atomic %</i>						
<i>site 1</i>	average	52,9	8,7	38,2	0,0	0,0	0,1	100,0
	std deviation	4,6	7,4	5,2	0,0	0,0	0,1	
<i>site 2</i>	average	57,0	22,5	0,0	0,0	0,0	20,5	100,0
	std deviation	2,9	6,2	0,0	0,0	0,0	4,3	
<i>site 3</i>	average	43,5	37,1	0,0	0,0	0,7	18,6	100,0
	std deviation	1,4	0,9	0,0	0,0	0,7	0,9	

Figure E7: SEM (BSE) and EDX analysis of Ti_3SiC_2 -cBN (20 vol.%, 100 μm) samples sintered at 30 MPa, 1300°C for 1 minute.



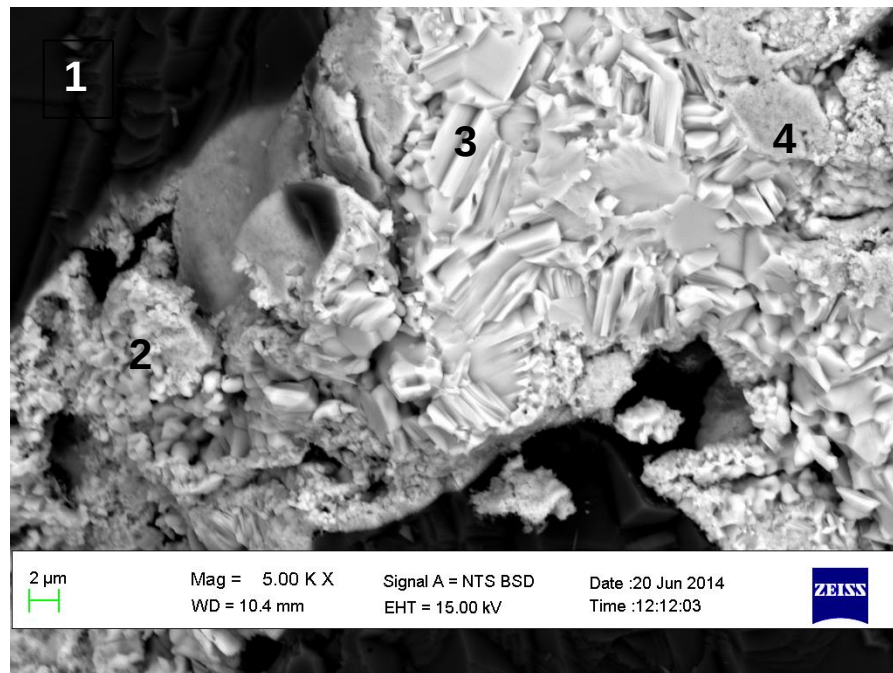
		<i>B</i>	<i>C</i>	<i>N</i>	<i>Al</i>	<i>Si</i>	<i>Ti</i>	<i>Total</i>
		<i>atomic %</i>						
<i>site 1</i>	average	62,0	0,0	38,0	0,0	0,0	0,0	100,0
	std dev	3,0	0,0	3,0	0,0	0,0	0,0	
<i>site 2</i>	average	58,6	23,1	0,0	0,0	0,0	18,3	100,0
	std dev	4,9	5,5	0,0	0,0	0,0	2,5	
<i>site 3</i>	average	50,4	31,3	0,0	0,0	0,4	17,9	100,0
	std dev	3,9	3,1	0,0	0,0	0,1	0,9	

Figure E8: SEM (BSE) and EDX analysis of Ti_3SiC_2 -cBN (20 vol.%, 100 μm) samples sintered at 30 MPa, 1300°C for 5 minutes.



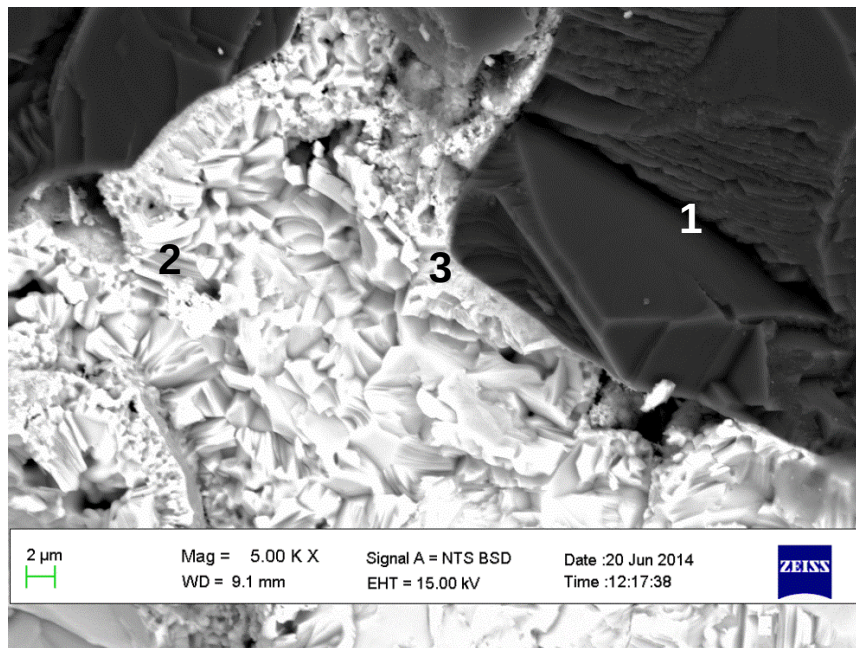
		<i>B</i>	<i>C</i>	<i>N</i>	<i>Al</i>	<i>Si</i>	<i>Ti</i>	<i>Total</i>
<i>atomic %</i>								
<i>site 1</i>	average	51,4	7,9	40,7	0,0	0,0	0,1	100,0
	std deviation	4,8	5,3	0,6	0,0	0,0	0,1	
<i>site 2</i>	average	56,8	22,8	0,0	0,0	0,0	20,4	100,0
	std deviation	2,6	1,7	0,0	0,0	0,0	3,2	
<i>site 3</i>	average	51,6	27,5	0,0	0,0	0,1	20,7	100,0
	std deviation	4,3	4,9	0,0	0,0	0,2	1,3	

Figure E9: SEM (BSE) and EDX analysis of Ti_3SiC_2 -cBN (20 vol.%, 100 μm) samples sintered at 30 MPa, 1300°C for 10 minutes.



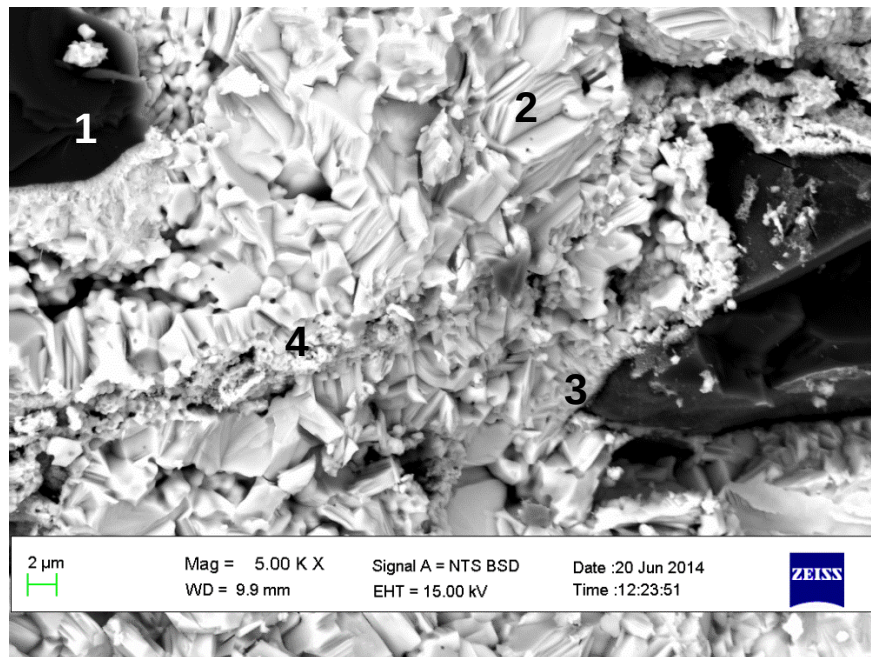
		<i>B</i>	<i>C</i>	<i>N</i>	<i>Al</i>	<i>Ti</i>	<i>Total</i>
		<i>atomic %</i>					
<i>site 1</i>	Average	49,0	11,1	39,0	0,2	0,8	100,0
	std deviation	1,7	9,0	9,3	0,3	0,9	
<i>site 2</i>	Average	28,6	40,6	1,7	1,4	27,7	100,0
	std deviation	8,2	16,3	4,1	1,8	4,5	
<i>site 3</i>	Average	26,9	19,0	0,0	9,5	44,5	100,0
	std deviation	8,6	10,6	0,0	6,1	15,5	
<i>site 4</i>	Average	23,4	38,7	4,5	2,5	30,8	100,0
	std deviation	1,6	13,1	10,2	2,3	13,4	

Figure E10: SEM (BSE) and EDX of Ti_2AlC -cBN (40 vol.%, 100 μm) samples sintered at 30 MPa, 1250°C and 5 minutes.



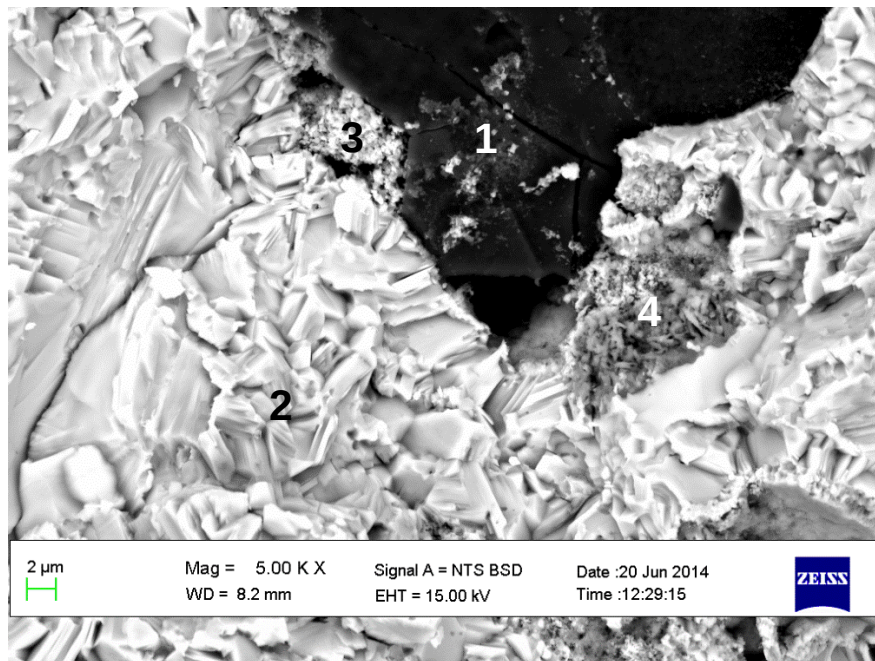
		<i>B</i>	<i>C</i>	<i>N</i>	<i>Al</i>	<i>Ti</i>	<i>Total</i>
		<i>atomic %</i>					
<i>site 1</i>	average	49,0	11,1	39,0	0,2	0,8	100,0
	std deviation	1,7	9,0	9,3	0,3	0,9	
<i>site 2</i>	average	28,0	25,1	0,6	7,0	39,2	100,0
	std deviation	6,3	9,5	1,8	4,1	16,6	
<i>site 3</i>	average	35,4	23,8	6,1	1,9	32,7	100,0
	std deviation	12,2	17,6	7,3	1,4	14,2	

Figure E11: SEM (BSE) and EDX of Ti_2AlC -cBN (40 vol.%, 100 μm) samples sintered at 30 MPa, 1250°C and 10 minutes.



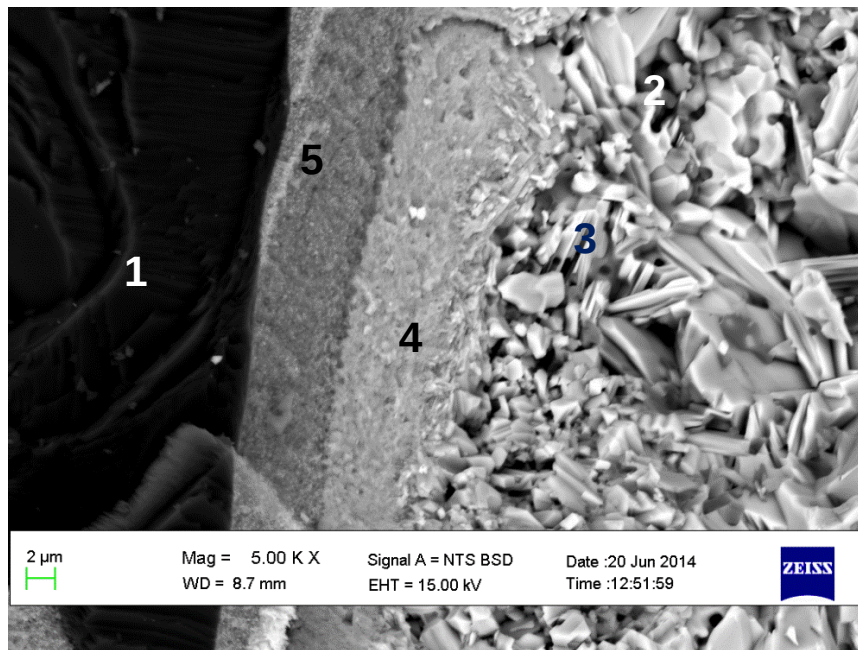
		<i>B</i>	<i>C</i>	<i>N</i>	<i>Al</i>	<i>Ti</i>	<i>Total</i>
		<i>atomic %</i>					
<i>site 1</i>	average	49,1	5,0	45,7	0,0	0,1	100,0
	std deviation	2,2	1,4	0,7	0,0	0,1	
<i>site 2</i>	average	42,3	30,1	0,8	3,9	22,9	100,0
	std deviation	13,5	9,5	2,2	3,4	15,0	
<i>site 3</i>	average	31,4	34,9	2,5	1,1	30,1	100,0
	std deviation	18,3	17,1	7,0	0,7	23,7	
<i>site 4</i>	average	23,0	26,5	0,0	10,1	40,3	100,0
	std deviation	5,6	13,1	0,0	2,0	19,2	

Figure E12: SEM (BSE) and EDX of Ti_2AlC -cBN (40 vol.%, 100 μm) samples sintered at 30 MPa, 1300°C and 5 minutes.



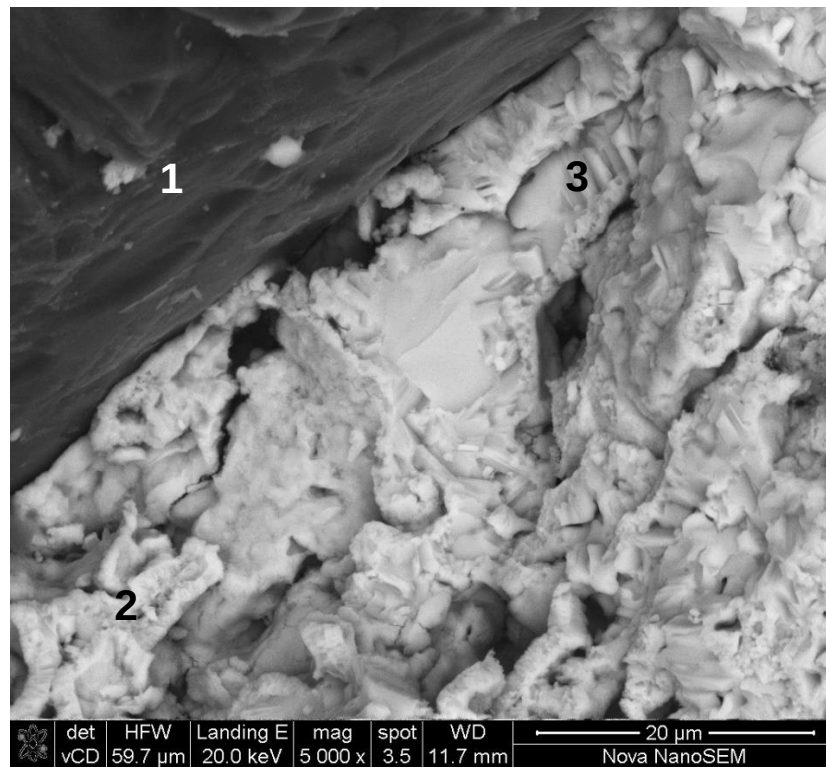
		<i>B</i>	<i>C</i>	<i>N</i>	<i>Al</i>	<i>Ti</i>	<i>Total</i>
		<i>atomic %</i>					
<i>site 1</i>	average	46,4	9,4	43,7	0,1	0,4	100,0
	std deviation	2,6	3,7	1,6	0,1	0,4	
<i>site 2</i>	average	34,4	34,5	0,9	9,1	21,1	100,0
	std deviation	4,5	10,0	2,5	5,4	6,6	
<i>site 3</i>	average	25,8	42,4	3,1	1,8	26,8	100,0
	std deviation	3,0	11,3	6,3	1,5	15,9	
<i>site 4</i>	average	30,8	29,7	0,0	7,5	32,0	100,0
	std deviation	3,2	8,8	0,0	3,6	11,3	

Figure E13: SEM (BSE) and EDX of Ti_2AlC -cBN (40 vol.%, 100 μm) samples sintered at 30 MPa, 1300°C and 10 minutes.



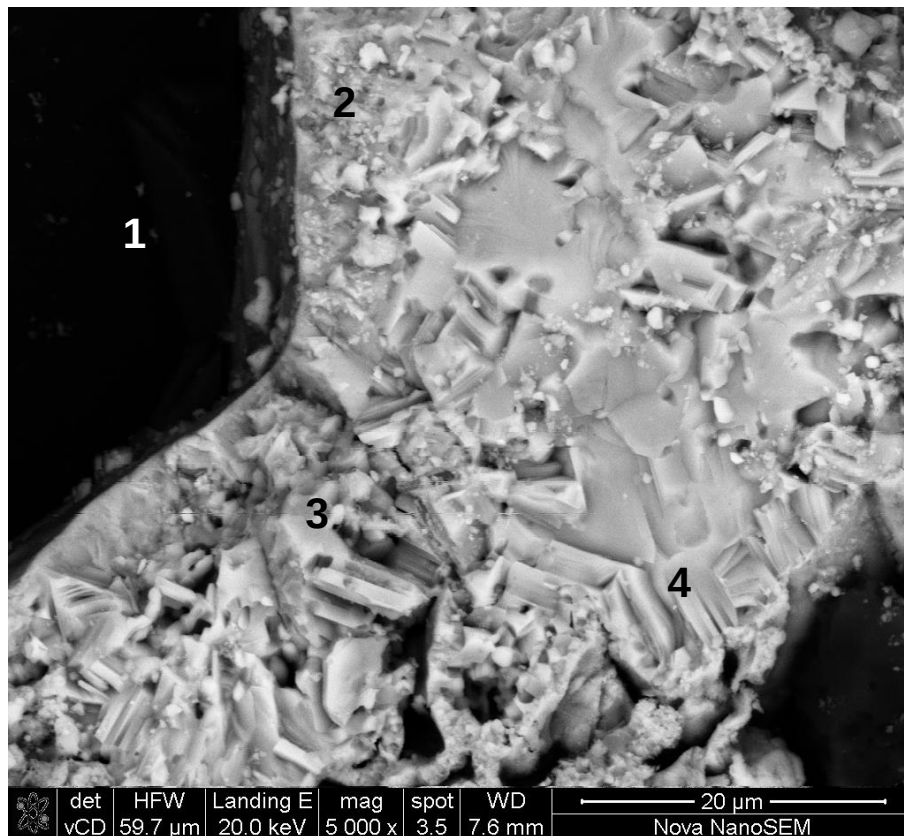
		<i>B</i>	<i>C</i>	<i>N</i>	<i>Al</i>	<i>O</i>	<i>Ti</i>	<i>Total</i>
<i>atomic %</i>								
<i>site 1</i>	average	48,7	7,8	34,2	8,5	0,4	0,4	100,0
	std deviation	2,7	3,9	7,0	6,1	0,4	0,8	
<i>site 2</i>	average	31,0	13,5	2,9	25,6	3,3	23,7	100,0
	std deviation	14,5	2,6	5,9	12,1	2,2	9,8	
<i>site 3</i>	average	17,4	20,3	0,0	30,1	5,5	26,7	100,0
	std deviation	3,7	9,9	0,0	9,2	1,3	6,7	
<i>site 4</i>	average	42,4	20,4	0,8	11,4	5,4	19,5	100,0
	std deviation	2,5	1,9	1,9	5,5	0,3	2,7	
<i>site 5</i>	average	41,5	10,3	13,9	11,3	14,2	8,7	100,0
	std deviation	5,4	3,5	4,1	8,9	1,2	1,7	

Figure E14: SEM (BSE) and EDX of Ti_2AlC -cBN (40 vol.%, 100 μm) samples sintered at 30 MPa, 1350°C and 10 minutes.



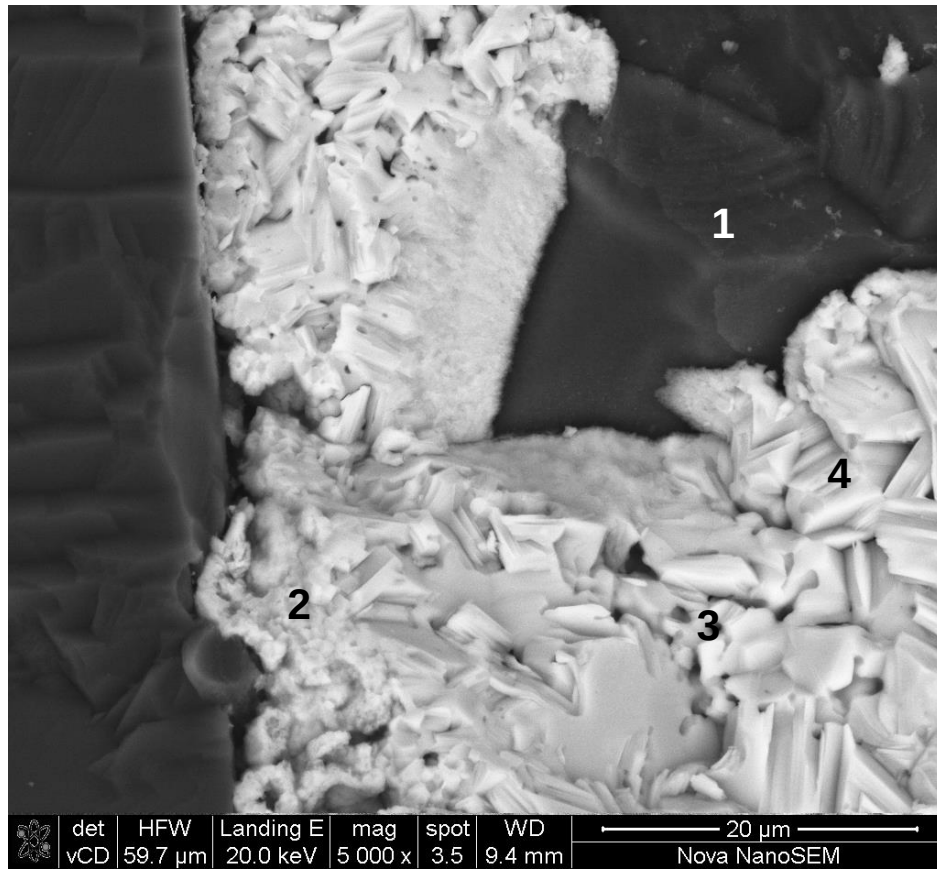
		<i>B</i>	<i>C</i>	<i>N</i>	<i>Al</i>	<i>Ti</i>	<i>Total</i>
		atomic %					
<i>site 1</i>	average	51,7	16,3	31,8	0,0	0,2	100,0
	std deviation	4,6	14,0	14,8	0,0	0,3	
<i>site 2</i>	average	41,0	45,8	0,0	0,6	12,6	100,0
	std deviation	4,9	7,0	0,0	0,8	2,1	
<i>site 3</i>	average	55,1	25,8	2,0	4,5	12,6	100,0
	std deviation	3,5	3,5	4,9	1,5	1,7	

Figure E15: SEM (BSE) and EDX analysis of $\text{Ti}_3\text{AlC}_2\text{-cBN}$ (40 vol.%, 100 μm) samples sintered at 30 MPa, 1250°C for 5 minutes.



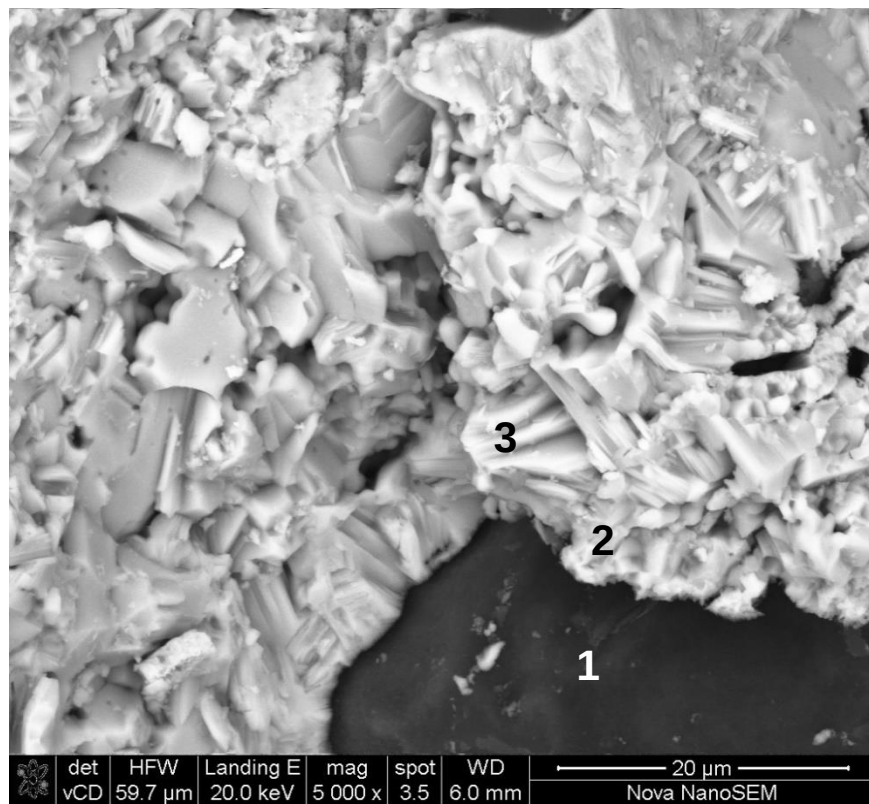
		<i>B</i>	<i>C</i>	<i>N</i>	<i>Al</i>	<i>Ti</i>	<i>Total</i>
		<i>atomic %</i>					
<i>site 1</i>	average	48,2	14,1	37,5	0,0	0,2	100,0
	std deviation	3,2	7,1	7,1	0,0	0,2	
<i>site 2</i>	average	42,9	44,7	0,0	0,9	11,5	100,0
	std deviation	4,7	6,5	0,0	0,7	3,0	
<i>site 3</i>	average	54,2	27,1	0,0	4,4	14,2	100,0
	std deviation	3,5	6,1	0,0	1,3	4,0	
<i>site 4</i>	average	53,4	29,1	0,0	4,1	13,3	100,0
	std deviation	2,1	1,7	0,0	1,3	1,5	

Figure E16: SEM (BSE) and EDX analysis of $\text{Ti}_3\text{AlC}_2\text{-cBN}$ (40 vol.%, 100 μm) samples sintered at 30 MPa, 1250°C for 10 minutes.



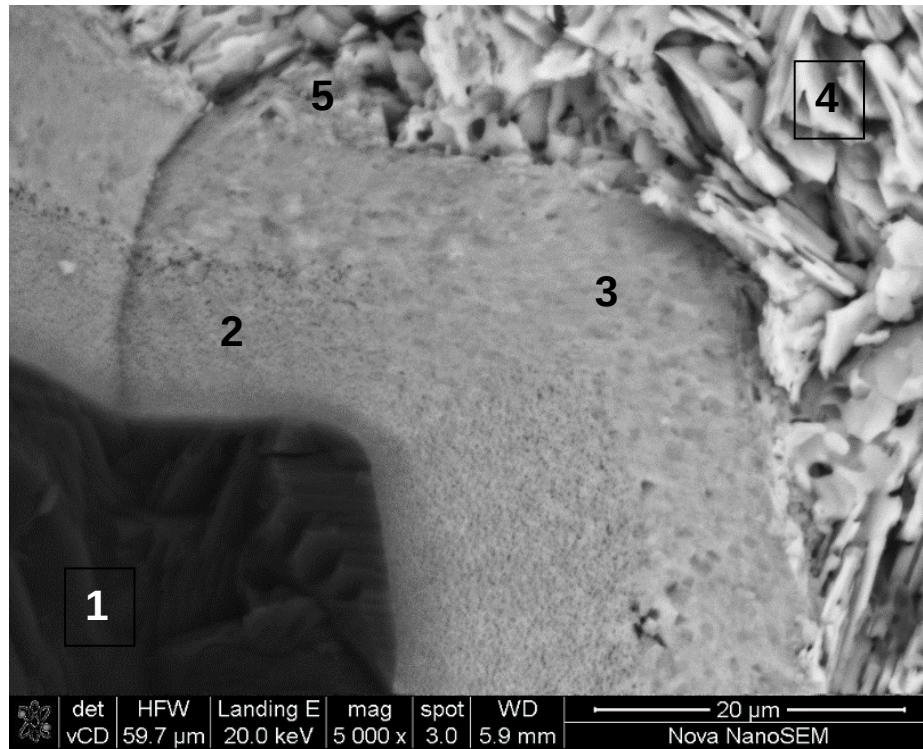
		<i>B</i>	<i>C</i>	<i>N</i>	<i>Al</i>	<i>Ti</i>	<i>Total</i>
		<i>atomic %</i>					
<i>site 1</i>	average	51,1	14,8	33,8	0,0	0,3	100,0
	std deviation	3,1	14,9	15,3	0,1	0,2	
<i>site 2</i>	average	43,1	39,5	6,3	0,7	10,4	100,0
	std deviation	4,6	10,2	9,8	1,2	4,2	
<i>site 3</i>	average	53,8	28,8	0,0	4,7	12,6	100,0
	std deviation	6,4	7,8	0,0	0,7	1,9	
<i>site 4</i>	average	50,9	32,0	0,0	4,6	12,5	100,0
	std deviation	2,8	4,4	0,0	0,6	2,3	

Figure E17: SEM (BSE) and EDX analysis of $\text{Ti}_3\text{AlC}_2\text{-cBN}$ (40 vol.%, 100 μm) samples sintered at 30 MPa, 1300°C for 5 minutes.



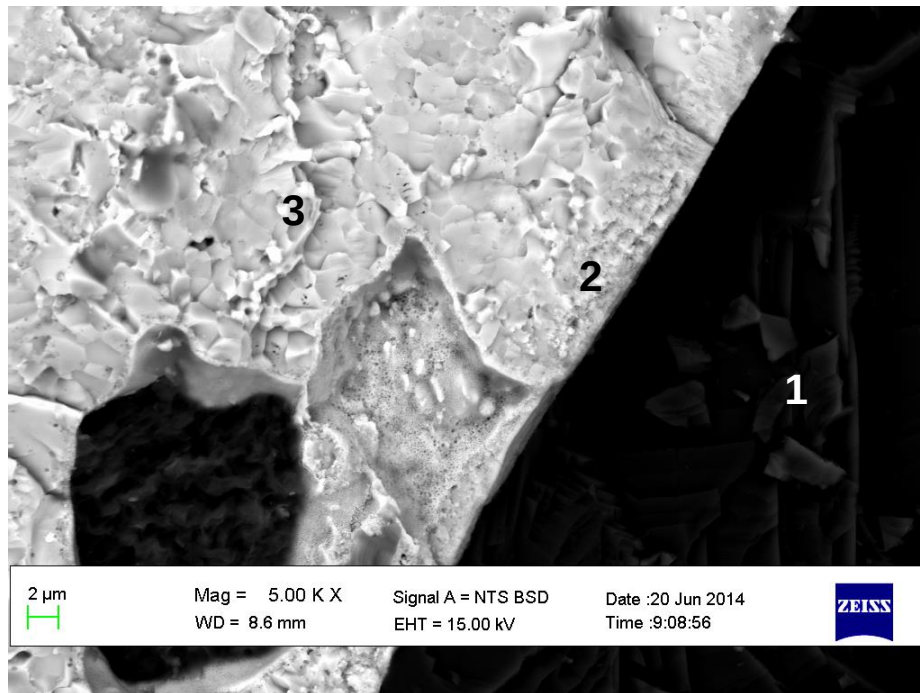
		<i>B</i>	<i>C</i>	<i>N</i>	<i>Al</i>	<i>Ti</i>	<i>Total</i>
		<i>atomic %</i>					
<i>site 1</i>	average	49,2	12,1	38,4	0,0	0,4	100,0
	std deviation	3,7	7,1	4,4	0,0	0,2	
<i>site 2</i>	average	44,5	41,3	0,0	1,0	13,2	100,0
	std deviation	3,4	5,6	0,0	0,8	3,4	
<i>site 3</i>	average	54,3	26,8	0,0	4,9	14,1	100,0
	std deviation	4,4	5,1	0,0	1,1	1,8	

Figure E18: SEM (BSE) and EDX analysis of $\text{Ti}_3\text{AlC}_2\text{-cBN}$ (40 vol.%, 100 μm) samples sintered at 30 MPa, 1300°C for 10 minutes.



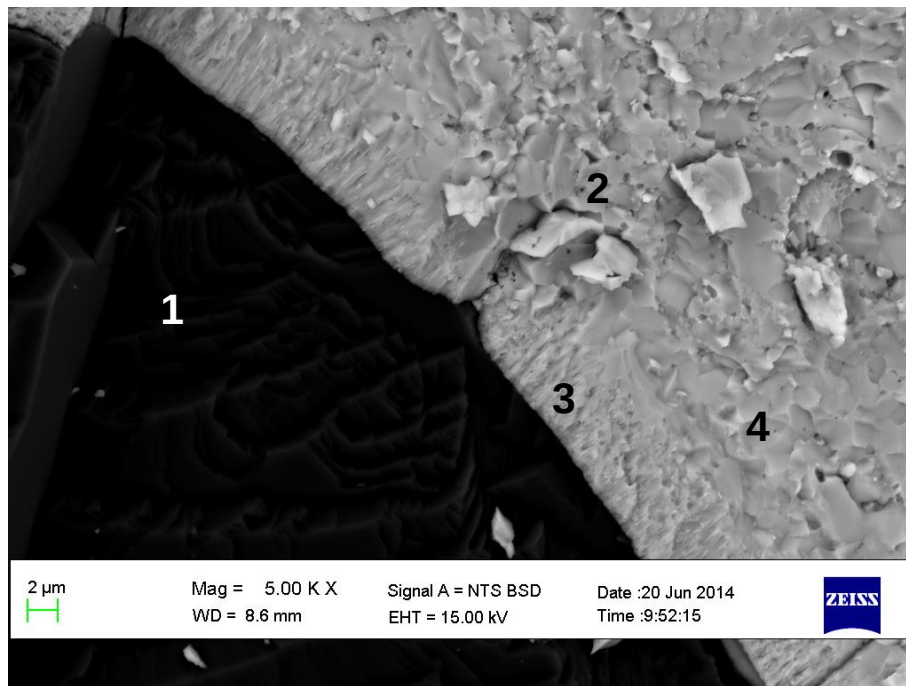
		<i>B</i>	<i>C</i>	<i>N</i>	<i>Al</i>	<i>Ti</i>	<i>Total</i>
		<i>atomic %</i>					
<i>site 1</i>	average	52,6	5,8	41,6	0,0	0,0	100,0
	std deviation	3,5	4,6	1,6	0,0	0,0	
<i>site 2</i>	average	62,9	19,9	5,9	1,5	9,8	100,0
	std deviation	7,1	2,1	9,1	0,3	2,7	
<i>site 3</i>	average	50,2	10,8	24,9	1,2	12,8	100,0
	std deviation	6,0	5,5	4,4	0,2	2,3	
<i>site 4</i>	average	46,5	36,4	2,7	3,2	11,2	100,0
	std deviation	3,3	4,3	6,5	0,5	1,7	
<i>site 5</i>	average	45,4	27,1	11,6	0,7	15,2	100,0
	std deviation	10,1	12,6	12,7	0,4	3,4	

Figure E19: SEM (BSE) and EDX analysis of $\text{Ti}_3\text{AlC}_2\text{-cBN}$ (40 vol.%, 100 μm) samples sintered at 30 MPa, 1350°C for 10 minutes.



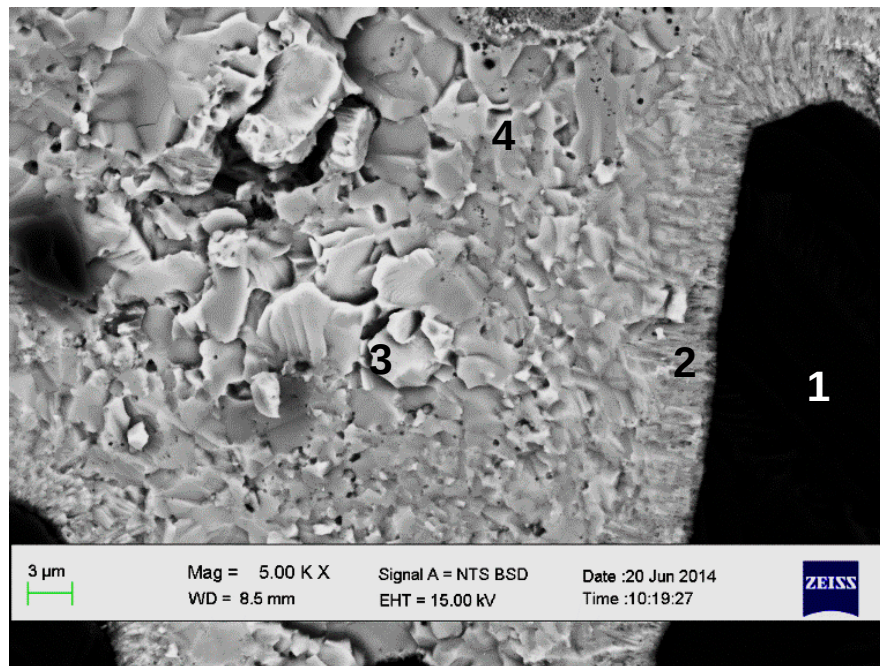
		<i>B</i>	<i>C</i>	<i>N</i>	<i>Si</i>	<i>Ti</i>	<i>Total</i>
		<i>atomic %</i>					
<i>site 1</i>	average	48,7	10,2	41,0	0,0	0,1	100,0
	std deviation	2,0	0,9	2,6	0,0	0,1	
<i>site 2</i>	average	62,0	19,5	0,0	0,1	18,5	100,0
	std deviation	2,5	4,5	0,0	0,1	2,7	
<i>site 3</i>	average	48,2	32,0	0,0	0,9	18,9	100,0
	std deviation	2,7	5,6	0,0	0,7	2,8	

Figure E20: SEM (BSE) and EDX analysis of Ti_3SiC_2 -cBN (40 vol.%, 100 μm) samples sintered at 30 MPa, 1250°C for 5 minutes.



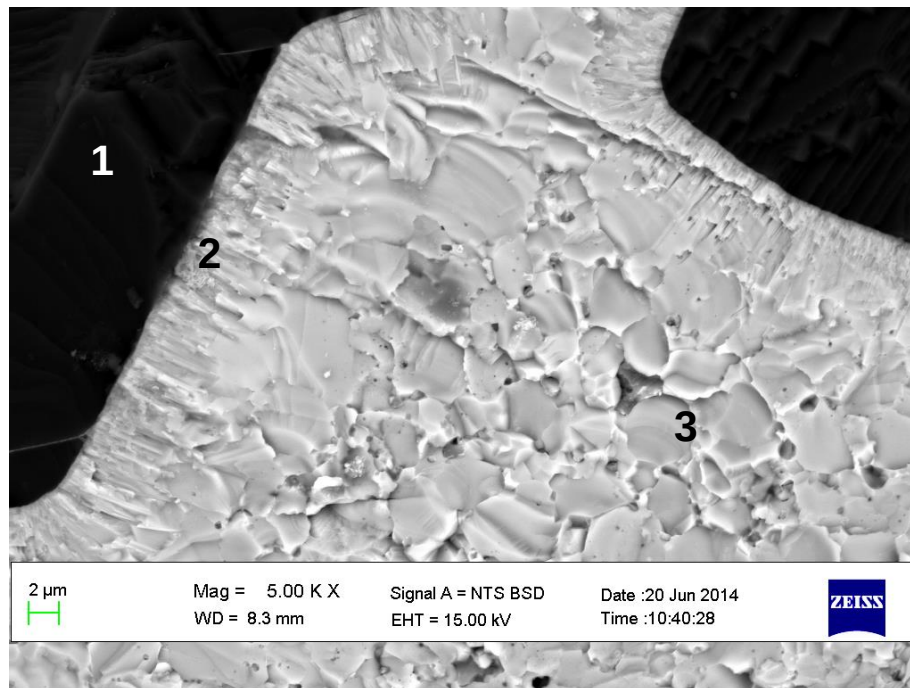
		<i>B</i>	<i>C</i>	<i>N</i>	<i>Si</i>	<i>Ti</i>	<i>Total</i>
		<i>atomic %</i>					
<i>site 1</i>	average	54,0	4,2	41,7	0,0	0,1	100,0
	std deviation	5,1	4,9	2,4	0,0	0,2	
<i>site 2</i>	average	56,9	22,4	0,0	3,8	16,8	100,0
	std deviation	1,4	0,9	0,0	0,8	1,5	
<i>site 3</i>	average	58,6	21,5	0,0	0,0	19,9	100,0
	std deviation	3,4	3,8	0,0	0,0	3,9	
<i>site 4</i>	average	47,6	31,2	0,0	0,6	20,6	100,0
	std deviation	3,2	2,6	0,0	0,4	0,9	

Figure E21: SEM (BSE) and EDX analysis of Ti_3SiC_2 -cBN (40 vol.%, 100 μm) samples sintered at 30 MPa, 1250°C for 10 minutes.



		<i>B</i>	<i>C</i>	<i>N</i>	<i>Si</i>	<i>Ti</i>	<i>Total</i>
		<i>atomic %</i>					
<i>site 1</i>	average	53,0	8,6	38,4	0,0	0,0	100,0
	std deviation	5,1	6,7	2,8	0,0	0,0	
<i>site 2</i>	average	55,7	23,1	0,0	0,0	21,1	100,0
	std deviation	4,6	5,7	0,0	0,0	6,6	
<i>site 3</i>	average	45,7	33,4	0,0	1,5	19,4	100,0
	std deviation	7,4	7,9	0,0	1,5	6,3	
<i>site 4</i>	average	48,8	26,0	0,0	0,9	24,3	100,0
	std deviation	1,5	0,8	0,0	1,2	1,5	

Figure E22: SEM (BSE) and EDX analysis of $\text{Ti}_3\text{SiC}_2\text{-cBN}$ (40 vol.%, 100 μm) samples sintered at 30 MPa, 1300°C for 5 minutes.



		<i>B</i>	<i>C</i>	<i>N</i>	<i>Al</i>	<i>Si</i>	<i>Ti</i>	<i>Total</i>
		<i>atomic %</i>						
<i>site 1</i>	average	51,1	8,5	40,3	0,0	0,0	0,1	100,0
	std deviation	2,4	5,8	3,9	0,0	0,0	0,1	
<i>site 2</i>	average	56,2	19,8	0,0	0,0	0,0	24,0	100,0
	std deviation	2,6	8,7	0,0	0,0	0,0	6,2	
<i>site 3</i>	average	42,7	39,5	0,0	0,0	0,5	17,3	100,0
	std deviation	4,4	6,6	0,0	0,0	0,3	2,7	

Figure E23: SEM (BSE) and EDX analysis of Ti_3SiC_2 -cBN (40 vol.%, 100 μm) samples sintered at 30 MPa, 1300°C for 10 minutes.

Appendix F: Supplementary data for EDX reported averages.

Spectrum	B	C	N	Si	Ti	Total
Atomic %						
Spectrum 1	33.2	13.4	43.0	3.5	6.9	100.0
Spectrum 2	47.6	14.0	21.0	0.3	17.1	100.0
Spectrum 3	28.8	16.1	31.4	2.9	20.8	100.0
Spectrum 4	36.8	10.6	36.2	2.1	14.2	100.0
Spectrum 5	41.8	21.5	14.5	1.8	20.3	100.0
avg	37.6	15.1	29.2	2.1	15.9	
std	7.3	4.1	11.5	1.2	5.7	

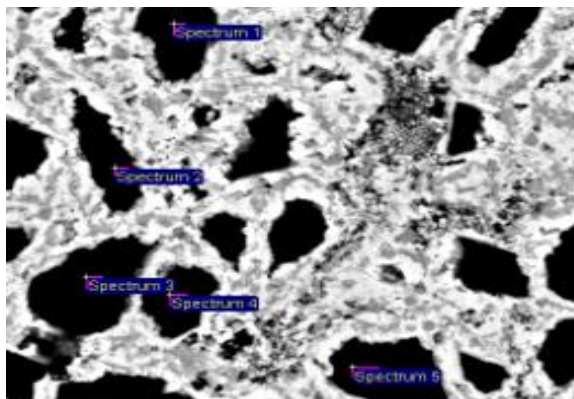


Figure F 1: EDX analysis of $\text{Ti}_3\text{SiC}_2\text{-cBN}$ (20 vol.%, 10 μm) sample sintered at 30 MPa, 1 minute and 1600°C. Site 1.

Spectrum	B	C	N	Si	Ti	Total
Atomic %						
Spectrum 1	43.1	25.6	9.4	3.6	18.2	100
Spectrum 2	36.9	21.7	17.4	1.5	22.5	100
Spectrum 3	22.9	23.0	31.5	3.3	19.3	100
Spectrum 4	25.2	32.7	16.9	4.9	20.4	100
Spectrum 5	37.1	21.9	16.0	2.6	22.3	100
avg	33.1	25.0	18.3	3.2	20.5	
std	8.6	4.6	8.1	1.3	1.9	

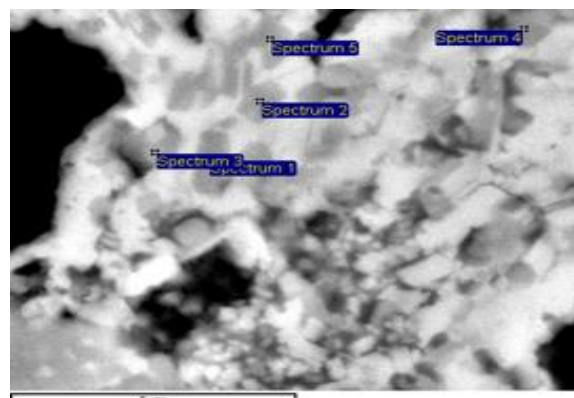


Figure F 2: EDX analysis of $\text{Ti}_3\text{SiC}_2\text{-cBN}$ (20 vol.%, 10 μm) sample sintered at 30 MPa, 1 minute and 1600°C. Site 2.

Spectrum	B	C	N	Si	Ti	Total
Atomic %						
Spectrum 1	27.6	32.5	14.8	9.2	15.9	100.0
Spectrum 2	32.7	40.3	0.0	10.8	16.2	100.0
Spectrum 3	32.8	20.3	25.6	0.5	20.9	100.0
Spectrum 4	30.7	25.2	22.1	4.5	17.5	100.0
Spectrum 5	38.6	21.6	15.7	0.8	23.2	100.0
avg	32.5	28.0	15.6	5.2	18.7	
std	4.0	8.4	9.8	4.7	3.2	

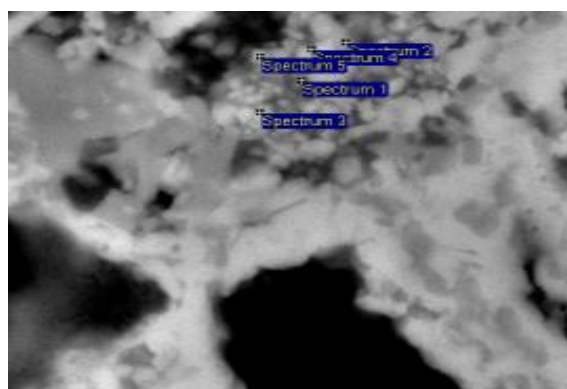


Figure F 3: EDX analysis of $\text{Ti}_3\text{SiC}_2\text{-cBN}$ (20 vol.%, 10 μm) sample sintered at 30 MPa, 1 minute and 1600°C. Site 3.

Spectrum	B	C	N	Si	Ti	Total
Atomic %						
Spectrum 1	28.7	20.7	25.8	3.2	21.5	100.0
Spectrum 2	33.6	23.9	18.4	1.8	22.2	100.0
Spectrum 3	54.6	20.9	0.0	4.0	20.5	100.0
Spectrum 4	28.8	17.1	38.2	3.0	12.8	100.0
Spectrum 5	23.5	21.9	30.8	0.9	22.9	100.0
avg	33.9	20.9	22.6	2.6	20.0	
std	12.1	2.5	14.6	1.2	4.1	

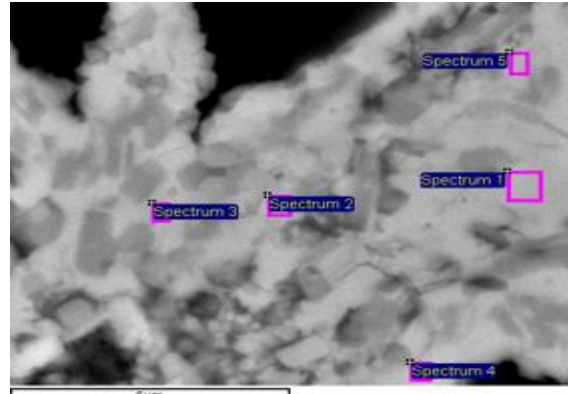


Figure F 4: EDX analysis of $\text{Ti}_3\text{SiC}_2\text{-cBN}$ (20 vol.%, 10 μm) sample sintered at 30 MPa, 1 minute and 1600°C. Site 4.

Spectrum	B	C	N	Al	Si	Ti	Total
atomic %							
Spectrum 1	47.2	11.8	40.9	0.0	0.0	0.1	100.0
Spectrum 2	60.1	0.0	39.8	0.0	0.0	0.1	100.0
Spectrum 3	47.0	10.7	42.1	0.0	0.0	0.2	100.0
Spectrum 4	22.5	77.3	0.0	0.0	0.0	0.2	100.0
Spectrum 5	55.9	0.0	43.9	0.0	0.0	0.2	100.0
Spectrum 6	42.7	15.9	41.3	0.0	0.0	0.1	100.0
avg	45.9	19.3	34.7	0.0	0.0	0.1	
std	13.2	29.2	17.0	0.0	0.0	0.0	

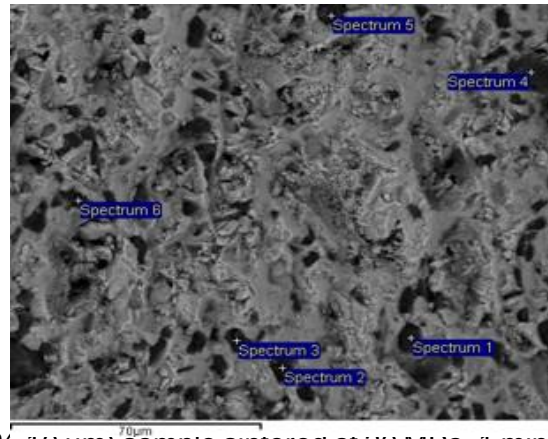


Figure F 5: EDX analysis of $\text{Ti}_3\text{SiC}_2\text{-cBN}$ (20 vol.%, 10 μm) sample sintered at 30 MPa, 1 minute and 1250°C. Site 1.

Spectrum	B	C	N	Al	Si	Ti	Total
atomic %							
Spectrum 1	48.3	31.4	0.0	0.0	0.0	20.3	100.0
Spectrum 2	49.4	29.1	0.0	0.0	0.7	20.7	100.0
Spectrum 3	53.0	29.2	0.0	0.2	1.4	16.2	100.0
Spectrum 4	56.5	19.0	0.0	0.0	2.4	22.0	100.0
Spectrum 5	41.8	24.2	17.8	0.2	0.8	15.2	100.0
avg	49.8	26.6	3.6	0.1	1.1	18.9	
std	5.5	5.0	8.0	0.1	0.9	3.0	

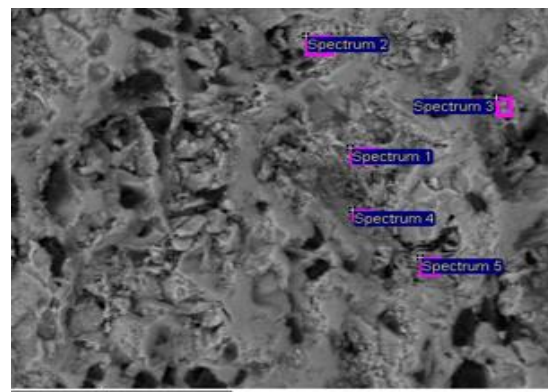


Figure F 6: EDX analysis of $\text{Ti}_3\text{SiC}_2\text{-cBN}$ (20 vol.%, 10 μm) sample sintered at 30 MPa, 1 minute and 1250°C. Site 2.

Spectrum	B	C	N	Al	Si	Ti	Total
atomic %							
Spectrum 1	51.7	37.5	0.0	0.0	9.7	1.1	100.0
Spectrum 2	60.1	17.1	0.0	0.0	0.0	22.8	100.0
Spectrum 3	61.7	19.0	0.0	0.0	0.0	19.3	100.0
Spectrum 4	51.8	37.9	0.0	0.0	8.8	1.6	100.0
avg	56.3	27.9	0.0	0.0	4.6	11.2	
std	5.3	11.4	0.0	0.0	5.3	11.5	

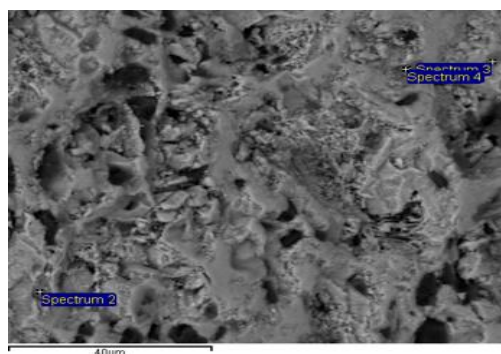


Figure F 7: EDX analysis of $\text{Ti}_3\text{SiC}_2\text{-cBN}$ (20 vol.%, 10 μm) sample sintered at 30 MPa, 1 minute and 1250°C. Site 3.

Spectrum	B	C	N	Al	Si	Ti	Total
atomic %							
Spectrum 1	56.0	24.0	0.0	0.0	1.0	19.0	100.0
Spectrum 2	40.3	17.8	26.5	0.0	0.0	15.4	100.0
Spectrum 3	37.3	23.6	26.1	0.0	0.3	12.7	100.0
Spectrum 4	40.3	16.2	26.5	0.0	1.3	15.7	100.0
Spectrum 5	49.2	29.9	0.0	0.0	0.0	20.9	100.0
Spectrum 6	34.5	18.2	30.8	0.0	0.0	16.4	100.0
avg	43.0	21.6	18.3	0.0	0.4	16.7	
std	8.1	5.2	14.3	0.0	0.6	2.9	

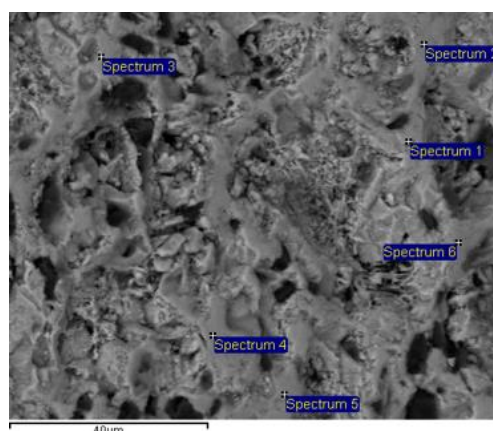


Figure F 8: EDX analysis of $\text{Ti}_3\text{SiC}_2\text{-cBN}$ (20 vol.%, 10 μm) sample sintered at 30 MPa, 1 minute and 1250°C. Site 4.

Spectrum	B	C	N	Si	Ti	Total
atomic %						
Spectrum 1						0
Spectrum 2						0
Spectrum 3	58.2	0.0	41.8	0.0	0.0	100.0
Spectrum 4	53.2	0.0	46.8	0.0	0.0	100.0
Spectrum 5						
avg	55.7	0.0	44.3	0.0	0.0	
std	3.6	0.0	3.6	0.0	0.0	

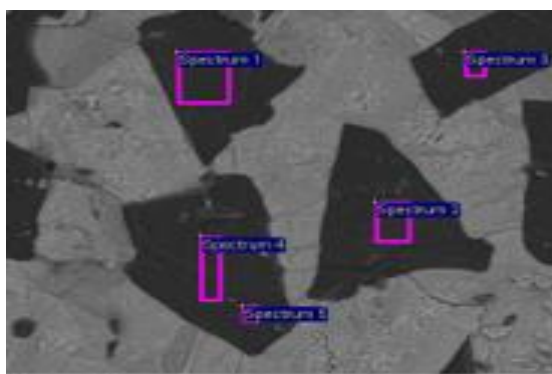


Figure F 9: SEM (BSE) and EDX analysis of $\text{Ti}_3\text{SiC}_2\text{-cBN}$ (20 vol.%, 100 μm) samples sintered at 30 MPa, 1250°C for 1 minute. Site 1.

Spectrum	B	C	N	Si	Ti	Total
atomic %						
Spectrum 1						
Spectrum 2						
Spectrum 3	63.1	17.5	0.0	0.0	19.5	100.0
Spectrum 4	54.4	26.7	0.0	0.0	18.9	100.0
Spectrum 5	64.1	21.8	0.0	0.0	14.0	100.0
avg	60.5	22.0	0.0	0.0	17.5	
std	5.4	4.6	0.0	0.0	3.0	

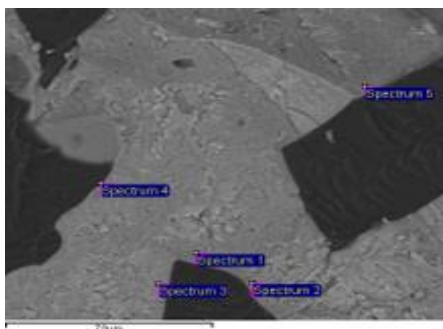


Figure F 10: SEM (BSE) and EDX analysis of Ti_3SiC_2 -cBN (20 vol.%, 100 μm) samples sintered at 30 MPa, 1250°C for 1 minute. Site 2.

Spectrum	B	C	N	Si	Ti	Total
atomic %						
Spectrum 1	57.0	19.4	0.0	7.1	16.5	100.0
Spectrum 2						
Spectrum 3	53.5	22.0	0.0	0.8	23.7	100.0
Spectrum 4	57.0	22.9	0.0	5.9	14.2	100.0
avg	55.8	21.4	0.0	4.6	18.2	
std	2.0	1.8	0.0	3.3	5.0	

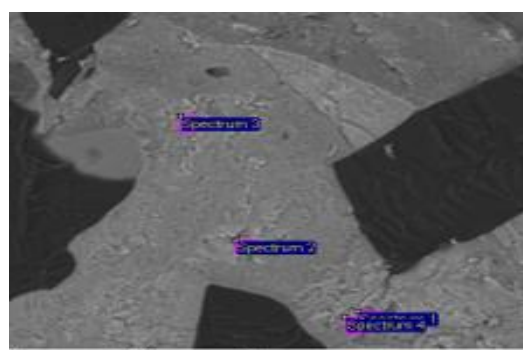


Figure F 11: SEM (BSE) and EDX analysis of Ti_3SiC_2 -cBN (20 vol.%, 100 μm) samples sintered at 30 MPa, 1250°C for 1 minute. Site 3.

Spectrum	B	C	N	Si	Ti	Total
atomic %						
Spectrum 1	40.9	38.3	0.0	0.3	20.5	100.0
Spectrum 2	48.0	31.6	0.0	0.3	20.1	100.0
Spectrum 3	42.1	43.9	0.0	0.4	13.6	100.0
Spectrum 4						
Spectrum 5						
Spectrum 6	38.8	44.9	0.0	0.7	15.7	100.0
avg	42.5	39.6	0.0	0.4	17.5	
std	4.0	6.1	0.0	0.2	3.4	

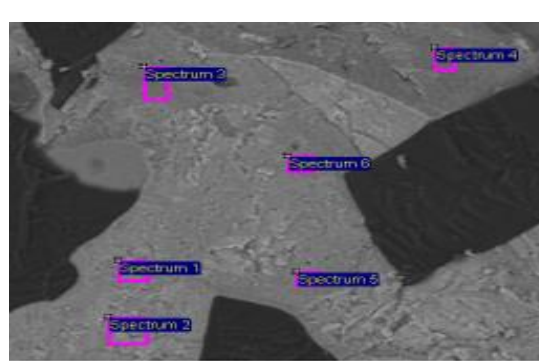


Figure F 12: SEM (BSE) and EDX analysis of Ti_3SiC_2 -cBN (20 vol.%, 100 μm) samples sintered at 30 MPa, 1250°C for 1 minute. Site 4.

Spectrum	B	C	N	Si	Ti	Total
atomic %						
Spectrum 1						
Spectrum 2	51.1	10.9	38.0	0.0	0.0	100.0
Spectrum 3						0.0
Spectrum 4	49.7	12.2	37.9	0.0	0.3	100.0
Spectrum 5	51.1	11.9	37.0	0.0	0.0	100.0
avg	50.6	11.7	37.6	0.0	0.1	
std	0.8	0.6	0.6	0.0	0.1	

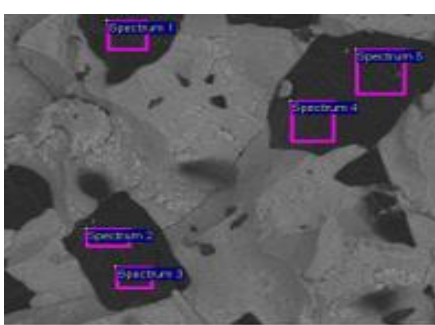


Figure F 13: SEM (BSE) and EDX analysis of Ti_3SiC_2 -cBN (20 vol.%, 100 μm) samples sintered at 30 MPa, 1250°C for 5 minute. Site 1

Spectrum	B	C	N	Si	Ti	Total
atomic %						
Spectrum 1	50.4	32.4	0.0	3.9	13.2	100.0
Spectrum 2	52.4	28.4	0.0	3.3	15.8	100.0
Spectrum 4	59.5	22.7	0.0	0.2	17.7	100.0
Spectrum 5						
avg	54.1	27.8	0.0	2.5	15.6	
std	4.8	4.9	0.0	2.0	2.2	

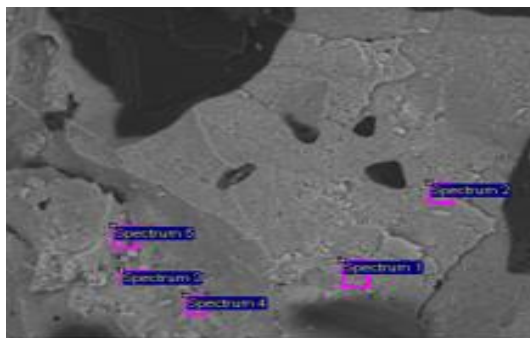


Figure F 14: SEM (BSE) and EDX analysis of Ti_3SiC_2 -cBN (20 vol.%, 100 μm) samples sintered at 30 MPa, 1250°C for 5 minute. Site 2

Spectrum	B	C	N	Si	Ti	Total
atomic %						
Spectrum 1						
Spectrum 2	60.8	18.1	0.0	0.0	21.2	100.0
Spectrum 3	65.4	16.0	0.0	0.0	18.7	100.0
Spectrum 5	59.6	28.4	0.0	0.0	12.1	100.0
avg	61.9	20.8	0.0	0.0	17.3	
std	3.1	6.6	0.0	0.0	4.7	

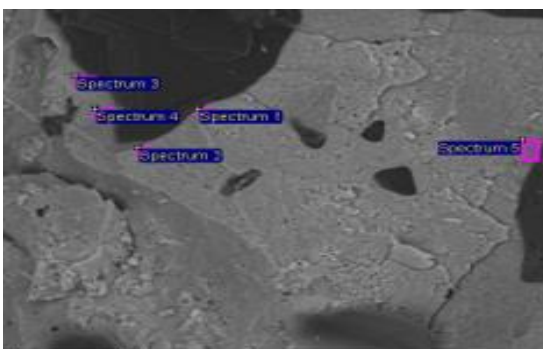


Figure F 15: SEM (BSE) and EDX analysis of Ti_3SiC_2 -cBN (20 vol.%, 100 μm) samples sintered at 30 MPa, 1250°C for 5 minute. Site 3.

Spectrum	B	C	N	Si	Ti	Total
atomic %						
Spectrum 1						
Spectrum 2	62.0	17.9	0.0	0.1	19.9	100.0
Spectrum 3	61.0	25.4	0.0	0.0	13.6	100.0
Spectrum 5	63.2	21.8	0.0	0.0	15.1	100.0
avg	62.1	21.7	0.0	0.0	16.2	
std	1.1	3.7	0.0	0.1	3.3	

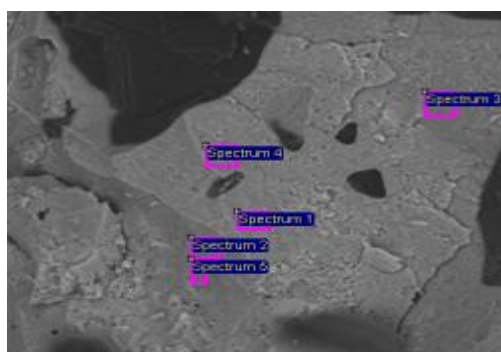


Figure F 16: SEM (BSE) and EDX analysis of Ti_3SiC_2 -cBN (20 vol.%, 100 μm) samples sintered at 30 MPa, 1250°C for 5 minute. Site 4

Spectrum	B	C	N	Si	Ti	Total
atomic %						
Spectrum 1	46.6	11.3	42.1	0.0	0.0	100.0
Spectrum 2	49.1	12.7	38.1	0.0	0.1	100.0
Spectrum 3	50.5	11.5	38.0	0.0	0.1	100.0
Spectrum 4	45.2	14.9	39.9	0.0	0.0	100.0
Spectrum 7	46.5	12.7	40.8	0.0	0.0	100.0
avg	47.8	12.9	39.2	0.0	0.1	
std	2.4	1.4	1.4	0.0	0.1	

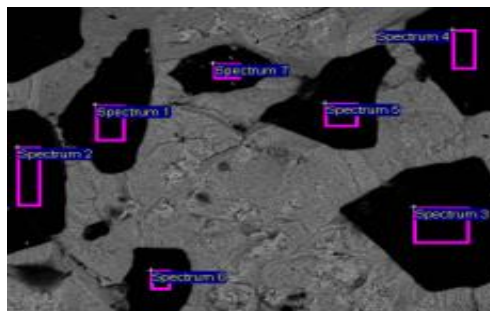


Figure F 17: SEM (BSE) and EDX analysis of $\text{Ti}_3\text{SiC}_2\text{-CBN}$ (20 vol.%, 100 μm) samples sintered at 30 MPa, 1250°C for 10 minute. Site 1.

Spectrum	B	C	N	Si	Ti	Total
atomic %						
Spectrum 1	66.5	17.2	0.0	0.0	16.3	100.0
Spectrum 2						
Spectrum 3	53.9	29.6	0.0	0.0	16.5	100.0
Spectrum 4	62.3	18.0	0.0	0.0	19.7	100.0
Spectrum 5	58.0	20.2	0.0	0.0	21.8	100.0
Spectrum 6	62.5	24.1	0.0	0.0	13.4	100.0
avg	60.6	21.8	0.0	0.0	17.5	
std	4.8	5.1	0.0	0.0	3.3	

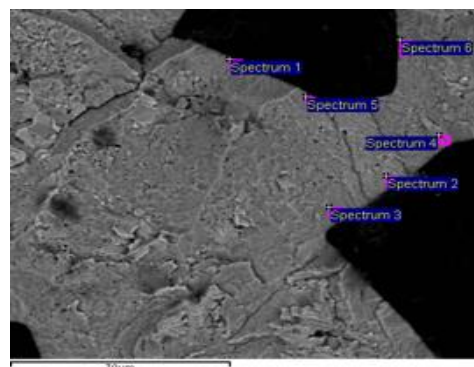


Figure F 18: SEM (BSE) and EDX analysis of $\text{Ti}_3\text{SiC}_2\text{-CBN}$ (20 vol.%, 100 μm) samples sintered at 30 MPa, 1250°C for 10 minute. Site 2.

Spectrum	B	C	N	Si	Ti	Total
atomic %						
Spectrum 1	52.7	30.6	0.0	3.8	12.8	100.0
Spectrum 2	49.5	26.0	0.0	2.5	22.1	100.0
Spectrum 4	49.0	32.3	0.0	3.7	15.0	100.0
Spectrum 6						
avg	50.4	29.6	0.0	3.3	16.6	
std	2.0	3.3	0.0	0.7	4.8	

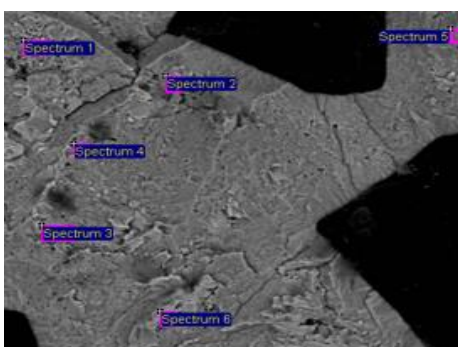


Figure F 19: SEM (BSE) and EDX analysis of $\text{Ti}_3\text{SiC}_2\text{-CBN}$ (20 vol.%, 100 μm) samples sintered at 30 MPa, 1250°C for 10 minute. Site 3.

Spectrum	B	C	N	Si	Ti	Total
atomic %						
Spectrum 1	59.7	17.9	0.0	0.0	22.4	100.0
Spectrum 2	60.6	17.5	0.0	0.0	21.9	100.0
Spectrum 3	60.2	15.6	0.0	0.0	24.2	100.0
Spectrum 4	59.1	19.6	0.0	0.0	21.3	100.0
Spectrum 6	58.7	26.2	0.0	0.0	15.1	100.0
avg	59.6	19.7	0.0	0.0	20.6	
std	0.9	4.6	0.0	0.0	3.9	

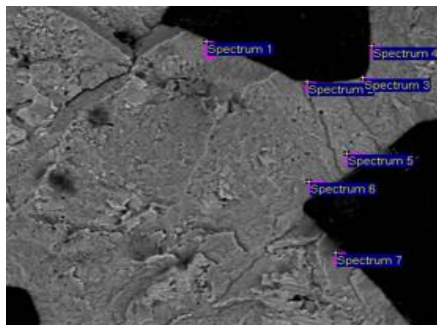


Figure F 20: SEM (BSE) and EDX analysis of $\text{Ti}_3\text{SiC}_2\text{-CBN}$ (20 vol.%, 100 μm) samples sintered at 30 MPa, 1250°C for 10 minute. Site 4.

Spectrum	B	C	N	Si	Ti	Total
atomic %						
Spectrum 1	48.2	31.2	0.0	1.4	19.2	100.0
Spectrum 2	53.8	23.0	0.0	0.6	22.7	100.0
Spectrum 3	46.6	32.7	0.0	0.6	20.2	100.0
Spectrum 4						
Spectrum 5	46.8	22.4	0.0	0.5	30.4	100.0
avg	48.8	27.3	0.0	0.8	23.1	
std	3.4	5.4	0.0	0.4	5.0	

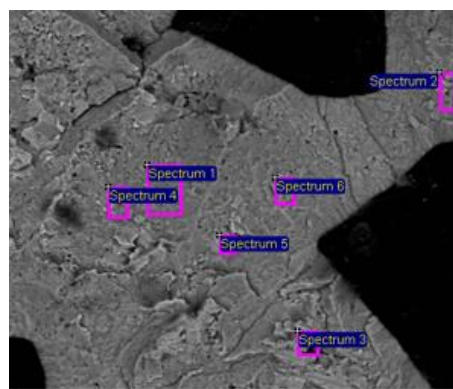


Figure F 21: SEM (BSE) and EDX analysis of $\text{Ti}_3\text{SiC}_2\text{-CBN}$ (20 vol.%, 100 μm) samples sintered at 30 MPa, 1250°C for 10 minute. Site 5.

Spectrum	B	C	N	Al	Si	Ti	Total
atomic %							
Spectrum 1	51.0	18.0	30.7	0.0	0.0	0.3	100.0
Spectrum 2	49.7	7.7	42.6	0.0	0.0	0.1	100.0
Spectrum 3							0.0
Spectrum 5	59.8	0.0	40.2	0.0	0.0	0.0	100.0
Spectrum 6	51.3	9.3	39.4	0.0	0.0	0.0	100.0
avg	52.9	8.7	38.2	0.0	0.0	0.1	
std	4.6	7.4	5.2	0.0	0.0	0.1	

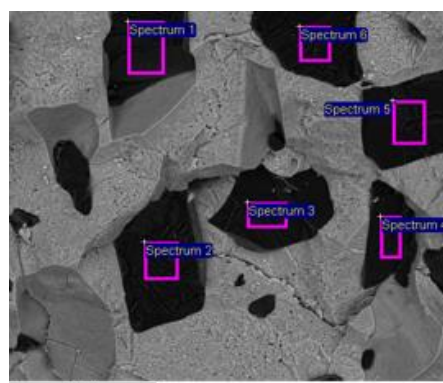


Figure F 22: SEM (BSE) and EDX analysis of $\text{Ti}_3\text{SiC}_2\text{-cBN}$ (20 vol.%, 100 μm) samples sintered at 30 MPa, 1300°C for 1 minute. Site 1.

Spectrum	B	C	N	Al	Si	Ti	Total
atomic %							
Spectrum 1	57.4	25.7	0.0	0.0	0.0	16.9	100.0
Spectrum 2	56.6	25.8	0.0	0.0	0.0	17.6	100.0
Spectrum 3	60.5	13.2	0.0	0.0	0.0	26.3	100.0
Spectrum 4	53.4	25.5	0.0	0.0	0.0	21.1	100.0
Spectrum 5							
avg	57.0	22.5	0.0	0.0	0.0	20.5	
std	2.9	6.2	0.0	0.0	0.0	4.3	

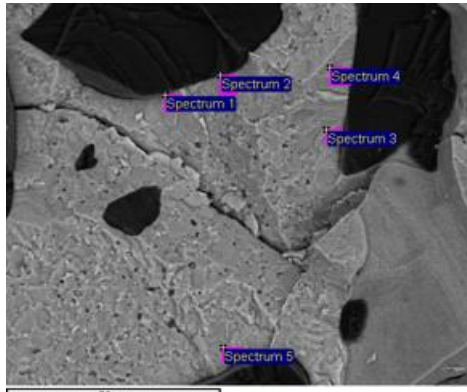


Figure F 23: SEM (BSE) and EDX analysis of Ti_3SiC_2 -cBN (20 vol.%, 100 μm) samples sintered at 30 MPa, 1300°C for 1 minute. Site 2.

Spectrum	B	C	N	Al	Si	Ti	Total
atomic %							
Spectrum 1	42.5	36.4	0.0	0.0	1.7	19.4	100.0
Spectrum 2	42.6	38.3	0.0	0.0	0.4	18.7	100.0
Spectrum 3							
Spectrum 5	45.5	36.5	0.0	0.0	0.7	17.3	100.0
Spectrum 6	43.5	37.4	0.0	0.0	0.2	18.9	100.0
avg	43.5	37.1	0.0	0.0	0.7	18.6	
std	1.4	0.9	0.0	0.0	0.7	0.9	

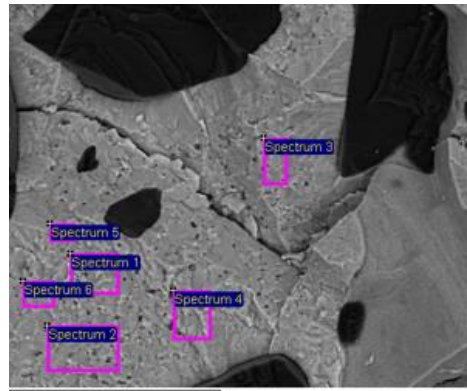


Figure F 24: SEM (BSE) and EDX analysis of Ti_3SiC_2 -cBN (20 vol.%, 100 μm) samples sintered at 30 MPa, 1300°C for 1 minute. Site 3.

Spectrum	B	C	N	Al	Si	Ti	Total
atomic %							
Spectrum 1	65.2	0.0	34.8	0.0	0.0	0.0	100.0
Spectrum 2	46.2	15.4	38.4	0.0	0.0	0.1	
Spectrum 3	61.7	0.0	38.3	0.0	0.0	0.0	100.0
Spectrum 4	59.3	0.0	40.7	0.0	0.0	0.0	100.0
Spectrum 5	46.4	14.9	38.7	0.0	0.0	0.0	
avg	55.7	6.1	38.2	0.0	0.0	0.0	
std	8.9	8.3	2.1	0.0	0.0	0.1	

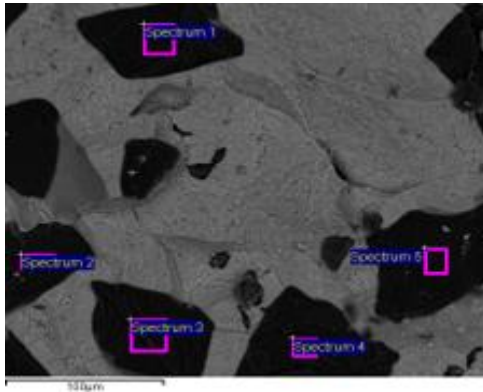


Figure F 25: SEM (BSE) and EDX analysis of Ti_3SiC_2 -cBN (20 vol.%, 100 μm) samples sintered at 30 MPa, 1300°C for 5 minute. Site 1.

Spectrum	B	C	N	Al	Si	Ti	Total
atomic %							
Spectrum 1	58.9	21.5	0.0	0.0	0.0	19.6	100.0
Spectrum 2	58.6	20.2	0.0	0.0	0.0	21.2	100.0
Spectrum 3	52.5	31.3	0.0	0.0	0.0	16.2	100.0
Spectrum 4	64.5	19.3	0.0	0.0	0.0	16.2	100.0
avg	58.6	23.1	0.0	0.0	0.0	18.3	
std	4.9	5.5	0.0	0.0	0.0	2.5	

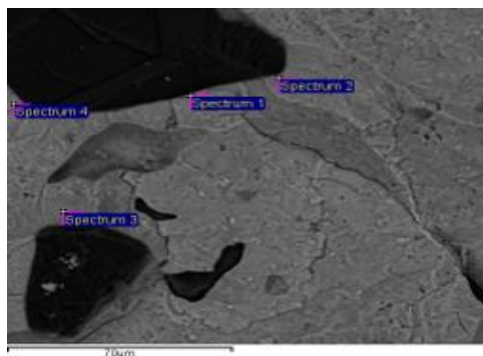


Figure F 26: SEM (BSE) and EDX analysis of $\text{Ti}_3\text{SiC}_2\text{-cBN}$ (20 vol.%, 100 μm) samples sintered at 30 MPa, 1300°C for 5 minute. Site 2.

Spectrum	B	C	N	Al	Si	Ti	Total
atomic %							
Spectrum 1	47.4	33.2	0.0	0.0	0.4	19.0	100.0
Spectrum 2	51.9	29.6	0.0	0.0	0.5	18.0	100.0
Spectrum 3	39.9	44.7	0.0	0.0	0.0	15.4	100.0
Spectrum 4	55.1	27.8	0.0	0.0	0.3	16.8	100.0
Spectrum 5	47.2	34.6	0.0	0.0	0.4	17.9	100.0
Spectrum 6	46.5	33.4	0.0	0.0	0.0	20.1	100.0
avg	48.0	33.9	0.0	0.0	0.3	17.9	
std	5.2	5.9	0.0	0.0	0.2	1.6	

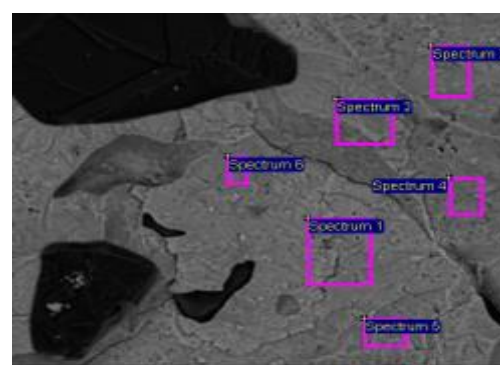


Figure F 27: SEM (BSE) and EDX analysis of $\text{Ti}_3\text{SiC}_2\text{-cBN}$ (20 vol.%, 100 μm) samples sintered at 30 MPa, 1300°C for 5 minute. Site 3.

Spectrum	B	C	N	Si	Ti	Total
atomic %						
Spectrum 1	46.9	9.7	43.3	0.0	0.1	100.0
Spectrum 2	57.2	0.0	42.7	0.0	0.1	100.0
Spectrum 3	47.2	9.8	43.0	0.0	0.1	100.0
Spectrum 4	51.9	10.6	37.3	0.0	0.2	100.0
Spectrum 5	49.1	11.5	39.4	0.0	0.1	100.0
Spectrum 6	48.4	9.3	42.3	0.0	0.1	100.0
avg	50.1	8.5	41.3	0.0	0.1	
std	3.9	4.2	2.4	0.0	0.1	

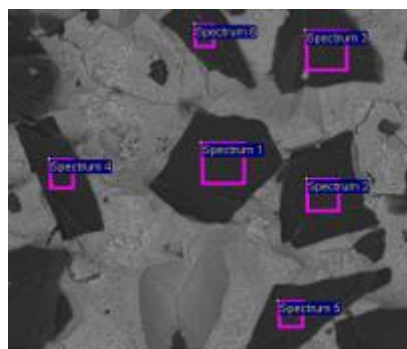


Figure F 28: SEM (BSE) and EDX analysis of $\text{Ti}_3\text{SiC}_2\text{-cBN}$ (20 vol.%, 100 μm) samples sintered at 30 MPa, 1300°C for 10 minute. Site 1.

Spectrum	B	C	N	Si	Ti	Total
atomic %						
Spectrum 1	64.5	13.5	0.0	0.0	22.0	100.0
Spectrum 2	48.9	17.5	15.2	0.0	18.4	100.0
Spectrum 3	61.7	22.9	0.0	0.0	15.4	100.0
Spectrum 4	63.1	18.6	0.0	0.0	18.4	100.0
Spectrum 5	58.6	22.9	0.0	0.3	18.2	100.0
avg	59.4	19.1	3.0	0.1	18.5	
std	6.2	4.0	6.8	0.1	2.3	

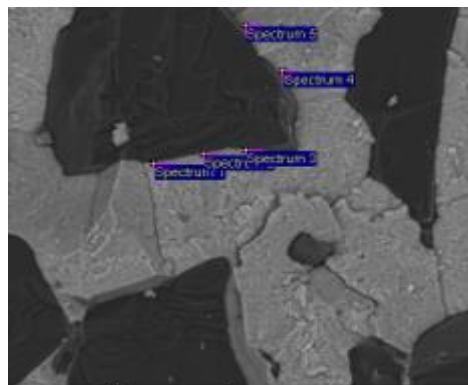


Figure F 29: SEM (BSE) and EDX analysis of Ti_3SiC_2 -cBN (20 vol.%, 100 μm) samples sintered at 30 MPa, 1300°C for 10 minute. Site 2.

Spectrum	B	C	N	Si	Ti	Total
atomic %						
Spectrum 1	50.5	25.7	0.0	1.7	22.1	100.0
Spectrum 2						
Spectrum 3	50.1	28.9	0.0	1.3	19.7	100.0
Spectrum 4	47.5	36.7	0.0	0.2	15.6	100.0
Spectrum 5	44.6	36.9	0.0	0.4	18.0	100.0
avg	48.2	32.0	0.0	0.9	18.9	
std	2.7	5.6	0.0	0.7	2.8	

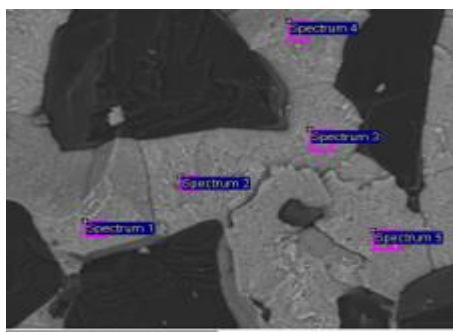


Figure F 30: SEM (BSE) and EDX analysis of Ti_3SiC_2 -cBN (20 vol.%, 100 μm) samples sintered at 30 MPa, 1300°C for 10 minute. Site 3.

Spectrum	B	C	N	Si	Ti	Total
atomic %						
Spectrum 1	53.8	0.0	46.1	0.0	0.1	100.0
Spectrum 2	55.3	0.0	44.7	0.0	0.0	100.0
Spectrum 3	49.8	8.3	41.9	0.0	0.0	100.0
Spectrum 4	52.1	19.5	28.4	0.0	0.0	100.0
Spectrum 5	60.7	0.0	39.0	0.0	0.3	100.0
Spectrum 6	50.3	8.6	41.0	0.0	0.1	100.0
Spectrum 7	52.8	27.2	19.8	0.0	0.2	100.0
avg	53.5	10.6	35.8	0.0	0.1	
std	4.0	10.9	9.7	0.0	0.1	

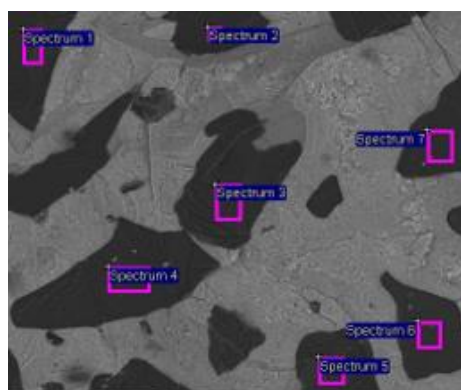


Figure F 31: SEM (BSE) and EDX analysis of Ti_3SiC_2 -cBN (40 vol.%, 100 μm) samples sintered at 30 MPa, 1250°C for 5 minute. Site 1.

Spectrum	B	C	N	Si	Ti	Total
atomic %						
Spectrum 1	56.1	22.4	0.0	2.9	18.6	100.0
Spectrum 2	58.9	21.4	0.0	4.5	15.2	100.0
Spectrum 3	55.9	22.2	0.0	4.5	17.4	100.0
Spectrum 4	56.7	23.7	0.0	3.5	16.1	100.0
avg	56.9	22.4	0.0	3.8	16.8	
std	1.4	0.9	0.0	0.8	1.5	

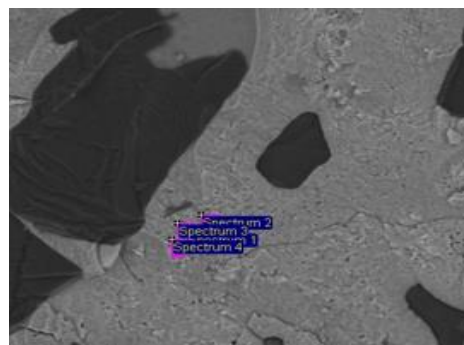


Figure F 32: SEM (BSE) and EDX analysis of Ti_3SiC_2 -cBN (40 vol.%, 100 μm) samples sintered at 30 MPa, 1250°C for 5 minute. Site 2.

Spectrum	B	C	N	Si	Ti	Total
atomic %						
Spectrum 1	56.2	26.0	0.0	0.0	17.8	100.0
Spectrum 2	56.8	21.6	0.0	0.0	21.6	100.0
Spectrum 3	53.7	23.4	0.0	0.0	22.8	100.0
Spectrum 4	51.5	29.8	0.0	0.3	18.5	100.0
Spectrum 5	59.3	21.8	0.0	0.0	18.9	100.0
Spectrum 6	61.1	25.5	0.0	0.0	13.4	100.0
Spectrum 7	62.2	15.3	0.0	0.0	22.5	100.0
avg	57.4	22.9	0.0	0.1	19.6	
std	4.2	4.8	0.0	0.1	3.5	

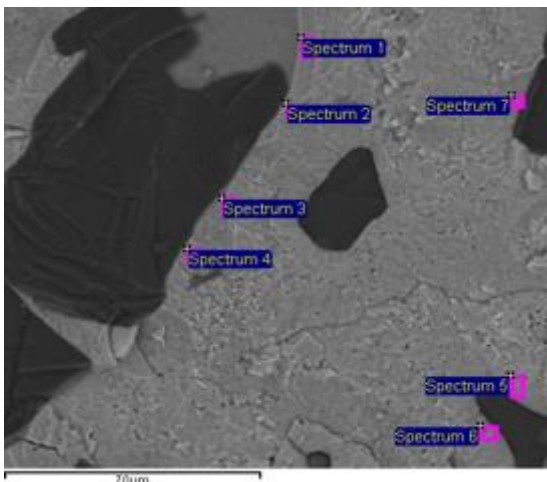


Figure F 33: SEM (BSE) and EDX analysis of Ti_3SiC_2 -cBN (40 vol.%, 100 μm) samples sintered at 30 MPa, 1250°C for 5 minute. Site 3.

Spectrum	B	C	N	Si	Ti	Total
atomic %						
Spectrum 1	49.9	29.3	0.0	0.9	20.0	100.0
Spectrum 2	45.4	33.0	0.0	0.3	21.3	100.0
Spectrum 3	45.8	33.6	0.0	0.0	20.6	100.0
Spectrum 4	49.3	28.1	0.0	0.0	22.6	100.0
Spectrum 5	47.4	34.4	0.0	0.0	18.2	100.0
avg	47.5	31.7	0.0	0.2	20.5	
std	2.0	2.8	0.0	0.4	1.6	

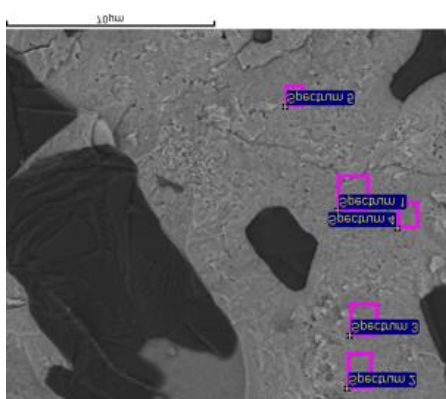


Figure F 34: SEM (BSE) and EDX analysis of Ti_3SiC_2 -cBN (40 vol.%, 100 μm) samples sintered at 30 MPa, 1250°C for 5 minute. Site 4.

Spectrum	B	C	N	Si	Ti	Total
atomic %						
Spectrum 1	51.3	9.5	39.2	0.0	0.0	100.0
Spectrum 2	60.5	0.0	39.5	0.0	0.0	100.0
Spectrum 3	49.3	16.3	34.4	0.0	0.0	100.0
Spectrum 4	57.3	0.0	42.6	0.0	0.1	100.0
Spectrum 5	50.6	10.3	38.9	0.1	0.1	100.0
Spectrum 6	50.7	8.6	40.6	0.0	0.0	100.0
avg	53.3	7.5	39.2	0.0	0.0	
std	4.5	6.4	2.7	0.0	0.1	

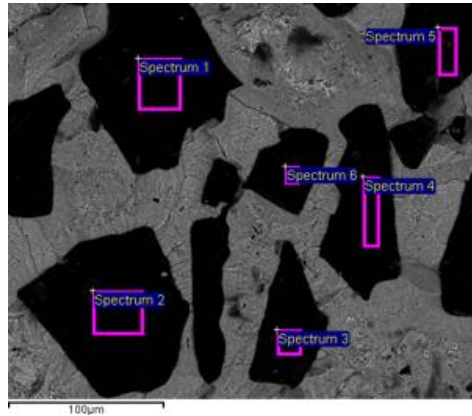


Figure F 35: SEM (BSE) and EDX analysis of Ti_3SiC_2 -cBN (40 vol.%, 100 μm) samples sintered at 30 MPa, 1250°C for 10 minute. Site 1.

Spectrum	B	C	N	Si	Ti	Total
atomic %						
Spectrum 1	52.0	15.2	0.0	0.0	32.8	100.0
Spectrum 2	63.1	19.7	0.0	0.0	17.2	100.0
Spectrum 3	51.7	29.2	0.0	0.0	19.2	100.0
Spectrum 4	59.4	18.3	8.5	0.0	13.7	100.0
Spectrum 5	56.3	24.3	0.0	0.0	19.5	100.0
Spectrum 6	55.7	27.2	0.0	0.0	17.1	100.0
avg	56.4	22.3	1.4	0.0	19.9	
std	4.4	5.4	3.5	0.0	6.6	

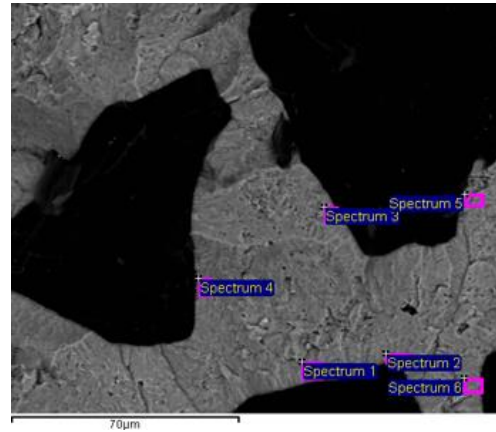


Figure F 36: SEM (BSE) and EDX analysis of Ti_3SiC_2 -cBN (40 vol.%, 100 μm) samples sintered at 30 MPa, 1250°C for 10 minute. Site 2.

Spectrum	B	C	N	Si	Ti	Total
atomic %						
Spectrum 1	51.5	32.6	0.0	3.2	12.7	100.0
Spectrum 2	37.4	41.7	0.0	0.5	20.5	100.0
Spectrum 3	48.2	25.9	0.0	0.9	25.1	100.0
Spectrum 4	52.6	26.8	0.0	0.2	20.4	100.0
avg	47.4	31.7	0.0	1.2	19.7	100.0
std	6.9	7.3	0.0	1.4	5.1	20.7

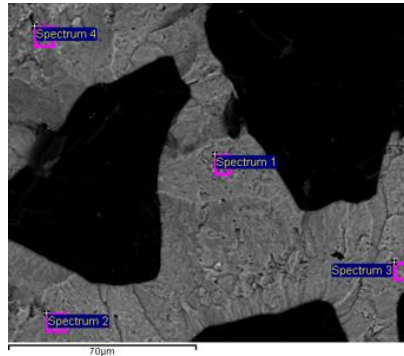


Figure F 37: SEM (BSE) and EDX analysis of Ti_3SiC_2 -cBN (40 vol.%, 100 μm) samples sintered at 30 MPa, 1250°C for 10 minute. Site 3.

Spectrum	B	C	N	Si	Ti	Total
atomic %						
Spectrum 1	50.6	30.0	0.0	0.0	19.4	100.0
Spectrum 2	48.3	25.3	0.0	0.4	26.0	100.0
Spectrum 3	49.1	32.9	0.0	0.0	18.0	100.0
Spectrum 4	50.4	25.9	0.0	0.0	23.7	100.0
Spectrum 5	47.6	27.0	0.0	2.2	23.2	100.0
avg	49.2	28.2	0.0	0.5	22.1	
std	1.3	3.2	0.0	1.0	3.3	

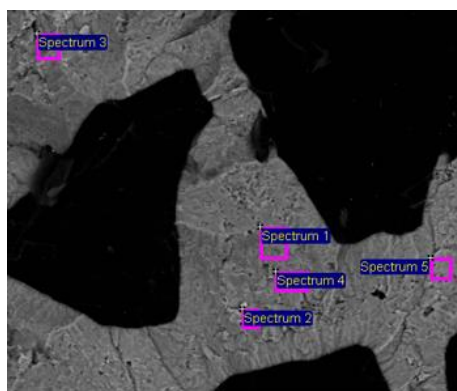


Figure F 38: SEM (BSE) and EDX analysis of Ti_3SiC_2 -cBN (40 vol.%, 100 μm) samples sintered at 30 MPa, 1250°C for 10 minute. Site 4.

Spectrum	B	C	N	Al	Si	Ti	Total
atomic %							
Spectrum 1	47.4	11.7	40.8	0.0	0.0	0.0	100.0
Spectrum 2	40.2	26.4	33.4	0.0	0.0	0.0	100.0
Spectrum 3	49.9	12.0	37.9	0.0	0.0	0.3	100.0
Spectrum 4	53.8	0.0	46.1	0.0	0.0	0.1	100.0
Spectrum 5	48.6	12.6	38.7	0.0	0.0	0.1	100.0
Spectrum 6	52.3	9.2	38.4	0.0	0.0	0.1	100.0
avg	48.7	12.0	39.2	0.0	0.0	0.1	
std	4.8	8.5	4.2	0.0	0.0	0.1	

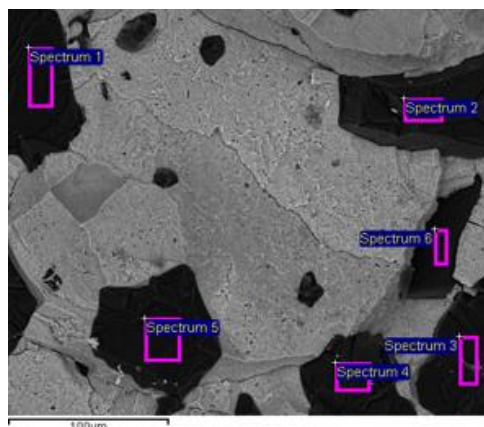


Figure F 39: SEM (BSE) and EDX analysis of Ti_3SiC_2 -cBN (40 vol.%, 100 μm) samples sintered at 30 MPa, 1300°C for 5 minute. Site 1.

Spectrum	B	C	N	Al	Si	Ti	Total
atomic %							
Spectrum 1	57.4	17.0	0.0	0.0	0.0	25.6	100.0
Spectrum 2	57.9	12.9	0.0	0.0	0.0	29.2	100.0
Spectrum 3	53.2	29.6	0.0	0.0	0.0	17.2	100.0
Spectrum 4	56.7	12.7	15.8	0.0	0.2	14.6	100.0
avg	56.3	18.1	3.9	0.0	0.1	21.6	
std	2.2	8.0	7.9	0.0	0.1	6.9	

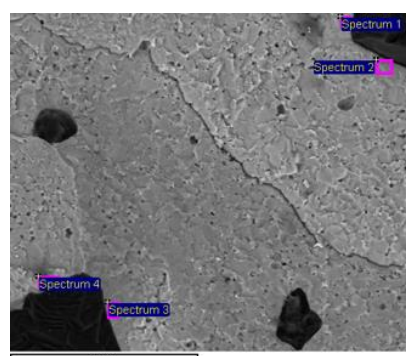


Figure F 40: SEM (BSE) and EDX analysis of Ti_3SiC_2 -cBN (40 vol.%, 100 μm) samples sintered at 30 MPa, 1300°C for 5 minute. Site 2.

Spectrum	B	C	N	Al	Si	Ti	Total
atomic %							
Spectrum 1	39.2	46.8	0.0	0.0	0.2	13.8	100.0
Spectrum 2	45.6	37.6	0.0	0.0	0.2	16.6	100.0
Spectrum 3	39.3	40.8	0.0	0.0	1.0	18.8	100.0
Spectrum 4	43.9	37.0	0.0	0.0	0.3	18.8	100.0
Spectrum 5	38.6	46.0	0.0	0.0	0.4	15.0	100.0
Spectrum 6	49.6	28.9	0.0	0.0	0.5	21.0	100.0
avg	42.7	39.5	0.0	0.0	0.5	17.3	
std	4.4	6.6	0.0	0.0	0.3	2.7	

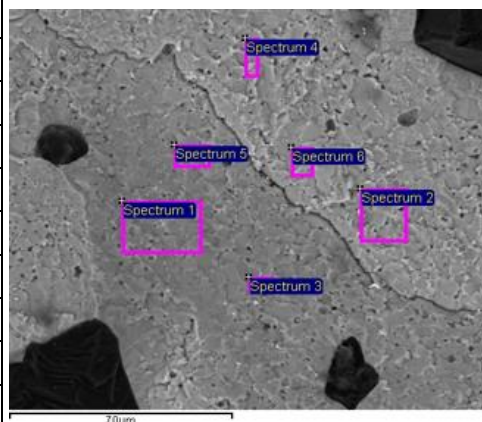


Figure F 41: SEM (BSE) and EDX analysis of $\text{Ti}_3\text{SiC}_2\text{-cBN}$ (40 vol.%, 100 μm) samples sintered at 30 MPa, 1300°C for 5 minute. Site 3.

Spectrum	B	C	N	Al	Si	Ti	Total
atomic %							
Spectrum 1	48.6	10.7	40.7	0.0	0.0	0.0	100.0
Spectrum 2	50.2	9.8	39.9	0.0	0.0	0.1	100.0
Spectrum 3	58.5	0.0	41.3	0.0	0.0	0.1	100.0
Spectrum 4	44.8	27.0	27.6	0.0	0.0	0.5	100.0
Spectrum 5	48.2	11.1	40.7	0.0	0.0	0.1	100.0
avg	50.1	11.7	38.1	0.0	0.0	0.2	
std	5.1	9.7	5.8	0.0	0.0	0.2	

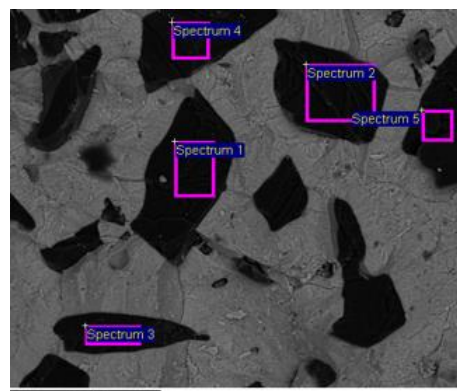


Figure F 42: SEM (BSE) and EDX analysis of $\text{Ti}_3\text{SiC}_2\text{-cBN}$ (40 vol.%, 100 μm) samples sintered at 30 MPa, 1300°C for 10 minute. Site 1.

Spectrum	B	C	N	Al	Si	Ti	Total
atomic %							
Spectrum 1	60.1	24.4	0.0	0.0	0.0	15.5	100.0
Spectrum 2	56.1	22.3	0.0	0.0	0.0	21.6	100.0
Spectrum 3	52.9	23.7	0.0	0.0	0.0	23.4	100.0
Spectrum 4	57.4	23.4	0.0	0.0	0.0	19.3	100.0
Spectrum 5	60.0	16.1	0.0	0.0	0.2	23.7	100.0
Spectrum 6	57.5	20.1	0.0	0.0	0.0	22.4	100.0
avg	57.3	21.7	0.0	0.0	0.0	21.0	
std	2.7	3.1	0.0	0.0	0.1	3.1	

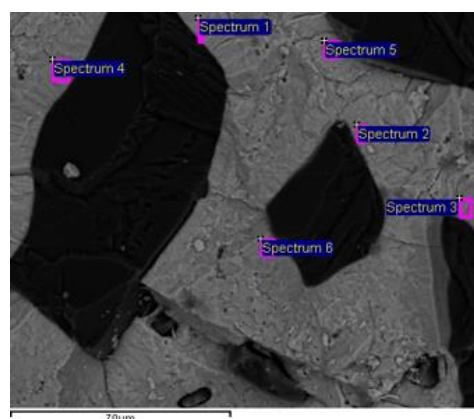


Figure F 43: SEM (BSE) and EDX analysis of $\text{Ti}_3\text{SiC}_2\text{-cBN}$ (40 vol.%, 100 μm) samples sintered at 30 MPa, 1300°C for 10 minute. Site 2.

Spectrum	B	C	N	Al	Si	Ti	Total
atomic %							
Spectrum 1	46.9	32.8	0.0	0.0	0.3	20.0	100.0
Spectrum 2	49.1	29.8	0.0	0.0	0.3	20.8	100.0
Spectrum 3	56.1	21.5	0.0	0.0	0.0	22.4	100.0
Spectrum 4	47.5	32.5	0.0	0.2	0.0	19.9	100.0
Spectrum 5	54.4	26.0	0.0	0.0	0.0	19.6	100.0
avg	50.8	28.5	0.0	0.0	0.1	20.6	
std	4.2	4.8	0.0	0.1	0.2	1.2	

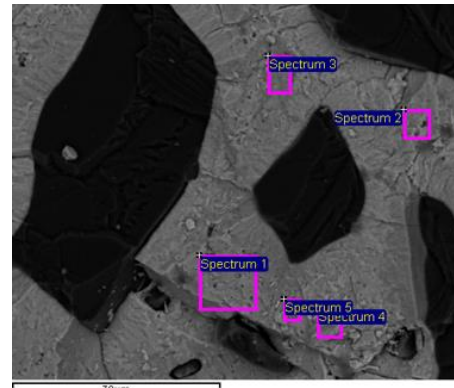


Figure F 44: SEM (BSE) and EDX analysis of Ti_3SiC_2 -cBN (40 vol.%, 100 μm) samples sintered at 30 MPa, 1300°C for 10 minute. Site 3.

Appendix G: Supplementary data for mechanical test results

Table G1: Sample identification and sample naming designation

cBN fraction and size in composite	MAX phase in composite	Naming designation
20 vol.% 10 μm cBN	Ti_2AlC	211(21)
	Ti_3AlC_2	312(21)
	Ti_3SiC_2	sic(21)
20 vol.% 100 μm cBN	Ti_2AlC	211(210)
	Ti_3AlC_2	312(210)
	Ti_3SiC_2	sic(210)
40 vol.% 100 μm cBN	Ti_2AlC	211(410)
	Ti_3AlC_2	312(410)
	Ti_3SiC_2	sic(410)

Table G2: Sample thicknesses for Ti₂AlC samples.

Different sample names	Thickness	Different sample names	Thickness	Different sample names	Thickness
211(21)-1	2,66	211(210)-1	3,50	211(410)-1	3,01
211(21)-2	2,66	211(210)-2	3,32	211(410)-2	3,70
211(21)-3	2,40	211(210)-3	3,40	211(410)-3	3,76
211(21)-4	2,42	211(210)-4	3,50	211(410)-4	3,01
211(21)-5	2,46	211(210)-5	3,28	211(410)-5	3,01
211(21)-6	2,50	211(210)-6	3,34	211(410)-6	3,80
211(21)-7	2,39	211(210)-7	3,44	211(410)-7	3,20
211(21)-8	2,56	211(210)-8	3,20	211(410)-8	3,01
211(21)-9	2,51	211(210)-9	3,48	211(410)-9	3,24
211(21)-10	2,67	211(210)-10	3,19	211(410)-10	3,36
211(21)-11	2,51	211(210)-11	3,41	211(410)-11	3,52
211(21)-12	2,42	211(210)-12	3,48	211(410)-12	3,11
211(21)-13	2,58	211(210)-13	3,35	211(410)-13	3,58
211(21)-14	2,40	211(210)-14	3,33	211(410)-14	3,72
211(21)-15	2,41	211(210)-15	3,45	211(410)-15	3,33
211(21)-16	2,46	211(210)-16	3,30	211(410)-16	3,63
211(21)-17	2,51	211(210)-17	3,41	211(410)-17	3,40
211(21)-18	2,61	211(210)-18	3,46	211(410)-18	3,09
211(21)-19	2,68	211(210)-19	3,29	211(410)-19	3,17
211(21)-20	2,40	211(210)-20	3,38	211(410)-20	3,56
Average	2,51	Average	3,38	Average	3,36

Table G3: Sample thickness for Ti_3SiC_2 samples.

Different sample names	Thickness	Different sample names	Thickness	Different sample names	Thickness
sic(21)_1	3,20	sic(210)_1	2,86	sic(410)_1	3,10
sic(21)_2	3,10	sic(210)_2	2,86	sic(410)_2	3,14
sic(21)_3	3,18	sic(210)_3	2,99	sic(410)_3	3,08
sic(21)_4	3,40	sic(210)_4	3,00	sic(410)_4	3,08
sic(21)_5	3,04	sic(210)_5	2,50	sic(410)_5	3,00
sic(21)_6	3,52	sic(210)_6	2,90	sic(410)_6	3,10
sic(21)_7	3,48	sic(210)_7	2,57	sic(410)_7	3,10
sic(21)_8	3,12	sic(210)_8	2,85	sic(410)_8	3,20
sic(21)_9	3,38	sic(210)_9	2,84	sic(410)_9	3,04
sic(21)_10	3,39	sic(210)_10	2,51	sic(410)_10	3,06
sic(21)_11	3,37	sic(210)_11	2,91	sic(410)_11	3,18
sic(21)_12	3,41	sic(210)_12	2,61	sic(410)_12	3,16
sic(21)_13	3,25	sic(210)_13	2,82	sic(410)_13	3,08
sic(21)_14	3,29	sic(210)_14	2,66	sic(410)_14	3,09
sic(21)_15	3,09	sic(210)_15	2,57	sic(410)_15	3,01
sic(21)_16	3,51	sic(210)_16	2,89	sic(410)_16	3,16
sic(21)_17	3,45	sic(210)_17	2,69	sic(410)_17	3,15
sic(21)_18	3,36	sic(210)_18	2,66	sic(410)_18	3,13
sic(21)_19	3,48	sic(210)_19	2,51	sic(410)_19	3,11
sic(21)_20	3,51	sic(210)_20	2,63	sic(410)_20	3,15
Average	3,33	Average	2,74	Average	3,11

Table G4: Sample thickness for Ti_3AlC_2 samples.

Different sample names	Thickness	Different sample names	Thickness	Different sample names	Thickness
312(21)-1	2,90	312(210)-1	3,20	312(410)-1	2,81
312(21)-2	2,80	312(210)-2	3,32	312(410)-2	2,77
312(21)-3	3,01	312(210)-3	3,36	312(410)-3	2,80
312(21)-4	3,32	312(210)-4	3,25	312(410)-4	2,91
312(21)-5	2,76	312(210)-5	3,08	312(410)-5	2,57
312(21)-6	3,40	312(210)-6	3,44	312(410)-6	2,93
312(21)-7	2,70	312(210)-7	3,31	312(410)-7	2,55
312(21)-8	3,09	312(210)-8	3,13	312(410)-8	2,83
312(21)-9	3,24	312(210)-9	3,29	312(410)-9	2,86
312(21)-10	2,89	312(210)-10	3,25	312(410)-10	2,69
312(21)-11	2,77	312(210)-11	3,37	312(410)-11	2,73
312(21)-12	3,08	312(210)-12	3,29	312(410)-12	2,70
312(21)-13	2,96	312(210)-13	3,32	312(410)-13	2,79
312(21)-14	3,08	312(210)-14	3,36	312(410)-14	2,71
312(21)-15	3,05	312(210)-15	3,22	312(410)-15	2,68
312(21)-16	3,26	312(210)-16	3,40	312(410)-16	2,87
312(21)-17	2,91	312(210)-17	3,35	312(410)-17	2,70
312(21)-18	3,29	312(210)-18	3,26	312(410)-18	2,85
312(21)-19	2,76	312(210)-19	3,26	312(410)-19	2,65
312(21)-20	3,03	312(210)-20	3,40	312(410)-20	2,69
Average	3,02	Average	3,29	Average	2,76

Table G5: Microhardness results for Ti₂AlC-CBN composites.

20 10		
211(21)-3	Hv	GPa
	488,8	4,8
	311,0	3,0
	357,5	3,5
	305,9	3,0
	489,9	4,8
	474,0	4,6
Average	404,5	4,0
211(21)-4	377,6	3,7
	385,3	3,8
	430,6	4,2
	463,0	4,5
	323,0	3,2
	559,7	5,5
Average	423,2	4,2
211(21)-5	541,6	5,3
	376,1	3,7
	421,5	4,1
	471,9	4,6
	449,3	4,4
	432,9	4,2
Average	448,9	4,4
overall average	417,1	4,1
overall std dev	72,7	0,7

20 100		
211(210)-1	Hv	GPa
	821,2	8,1
	670,0	6,6
	806,8	7,9
	440,5	4,3
	405,8	4,0
	496,2	4,9
Average	606,8	6,0
211(210)-4	388,1	3,8
	507,3	5,0
	737,8	7,2
	451,3	4,4
	460,4	4,5
	598,8	5,9
Average	524,0	5,1
211(210)-5	505,5	5,0
	396,2	3,9
	414,8	4,1
	759,0	7,4
	390,9	3,8
	361,7	3,5
Average	471,4	4,6
overall average	522,1	5,1
overall std dev	152,2	1,5

40 100		
211(410)-1	Hv	GPa
	423,3	4,2
,	469,2	4,6
	506,1	5,0
	566,6	5,6
	724,4	7,1
	413,9	4,1
Average	517,3	5,1
211(410)-2	934,4	9,2
	422,4	4,1
	439,1	4,3
	781,2	7,7
	570,1	5,6
	505,5	5,0
Average	608,8	6,0
211(410)-6	330,0	3,2
	521,2	5,1
	617,4	6,1
	772,2	7,6
	513,3	5,0
	891,4	8,7
Average	607,6	6,0
overall average	577,9	5,7
overall std dev	168,8	1,7

Table G6: Microhardness results for Ti_3AlC_2 -cBN composites.

20 10			20 100			40 100		
	Hv	GPa		Hv	GPa		Hv	GPa
312(21)-1	558,3	5,5	312(210)-1	438,6	4,3	312(410)-1	348,9	3,4
	349,2	3,4		378,0	3,7		277,5	2,7
	417,5	4,1		497,4	4,9		407,5	4,0
	521,2	5,1		307,3	3,0		496,2	4,9
	442,0	4,3						
	435,8	4,3						
Average	454,0	4,5	Average	405,3	4,0	Average	382,5	3,8
312(21)-2	370,8	3,6	312(210)-3	507,3	5,0	312(410)-2	369,4	3,6
	398,2	3,9		339,3	3,3		311,8	3,1
	475,1	4,7		438,1	4,3		318,2	3,1
	541,6	5,3		292,7	2,9		309,0	3,0
	383,8	3,8		442,9	4,3		481,6	4,7
	302,9	3,0		342,5	3,4			
Average	412,1	4,0	Average	393,8	3,9	Average	358,0	3,5
312(21)-3	376,5	3,7						
	376,1	3,7		396,2	3,9		864,4	8,5
	421,5	4,1		414,8	4,1		955,5	9,4
	471,9	4,6		759,0	7,4		1477,6	14,5
	449,3	4,4		390,9	3,8		1403,8	13,8
	432,9	4,2		361,7	3,5		1178,4	11,6
Average	448,9	4,4	Average	471,4	4,6	Average	1215,7	11,9
overall average	417,1	4,1	overall average	522,1	5,1	overall average	1349,6	13,2
overall std dev	72,7	0,7	overall std dev	152,2	1,5	overall std dev	403,1	4,0

Table G7: Microhardness results for Ti_3SiC_2 -cBN composites.

20 10		
sic(21)_1	Hv	GPa
	897,0	8,8
	828,6	8,1
	922,6	9,0
	855,3	8,4
	641,2	6,3
	836,1	8,2
Average	830,1	8,1
sic(21)_2	669,1	6,6
	593,5	5,8
	749,3	7,3
	1009,9	9,9
	693,1	6,8
	704,6	6,9
Average	736,6	7,2
sic(21)_4	757,9	7,4
	539,0	5,3
	628,7	6,2
	448,3	4,4
	627,9	6,2
	573,7	5,6
Average	595,9	5,8
overall average	731,4	7,2
overall std dev	143,9	1,4

20 100		
	Hv	GPa
sic(210)_3	888,7	8,7
	2561,6	25,1
	1115,9	10,9
	1161,8	11,4
	1454,2	14,3
	924,1	9,1
Average	1351,1	13,2
sic(210)_4	2001,1	19,6
	1332,8	13,1
	1239,5	12,2
	1250,9	12,3
	1421,1	13,9
	1606,3	15,8
Average	1475,3	14,5
sic(210)_5	1414,7	13,9
	864,4	8,5
	955,5	9,4
	1477,6	14,5
	1403,8	13,8
	1178,4	11,6
Average	1215,7	11,9
overall average	1349,6	13,2
overall std dev	403,1	4,0

c 30 100		
	Hv	GPa
sic(410)_1	535,7	5,3
	1730,1	17,0
	738,8	7,2
	329,1	3,2
	615,1	6,0
	1106,3	10,8
Average	842,5	8,3
sic(410)_2	629,6	6,2
	1141,5	11,2
	978,9	9,6
	912,5	8,9
	539,6	5,3
	648,9	6,4
Average	808,5	7,9
sic(410)_3	1145,5	11,2
	1483,5	14,5
	452,8	4,4
	993,4	9,7
	880,5	8,6
	375,1	3,7
Average	888,5	8,7
overall average	883,6	8,7
overall std dev	369,8	3,6

Table G8: Bulk hardness results for all composites.

Composite	Indent #	Hv	GPa		Composite	Indent #	Hv	GPa
211(410)-5	1	323,0	3,2		312(21)-5	1	395,3	3,9
	2	338,0	3,3			2	457,8	4,5
	3	303,1	3,0			3	374,9	3,7
	4	552,2	5,4			4	474,6	4,7
Average		379,1	3,7		Average		425,7	4,2
std dev		100,0	1,0		std dev		42,0	0,4
sic(21)_3	1	342,8	3,4		sic(410)-6	1	674,5	6,6
	2	538,3	5,3			2	684,6	6,7
	3	656,7	6,4			3	510,3	5,0
	4	582,4	5,7			4	470,8	4,6
Average		530,1	5,2		Average		585,1	5,7
std dev		116,0	1,1		std dev		96,0	0,9
211(21)-2	1	359,2	3,5		312(210)-5	1	1513,0	14,8
	2	472,4	4,6			2	1273,0	12,5
	3	554,9	5,4			3	1060,0	10,4
	4	271,3	2,7			4		
Average		414,5	4,1		Average		1282,0	12,6
std dev		107,0	1,1		std dev		180,0	1,8
211(210)-3	1	598,8	5,9		312(410)-3	1	1470,0	14,4
	2	438,6	4,3			2	1381,0	13,5
	3	427,8	4,2			3	1549,0	15,2
	4	326,6	3,2			4		
Average		448,0	4,4		Average		1466,7	14,4
std dev		97,0	1,0		std dev		70,0	0,7
sic(210)-1	1	1028,5	10,1					
	2	790,4	7,8					
	3	890,1	8,7					
	4	743,0	7,3					
Average		863,0	8,5					
std dev		109,0	1,1					

Table G9: Wear results and calculations.

		Mass (g)										
Sample	Thickness (mm)	Before	After	Loss	L (mm)	r (mm)	h(mm)	$\frac{(R-h)}{R}$	Ar-cos	Area (mm ²)	volume loss (mm ³)	Wear rate (mm ³ /N)
211(410)-3	3,76	3,4276	3,4160	0,0115	5,20	14,77	0,23	0,98	0,17	0,79	4,10	0,98
sic(21)-5	3,04	3,7921	3,7731	0,0189	6,20	14,68	0,32	0,98	0,21	1,34	8,32	1,98
211(21)-1	2,66	3,0713	3,0419	0,0295	7,74	14,49	0,51	0,97	0,26	2,63	20,35	4,85
211(210)-2	3,32	3,8010	3,7905	0,0104	5,44	14,75	0,25	0,98	0,18	0,90	4,91	1,17
sic(210)-2	2,86	3,8792	3,8768	0,0023	5,24	14,77	0,23	0,98	0,18	0,81	4,23	1,01
312(21)-4	3,32	3,3354	3,2888	0,0467	9,00	14,31	0,69	0,95	0,30	4,16	37,48	8,94
sic(410)-4	3,08	3,8977	3,8957	0,0020	4,14	14,86	0,14	0,99	0,14	0,40	1,64	0,39
312(210)-2	3,09	3,84	3,83	0,0064	5,34	14,76	0,24	0,98	0,18	0,85	4,56	1,09
312(410)-5	3,42	3,66	3,66	0,0068	4,67	14,82	0,18	0,99	0,16	0,57	2,66	0,63



Investigation of MAX phase/c-BN composites

Tokoloho Rampai^{a,b}, C.I. Lang^{a,*}, Iakovos Sigalas^{b,c}

^aCentre for Materials Engineering, Department of Mechanical Engineering, University of Cape Town, Cape Town, South Africa

^bDST/NRF Centre of Excellence in Strong Materials, University of the Witwatersrand, Johannesburg, South Africa

^cSchool of Chemical and Metallurgical Engineering, University of the Witwatersrand, Johannesburg, South Africa

Received 17 August 2012; received in revised form 31 October 2012; accepted 31 October 2012

Available online 11 January 2013

Abstract

We have successfully fabricated novel MAX phase/c-BN composite materials, which have the potential to improve significantly on current grinding and cutting materials. The synthesis conditions include elevated temperatures and moderate pressure, which allows for good bonding of the carrier to the abrasive. Preliminary results show that MAX phase ceramics offer outstanding benefits as carrier materials for c-BN abrasive particles.

© 2012 Elsevier Ltd and Techna Group S.r.l. All rights reserved.

Keywords: B. Composites; E. Cutting tools; c-BN; MAX phases

1. Introduction

Current backing materials in grinding and cutting tools are either ceramics or metals; however ceramics have the disadvantage of low toughness, and many metals have the disadvantages of high density and intolerance to extreme temperatures. The utilization of composite cutting materials, in which hard abrasive particles are embedded in a softer carrier material, is currently limited by the properties of the available carrier materials. Carrier materials which are soft can lose cutting efficiency as the abrasive particles are lost or alternatively penetrate the carrier; those which are hard may suffer loss of abrasive through fracture; metallic carrier materials commonly experience high friction with the work piece; and the bonding between carrier material and abrasive may be insufficient, resulting in reduced processing power of the cutting tool [1].

MAX phase ceramics have both metallic and ceramic properties [1]: they are relatively ductile and machinable, yet also heat-tolerant, strong and lightweight [2,3]. They accordingly have unique potential as carrier materials for

abrasive media such as cubic boron nitride (c-BN), a widely used abrasive in cutting tools which is exceeded in hardness only by diamond [4,5]. Composites of MAX phase ceramics with c-BN may thus offer outstanding advantages in the tooling industry.

MAX phases are carbide and nitride ternary ceramics with the general formula $M_nA_{n-1}X_m$, where M = early transition metal; A = group A element, usually IIIA or IVA; X = C or N;

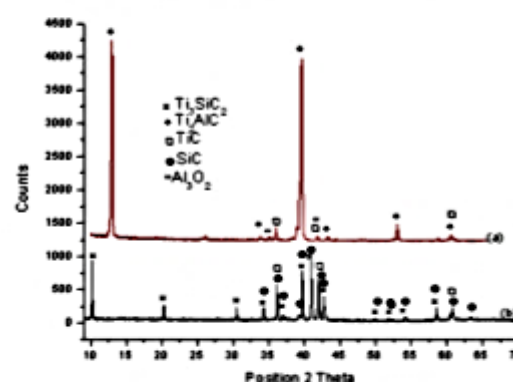


Fig. 1. X-ray diffractogram of: (a) Ti_2AlC and (b) Ti_2SiC_2 synthesized at 1400 °C, 30 MPa, 120 min.

*Corresponding author. Current address: Department of Engineering, Macquarie University, NSW 2109, Australia. Tel.: + 61 298509149; fax: + 61 298509128.

E-mail address: cundace.lang@gmail.com (C.I. Lang).

Appendix I: First draft paper written from PhD work: submitted to International Journal of Ceramic Engineering and science after reviewer comment (30/09/2020)

Utilisation of moderate pressure and elevated temperatures in the optimisation of Ti_2AlC -cBN composites using SPS technique.

Tokoloho Rampai^{a,b,c,*}, Iakovos Sigalas^{a,c}, David Whitefield^{a,c},

^a DST-NRF Centre of Excellence in Strong Materials, University of the Witwatersrand, Johannesburg, South Africa.

^b * Department of Chemical Engineering University of Cape, Town, Rondebosch, 7701, South Africa.

+27 216501807 School of Chemical and Metallurgical Engineering, University of the Witwatersrand, Johannesburg, South Africa

*Corresponding author: Email: motaung@gmail.com Tel: +27 21 6508107

Abstract:

The formation reaction mechanism of Ti_2AlC -cubic-boron-nitride (cBN) composite materials was investigated using different particle sizes at different volume percentages of cBN (20 and 40 vol%), at a constant moderate pressure while varying time and temperature. The results show that, under the investigated conditions, Ti_2AlC decomposed at 1300°C with a simultaneous hexagonalisation of the cBN, resulting in the creation of secondary phases including TiB_2 , TiC , TiN and AlN . It was observed that the optimum time and temperature for fabricating Ti_2AlC -cBN composites, where both phases were abundantly present, was 1250°C for 5 minutes for all composites. Under these conditions, there was no hBN in the resulting composites. Increasing the average particle size of cBN powder enhanced the stability of the Ti_2AlC and cBN in the samples. Also, the increase in volume fraction of cBN was observed to further promote the stability of Ti_2AlC and cBN in the samples. This was due to the decrease in surface area of cBN, which hampered hexagonalisation of cBN. Whatever excess hBN present reacted completely with the MAX phase in the final composites. The secondary phases formed in the samples were TiAl_2 , Ti_3Al , TiC_b , TiB_2 , TiC_xN_y (in samples containing $100\text{ }\mu\text{m}$ cBN) and TiN (in samples containing 20 vol.% cBN). The reaction area between Ti_2AlC and cBN was strongly bonded to the cBN and Ti_2AlC phases. A controlled method of simultaneous hexagonalisation of cBN and reaction of the resultant hBN with Ti_2AlC has proved superior in forming composites of Ti_2AlC with cBN.

Keywords:

Spark Plasma Sintering, MAX phases, cBN, Ti_2AlC

1. Introduction

MAX phases are ternary compounds with both metallic and ceramic properties¹. Ceramic material consisting of MAX phases are relatively ductile and machinable, yet also heat-tolerant, strong and lightweight^{1,2}. Among the MAX phases reported so far, aluminium containing Ti_2AlC and Ti_3AlC_2 , are two of the most lightweight and oxidation resistant²⁻⁶. These two compositions show promise for many

applications especially in the field of high temperature heat resisting materials⁴. Composites of Ti_2AlC with other ceramics, such as TiAl , TiC and Al_2O_3 , have been investigated using temperature ranges from 950 to 1350°C⁷⁻⁹. In previous work¹⁰ the authors have reported synthesising Ti_2AlC -cBN composites via making the Ti_2AlC , then reacting this with cBN. In this work the authors used SPS at 1500°C for 10 minutes at 10 MPa, and the result was a complete decomposition of the MAX phase, but the presence of a limited quantity of cBN was observed. The major phases listed from most to least in the sample were: TiN , TiB_2 , TiC and AlN ¹⁰.

Therefore, there was an expected advantage to investigating composites of the Ti_2AlC MAX phase and cubic boron nitride (cBN). cBN has excellent physical properties, in particular a high hardness 50 GPa, second only to diamond, at 90 GPa¹¹⁻¹³. cBN does not react with carbon the way diamond does at high temperatures, which rapidly deteriorates diamond cutting tools but not cBN tools. However, there are some challenges to still to overcome when using cBN abrasive grinding wheels in industry, such as the expensive manufacture route^{14,15}. Other properties of cBN include high thermal conductivity, and chemical and thermal stability, the latter two outranking even diamond^{11,12}. Sintering of cBN is difficult due to the predominantly covalent bonding^{11,16}. Extremely high pressures and temperatures of 7.5–8 GPa and >2000°C are required to obtain complete densification of the cBN parts after sintering^{11,17}.

This work shows a simple and versatile approach for the formation of Ti_2AlC -cBN composites without excess hBN formation in the samples. The synthesis of Ti_2AlC -cBN composites was evaluated using different particle sizes at different volume percentages of cBN (20 and 40 vol%) at a constant moderate pressure with varying time and temperature. The reaction mechanism was noted and a simultaneous hexagonalisation and reaction of the cBN with Ti_2AlC was found to be the superior method to achieve Ti_2AlC -cBN composites. An optimum combination of time and temperature ensured the coexistence of cBN and Ti_2AlC as the major phases, without excess hBN formation. XRD measurements did not only confirm the absence of hBN but also gave a clear indication of the presence of Ti_2AlC and cBN. From the SEM results, the presence of a strong bonded reaction area was observed.

In addition, SEM-EDS investigations showed the phase distribution of the secondary phases formed in the matrix and reaction area.

2. Materials and methods

The Ti_2AlC -cBN composites were synthesised from the titanium (44 μm , 99wt% pure, Alfa Aesar), aluminium (44 μm , 99.97wt% pure, Alfa Aesar), activated carbon (13.2 μm , 99wt% pure, ABCR), cBN (10 μm , ABN, Element Six) and cBN (100 μm , ABN 800, Element Six). A stoichiometric combination of the MAX phase precursor powders was mixed and milled in a planetary ball mill for six hours using a zirconia milling pot, at 300 rpm.

The milled and dried powders were dry mixed with 10 μm cBN, to give a composition of 20 vol% cBN, in a tubular mixer (at 67 rpm) for four hours. The resulting mixture was compacted in a 20 mm round graphite die, then placed into a Spark Plasma Sintering (SPS) furnace (FCT System GmbH HP-D5 spark plasma sintering furnace) for sintering. The sintering pressure was held constant at 30 MPa for all reactions as this was shown in previous work¹⁰ to be adequate pressure for densification for this system. The sintering time was varied from 1 minute up to 10 minutes. And the temperature ranged from 660°C (which is the melting temperature of aluminium) to 1600°C (which is given as the decomposition temperature of the MAX phase¹⁰).

These settings were used to evaluate the reactivity of the MAX phase with cBN and the optimum conditions to obtain a Ti_2AlC -cBN composite with the two phases abundantly present. Further experiments were done with ten times the initial size of the cBN (100 μm) to evaluate the effect of cBN surface area on the phase content of the composites. The cBN content was also increased to 40 vol.% to evaluate the effect of cBN on the phase content of the composites. The powder processing for all experiments was kept the same. All synthesised samples are shown in Table 1 with the naming convention for the variation of cBN, soaking temperature and time.

Samples had their density determined by Archimedes' method and were then fractured into two halves for analysis. One of the fracture surfaces was ground and polished for phase analysis, along the

cross-sectional area, using a Scanning Electron Microscope (SEM) and Energy-dispersive X-ray Spectroscopy (EDX). For all the samples containing 100 μm cBN, only the fracture surface was analysed for reaction area, fractography and phases present (SEM/EDS- Zeiss Sigma Field Emission Scanning Electron Microscope). X-ray diffractograms for all samples synthesised were collected using a Bruker D2 Phaser desktop diffractometer with $\text{Co(K}\alpha\text{)}$ radiation produced at 40 KV and 20 mA, over a 2θ range of 10° - 70° using a 10 min., no spin profile for phase analysis.

3. Results and discussion

3.1 Ti_2AlC -cBN composites with 20 vol% of 10 μm cBN

To establish the most effective temperature for sintering the Ti_2AlC -cBN composites, the dwell time and the pressure were kept constant at 1 minute and 30 MPa respectively, while the temperature was varied up to 1500°C , Figure 1. The piston displacement, as well as the displacement's derivative with time curves from the SPS during sintering were shown in Figure 1a, and 1b respectively. From Figure 1a, all sintering temperature profiles showed sample volume change takes place at around 680°C . At this temperature range a reaction peak was also observed in the "piston derivative's with time" curve (Figure 1b). This was associated with the formation of Ti-Al intermetallic phases such as TiAl_3 , Ti_3Al and TiAl_2 , which occur as a result of the melting of the aluminium at 660°C ¹⁸. The presence of these phases and the unreacted Ti and cBN was determined by XRD in a sample A70-1 (Figure 2).

In Figure 1a, the samples sintered at 1300°C and above all showed an additional increase in the densification rate of approximately 1.5 mm at about 1300°C . After this fast densification, no further densification was observed in the materials. In this temperature range, there was a corresponding reaction peak observed in the "piston derivative's with time" curve (Figure 1b). These peaks were related to the reaction of the MAX phase with the cBN. This is supported by the absence of MAX phases in samples sintered at and above 1300°C (Figure 3), and the presence of MAX phases in samples sintered below 1300°C (Figure 4). The cBN content was also gravely reduced due to this reaction (at 1300°C) and subsequently, phases containing Ti and B and N were increased and AlN was also formed.

This exothermic peak can be attributed to the reaction of Ti with BN to form TiB_2 and TiC_xN_y , which are both exothermic reactions¹⁹. The sudden increase of the temperature, due to the heat released, could have driven the degradation of the MAX phase and more dramatic hexagonalisation of the cBN, which would further promote the formation of these phases. hBN was only observed in samples sintered at and above the reaction temperature of 1300°C (Figure 3). The exception was the sample A150-1, and this could have been due to all the hBN possibly reacting completely to further form the B and N based reaction products.

Figure 1a shows that the Ti_2AlC densification curve has a small but constant densification from approximately 900°C until 1300°C (shown by the densification curves changing from horizontal to diagonal). This was due to the gradual reaction of the formed Ti-Al intermetallics, Ti and C forming the MAX phase. This was likely since the gradual increase indicates that the pistons are moving relative to each other, thus a volume change was occurring. This would happen as the formation of the MAX phase from TiAl_3 and TiAl_2 would induce a volume change because the MAX phase has a higher density than the intermetallics (Table 2). In these composites, two MAX phases were observed, Ti_2AlC and Ti_2AlN as shown in Figure 4 for samples A115-1 and A125-1. The presence of Ti_2AlN was possible since hBN present in the samples provided the N for the formation of this MAX phase.

Chen et al.,²⁰ and Lin et al.,²¹ both noted that the formation of Ti_2AlC and Ti_2AlN occurred through the reaction of Ti-Al intermetallics and a C or N source respectively. The formation of Ti_2AlN was limited by the amount of hBN available, thus it was found in lesser amounts than the Ti_2AlC since there was more abundant C found in the sample. The piston displacement curves of the SPS sintering for the composite samples sintered at 1300°C and above showed a small but constant densification, followed by a sudden significant increase at 1300°C. The piston displacement curves of samples A115-1 and A125-1 (Figure 1a) do not show this sudden increase, due to the lower maximum temperatures that samples were sintered.

The major phases (TiC_xN_y , TiB_2) in the samples sintered at 1300°C and above were denser than the major phases (Ti_2AlC , TiAl_2 and cBN) in samples A115-1 and A125-2, Figure S1 in supplementary

data and Table 2. Thus, this shows the formation of phases that are denser forming at 1300°C, which was corroborated with the measured densities of samples A130-1, A140-1 and A150-1, Figure S1 in supplementary data. It was seen in Figure S1(in supplementary data) that the densities of the samples increase at 1300°C and stay more or less constant above this temperature. The samples sintered at 1300°C and above showed no further densification during heating. This was indicated by the pistons of the SPS sinter press no longer moving relative to each other, and thus the samples were assumed to have reached relative complete densification.

The SEM images, Figure 5 corroborated the XRD results that showed the cBN proportions decreased with increased temperature. Also, these images show that for samples A130-1, A140-1 and A150-1 had a clear reaction area. This further shows that the exothermic reaction at 1300°C promoted the hexagonalisation of the cBN, and hBN is more prone to react with the MAX phases to form the reaction products (Figure 3)

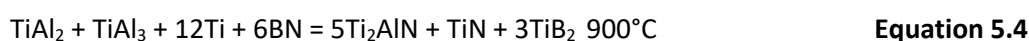
Wolfrum et al.,²² noted that the hexagonalisation of the cBN started at the surface of the cBN and moved inwards, this was seen in these samples where the outer dimensions of the reaction area was constant at around 10 µm for all the samples (Figure 5). And the actual outline of the BN phase seen was some distance from the original outline (Figure 5) in samples A130-1, A140-1 and A150-1. Reaction products such TiC_xN_y and TiB_2 were found both in the reaction area and the matrix, Figure S2 in supplementary data. The proportions found in the matrix could have been formed as the MAX phases were formed, and those in the reaction area could more likely be the product of the exothermic reaction at 1300°C. The AlN phase was found around the original outline of the BN phase (dark outline) in samples A130-1, A140-1 and A150-1 (Figure 5). Thus, it was assumed that there was a migration of the loosely bound Al in the MAX phase¹⁹ towards the cBN high reaction site. Hence AlN was found in the area around the reaction area surrounding the cBN particles (Figures 5 and S2). This triggers B in the BN to migrate into the MAX matrix and react with the Al deficient MAX phase to form TiB_2 and thus TiC_a/TiC_xN_y , which were mostly observed in the matrix (Figure S2 in supplementary data), and were also confirmed to be present in the samples by the XRD results (Figure 4).

Yoshida et al.,²⁴ reported that the solid-liquid angle between the Al(l) and C(s) was more than 100°, therefore, wetting was unfavorable and the reaction between Ti and C could not occur. However, this angle decreases with increasing temperature above 900°C. The solid-liquid angle between the Al(l) and C(s) in this case decreased to approximately 60° which promoted the formation of TiC. At temperatures of approximately 1100°C and above the formation of the Ti₂AlC from Ti-Al and TiC occurred. The hypothesised reaction of Ti₂AlC or Ti₂AlN with cBN was that the cBN first hexagonalises, this is shown in Equation 1 where under 30 MPa and temperature ranges investigated that cBN would hexagonalise. This hexagonalisation was simultaneously accompanied by the hBN reacting with the present Ti and Ti-Al intermetallics. This can occur, since the hBN was much more susceptible to diffusion processes and reactions than cBN at these temperatures, owing to the bonds in the hBN being less strong than those in cBN. This was also noted by **Li et al.,²⁵** that, in a Ti-Al-C-cBN system, cBN would hexagonalise under these conditions. This could happen only in small amounts on the surface of the cBN under these conditions. Below 1300°C, the simultaneous hexagonalisation of the cBN and the reaction of the hBN with Ti₂AlC was most likely to occur in a complementary manner, leaving no excess unreacted hBN on the surface of the cBN, Figure 4.

$$P \text{ (kbar)} = 0.030 T(K) - 10.3, (1 \text{ kbar} = 0.1 \text{ GPa})$$

Equation 5.4²⁶

The reaction mechanism hypothesised from these results was shown in Equations 2 to 5, with the formation of TiC in Equation 3 from **Chen et al.,²⁰** and reflects what was seen in this study.



Since sample A125-1 contained the most Ti_2AlC , it was decided to use this temperature and vary the dwell time, Figure 6. This was done in order to optimise the proportion of Ti_2AlC and minimise the Ti-Al intermetallic phases, without compromising the presence of the cBN. For all composites, Ti_2AlC , Ti_2AlN and cBN were present with no hBN in any samples. However, samples A125-5 and A125-10 contained Ti_3Al_5 and the sample A125-10 also contained Ti_3AlC_2 . The presence of TiAl_3 , TiN_b , TiC_a , TiB_2 and Ti_2Al secondary phases were observed in all of the composites, with the Ti-Al phases decreasing with increased dwell time (Figure 7). Thus, the optimum sintering time at 1250°C was 1 minute, which gave the highest amounts of Ti_2AlC without compromising too much cBN content, and small amounts of the secondary phases with no Ti_3AlC_2 .

The densities of samples A125-1, A125-5 and A125-10 were 3.99 g/cm^3 , 3.46 and 3.49 g/cm^3 respectively Figure S3 in supplementary data. The density of sample A125-1 was higher than that for samples A125-5 and A125-10. This might be due to the fact that there was a higher content of the Ti-Al intermetallics on sample A125-1 (Figure 7) compared to the other two samples which had similar densities. The fact that the densities of samples A125-5 and A125-10 was similar, does not indicate that the phase content was the same, but rather that the phases present in sample A125-5 were similar in density to the phases in sample A125-10. For example, Ti_2AlC and Ti_3Al (Table 2).

The SEM images of samples A125-1, A125-5 and A125-10, Figure 8, shows that there was a reaction area in samples A125-5 and A125-10 only (between red and blue outline). In sample A125-1, the fracture propagated around the cBN particles, which implied that there was not a strong bond between the cBN and the matrix, as the crack would travel a path of least resistance. The polished surface also confirms this, because unlike A125-5 and A125-10, there was no reaction area in A125-1. The samples A125-5 and A125-10 had reaction areas with strong bonds to both Ti_2AlC and cBN, and thus the cracks would propagate through or at the interface of the cBN as this would be the path of least resistance in these cases.

In samples A125-5, the reaction area was approximately $1 \mu\text{m}$ thick, and in the sample A125-10 the reaction area was approximately $2 \mu\text{m}$ thick (Figure 8). These samples did not have the dark ring

around the outer surface of the reaction area because they did not contain AlN as in the samples sintered at 1300°C and above (Figures 3 and 5). They did, however, have the same phase distribution of the Ti-Al phases in the reaction area and TiC_a , TiN_b or (TiC_xN_y) and TiB_2 in the matrix, with the matrix mostly consisting of Ti_2AlC and Ti_2AlN in this case (Figure 3 and 6). Samples A125-1 and A125-5 displayed a large amount of a layered Ti_2AlC phase in the matrix. Sample A125-10 shows more evidence of a porous structure, this could be due to the formation of Ti_3AlC_2 from the Ti_2AlC grains leaving the matrix porous since the Ti_2AlC is less dense than Ti_3AlC_2 .

From sample A125-5, it was concluded from XRD and SEM/EDX data that the Ti_2AlC -cBN interface had a reaction area as required, but also the MAX phase and cBN were present.

3.2 Increase in particle size (10 to 100 μm) and volume fraction of the 100 μm cBN (20 to 40 vol%).

The 1250°C sintering condition was used to sinter samples with 20 vol.% of 100 μm cBN as recommended in Section 4.1. In addition, samples were also sintered at 1300°C in order to evaluate the interaction reaction of Ti_2AlC and cBN for a decrease in surface area of the cBN.

Decreasing the surface area of the cBN, by increasing the cBN particle size, did not have a significant effect on the phases present in samples B125-5 and B125-10, Figure 6 and 9. Figure S4 in supplementary data shows the XRD results for the samples sintered at 1300°C. The first notable difference was the complete lack of Ti_2Al_5 and presence of TiC_xN_y in the sample with 100 μm cBN particles compared with those with 10 μm cBN particles (Figure 9). This could have been due to the low availability of surface area of the cBN, leading to less hBN forming on the surface. Thus, the Ti-Al phases had a higher likelihood to react with the TiC_a to form more Ti_2AlC , instead of reacting with hBN to form TiN_b and TiB_2 as shown in Figure 9. The second notable difference was the presence of hBN in B125-10. In Figure 10 it was observed that the proportion of the cBN was higher in sample B125-10. The likely reason is that the proportion reported in vol.% and the phases formed in sample B125-10

have a higher density than cBN (Figure S5 in supplementary data and Table 2). Thus, the cBN, having lower density would likely occupy more volume in the sample, but the actual content of cBN reduces.

Another notable difference in decreasing the surface area was that the exothermic reaction observed at 1300°C in Figure 1b occurred at a higher temperature than 1300°C in these composites (Figure S4 in supplementary data). This reaction related to the complete decomposition of Ti_2AlC and Ti_2AlN , Figure 2, but in this case Ti_2AlC and Ti_2AlN were found in samples sintered at 1300°C (Figure S4 in supplementary data). This suggests that the high surface area of the cBN promoted the exothermic reaction to occur at 1300°C, and the low surface area suppressed the exothermic reaction at the same temperature and shifted it to a higher temperature, not investigated in this work. It was observed, however, that there was also excess hBN found in all samples sintered 1300°C for samples with both high and low surface area of cBN (Figure S4 in supplementary data). This may have been due to the increase in temperature (at 30 MPa) promoting the hexagonalisation of cBN (as described by Equation 1).

Figure 11 shows the SEM (BSE) images of the Ti_2AlC -cBN samples sintered at 1250°C and 1300°C. All samples showed that the crack propagated through the cBN (blue arrow), indicating that the bond between the cBN and the MAX phase was strong. Also, all samples displayed crack propagation around the cBN (red arrows), this may indicate that the bond of the reaction area was weaker in these places. Samples B125-1 and B125-5 also showed possible evidence of cBN pull-out (green arrows), indicating a weak bond between the reaction area and cBN. All samples displayed cBN and different textured phases in the matrix.

shows the EDX analysis was undertaken on sample B125-5 (Figure S6), which had a combination of high MAX phase content with minimal hBN. The EDX analysis of the reaction area (Site 4) showed some high content of B, this could be because the cBN was close to the area detected. There was high Ti content observed, this was where the TiC_x and TiB_2 were also found. Site 3 and 5 was Ti_2AlC and more TiB_2 and TiC_xN_y were found in the matrix (Site 2). A similar phase distribution was observed in samples B125-1, B125-5, B125-10, B130-1, B130-5 and B130-10, Figures S6 and S7 in supplementary data.

Increasing the surface area of the cBN altered the reactivity of the cBN with the MAX phases. In this case, as shown in Figures 8 and 11, there was no reaction area observed in the samples containing 100 μm compared to those containing 10 μm cBN. When considering the composites containing 20 vol.% of 100 μm cBN, there was no significant difference in the microstructure in the samples sintered at 1250°C and 1300°C (Figure 11).

This indicates that for samples sintered with 20 vol.% of 100 μm cBN, the optimum condition for sintering the Ti_2AlC -cBN composites was also 1250°C for 5 minutes. This was due to the fact that the Ti_2AlC content was at its highest with an acceptable proportion of cBN. Thus, the same sintering conditions were also used to sinter samples with 40 vol.% of 100 μm cBN. In addition, samples were also sintered for 10 minutes and 1300°C and 1350°C in order to evaluate the interaction reaction of Ti_2AlC and cBN with an increase in the amount of cBN.

The first notable difference in increasing the cBN proportion was that TiN_b was not formed in the samples containing 100 μm of 40 vol.% cBN as shown in Figures 12 and S8. Also, sample C135-5 (Figure 12) contained the Ti_3AlC_2 phase. This phase was not observed in samples C135-10, Figure S8 in supplementary data. In addition, increasing the proportion of the cBN in the samples further suppressed the presence of Ti-Al , TiB_2 and TiC_xN_y phases, Figures 10 and 13. In samples C125-5, C125-10, C130-5 and C130-10, cBN remained the major phase and was surpassed by hBN, TiC_a , TiN_b and TiC_xN_y in samples C135-5 and C135-10 (Figure 13). This change in major phase was also reflected in the density changes in the samples (Figure S9 in supplementary data), where the density of samples C125-5, C125-10, C135-5 and C130-10 was approximately 3.5 g/cm^3 . But the density increased for samples C135-5 and C135-10 (approximately 3.8 g/cm^3) as the major phases here have a higher density than cBN (Table 2). The Ti_2AlC decomposition temperature was also observed to be above 1300°C for samples containing 40 vol.% cBN (Figures 12 and S8).

There was no hBN in samples C125-5 and C125-10, but there was for samples C135-5 and C135-10 (Figures 12 and S8). However, for sample C130-5 there was no hBN present (Figure 12), but there was hBN in sample C130-10 (Figure S8 in supplementary data). Thus, increasing the volume fraction of the

cBN in the samples further suppressed the formation of hBN in the samples sintered using these conditions. For samples sintered at 1300°C for 5 minutes, there was hBN found in the sample containing 20 vol.% of 100 µm cBN but not in the sample containing 40 vol.% of 100 µm cBN.

Figure 14 shows the SEM (BSE) images of the Ti_2AlC -cBN samples sintered for 5 minutes and 10 minutes. Samples C125-5, 125-10, C130-5 and C130-10 look similar in terms of the matrix and cBN morphology. However, the samples C135-5 and C135-10 have a clear reaction area (between red and blue outline) which was approximately 8-9 µm for the sample sintered for 5 minutes and approximately 10-12 µm for the sample sintered for 10 minutes. In all samples it was observed that there was evidence of crack propagation through cBN (blue arrow) which indicates that the bond of the matrix to the cBN was strong. It was also observed that samples C125-5 and C130-5 had some evidence of crack propagating between the cBN and the matrix (blue arrow) indicating that, in these cases, the bond was weak. The matrix of samples C135-5 and C135-10 displayed some layered structure (Figure 14), but also a large number of pores that could be due to the weight loss of Al at high temperature²⁷ as it vaporised.

EDX analysis was also undertaken on sample C135-5, Figure S10, as samples C125-5, C125-10, C130-5 and C130-10 look similar in morphology as the samples containing 20 vol.% of cBN. The EDX analysis shows that in Site 1 there was a BN phase and some C observed from the EDX data, this could be due to the electrons from the neighbouring phases. Site 2 and 3 show that Ti_3AlC_2 , TiC_α and TiB_2 could be found here, and all around in the matrix. Sites 5 and 6 show evidence of AlN, with Site 6 showing signs of TiB_2 and Site 5 showing more evidence of BN phase. Site 4 shows some evidence of possible TiC_xN_y and TiB_2 .

This shows that for samples sintered with 40 vol.% of 100 µm cBN, the optimum conditions for sintering the Ti_2AlC -cBN composites was 1250°C for 5 minutes. Even though sample C125-10 had a good proportion of Ti_2AlC and cBN, with no hBN, sample C125-5 had a much higher Ti_2AlC proportion. However, samples C130-5 and C130-10 also proved successful for this work's intended purposes.

3.3 Overall discussion.

Figure 15 shows the cBN hexagonalisation and MAX phase proportion in the samples that were deemed successful (Figure 16). The hexagonalisation of the cBN was estimated by taking the gradient of the cBN graph in each respective Rietveld analysis results shown in Figures 7, 10 and 13. This was done because estimation from the presence of hBN would not be logical as in all cases, hBN had already reacted to form Ti-B/N phases.

Generally, it was observed that there was a reduction in cBN with increase in dwell time or sintering temperature. **Garrett et al.**,²⁸ also used 10 and 100 μm cBN at 30 MPa to make composites with Sialon, they found that hexagonalisation decreases with sintering temperature, whereas this work agreed more with work done by **Sachdev et al.**,²⁹ where they demonstrated that the hexagonalisation increased with increase in temperature. The phase proportions in Figure 15 were just reported as shown in the respective Rietveld analysis graphs in on the samples. The Ti_2AlC proportion reported is the sum of Ti_2AlC and Ti_2AlN as they were both found in the samples.

In the Ti_2AlC based composites the cBN hexagonalisation rate increased with increased cBN size whereas a decrease in hexagonalisation rate was observed with an increase of the cBN size. The decrease in the MAX phase proportion in the composites with samples containing 40 vol.% was probably due to the doubling in the cBN content rather than the absolute decrease of the MAX phase.

4. Conclusions

The following conclusions can be drawn from this work:

- Elevated temperatures and moderate pressures can be used to fabricate Ti_2AlC -cBN composites, by a controlled method of simultaneous hexagonalisation of cBN and reaction of the cBN with Ti_2AlC .
- The Ti_2AlC -cBN (20 vol.% of 10 μm) composite can be successfully synthesised with the cBN and the MAX phase as major phases. The optimum conditions were 1250°C, at 30 MPa

pressure, for 5 minutes. These conditions produce clearly visible reaction zones and the composite also comprised TiC, TiAl₂, TiN, Ti₃Al and TiB₂.

- The Ti₂AlC-cBN (20 vol.% of 100 µm) composite was successfully synthesised with mainly the cBN and the MAX phase present. Using the results from the Ti₂AlC-cBN (20 vol.% of 10 µm) studies, it was correctly predicted that the conditions that would be appropriate for synthesising these samples were 1250°C, at 30 MPa pressure, for 5 minutes. These conditions also comprised limited amounts of TiC, TiAl₂, TiN, Ti₃Al and TiB₂.
- The Ti₂AlC-cBN (40 vol.% of 100 µm) composite was successfully synthesised with the cBN and the MAX phase present as major phases. Using the results from the Ti₂AlC-cBN (20 vol.% of 100 µm) studies, it was predicted that the conditions for producing these samples were 1300°C, at 30 MPa pressure, for 5 minutes. These composites also contain small amounts of TiC, TiAl₂, TiN, Ti₃Al and TiB₂.
- Increase in the size of the cBN decreases the extent of hexagonalisation of the cBN. This is because the exposed surface area of the cBN is reduced and thus less cBN is available to hexagonalise.
- Increasing the fraction of the cBN in the MAX – cBN composites promotes the formation of all MAX phases. This is because as more cBN is present in the samples the less heat the MAX phase is exposed to and thus cBN provides thermal shielding.
- Increasing the volume fraction of the cBN particles promoted the formation of the MAX phase, by reducing the hexagonalisation of cBN, thus keeping the secondary phase amounts low and suppressing the formation of hBN at lower temperatures.
- The SEM micrographs of the wear sites and fracture surfaces of the optimum composites selected showed good potential for the composites for cBN based grinding wheels by demonstrating that pull-out of the cBN in the composites was highly unlikely due to the strong bond of the reaction area to both the cBN and respective MAX phase.

Acknowledgements: The financial support of Element 6, the Department of Science and Innovation and the National Research Foundation (NRF), South Africa, was gratefully acknowledged. The Centre of Excellence (CoE) in hard materials is also gratefully acknowledged for their financial support.

REFERENCES

1. M. W. Barsoum, in *Encyclopedia of Materials: Science and Technology*, K. H. Jürgen Buschow, R. W. Cahn, M. C. Flemings, B. Ilshner, E. J. Kramer, S. Mahajan, P. Veyssière (Eds.), Elsevier, Oxford, 2006, pp. 1-16.
2. I. Kero, *Licentiate thesis*, Luleå University of Technology, 2007.
3. X. H. Wang, Y.C. Zhou, *Layered Machinable and Electrically Conductive Ti_2AlC and Ti_3AlC_2 Ceramics: a Review*, Journal of Materials Science & Technology **26**(5) (2010) 385–416.
4. X. H. Wang, Y.C. Zhou, *Oxidation behavior of Ti_3AlC_2 at 1000–1400 °C in air*, Corrosion Science **45** (5) (2003) 891-907.
5. X.H. Wang, Y.C. Zhou, *Microstructure and properties of Ti_3AlC_2 prepared by the solid–liquid reaction synthesis and simultaneous in-situ hot pressing process*, Acta Materialia **50** (2002) 3141-3149.
6. X.H. Wang, Y.C. Zhou, *High-Temperature Oxidation Behavior of Ti_2AlC in Air*, Oxidation of Metals **59** (3-4) (2003) 303-320.
7. C. Yang, F. Wang, T. Ai, J. Zhu, *Microstructure and mechanical properties of in situ $TiAl/Ti_2AlC$ composites prepared by reactive hot pressing*, Ceramics International **40** (6) (2014) 8165–8171.
8. J. Zhu, L. Ye, L. He, *Microstructure and mechanical properties of in situ synthesized Ti_2AlC/Al_2O_3 composites*, Materials Science and Engineering A **547** (15) (2012) 6–11.
9. J. Wang, N. Zhao, P. Nash, E. Liu, C. He, C. Shi, J. Li, *In situ synthesis of $Ti_2AlC-Al_2O_3/TiAl$ composite by vacuum sintering mechanically alloyed $TiAl$ powder coated with CNTs*, Journal of Alloys and Compounds. **578** (2013) 481–487.
10. T. Rampai, C. Lang and I. Sigalas, *Investigation of MAX phase/c-BN composites*, Ceramics International **39** (5) (2013) 4739-4748.

11. A. McKie, J. Winzer, I. Sigalas, M. Herrmann, L. Weiler, J. Rodel, N. Can, *Mechanical properties of cBN–Al composite materials*, *Ceramics International* **37** (1) (2011) 1–8.
12. R. Riedel, *Handbook of Ceramic Hard Materials*, Wiley-VCH, 2002.
- 13 J. Haines, J.M. Leger, G. Bocquillon, *Synthesis and Design of Superhard Materials*, *Annual Review Materials Research* **31** (2001) 1–23.
- 14 H.K. Tonshoff, B. Karpuschewski, P. Andrae, A. Turich, *Grinding performance of superhard abrasive wheels- final report concerning CIRP co-operative work in STC "G"*, *Annals of the CIRP* **47**: (1998) 723–732.
15. X. Chen, W.B. Rowe, R. Cai, *Precision grinding using CBN wheels*, *International Journal of Machine Tools & Manufacture* **42** (2002) 585–593.
16. T.K. Harris, E.J. Brookes, C.J. Taylor, *The effect of temperature on the hardness of polycrystalline cubic boron nitride cutting tool materials*, *International Journal of Refractory Metals and Hard Materials* **22** (2–3) (2004) 105–110.
17. T. Taniguchi, M. Akaishi, S. Yamaoka, *Sintering of cubic boron nitride without additives at 7.7 GPa and above 2000 °C*, *Journal of Materials Research* **14** (1) (1999) 162–169.
18. Školáková, A., Salvetr, P., Novák, P. & Vojtěch, D. 2018. Formation of Ti–Al Phases during SHS Process. *Acta Physica Polonica A*, 134 743 – 747.
19. W.B. Zhou, B.C. Mei, J.Q. Zhu, X.L. Hong, *Rapid synthesis of Ti₂AlC by spark plasma sintering technique*, *Materials Letters* **59** (1) (2005) 131-134
20. Y.-L. Chen, M. Yan, Y.-M. Sun, B.-C. Mei, J.-Q. Zhu, *The phase transformation of TiAl/Ti₂Al composites caused by hot pressing*, *Ceramics International* **35** (2009) 1807–1812.
21. Lin, Z.J., Zhuo, M.J., Li, M.S., Wang, J.Y. & Zhou, Y.C. 2007. Synthesis and microstructure of layered-ternary Ti₂AlN ceramic. *Scripta Materialia*. 56 :1115-1118

22. A. Wolfrum, B. Matthey, A. Michaelis and M. Herrmann, *On the Stability of c-BN-Reinforcing Particles in Ceramic Matrix Materials*, *Materials* **11** (2018), 255
23. A. Zhou, C. Wang and Y. Huang, *A possible mechanism on synthesis of Ti_3AlC_2* , *Materials Science and Engineering* **A352** (2003) 333-339.
24. Yoshida, M., Hoshima, Y., Ommyoji, J. & Yamagichi, A. 2010. Reaction mechanism for the synthesis of Ti_3AlC_2 through an intermediate carbide of Ti_3AlC from elemental Ti, Al and C powder mixture. *Journal of the Ceramic Society of Japan*, 118: 37-42.
25. L. Li, A. Zhou, L. Wang, S. Li, D. Wu, C. Yan. 2012. In situ synthesis of cBN– Ti_3AlC_2 composites by high-pressure and high-temperature technology. *Diamond & Related Materials*, 29: 8–12.
26. L. Vel, G. Demazeau and J. Etourneau. 1991. Cubic boron nitride: synthesis, physicochemical properties and applications. *Materials Science and Engineering*, B10:149-164.
27. A. Zhou, C. Wang and Y. Huang. 2003. Synthesis and mechanical properties of Ti_3AlC_2 by spark plasma sintering. *Journal of Materials Science*, 38: 3111-3115.
28. Garrett, J.C., Sigalas, I., Wolfrum, A.K. & Herrmann., M. 2015. Effect of cubic boron nitride grain size in the reinforcing of α -Sialon ceramics sintered via SPS. *Journal of the European Ceramic Society*, 35: 451–462.
29. Sachdev, H., Haubner, R., Noth, H. & Lux, B. 1997. Investigation of the c-BN/h-BN phase transformation at normal pressure. *Diamond Related Materials*, 6: 286-292.
30. Springer. 2016. https://materials.springer.com/isp/crystallographic/docs/sd_1013340 [ACCESS 1 December 2018].

Tables:

Table 3: Ti₂AlC-cBN composites naming convention.

Sample name	cBN fraction (vol.%)	cBN size (μm)	Soaking temperature (°C)	Soaking time (min)
A70-1	20	10	700	1
A115-1	20	10	1150	1
A125-1	20	10	1250	1
A130-1	20	10	1300	1
A140-1	20	10	1400	1
A150-1	20	10	1500	1
A125-5	20	10	1250	5
A125-10	20	10	1250	10
B125-1	20	100	1250	1
B125-5	20	100	1250	5
B125-10	20	100	1250	10
B130-1	20	100	1300	1
B130-5	20	100	1300	5
B130-10	20	100	1300	10
C125-5	40	100	1250	5
C125-10	40	100	1250	10
C130-5	40	100	1300	5
C130-10	40	100	1300	10
C135-5	40	100	1350	5
C135-10	40	100	1350	10

Table 2: Density of the secondary phases, listed in descending order, found in the sintered samples, as well as cBN, hBN, Ti₂AlC and Ti₃AlC₂ phases near the triple border for comparison³⁰.

Phase	Density (g/cm ³)	Phase	Density (g/cm ³)
TiN	5.39	TiAl ₂	3.51
TiB ₂	4.53	TiAl ₃	3.36
TiC	4.09	AlN	3.26
TiC _{0.3} N _{0.7}	5.25		
Ti ₃ AlC ₂	4.25	cBN	3.49
Ti ₂ AlC	4.07	hBN	2.26

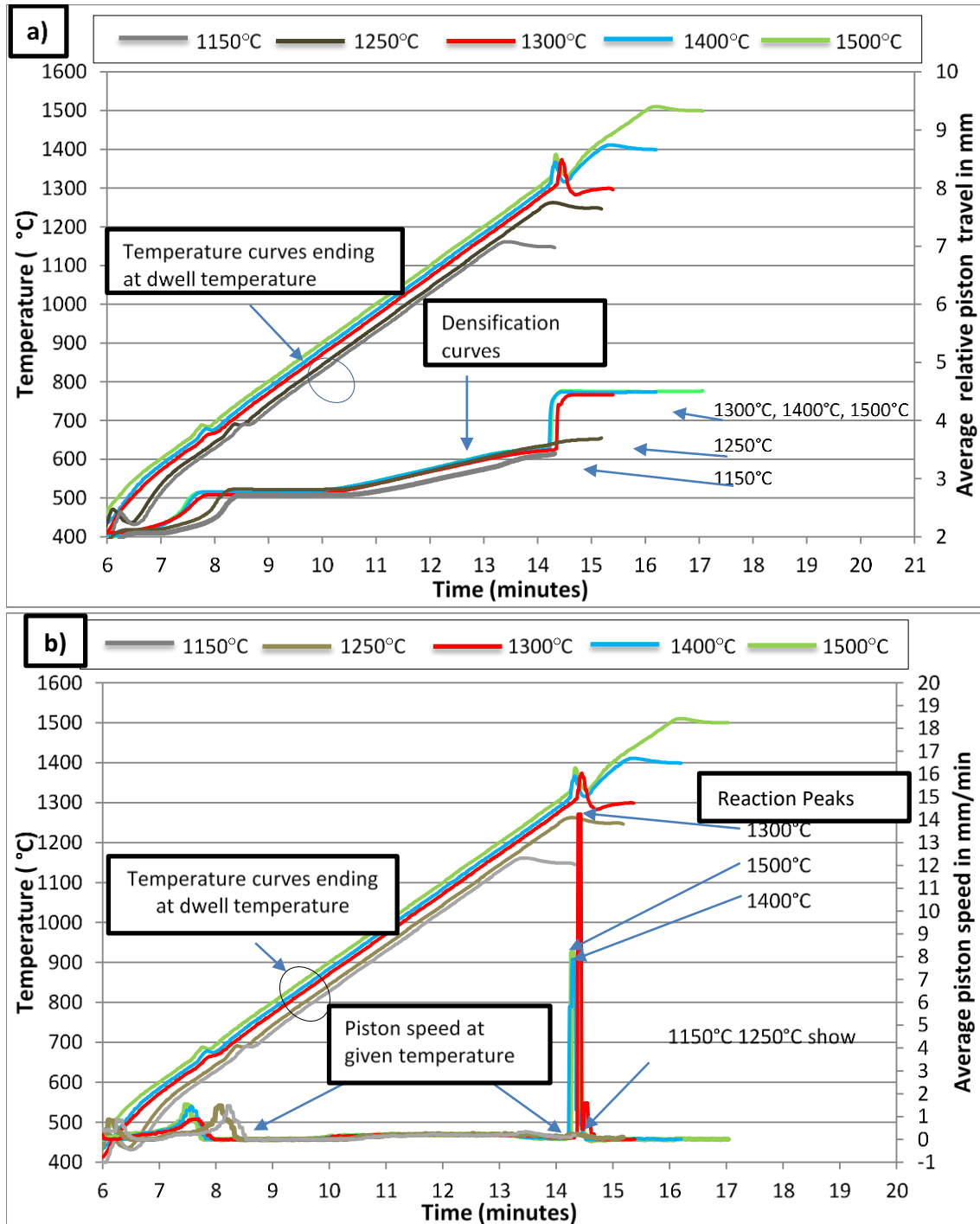
Figures:

Figure 1: $\text{Ti}_2\text{AlC-CBN}$ (20 vol.%, 100 μm) curves from the SPS runs at 1 min and different temperatures. **a)** piston displacement curves, **b)** piston displacement time derivative curves.

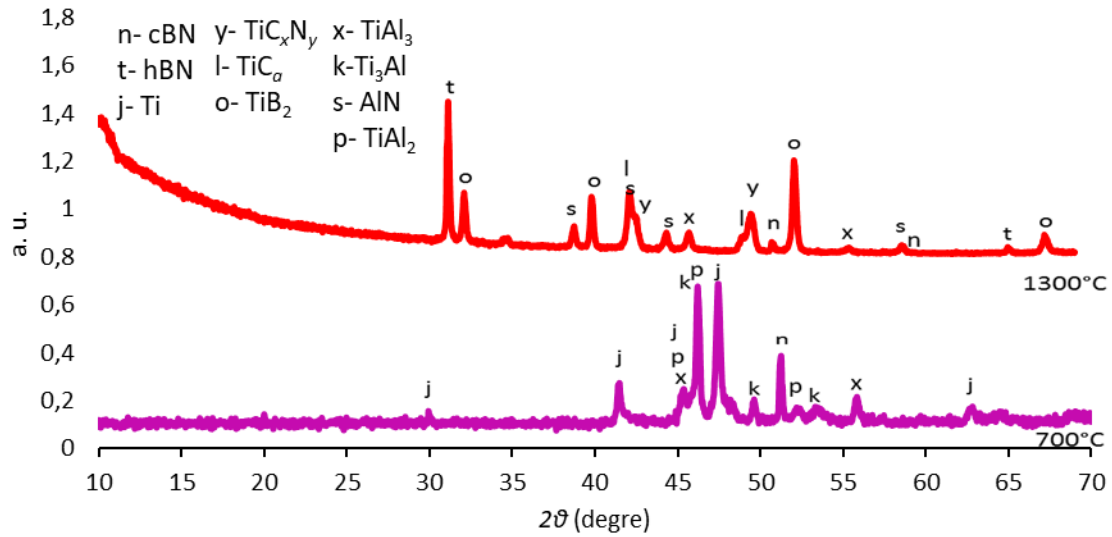


Figure 2: XRD diffractograms of Ti_2AlC -cBN (20 vol.%, 10 μm) samples, sintered at 30 MPa, 1 minute and different reaction peak temperatures, showing the phase development as a result of the two exothermic reactions at 680°C and 1300°C.

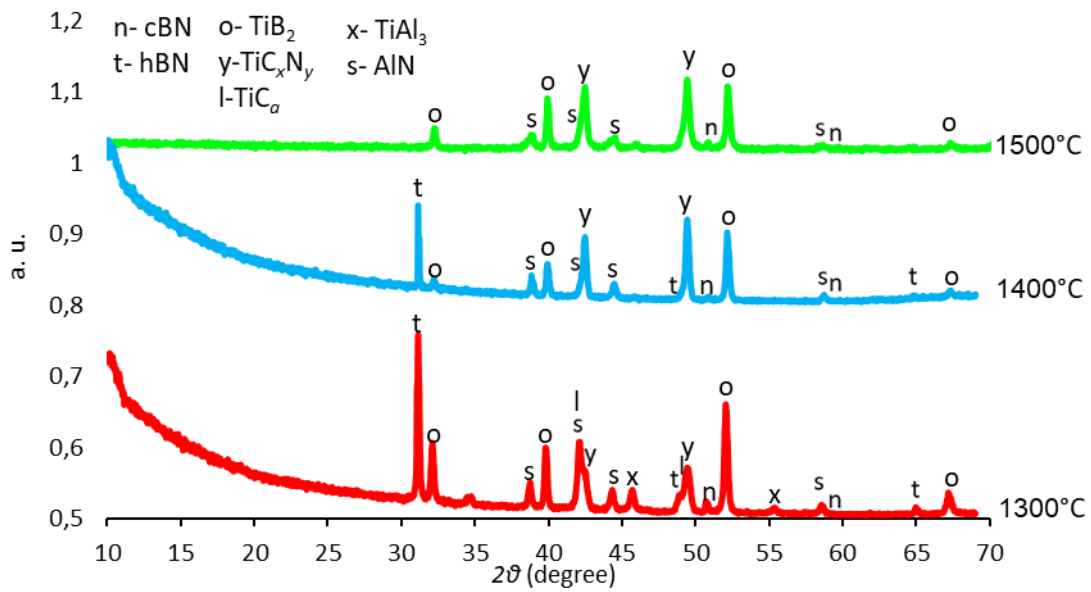


Figure 3: XRD diffractogram of Ti_2AlC -cBN (20 vol.%, 10 μm) samples, sintered at 30 MPa, 1 minute and different temperatures, showing the phase development and MAX phase decomposition when increasing temperature from 1300°C to 1500°C.

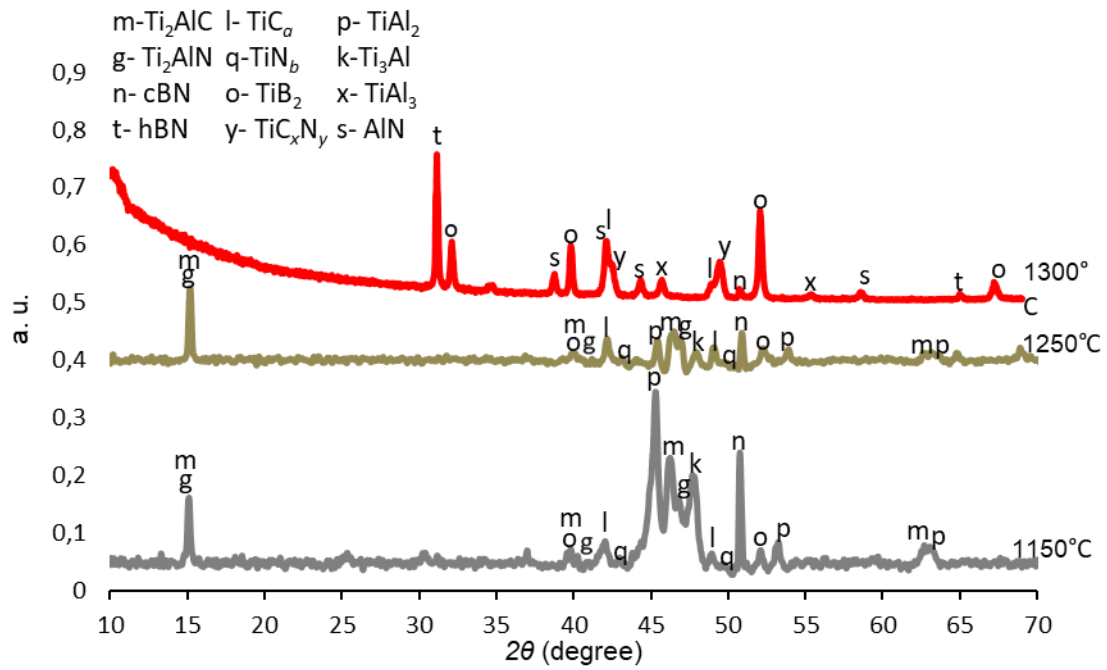


Figure 4: XRD diffractogram of Ti_2AlC -cBN (20 vol.%, 10 μm) samples, sintered at 30 MPa, 1 minute and different temperatures, showing the phase development and MAX phase decomposition when increasing temperature from 1150°C to 1300°C.

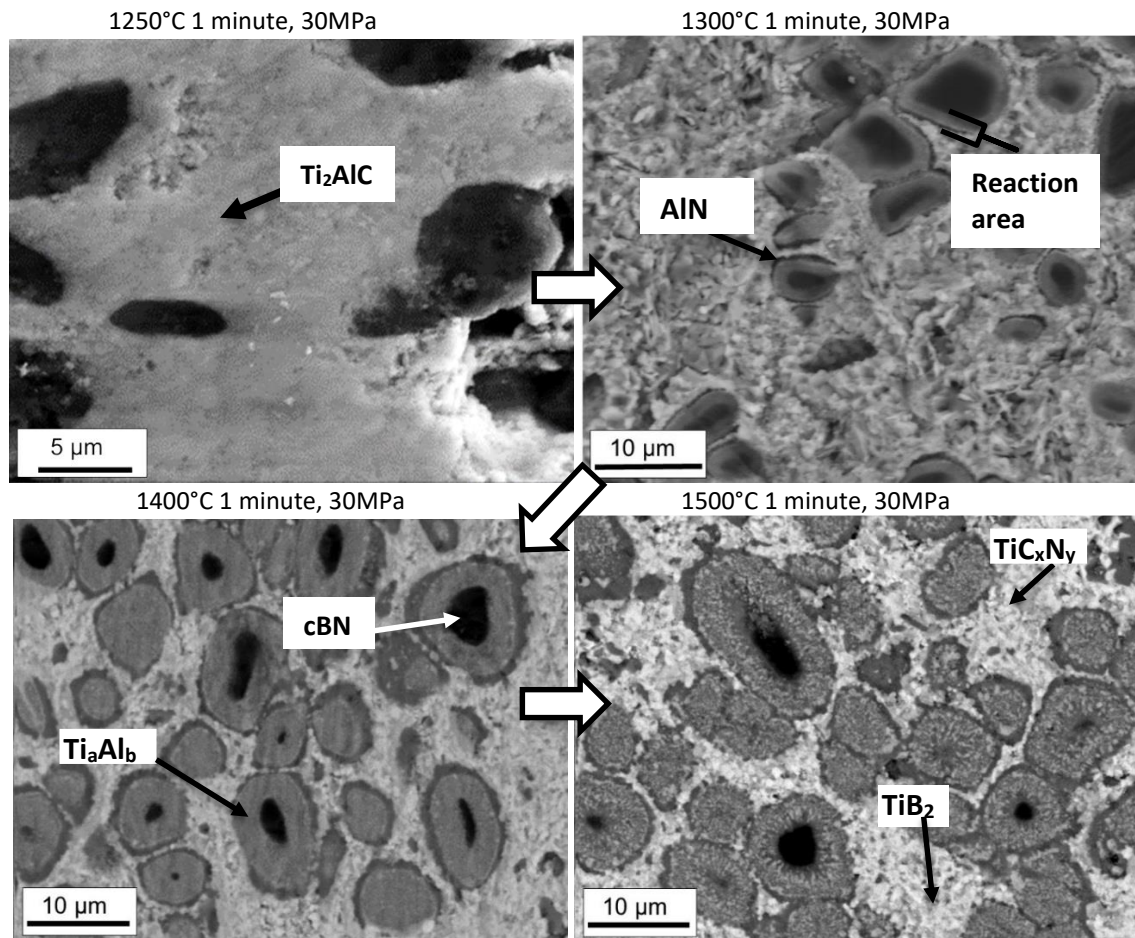


Figure 5: SEM micrographs of Ti_2AlC -cBN (20 vol.%, 10 μm) samples sintered at 30 MPa, 1 minute and different temperatures, showing the migration of phases in the sample when temperature was increased from 1250°C to 1500°C.

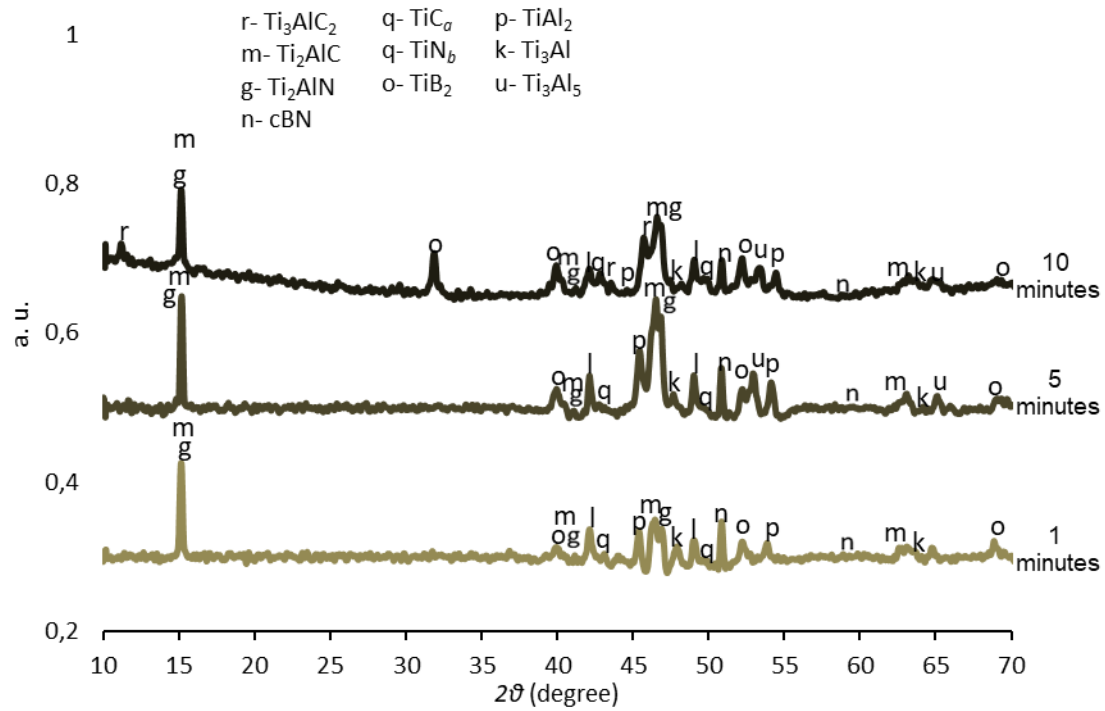


Figure 6: XRD diffractogram of Ti_2AlC -cBN (20 vol.%, 10 μm) samples sintered at 30 MPa, 1250°C and different time profiles, showing the increase of Ti_2AlC with increase in time, and also the development of Ti_3AlC_2 for 10 minutes samples.

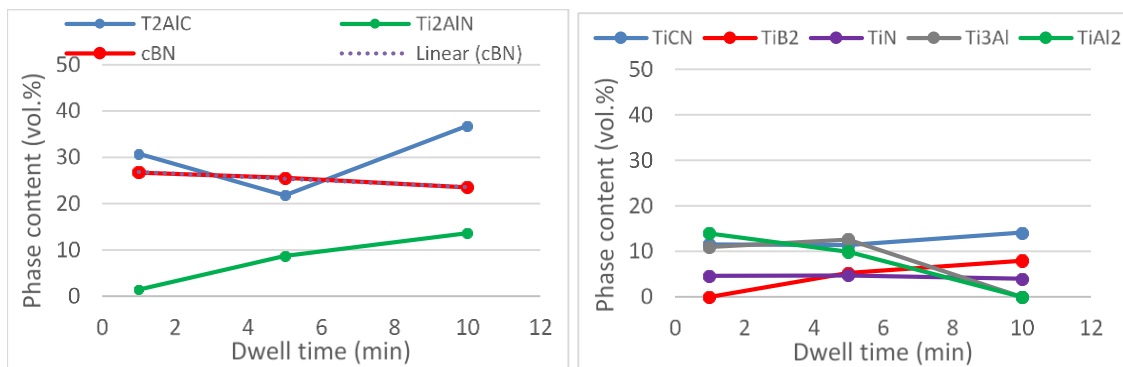


Figure 7: Phase quantities, determined by Rietveld analysis, of Ti_2AlC -cBN (20 vol.%, 10 μm) samples sintered for different times at 1250°C.

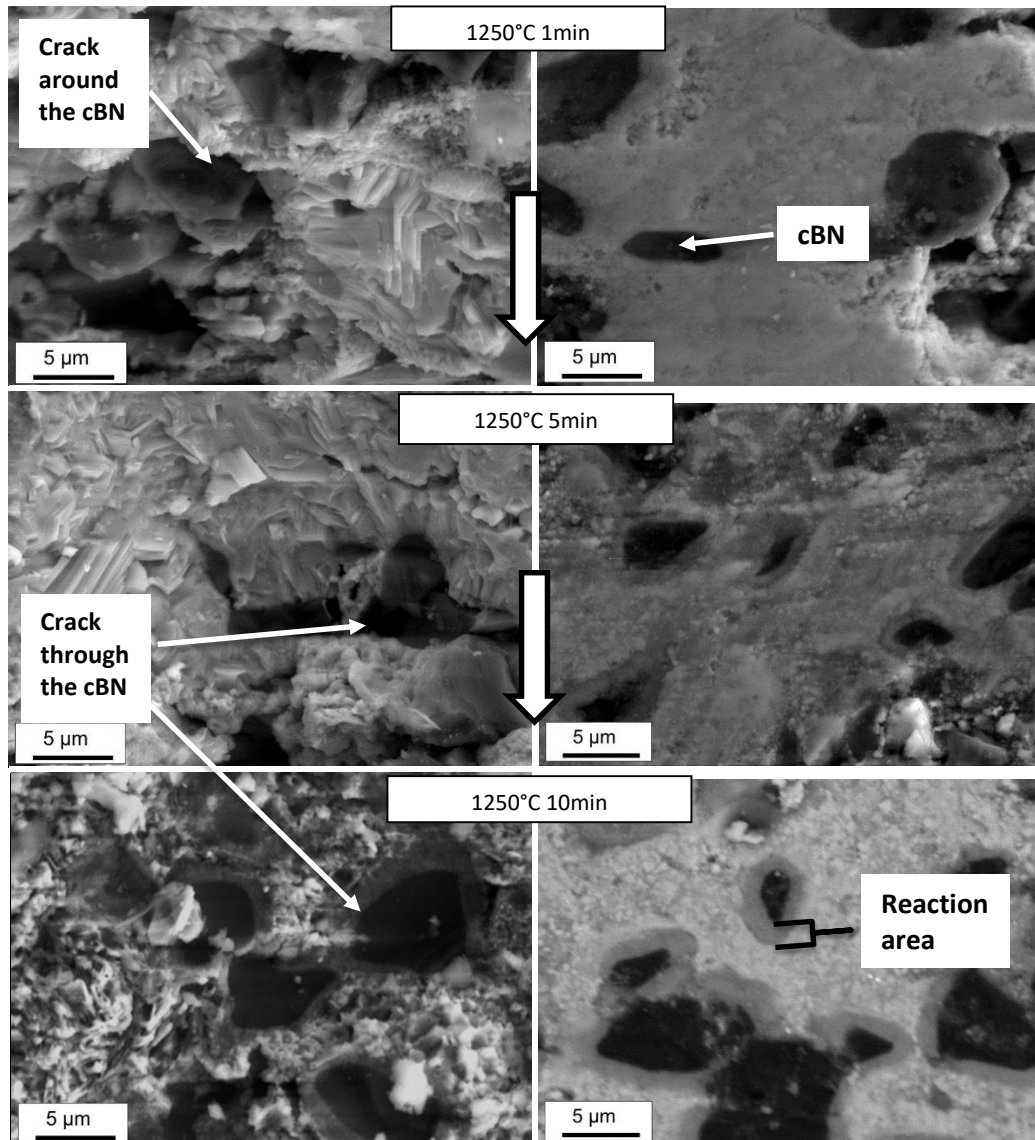
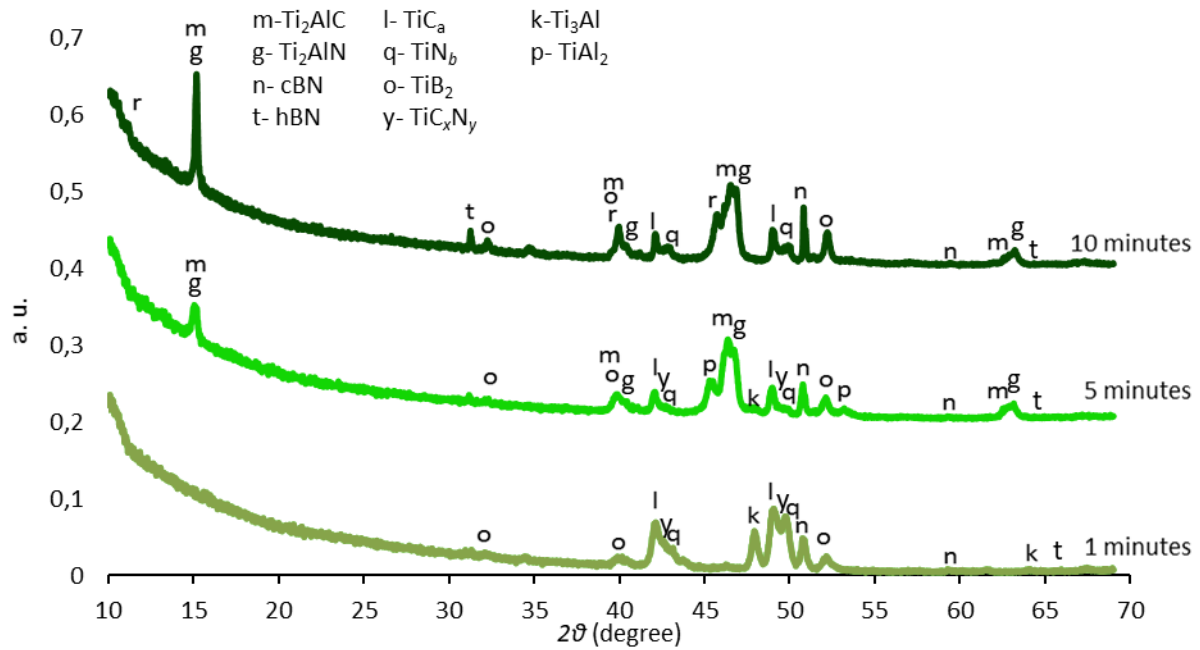


Figure 8: SEM (BSE) of fractured (left) and polished (right) Ti_2AlC -cBN (20 vol.%, 10 μm) samples sintered at 30 MPa 1300°C and different times. Blue arrows indicate crack propagation between cBN and matrix indicating strong bond between cBN and matrix, red arrows indicate crack propagating through the cBN and orange arrows indicate porosity in the matrix.



9 Figure 9: XRD traces of Ti_2AlC -cBN (20 vol.%, 100 μm) samples sintered at 30 MPa, 1250°C for different times.

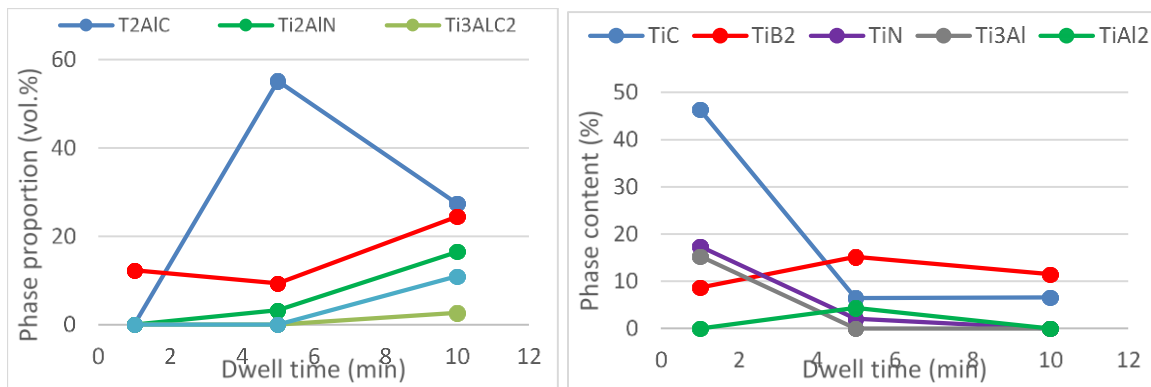


Figure 10: Phase quantities, determined by Rietveld analysis, of Ti_2AlC -cBN (20 vol.%, 100 μm) samples sintered for different times at 1250°C.

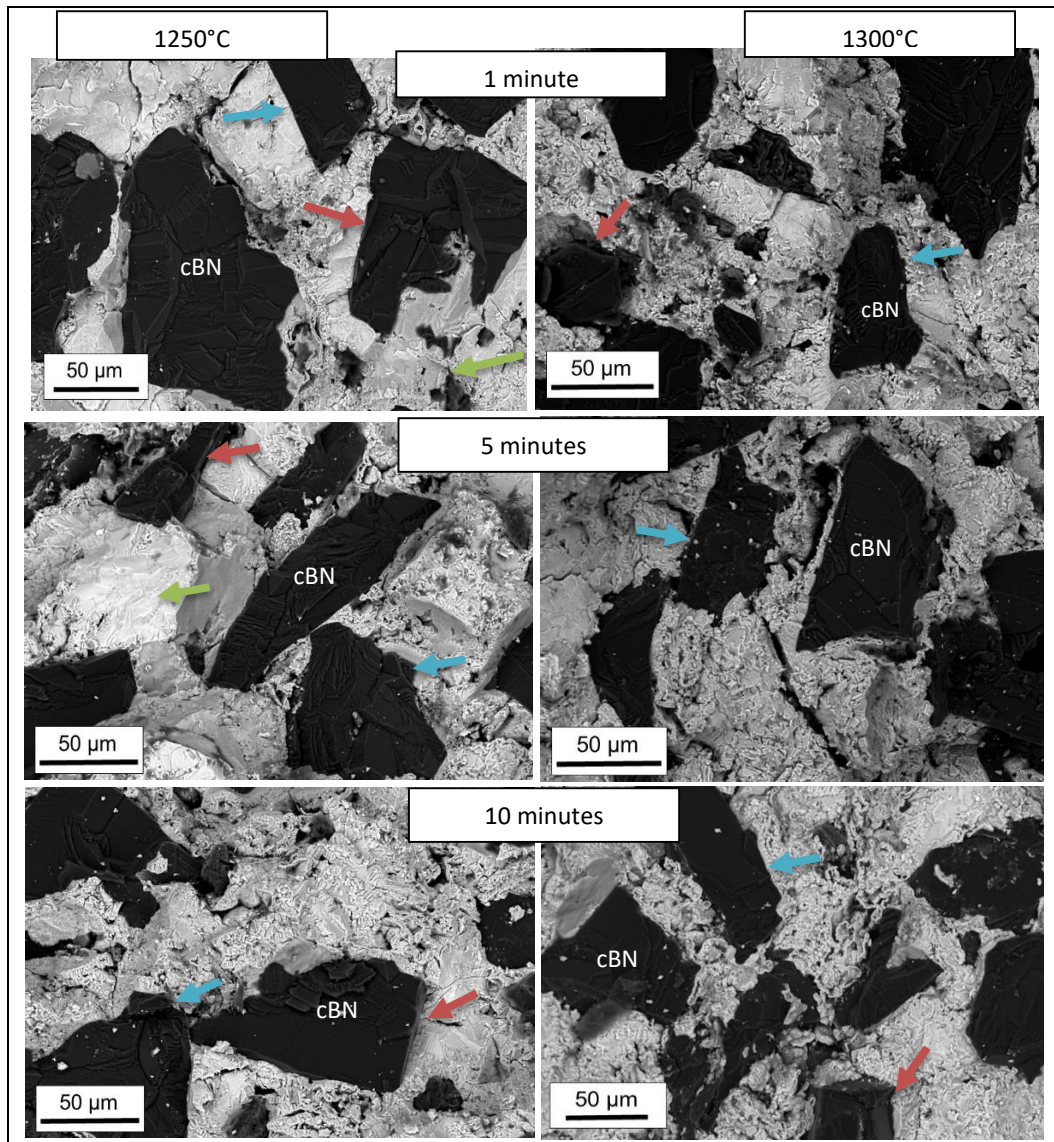


Figure 11: SEM (BSE) images of Ti_2AlC -cBN (20 vol.%, 100 μm) samples sintered for different times at 1250°C (left column) and 1300°C (right column). Blue arrows indicate crack propagation between cBN and matrix, red arrows indicate crack propagating through the cBN and Green arrows indicate possible cBN pull-out.

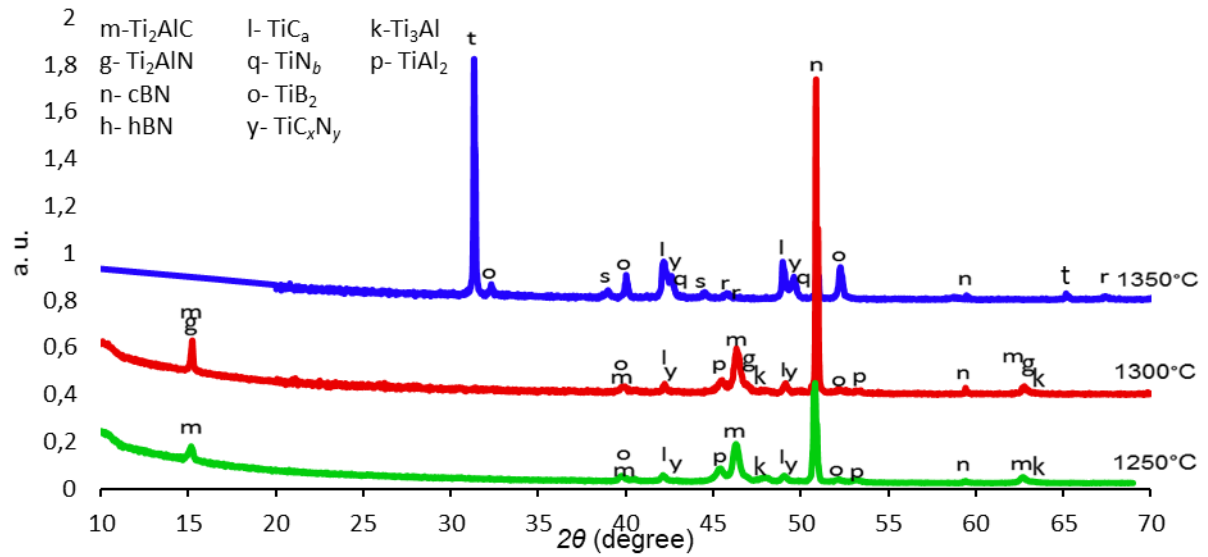


Figure 12: XRD traces of Ti₂AlC-cBN (40 vol.%, 100 μm) samples sintered at 30 MPa, 5 minutes and different temperatures.

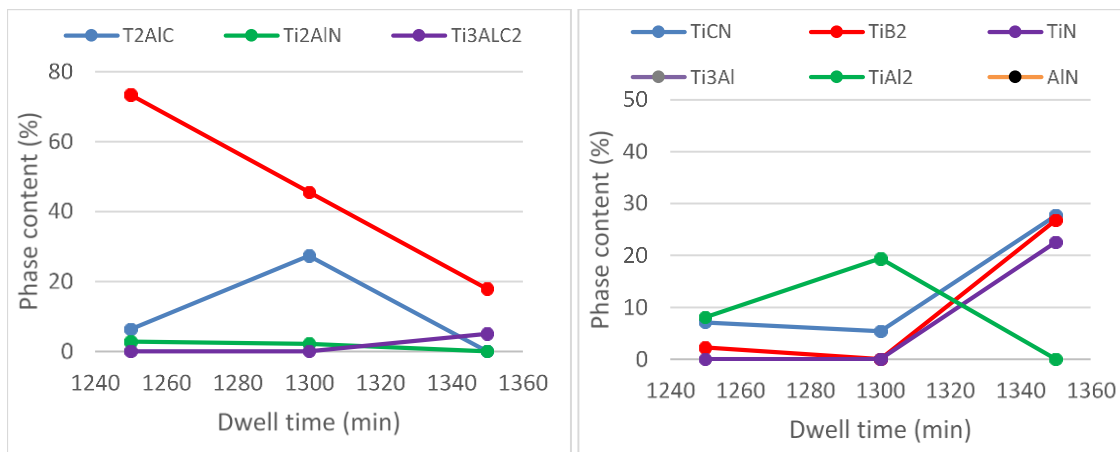


Figure 13: Phase quantities, determined by Rietveld analysis, of Ti₂AlC-cBN (40 vol.%, 100 μm) samples sintered for 5 minutes at different temperatures.

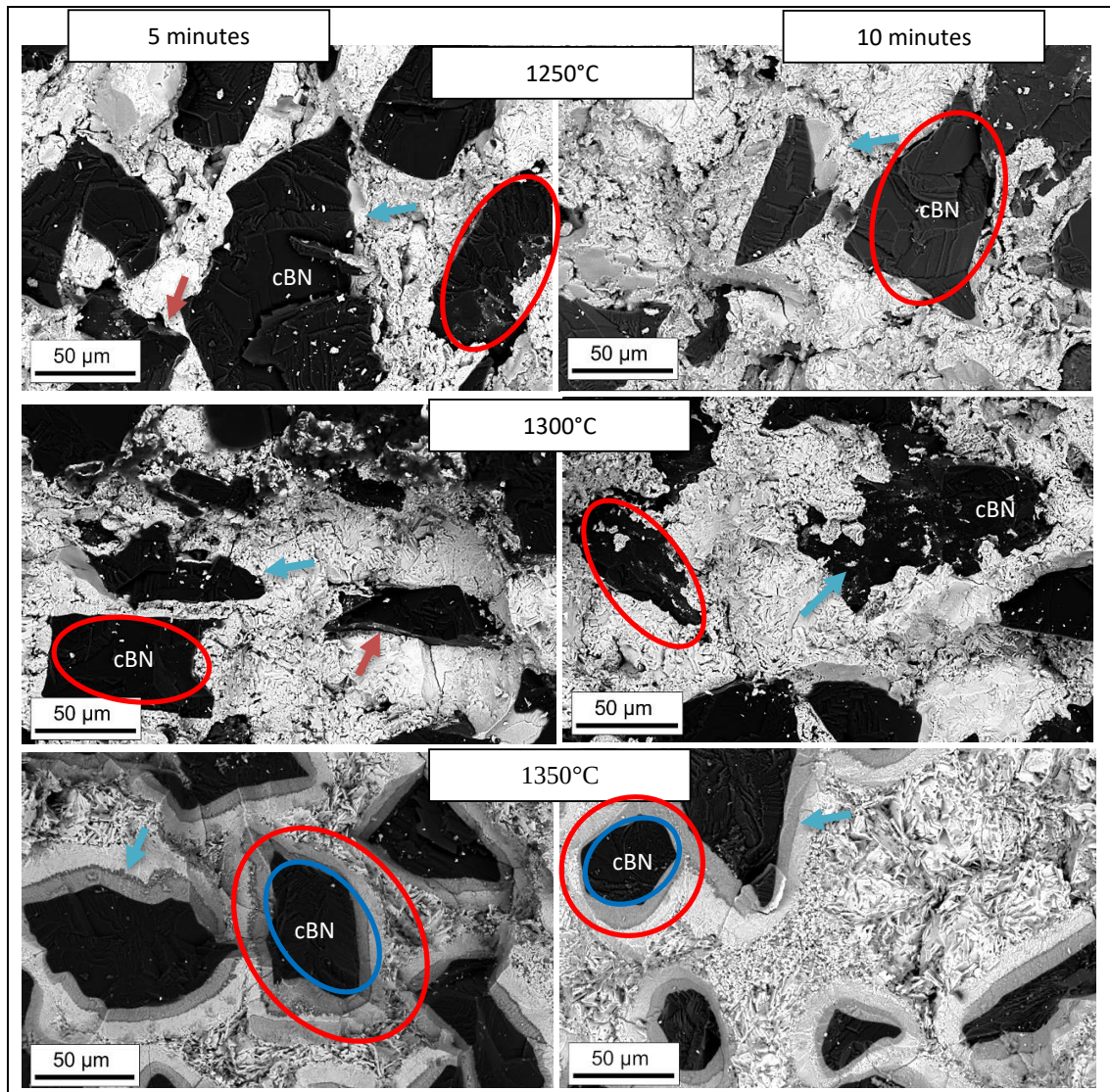


Figure 14 SEM (BSE) of Ti_2AlC -cBN (40 vol.%, 100 μm) samples sintered at 30 MPa and different temperatures for 5 minutes (left) and 10 minutes (right).

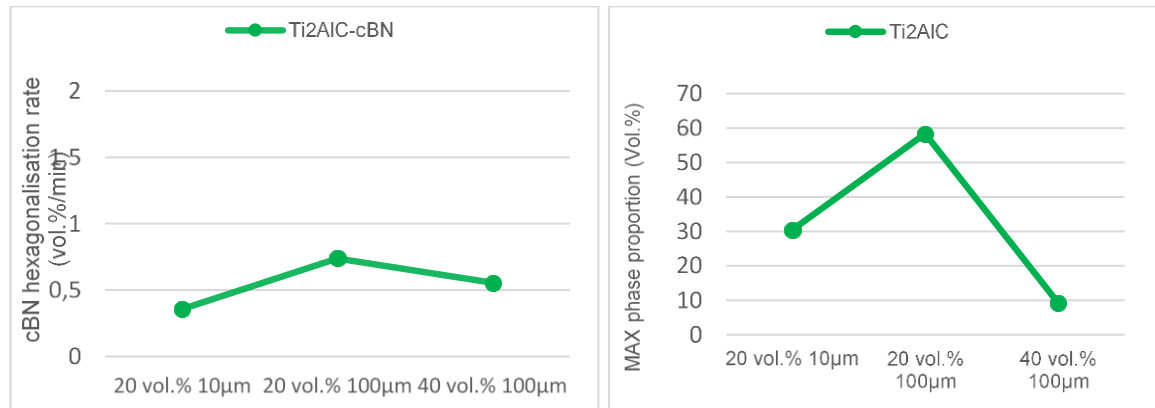


Figure 15: Graphs showing the rate of cBN hexagonalisation (left) and proportion of MAX phases formed (right) in all successful composites selected for mechanical tests.

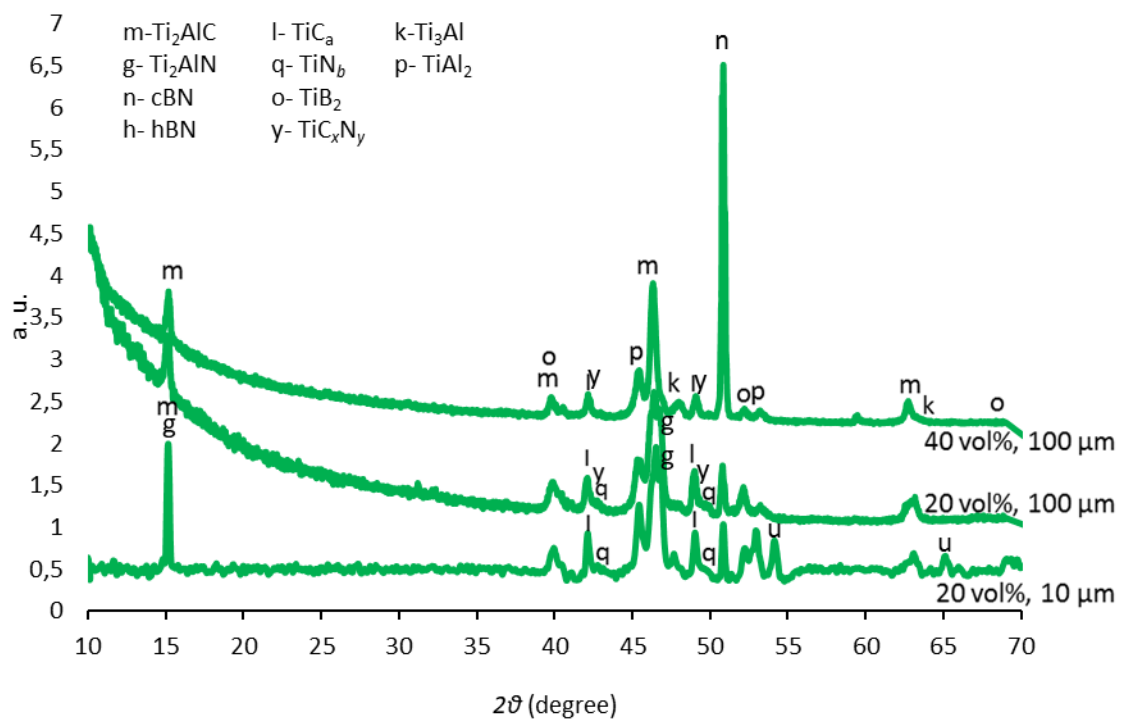


Figure 16: XRD traces of Ti₂AlC-cBN samples sintered at 1300°C for 10 minutes, showing different volume fraction (20 or 40 vol%) and different size (10 and 100 µm) cBN, also included is the successful sample at the 40 vol% cBN sample sintered at 1350°C for 5 minutes.

Appendix J: Second Publication form PhD work: submitted to Journal of American Ceramics Society (30/06/2020)

Ti₃AlC₂-cBN composite synthesis using SPS at elevated temperatures and moderate pressures, by control of cBN surface area and content.

Tokoloho Rampai^{a,b,c,*}, Iakovos Sigalas^{a,c}, David Whitefield^{a,c}

^a DST-NRF Centre of Excellence in Strong Materials, University of the Witwatersrand, Johannesburg, South Africa.

^bDepartment of Chemical Engineering, University of Cape Town, Cape Town. South Africa

^cSchool of Chemical and Metallurgical Engineering, University of the Witwatersrand, Johannesburg, South Africa

*Corresponding author: Department of Chemical Engineering, University of Cape Town, Rondebosch, 7701, South Africa.

Email: motaung@gmail.com

Tel: +27 216501807

Abstract:

The formation of Ti_3AlC_2 -cubic-boron-nitride (cBN) composites was investigated by varying the volume fraction of the cBN (20 and 40 vol%), as well as varying the surface area of the cBN particles. The investigation was carried out at a constant and moderate pressure, while varying time and temperature. The results show that, under the applied conditions, Ti_3AlC_2 decomposed at 1360°C with a simultaneous drastic reduction of the cBN. This resulted in the creation of secondary phases including TiB_2 , TiC , TiC_xN_y and AlN . It was observed that the optimum time and temperature for fabricating Ti_3AlC_2 -cBN composites, where both phases are abundantly present, was 1300°C for 10 minutes for composites containing 20 vol.% cBN. In composites containing 40 vol.% cBN particles the optimum temperature was 1350°C for 5 to 10 minutes. At these conditions there was little or no presence of hBN. Furthermore, the increase in particle size of the 20 vol.% cBN (from 10 to $100\text{ }\mu\text{m}$) in the composites was observed to enhance the stability of Ti_3AlC_2 and cBN. Also, the increase in volume fraction of the $100\text{ }\mu\text{m}$ cBN (from 20 to 40 vol.%) in the composites was observed to further enhance the stability of Ti_3AlC_2 and cBN by suppress the decomposition temperature of the Ti_3AlC_2 . This was due to the decrease in surface area of cBN, which hampered hexagonalisation and thus limited hBN formation. The secondary phases formed in the samples were TiC , TiC_xN_y , TiB_2 and TiN . The reaction area between Ti_3AlC_2 and cBN was strongly bonded to both the cBN and Ti_3AlC_2 phases. A controlled method of simultaneous partial hexagonalisation of cBN and reaction of the formed hBN with Ti_3AlC_2 has proved superior in forming composites of Ti_3AlC_2 with cBN. This promotes the viability of Ti_3AlC_2 as an alternative for a vitrified bond in cBN-based grinding wheels.

Keywords:

Spark Plasma Sintering (SPS), MAX phases, cubic boron nitride, Ti_3AlC_2

1. Introduction and review of literature

MAX phases are ternary compounds with both metallic and ceramic properties[1,2]. Ceramic materials consisting of MAX phases are relatively ductile and machinable, yet they are also heat-tolerant, strong and lightweight[1,2]. Among the MAX phases reported so far, aluminium containing Ti_2AlC and Ti_3AlC_2 , are the most lightweight and oxidation resistant[3,4,5]. These two compositions show promise for many applications especially in the field of high temperature heat resisting materials[6]. Synthesis of Ti_3AlC_2 and other hard ceramics, such as TiB_2 and cBN, has been investigated to further better the properties of these MAX phases.

Synthesis of Ti_3AlC_2 -cBN composites from base powders Ti, Al and C have been investigated at elevated temperatures $\sim 1050 - 1350^\circ C$ [7, 8,9,10,11]. However, in some cases the sintering temperatures are coupled with high pressure (3 - 5.5 GPa) and longer soaking times (10 – 12 minutes)[9,10,11]. And in the cases reported by Yang et. al.,[12] and Yue et. al.,[11] the presence of Ti_3AlC_2 in the resultant composite was questionable from the provided XRD data. Yang et. al.,[8] and Zhou et. al.,[7] showed that the Ti_3AlC_2 can be synthesised at temperatures ranging from as low as $1050^\circ C$ to $1250^\circ C$ and at pressures as low as 22 - 35 MPa. However, its noted that these conditions needed to be coupled with; either mechanical alloying of the starting powders, or first synthesising Al_4C_3 and then reacting it with Ti and C[8,7]. All these works demonstrate the difficulty in synthesising Ti_3AlC_2 composites via SPS method, using moderate pressures and elevated temperatures. There was also the difficulty of introducing high volume fractions of the abrasive in the Ti_3AlC_2 matrix.

In this current work, we investigated the reactivity of Ti_3AlC_2 and cBN in order to evaluate the feasibility of using these composites in grinding wheel applications. It will be demonstrated that Ti_3AlC_2 -cBN composites can be successfully synthesised using moderate pressures and elevated temperatures. The mechanism used here is through controlling the volume fraction and particle size of the cBN in order to stabilise the Ti_3AlC_2 content in the composite. Firstly, a reactivity study of the cBN and Ti_3AlC_2 with 20 vol.% of $10\ \mu m$ cBN particles was carried out. Then, the $10\ \mu m$ cBN particles were replaced with the $100\ \mu m$ cBN particles to evaluate how a decrease in the surface area of the cBN affects the extent of hexagonalisation of cBN, and optimisation of the Ti_3AlC_2 phase in the

composites. Finally, the volume fraction of the 100 μm cBN was increased to 40 vol.% to evaluate the effect of the cBN content in promoting the desired Ti_3AlC_2 phase and limiting excess hBN in the samples. XRD was used to confirm the presence of Ti_3AlC_2 and cBN in the samples, SEM-EDS investigations showed the phase distribution of the formed secondary phases in the matrix and reaction area between the two phases.

2. Materials and methods

The Ti_3AlC_2 -cBN composites were synthesised from titanium (44 μm , 99wt% pure), aluminium (44 μm , 99.97wt% pure), activated carbon (13.2 μm , 99wt% pure) and cBN (10 μm , ABN) or cBN (100 μm , ABN 800). The powders were weighed out in a 3:1,2:2 ratio of Ti:Al:C and mixed/milled using a planetary ball mill for six hours at 300 rpm.

The milled and dried powders were then dry mixed with cBN, to give a composition of 20 vol% or 40 vol% cBN, in a turbular mixer at 67 rpm for four hours. The resulting mixture was weighed and compacted in a 20 mm round die, which placed into a spark plasma sintering (SPS) machine (FCT System GmbH HP-D5 spark plasma sintering furnace) for sintering. The sintering pressure was held constant at 30 MPa for all reactions, since the aim was to use moderate pressures in this study without any mechanical alloying as seen in studied done by **Yang et. al.,[8]** and **Zhou et. al.,[7]**. The initial reactivity studies were done using 20 vol.% of the 10 μm , with soaking times kept constant at 1 minute. The soaking temperature was initially applied up to 1600°C in order to evaluate any change/reaction within the system in this temperature range. Thereafter, samples were sintered at the temperatures where reactions were noted (660°C and 1360°C). Finally, sintering temperatures were carried from 1150°C to 1500°C in order to evaluate the evolution of phases in the composites with. Optimal temperatures where selected and the soaking time, at these temperatures, increased from 1 to 10 minutes. This was done in order to evaluate the phase changes in the sample with change in time, and the optimum time to obtain the desired phases. The optimum temperatures chosen from the reactivity study were also used to sinter samples with 100 μm cBN.

The resultant samples were first taken through a sand blaster to remove the graphite sheets and hBN coating used in the sintering process. Secondly all the surfaces in the samples were ground to remove the portion of the samples that were in contact with the graphite sheets. This was done in order to eliminate any differential phase formation, from surface to centre of the samples, due to this interaction at elevated temperatures.

The ground samples were analysed by Archimedes' method for density and XRD analysis. The X-ray diffractograms for all samples synthesised were collected using the Bruker D2 Phaser desktop Diffractometer with Co(K α) radiation produced at 40 KV and 20 mA, over a 2θ range of 10° - 70° using a 10 min., no spin profile for phase analysis. All samples were then fractured in half to analyse the fracture surface using a scanning electron microscope (SEM) and phase analysis using Energy-dispersive X-ray spectroscopy (EDS) analysis. For the samples containing 10 μm cBN one of the fractured halves were ground and polished to analyse the reaction area and do further phase analysis. For all samples SEM/EDS was carried out using Zeiss Sigma Field Emission Scanning Electron Microscope.

3. Results and discussion

3.1 Ti₃AlC₂-cBN composites with 20 %vol of 10 μm cBN

Figure 1 shows the sintering profiles of the Ti₂AlC-cBN composites from the SPS sintering runs obtained at different temperatures as discussed in Section 2, the temperature indicated is the chamber temperature during sintering. The temperature curves, indicated on both Figure 1a and 1b, show the rate of increase of temperature for all samples was consistent. They also indicate the final sintering temperature for each run, ending in a vertical section which indicates the soaking time (1 minute) at the different soaking temperatures. In both figures, it was observed that the chamber temperature spiked at two temperatures (~ 680 and $\sim 1300^\circ\text{C}$). This may indicate an exothermic reaction as the sudden increase in temperature was not due to the SPS as it was set to increase the temperature at a

set rate. Therefore, the spike can only be attributed to the sample itself giving off heat, thus an exothermic reaction is indicated.

Figure 1a shows the piston displacement curves (traces at the bottom of the graph), which indicate the relative piston movement with increase in temperature. This may be used as an indication of volume changes of the samples with increase in temperature, and in a sense the densification or density changes in the samples with increase in temperature. Figure 2 shows the densities of samples with increase in temperature, this was used to corroborate the density changes observed in Figure 1a. The errors associated with the density measurements were very small, indicating that the average densities obtained for these samples were very accurate. Figure 1b shows SPS traces indicating piston displacement-time-derivative curves (traces at the bottom of the graph), these indicate the rate of travel of the piston with increase in temperature. These curves, in combination with the temperature curves, were utilised to estimate temperatures where reactions in the Ti_2AlC -cBN composites may have occurred. Figure 3 shows the XRD traces for samples sintered at or near the reaction temperature, the XRD data was used to show the resultant phases of the reactions observed in Figure 1b.

Školáková et al.,[13] noted that, in the self-propagating high-temperature synthesis (SHS) of Ti-Al intermetallics, there is an endothermic reaction at 660°C (melting of Al). An immediate exothermic reaction (formation of Ti-Al intermetallics) at ~ 680 thereafter with $T_{\text{onset}} 660^\circ\text{C}$ and $T_{\text{offset}} 682^\circ\text{C}$ was observed. This trend was also observed in the SPS data in this study, the peak indicating the melting of aluminium was not clearly seen, but it was also observed that the exothermic peak was at $\sim 680^\circ\text{C}$ with $T_{\text{onset}} 660^\circ\text{C}$ and $T_{\text{offset}} 686^\circ\text{C}$. **Skolakova et al.,[13]** also noted that the endothermic reaction was less intense and dwarfed by the exothermic reaction, and they could only see the endothermic reaction using the TGA analyses. However, the exothermic reaction could only occur as a result of the melting of aluminium, and an analysis of samples sintered at 700°C (Figure 3) shows the resultant phases; Ti, TiAl_3 , Ti_3Al , TiAl_2 from these simultaneous reactions. Figure 1a show the movement of the pistons relative to one another moving at a faster rate, also indicating that the formation of phases with a lesser density than the starting powder, further supporting the abovementioned, and XRD data.

Figure 1a further shows that the curves for samples sintered at 1150°C and 1250°C soaking temperatures did not have the ~1 mm increase at about 14 minutes; this only occurred for samples sintered at soaking temperatures of 1300°C and above. Figure 2 conforms this observation as densities of the samples stay constant with temperature until 1300°C, where the densities suddenly increased and stayed constant. The open porosity in this case was also observed to follow the same trend as the density, except the porosity decreases above 1300°C. The trend observed with the open porosity of the samples could be due to the formation of the denser phases from the less dense phases, causing cavitation. This sudden ~1 mm increase was attributed to the reaction peaks observed in Figure 1b for these samples which correlate to the complete degradation of the MAX phase in these composites (Figure 4). This indicated the formation of major phases found in these samples (TiC_xN_y and TiB_2), which are denser than the major phases in the samples sintered at 1250°C and below (Ti_2AlC and cBN) Figure 2 and 4 and Table 1.

For the samples sintered at 1400°C and above (densities of 4.21 and 4.18 g/cm³ respectively), the traces in Figure 1a were a flat line after the observed 1 mm increase. This indicated that the pistons of the SPS machine (during sintering) were no longer moving relative to each other, and that the samples had reached relative full densification. The sample sintered at 1150, 1250 and 1300°C (density of 3.30 g/cm³) showed the opposite, indicating full that densification had not been reached.

There was also a clear presence of the Ti_2AlC (instead of Ti_3AlC_2) phase and cBN in the samples sintered at 1150°C and 1250°C(not shown here), and secondary phases present included TiC_a , TiN_b , TiB_2 , Ti_3Al and TiAl_2 . The content of N and C in the TiN and TiC fluctuated with increase in temperature ($a=0.65$ to 1 and $b = 0.9$ to 1). The TiC peak shifted to the left with increase in C in the phase. And the TiN peak shifted to the right with the increase of N in the phase. The TiC_xN_y phase observed at temperatures above 1300°C also displayed similar trends. The peak shifted to the right with increase in N and to the left with increase in the C. It was also observed, from this XRD analysis, that Ti_2AlN was present in these samples. **Chen et al.,[14]** and **Lin et al.,[15]** noted that the formation of Ti_2AlC and Ti_2AlN both occurred through the reaction of the Ti-Al intermetallic compounds and $\text{TiC}_a/\text{TiN}_b$.

Skolakova et al.,[13] noted the difficulty in determining the resultant Ti-Al phases from the exothermic reaction at $\sim 680^{\circ}\text{C}$, however, in this study it was observed that the thermodynamically favourable phases were Ti_3Al , TiAl_2 and TiAl_3 . Both the TiAl_2 and TiAl_3 showed varying, non-stoichiometric, fractions of the Al in the system with varying temperature and Ti_3Al did not. The respective peaks shifted to the right with a decrease in the Al in each phase. A crude estimation of the phase development at different temperatures was made using the relative peak intensity ratio of the phase of interest in this section compare to the other phases. A more detailed analysis, Rietveld, was used in the optimisation studies, where phase quantification is more crucial. Using this method, it was found that TiAl_2 occurs as one of the major phases as a result of the exothermic reaction at 680°C (Figure 3). this phase then decreased with increase in temperature and finally depleted at 1300°C , with the same trend observed with Ti_3Al . TiAl_3 , however, was initially one of the minor phases (Figure 4) and remained even after the reaction at 1360°C .

As noted by **Yoshida et al.,[16]**, the reaction of Ti-Al intermetallics with TiC occurs at 1100°C . **Zhou et al.,[17]**, **Mei et al.,[18]** and **Kulkarni et al.,[19]** all indicated the synthesis of Ti_2AlC below 1200°C through the reaction of TiC and the resultant Ti-Al intermetallics. Similarly, **Liu et al.,[20]** noted the formation of Ti_2AlN from TiN and Ti-Al intermetallics at temperatures around 700°C . This can occur in this case since the cBN has transformed into hBN (according to Equation 1), which provides a N-rich environment. **Tomashik. & Perrot,[21]** noted that the N solubility is high in Ti, and that the Gibbs free energy of formation of the Ti_2AlN system is $-135.5 \text{ kJ.mol}^{-1}$ of atoms at 850°C . **Yoshida et al.,[16]** reported that the solid-liquid angle between the Al(l) and C(s) is more than 100° , therefore, wetting is unfavorable and the reaction between Ti and C could not occur. However, this angle decreases with increasing temperature above 900°C . The solid-liquid angle between the Al(l) and C(s) in this case decreased to approximately 60° which promoted the formation of TiC. At temperatures of approximately 1100°C and above the formation of the Ti_2AlC from Ti-Al and TiC occurred. Both the formation of the Ti_2AlC and the Ti_2AlN were observed in this study (Figure 4), with both phases present at 1150°C , along with TiN, TiC and Ti-Al intermetallics. **Tomashik. & Perrot,[21]** noted that Ti_2AlN is

thermodynamically more favorable to form at lower temperatures (~850°C) than Ti₂AlC (~1000°C). However, the formation of Ti₂AlN was limited by the available hBN here, thus Ti₂AlC formed more extensively as there was a higher content of C. Both these phases increased with increased temperature until 1250°C(not shown here).

$$P \text{ (kbar)} = 0.030 T(K) - 10.3, \quad (1 \text{ kbar}=0.1 \text{ GPa}) \quad \text{Equation 7[22]}$$

The exothermic reaction at 1300°C caused a more drastic cBN → hBN transformation and the decomposition of both Ti₂AlC and Ti₂AlN. This forms TiC_xN_y, AlN and more TiB₂. The TiC and TiAl₃ still remain in the system from 1300°C. in this case, unlike in temperatures below 1300°C, there is an excess of hBN observed in the composites which reduces and finally depleted as to forms the N and B phases.

The reaction temperature evaluations here showed that the optimisation of the Ti₂AlC – cBN composite would be at 1250°C since there is more Ti₂AlC in the system and no hBN observed.

Equations 2 to 5 show the predicted reaction sequence for the synthesis of the MAX phase and the reaction of Ti₂AlC with BN under the investigated conditions.



As shown in studies by **Yang et. al.,[10]** and **Yue et. al.,[11]** there was no MAX phase in their samples after sintering at 1350°C for 12 minutes, this study showed that at 1350°C the exothermic reaction would have already occurred and a soaking time of 1 minute or more increased the undesirable secondary phases in the samples. It was also observed that under the conditions studied here, Ti₂AlC rather than Ti₃AlC₂ was formed in the composites. The phase content of the composites

indicates that the reaction path proposed by **Zhou et. al.,[23]** in Equation 6 was preferred as temperatures lower than 1600°C were used to sinter the composite. **Zhou et. al.,[23]** also noted that the fabrication of Ti_3AlC_2 was more a kinetic than a thermodynamic based synthesis. In a Ti-Al-C system, Ti_2AlC was easier to form since it had a lower activation energy of formation, therefore in the optimisation of the Ti_3AlC_2 -cBN composites, optimising the kinetics of the system was required.



Figure 5 shows the SEM (BSE) images of the samples sintered at 1250°C, 1300°C, 1400°C, and 1500°C. The images confirm the XRD results, in Figure 3 and 4, that the cBN quantities decreased with increased temperature. The hexagonalisation of cBN occurred from the surface of the cBN and migrated inwards, indicating the shrinking core model for the transformation of cBN to hBN. This was observed from the outline of the reaction area, which is the original outline of the cBN (red outline Figure 5) staying constant at approximately 10 µm throughout all samples. The outline of the actual cBN after the hexagonalisation was some distance from the original position (indicated by the blue outline). This is not unlikely, since it is well known that the hexagonalisation of cBN occurs at the surface of the cBN particle as indicated in the work done by **Wolfrum et al.,[24]**. It was also noted by **Li et al.,[9]** that, in a Ti-Al-C-BN system, cBN would hexagonalise at temperatures as low as 1150°C if it was in contact with a suitable reagent, in this case it is Ti as N is significantly soluble in Ti. This is further supported by Equation 2.12 that under 30 MPa, cBN would hexagonalise at temperatures as low as 800°C. This thus leads to the likely reaction of the cBN to the MAX phase to be through $\text{cBN} \rightarrow \text{hBN}$, the hBN would then react with Ti as hBN is more likely to participate in diffusion processes under these conditions than cBN.

The sample sintered at 1250°C had no apparent reaction area (Figure 5), and therefore the cBN original size was the same as the outline after sintering. This indicated that there may have not been any reaction between cBN and the MAX phase. However, from the XRD analysis, it was observed that

some of the secondary phases included TiN and TiB₂ which indicate that the BN phase has participated in some reactions. The likely reason for the observation would be that the reaction area is very thin and is not easily apparent from the SEM images. The reaction area, thereafter, increases with increase in temperature, it started ~1 µm at 1300°C, then ~3 µm and finally ~3.5 µm at 1500°C. The different phases that occurs in the matrix seen in temperatures above 1300°C (seen as different shades of grey) appear to all be less than 1 µm. This may be due to the FAST (SPS) method facilitating the sintering times as low as 1 minute. This translates to thermal exposure for shorter time period, thus retarding grain growth.

Figure 6 shows the EDX analysis of the sample sintered at 1500°C for 1 minute. This was done in order to determine the distribution of the secondary phases given by XRD analysis. The error associated with the given EDX data was not too significant in the 5 measurements made per phase. This indicates that there was not too much variation in the analysed phases. The only significant errors were associated with the N content in site 2, this was observed because the N varies from 0 to 42 at.%. This observed error could also be a result of the beam picking up reflected electrons from the neighbouring atoms. Thus, the nitrogen content on this site was considered cautiously when interpreting the data for this site. The sample sintered at 1500°C was analysed as the secondary phases in this sample are more pronounced. The EDX was taken with a beam intensity of 20keV because the sample was thick. However, because of the small sizes of the phases analysed, the beam could also have picked up the electrons reflected from the neighbouring and/or underlying phases. The levels of C were also observed to be high even in phases that were not expected to contain C (such as cBN), thus the presence/content of C in each scan was cautiously considered.

Site 1 was observed to be cBN as expected since BN would be the phase with the lowest density. Site 2 displayed more Ti, and could be the TiB₂ and TiC_xN_y phases. Sites 3 and 5 containing more Al than Ti, this could be where AlN is found. This is not unlikely as AlN was determined to be in samples sintered at 1300°C (Figures 4) and above, and the phases in and around the reaction area are only observed in samples sintered at and above 1300°C (Figure 5). **Cui et. al.,[25]** noted that, in their study, the loosely

bound Al in the Ti_2AlC layered structure was the first to leave the Al plane to react with O_2 . The Ti would only react thereafter when the Ti_2AlC structure had low quantities of Al. In this study, the Al was the first to leave the Ti_2AlC layered structure migrating towards the BN to form AlN. site 4 displays high contents of Ti, B and C. This is further demonstration that the TiC, TiB_2 phases are also found in the matrix. This suggests that the Al migrates towards the BN, and the B would migrate outwards to react with the Al deficient MAX phase to form TiB_2 and thus TiC. However, there is also a presence of B within the reaction area, which suggests that some TiB_2 is also found in the reaction area. This further confirms the observations made by Cui et. al.,[25] that Ti also migrated towards the BN when the structure had a deficiency of Al.

Figure 7 shows the XRD results of samples sintered at $1300^\circ C$ for different times. Figure 8 shows the Rietveld analysis of the samples analysed in Figure 7. At $1250^\circ C$ and the investigated soaking times no Ti_3AlC_2 was observed, however, there was a clear presence of Ti_2AlC and Ti_2AlN , and cBN. The samples sintered at $1300^\circ C$, however, showed a gradual transforming the Ti_2AlC to the Ti_3AlC_2 . For all three soaking times Ti_2AlC , cBN, TiN, TiC and TiB_2 were present, with Ti_3AlC_2 , cBN and Ti_2AlC becoming the dominant phases in the sample sintered for 10 minutes. Ti_2AlC was the dominate phase for samples sintered for 1 and 5 minutes and is second to Ti_3AlC_2 in the sample sintered for 10 minutes. Ti_3AlC_2 phase was only found in the samples sintered for 5 and 10 minutes. hBN was only seen in the sample sintered for 5 minutes.

Figure 8 shows the Rietveld analysis of the phase content of the samples sintered at $1300^\circ C$. It was observed that the cBN and TiC_a decreased with increase in temperature where as Ti_2AlN and hBN increased with temperature. In the sample sintered for 5 minutes, there is hBN, however, this was not observed at samples sintered at 10 minutes. It was observed that the TiN content increased at 10 minutes soaking times, and this could be the reason why there is no excess hBN. Figure 9 shows the densities of the samples sintered at $1250^\circ C$ and $1300^\circ C$. It was observed that the error in these samples was not too large, indicating that the values reported were reliable. The densities and open porosities of all samples sintered at $1200^\circ C$ remained the same and 3.2 g/cm^3 and 12 %, respectively. This was

expected since there were no major phase changes within these samples. The samples sintered at 1300°C showed an increase in the density at 5 minutes from 3.4 to 4.2 g/cm³. And back down to 3.4 g/cm³. This can be attributed to the fact that at 5 minutes, the sample had more TiAl₃ than in the other samples, this has a higher density than the other major phases at 1- and 10-minutes soaking times.

Figure 10 shows the SEM (BSE) images of the samples sintered at 1300°C, both for polished and untreated fracture surfaces. For the samples sintered for 1 minute, the fracture seems to have propagated around the cBN particles (red arrow) in an intergranular manner. The samples sintered for 5 and 10 minutes displaying the crack propagating through (trans granular) the cBN (blue arrow).

The polished surfaces show there was a reaction area (between the red and blue outline) only for the sample sintered for 10 minutes, which was approximately 2 µm in size. The fracture of the samples sintered for 1 and 5 minutes show a laminar structure within the matrix, this was not as pronounced in the sample sintered for 10 minutes and a severe extent of porosity was also observed (orange arrow) throughout the matrix.

From the sample sintered at 1300°C for 10 minutes it was concluded by using XRD and SEM/EDS data that the reaction area was satisfactory and that the MAX-cBN interface has a reaction area which promotes the bond of the abrasive in the matrix, the Ti₃AlC₂ and cBN were abundantly present.

3.2 Increase in particle size (10 to 100 µm) and volume fraction of the 100 µm cBN (20 to 40 vol%).

The 1300°C, 10 minutes sintering condition was used to sinter samples containing 20 vol% of 100 µm cBN as recommended in Section 3.1.

Figure 11 shows the XRD diffractograms of the samples sintered at a constant temperature of 1300°C and a pressure of 30 MPa and three different soaking times (1, 5 and 10 minutes). This was done to obtain and optimise the Ti₃AlC₂ phase in the samples without compromising the cBN content. Figure 12 shows the Rietveld analysis and Figure 13 the density of the samples analysed in Figure 11. For all three soaking times cBN, AlN, TiN_b, TiC_xN_y and TiB₂ were present, with TiC_xN_y, TiC_o and TiB₂ becoming the dominant phases in the sample sintered for 10 minutes (Figure 12). The peak for TiC_xN_y

shifts to the right as the N content within the sample increased, and the TiN_b content remained lower than 1.5 vol.% in all samples (Figure 12). Ti_2AlC was the dominant phase for samples sintered for 1 and 5 minutes and diminished in the sample sintered for 10 minutes. The hBN phase was only found in the samples sintered for 5 and 10 minutes. And the Ti_3AlC_2 phase was seen only in the sample sintered for 10 minutes and was the only MAX phase in the sample.

Figure 13 Shows that the error for the densities was small and thus the reported values are reliable. However, the error for the open porosities was large, and that indicated that the values should be considered with caution. The density of the samples increased (383 to 4.00 g/cm³) with soaking time from 1 to 5 minutes and decreased again (3.54 g/cm³) as the time was increased to 10 minutes. This trend seemed to follow that of the Ti_2AlC and Ti_2AlN phases, as seen in Figure 12, the phase increased from 35 to 38 vol.% from 5 to 10 minutes respectively. Then it reduced again to depletion as the Ti_3AlC_2 phase is present at 21 vol%. Since these are the dominant phases in the respective samples, they have the most significant effect on the density of the samples. The open porosity of all samples remains more or less the same as the temperature in increased from 1 to 10 minutes.

Figure 14 shows the SEM (BSE) images of the Ti_3AlC_2 -cBN samples sintered at 1300°C. All samples showed the crack propagating through the cBN (blue arrow), which may be an indicator that the bond between the cBN and the MAX phase was strong. But, there also seemed to be crack propagating between the cBN and matrix (red arrow) and also possible abrasive pull-out (green arrow). This is indicated that: in some cases, the bond between the cBN and the matrix is not strong. All samples displayed cBN and a phase with a layered structure further away from the cBN.

Figure 15 show the EDX analysis the sample sintered at 1300°C for 10 minutes. The EDX analysis of the reaction area mainly consisted of TiC, site 2, and the cBN also seen, site 1. Site 3 shows a Ti, Al and C distribution in the ratio of 2:1:1,3 which indicates the Ti_2AlC MAX phase. Similar phase distribution was seen in the rest of the samples sintered at for 1 and 5 minutes.

The notable difference in decreasing the surface area of the cBN is that the content of hBN in the sample sintered with 100 μm powder was much lower than that of samples sintered with 10 μm cBN,

Figures 7 and 10. This could be due to the smaller available surface area of the cBN leading to less hBN forming on the surface. This also resulted in a sharper transformation of Ti_2AlC to Ti_3AlC_2 at longer soaking times. Thus, the samples sintered at 1300°C for 10 minutes sintering condition were further used to sinter samples with 40 vol% of 100 μm cBN. In addition, samples were also sintered for 5 minutes in order to evaluate kinetics when Ti_3AlC_2 and cBN interact with an increase in the amount of the cBN.

Figure 16 shows the XRD diffractograms of the samples sintered for a constant time of 5 minutes and a pressure of 30 MPa and three different temperatures. This was done to obtain and optimise the Ti_3AlC_2 phase in the sample without compromising the cBN content. For all three sintering temperatures, TiC_xN_y , AlN and cBN phases were present, with Ti_2AlC and Ti_3Al present in the samples sintered at 1250°C and 1300°C. The Ti_3AlC_2 , TiN_b and TiC_a phases were observed in the sample sintered at 1350°C, and $TiAl_2$ observed only in sample sintered at 1250°C. It was observed that the TiC_xN_y peak shifted to the left as the N content increased in the phase. Similar trends were observed for samples sintered for 10 minutes.

Figure 17 shows the results of the Rietveld analysis of the samples analysed in Figure 16. It was observed that the TiC_a , TiB_2 and AlN increased with temperature, and cBN and $TiAl_2$ decreased with increase in temperature. Figure 18 shows the density of samples sintered at all temperatures and for all soaking times. It was observed that for both 5- and 10-minutes soaking times, the densities of the samples were the same. Also, samples sintered at 1250°C to 1350°C also had similar densities, this was not unexpected as the phase content of the samples was very similar. The open porosities for all samples displayed a large error, thus the values observed were considered with caution. For samples sintered for 10 minutes, the open porosity decreased with increase in sintering temperature. Whereas, the samples sintered for 5 minutes the open porosity first increased then decreased. The decrease of porosity with temperature is expected as the increase in temperature promotes densification and thus decreases porosity.

Figure 19 shows the SEM (BSE) analysis of the Ti_3AlC_2 -cBN samples sintered for 5 minutes and 10 minutes. The samples sintered at 1250°C and 1300°C look similar in morphology as the samples with 20 vol.% cBN. However, the samples sintered at 1350°C had a clear reaction area (between red and blue outline) which was approximately 8-9 μm for the sample sintered for 5 minutes and approximately 10-12 μm for the sample sintered for 10 minutes. It was also observed in Figure 19 that in all sample there were instances where the crack propagated through the cBN (blue arrow) indicating that the bond between the cBN and the matrix was strong. And in samples below 1350 showed evidence of the crack propagating between the cBN and the matrix (red arrows) which indicated that the bond between the cBN and the matrix was not strong in these cases.

Figure 20 shows the EDX analysis of the two samples sintered at 1350°C for 5 minutes as the samples sintered at 1250°C and 1300°C look similar morphology in relation presented in sections 4.3.2. Site 1 displays the cBN phase, whereas site 2 and 5 display similar phase content. In these sites, some TiC_a , TiB_2 and TiN_b could be found. Site 4 shows evidence of Ti_2AlC and possibly a BC phase.

Increasing the volume fraction of the low surface area cBN has a significant effect on the phase content, Figure 21. The samples sintered with 40 vol% of the cBN have no excess hBN found in the samples, also, at 1300°C they have Ti_2AlC present as the only MAX phase. Increasing the temperature to 1350°C results in the formation of Ti_3AlC_2 as the only MAX phase in the sample and as one of the major phases with cBN. Therefore, increasing the volume fraction of cBN suppresses the reaction kinetics to form Ti_3AlC_2 at these conditions, and promotes a larger extent of hexagonalisation of the cBN. This could be due to the increase in the available cBN leading to more hBN forming.

In the wake of the results seen for 1300°C soaking temperature, composites were also sintered at 1350°C in order to optimise the formation of Ti_3AlC_2 and its reaction with cBN with a higher content of cBN. Increasing the temperature to 1350°C results in the formation of Ti_3AlC_2 as the only MAX phase in the composite (Figure 21) and as one of the major phases with cBN. This was, however, coupled with the slight increase in the excess hBN in the resultant composite. The noteworthy result here is that at 1350°C, the MAX phase and the cBN are still abundantly present in the composites with 40 vol%

of the 100 μm cBN particles. Unlike in the 10 vol% of the 10 μm cBN particles where, at 1350°C, the MAX phase completely decomposed into secondary phases.

However, the presence of a reaction area and the cBN-reaction area- Ti_3AlC_2 bond was similar to samples sintered with 20 vol% of the 100 μm cBN. Also, the phase distribution in the samples sintered at 1350°C was similar to the samples sintered with 20 vol% of the 100 μm cBN. This shows that for samples sintered with 40 vol% of 100 μm cBN, the optimum conditions for sintering the Ti_3AlC_2 -cBN composites was 1350°C for 10 minutes

4. Conclusions

- Elevated temperatures (1300°C-1350°C) and moderate pressure (30 MPa) can be used to fabricate Ti_3AlC_2 -cBN composites, by a controlled method of simultaneous partial hexagonalisation of cBN and reaction of the hBN with Ti_3AlC_2 .
- Ti_3AlC_2 -cBN (20 vol% of 10 μm) composites can be fabricated with both phases present in the sample. This, however, was coupled with the presence of the Ti_2AlC and Ti_2AlN phases.
- Ti_3AlC_2 -cBN (20 vol% of 100 μm) composites proved difficult to manufacture with the two phases present as the major phases. However, composites were successfully made where both phases were clearly present in the resulting samples.
- The Ti_3AlC_2 -cBN (40 vol% of 100 μm) composite can be successfully synthesised with the cBN and Ti_3AlC_2 abundantly present. Using the predicted results from the Ti_3AlC_2 -cBN (20 vol% of 100 μm) studies, it was predicted accurately that the conditions appropriate for the manufacture of these samples were 1350°C, at 30 MPa pressure, for 5 minutes. These conditions gave reaction zones between the cBN and Ti_3AlC_2 and the composite also contains small amounts of TiC , TiN , AlN and TiB_2 .
- Decreasing the surface area of cBN particles promotes the formation of the Ti_3AlC_2 , by reducing the extent of hexagonalisation of cBN, thus limiting the reaction of hBN and Ti_3AlC_2 and keeping the secondary phases content low.

- Increasing the content of cBN particles suppresses the decomposition temperature of the MAX phase and promotes the formation and increase of the Ti_3AlC_2 , at slightly higher temperature of 1350°C.
- The SEM micrographs of the optimum composites selected show good potential for the composites for cBN based grinding wheels by demonstrating that pull-out of the cBN in the composites was highly unlikely due to the strong bond of the reaction area to both the cBN and the respective MAX phase.

Acknowledgements: The financial support of Element 6, the Department of Science and Technology and the National Research Foundation (NRF), BAAP South Africa, is gratefully acknowledged. The Centre of Excellence (CoE) in hard materials is also gratefully acknowledged for their financial support.

REFERENCES

1. Barsoum, M.W. 2006. in Encyclopedia of Materials: Science and Technology, K. H. Jürgen Buschow, R. W. Cahn, M. C. Flemings, B. Ilchner, E. J. Kramer, S. Mahajan, P. Veyssi re (Eds.), Elsevier, Oxford, 1-16.
2. Barsoum, M.W, Farber L., El-Raghy T., 1999. Dislocations, kink bands, and room-temperature plasticity of Ti_3SiC_2 . *Metallurgical and Materials Transactions*, **A 30**: 1727-1738.
3. Wang X.H., Zhou Y.C. 2002. Microstructure and properties of Ti_3AlC_2 prepared by the solid-liquid reaction synthesis and simultaneous in-situ hot pressing process, *Acta Materialia*. **50**: 3141-3149.
4. Wang X. H. & Zhou Y.C. 2003a., Oxidation behavior of Ti_3AlC_2 at 1000–1400 °C in air, *Corrosion Science*, **45**: 891-907
5. Wang X.H. & Zhou Y.C. 2003b. High-Temperature Oxidation Behavior of Ti_2AlC in Air, *Oxidation of Metals* **59**: 303-320.
6. Wang X. H. & Zhou Y.C. 2010. Layered machinable and electrically conductive Ti_2AlC and Ti_3AlC_2 ceramics: a review. *Journal of Materials Science & Technology*, **26**: 385–416.
7. Zhou, A., Wang, C. & Huang, Y. 2003a. Synthesis and mechanical properties of Ti_3AlC_2 by spark plasma sintering. *Journal of materials science*, **38**: 3111-3115.
8. Yang, C., Jin, S.Z., Liang, B.Y., Jia, S.S. 2009. Low-temperature synthesis of high-purity Ti_3AlC_2 by MA-SPS technique. *Journal of the European Ceramic Society*, **29**: 181-185.
9. Li, L., Zhou, A., Wang, L., Li, S., Wu, D. & Yan, C. 2012. In situ synthesis of cBN– Ti_3AlC_2 composites by high-pressure and high-temperature technology. *Diamond & Related Materials*, **29**: 8–12.

10. Yang, L., Gong, J., Yue, Z. & Chu, X. 2016. Preparation and characterization of cBN-based composites from cBN-Ti₃AlC₂ mixtures. *Diamond & related Materials*, **66**: 183-187.
11. Yue, Z., Yang, L., Gong, J. & Gao, J. 2018. Synthesis and Comparison of Two cBN Composites with Starting Ternary Carbide Binders. *Journal of Materials Engineering and Performance*, **27**: 2124-2130.
12. Yue, Z. & Chu, X. 2016. Preparation and characterization of cBN-based composites from cBN-Ti₃AlC₂ mixtures. *Diamond and related Materials*, **66**: 183-187.
13. Školáková, A., Salvetr, P., Novák, P. & Vojtěch, D. 2018. Formation of Ti–Al Phases during SHS Process. *ACTA PHYSICA POLONICA A*, **134** 743 – 747.
14. Chen Y.-L., Yan M., Sun Y.-M., Mei B.-C., Zhu J.-Q. 2009. The phase transformation of TiAl/Ti₂AlC composites caused by hot pressing. *Ceramics International*, **35**: 1807–1812.
15. Lin, Z.J., Zhuo, M.J., Li, M.S., Wang, J.Y. & Zhou, Y.C. 2007. Synthesis and microstructure of layered-ternary Ti₂AlN ceramic. *Scripta Materialia*. **56** :1115-1118
16. Yoshida, M., Hoshima, Y., Ommyoji, J. & Yamagichi, A. 2010. Reaction mechanism for the synthesis of Ti₃AlC₂ through an intermediate carbide of Ti₃AlC from elemental Ti, Al and C powder mixture. *Journal of the Ceramic Society of Japan*, **118**: 37 – 42.
17. Zhou, W.B., Mei, B.C., Zhu, J.Q. & Hong, X.L. 2005. Rapid synthesis of Ti₂AlC by spark plasma sintering technique. *Materials Letters*, **59**: 131-134.
18. Mei, B., Zhou, W., Zhu, J. & Hong, X. 2004. Synthesis of Ti₂AlC by hot pressing and its mechanical and electrical properties. *Journal of materials science*, **39**: 1471-1472 .
19. Kulkarni, S. & Datye, A. 2010. Synthesis of Ti₂AlC by spark plasma sintering of TiAl–carbon nanotube powder mixture. *Journal of alloys and compounds*, **490**: 155-159 .
20. Liu, L., Li, Y., Li, F., Cui, H., Zhang, L. & Guo, S. 2017. Synthesis and microstructure of Ti₂AlN ceramic by thermal explosion. *Ceramics International*, **43**: 13618–13621.

21. Tomashik, V. & Perrot, P. 2005. Aluminium-Nitrogen-Titanium. *Springer London. Landolt-Bornstein*, **11A3**: 322-333.
22. Vel, L., Demazeau, G. & Etourneau, J. 1991. Cubic boron nitride: synthesis, physicochemical properties and applications. *Materials Science and Engineering B*, **10**: 149-164
23. Zhou, A., Wang, C., Huang, Y. 2003b. A possible mechanism on synthesis of Ti_3AlC_2 . *Materials Science and Engineering*, **A352**: 333-339.
24. Wolfrum A., Matthey B., Michaelis A. & Herrmann M. 2019. On the Stability of c-BN-Reinforcing Particles in Ceramic Matrix Materials. *Materials*, **11**: 255.
25. Cui, B., Jayaseelan, D.D., Lee, W. E. 2011. Microstructural evolution during high-temperature oxidation of Ti_2AlC ceramics. *Acta Materialia*, **59**: 4116–4125.
26. Springer. 2016. https://materials.springer.com/isp/crystallographic/docs/sd_1013340 [ACCESS 1 December 2018].

Tables:

Table 4: Density of the secondary phases, listed in descending order, found in the sintered samples, as well as cBN, hBN, Ti_2AlC and Ti_3AlC_2 phases near the triple border for comparison[26].

Phase	Density (g/cm ³)	Phase	Density (g/cm ³)
TiN	5.39	TiAl ₂	3.51
TiB ₂	4.53	TiAl ₃	3.36
TiC	4.09	AlN	3.26
TiC _{0.3} N _{0.7}	5.25		
Ti ₃ AlC ₂	4.25	cBN	3.49
Ti ₂ AlC	4.07	hBN	2.26

Figures:

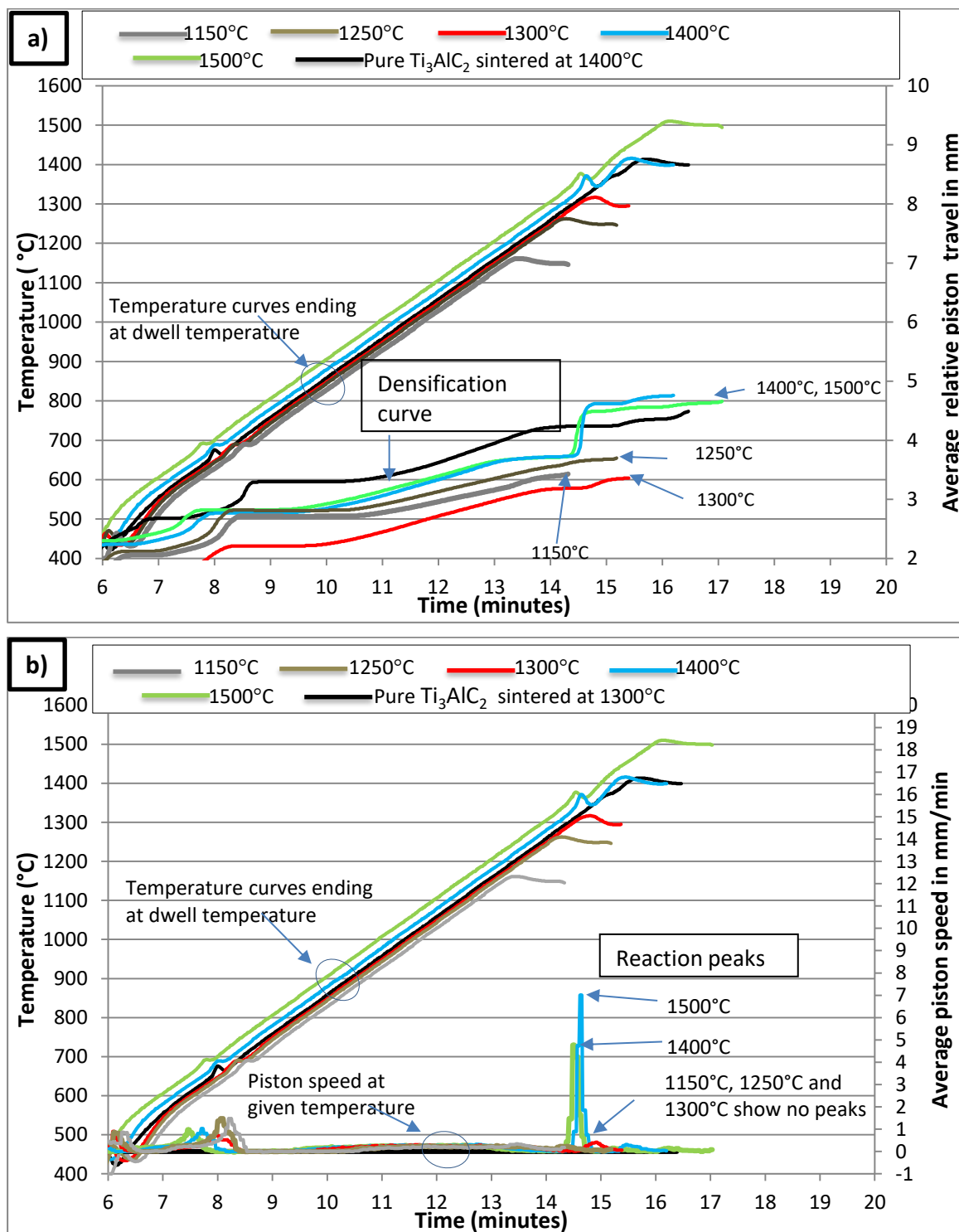


Figure 1: $\text{Ti}_3\text{AlC}_2\text{-cBN}$ (20 vol%, 10 μm) curves from the SPS runs at 1 min and different temperatures. **a)** piston displacement curves, **b)** piston displacement time derivative curves.

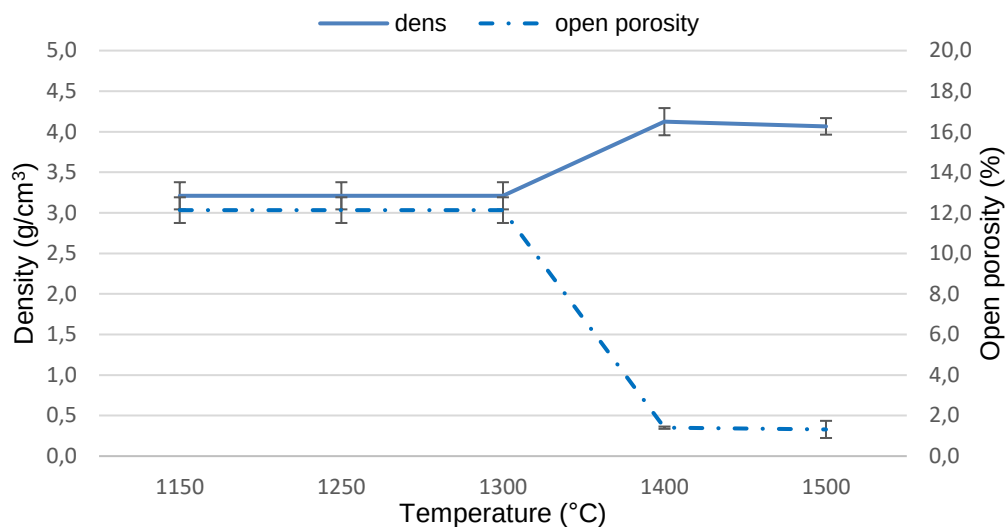


Figure 2: Densities and open porosities of Ti_3AlC_2 -cBN (20 vol.%, 10 μm) samples sintered at different temperatures with 1 minute dwell time.

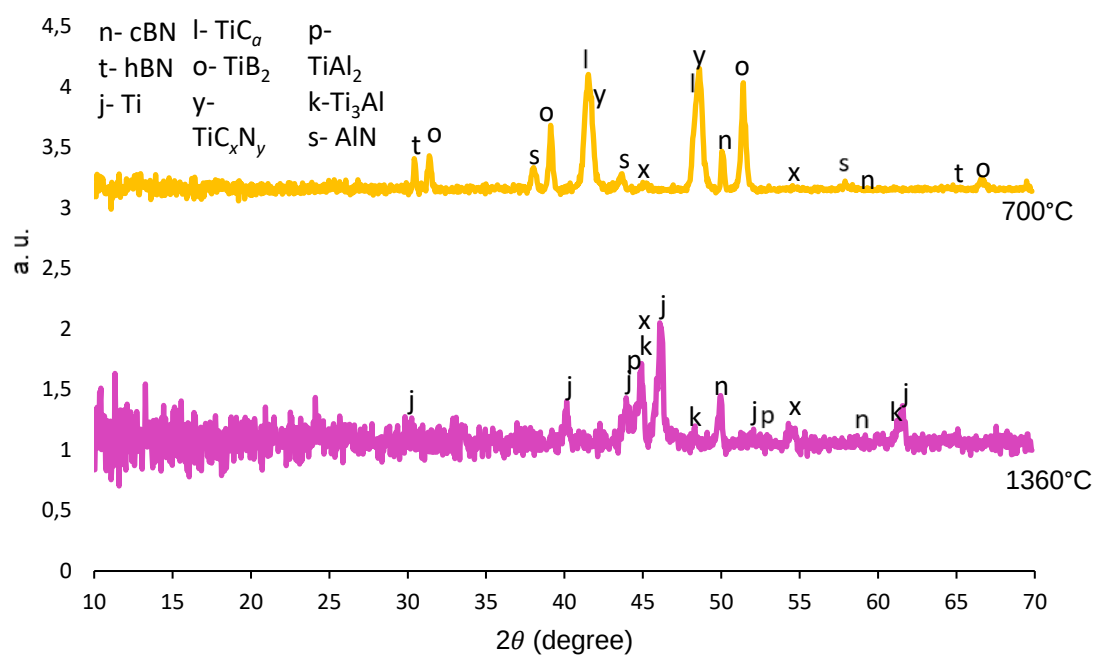


Figure 3: XRD diffractograms of Ti_3AlC_2 -(20 vol% of 10 μm) cBN samples, sintered at 30 MPa, 1 minute and different reaction peak temperatures, showing the phase development as a result of the two exothermic reactions at 680°C and 1350°C.

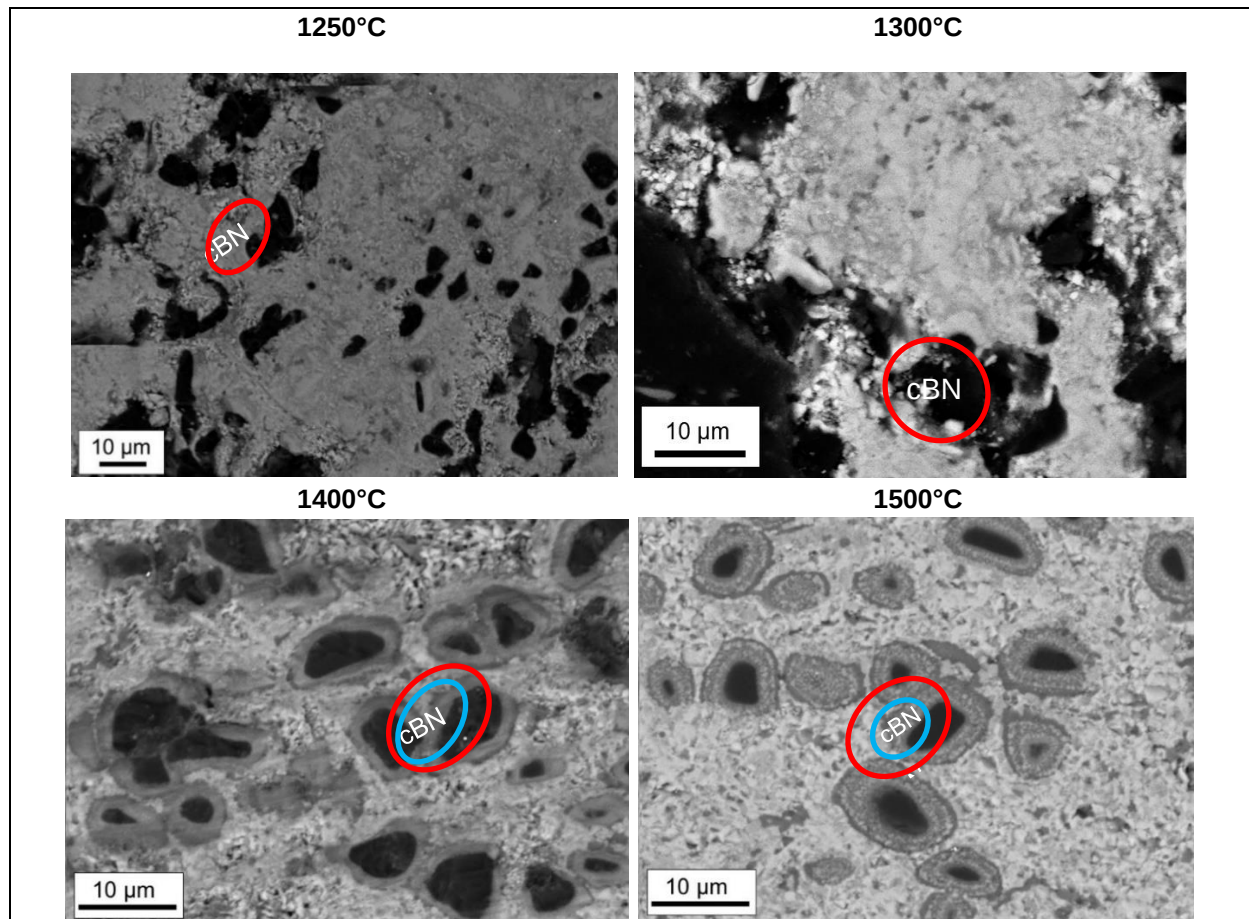
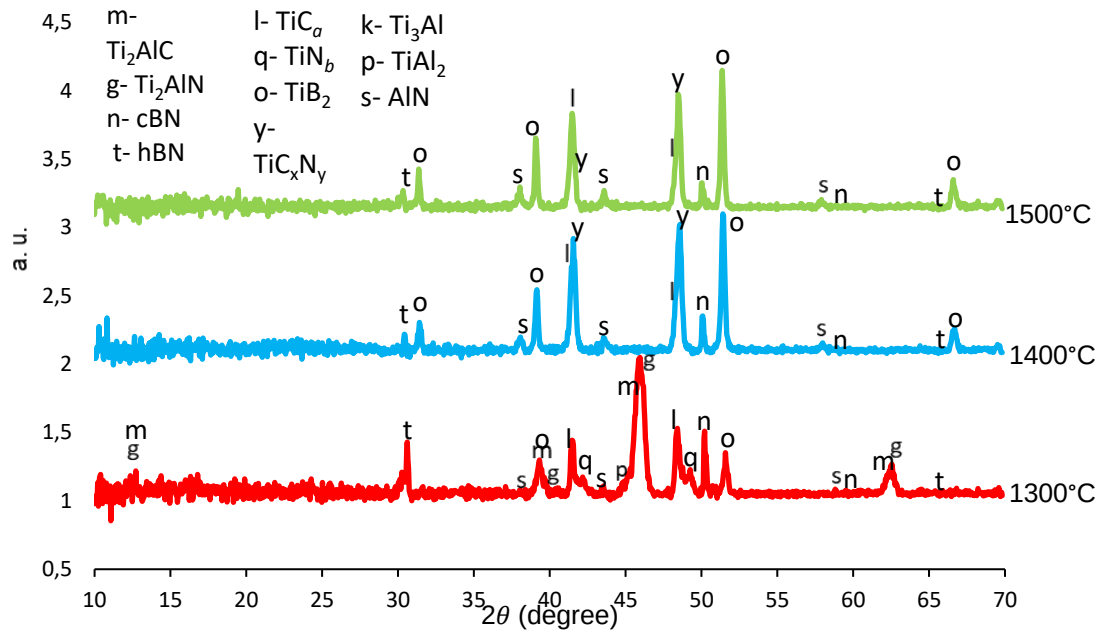
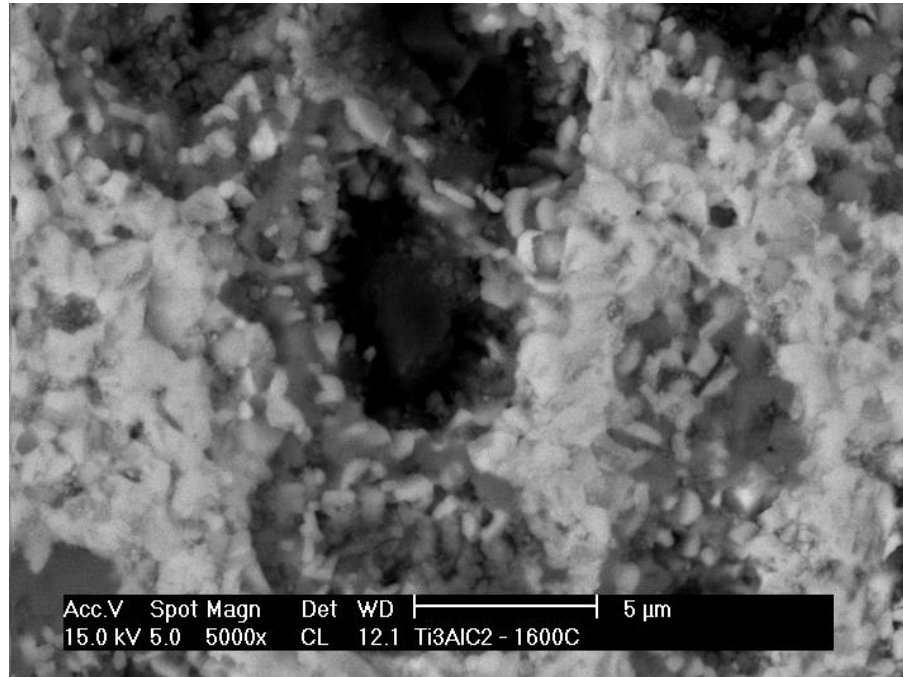


Figure 5: SEM micrographs of Ti_3AlC_2 -(20% of 10 μm) cBN samples sintered at 30 MPa, 1 minute and different temperatures, showing the migration of phases in the sample when temperature was increased from 1250°C to 1500°C.



		<i>B</i>	<i>C</i>	<i>N</i>	<i>O</i>	<i>Al</i>	<i>Si</i>	<i>Ti</i>	<i>Total</i>
<i>atomic %</i>									
<i>site 1</i>	average	50,2	8,4	32,1	0,6	5,7	0,0	3,0	100,0
	std deviation	8,0	7,3	13,6	1,3	4,3	0,0	2,8	
<i>site 2</i>	average	22,8	41,5	0,0	11,3	2,2	0,0	22,1	100,0
	std deviation	18,8	6,3	0,0	16,5	1,6	0,1	16,5	
<i>site 3</i>	average	15,7	35,5	0,0	12,5	2,0	0,2	34,1	100,0
	std deviation	19,6	12,5	0,0	15,8	1,2	0,2	14,8	
<i>site 4</i>	average	24,3	32,3	6,8	0,0	5,6	0,1	30,9	100,0
	std deviation	21,0	16,0	13,6	0,0	4,6	0,2	24,1	
<i>site 5</i>	average	29,1	20,9	19,9	1,3	6,4	0,1	22,4	100,0
	std deviation	24,5	16,8	17,1	1,7	2,7	0,1	24,5	

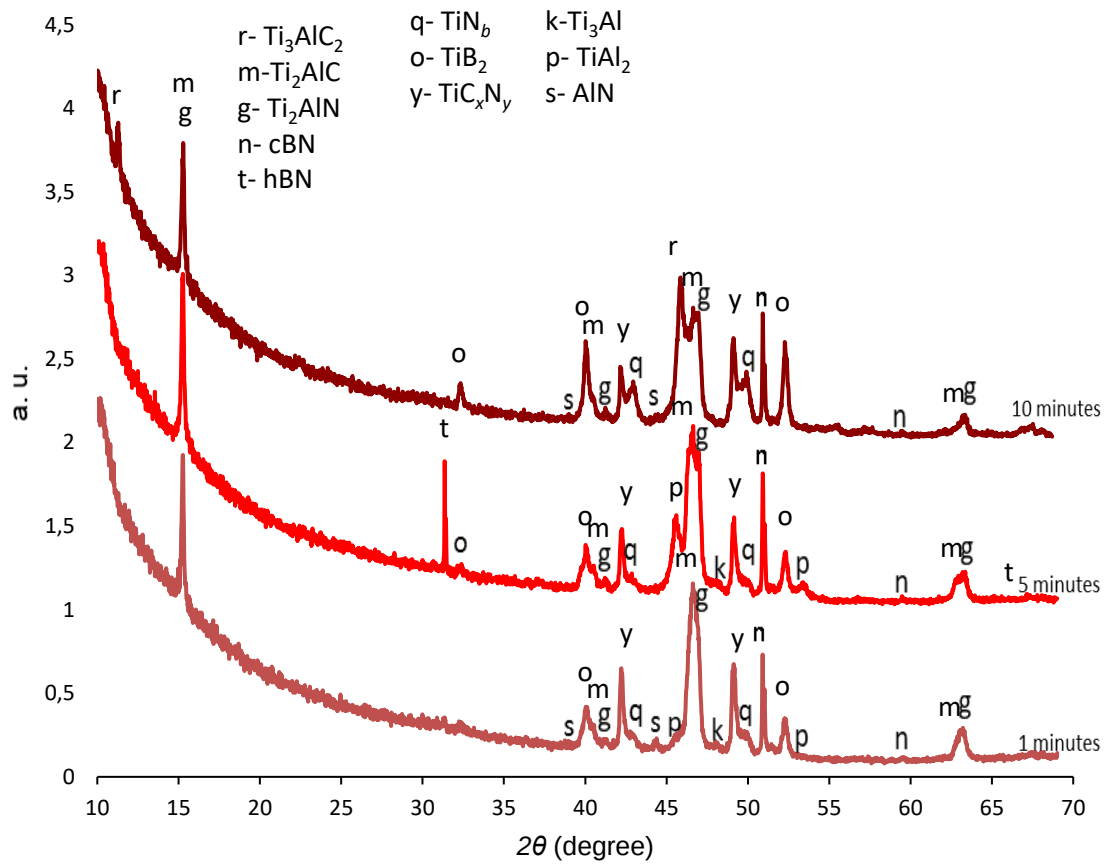
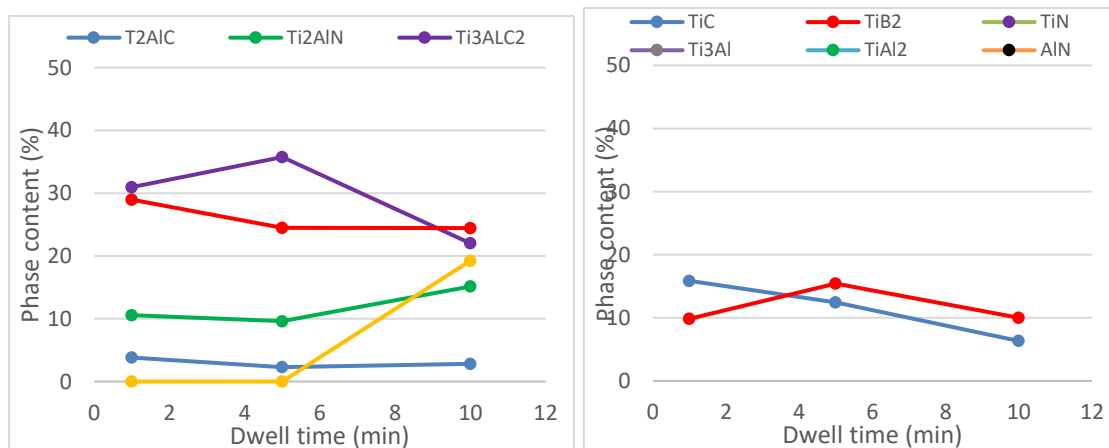
Figure 6: EDX analysis of Ti_3AlC_2 -cBN (20 vol.%, 10 μm) samples sintered at 30 MPa, 1 minute and 1600°C.Figure 7: XRD diffractogram of Ti_3AlC_2 -(20 vol% of 10 μm) cBN samples sintered at 30 MPa, 1300°C and different time profiles, showing the development of Ti_3AlC_2 from 5 to 10 minutes dwell times.

Figure 8: Phase quantities, determined by Rietveld analysis, of Ti_3AlC_2 -cBN (20 vol.%, 10 μm) samples sintered for different times at 1250°C.

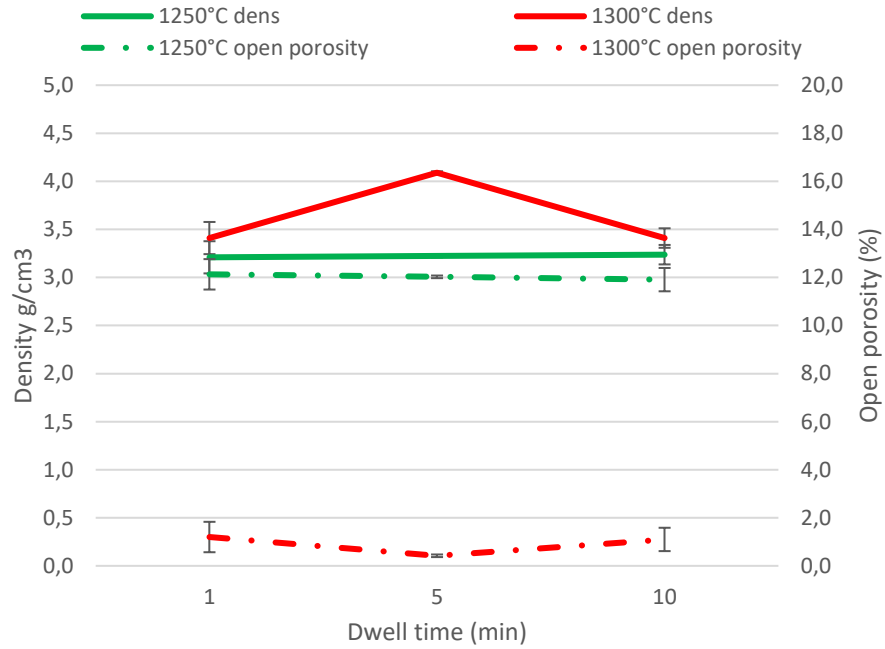


Figure 9: Densities and open porosities Vol.% of Ti_3AlC_2 -cBN (20 vol.%, 10 μm) samples sintered at different temperatures and for different dwell time.

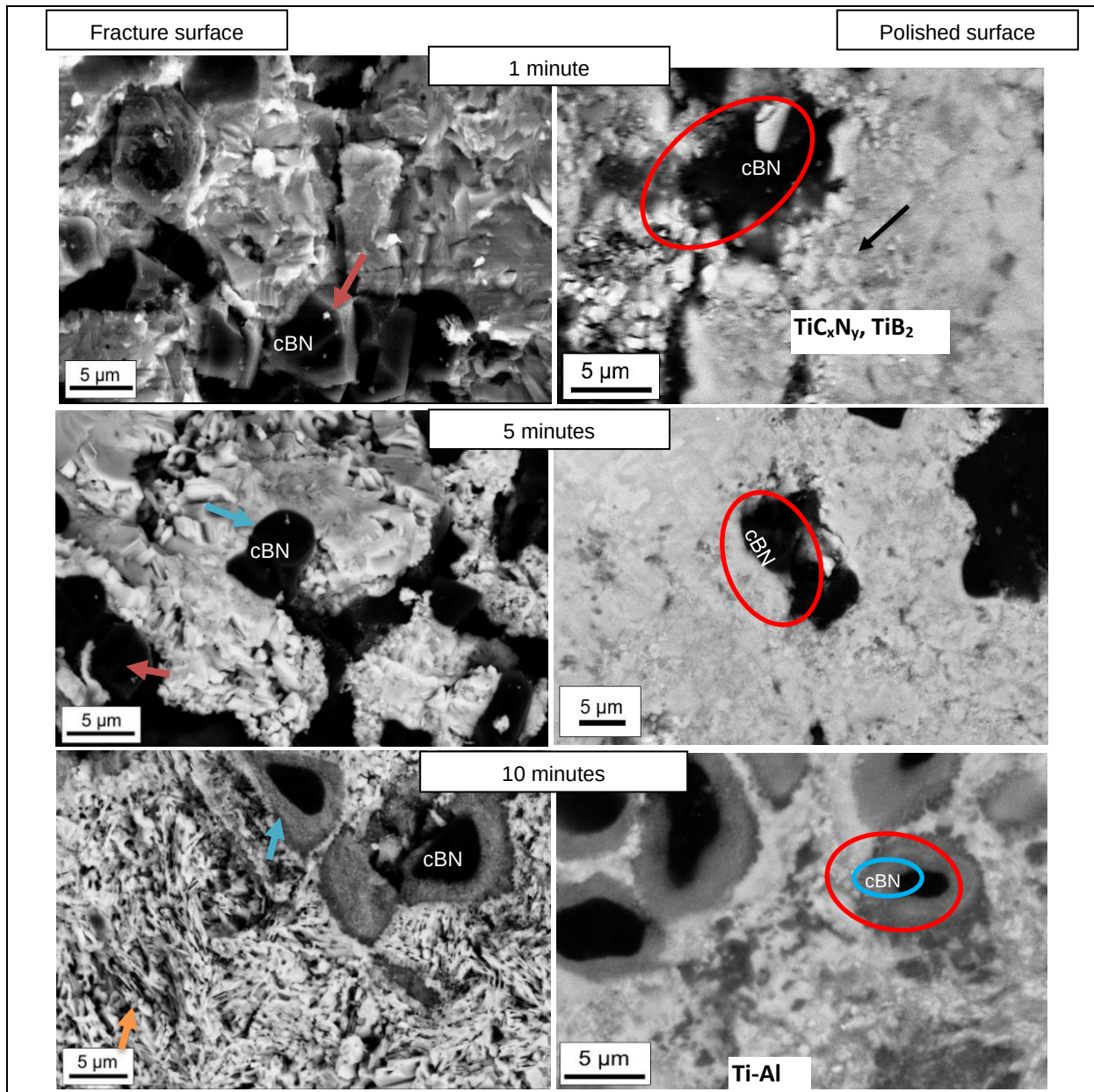


Figure 10: SEM (BSE) of fractured (left) and polished (right) Ti_3AlC_2 -cBN (20vol.%, 10 μm) samples sintered at 30 MPa 1300°C and different times. Blue arrows indicate crack propagation between cBN and matrix indicating strong bond between cBN and matrix, red arrows indicate crack propagating through the cBN and orange arrows indicate porosity in the matrix.

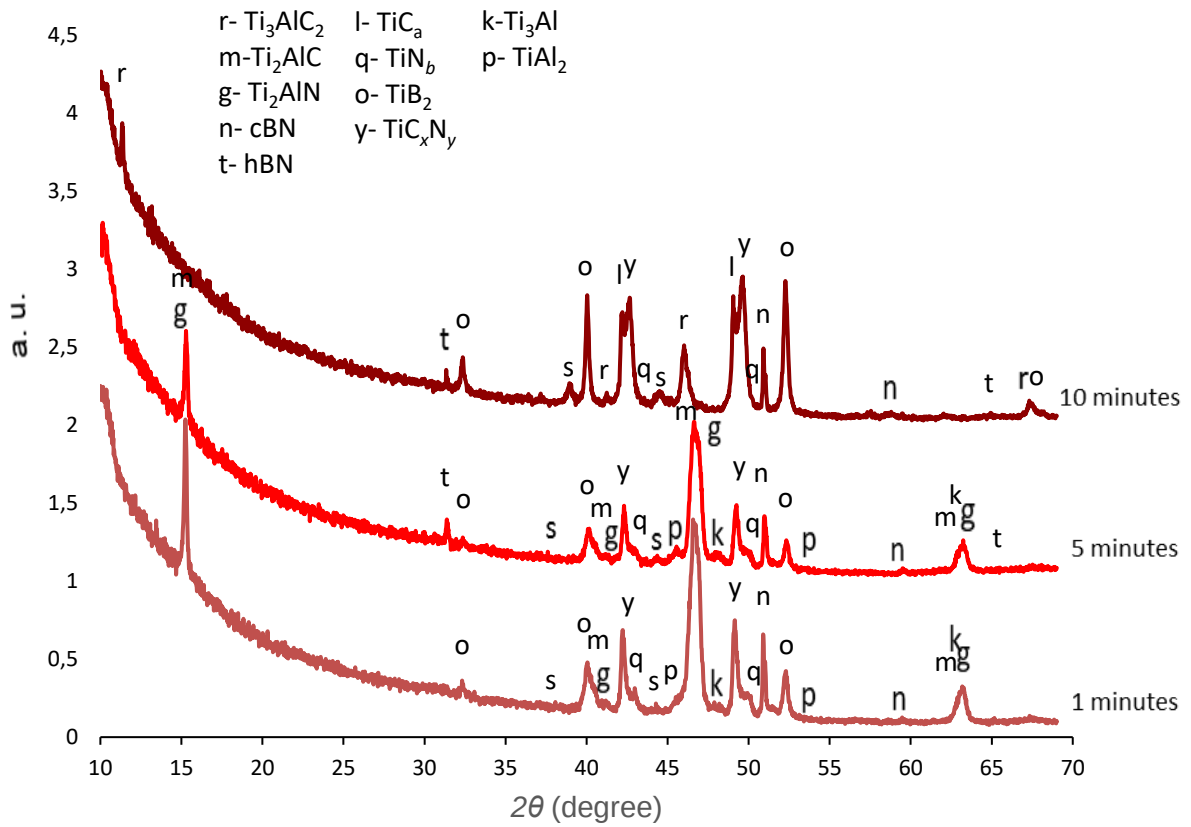


Figure 11: XRD traces of Ti_3AlC_2 -cBN (20 vol.%, 100 μm) samples sintered at 30 MPa, 1300°C for different times.

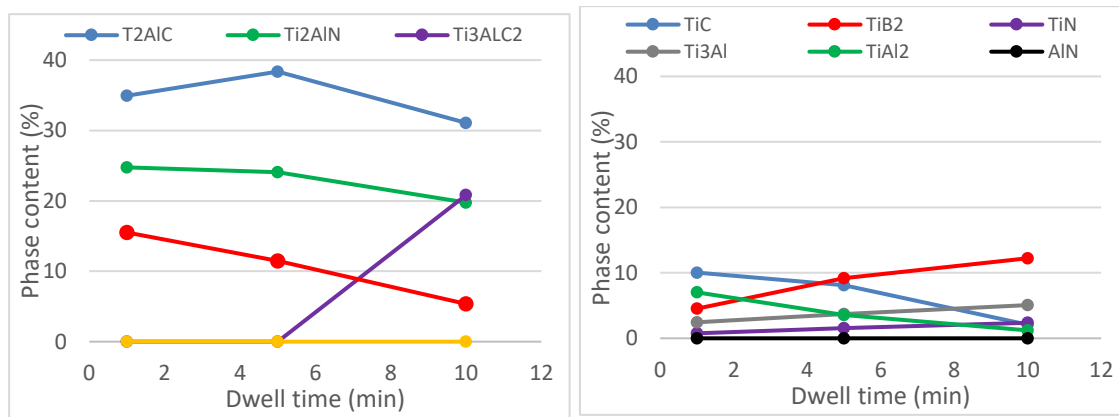


Figure 12: Phase quantities, determined by Rietveld analysis, of Ti_3AlC_2 -cBN (20 vol.%, 100 μm) samples sintered for different times at 1300°C.

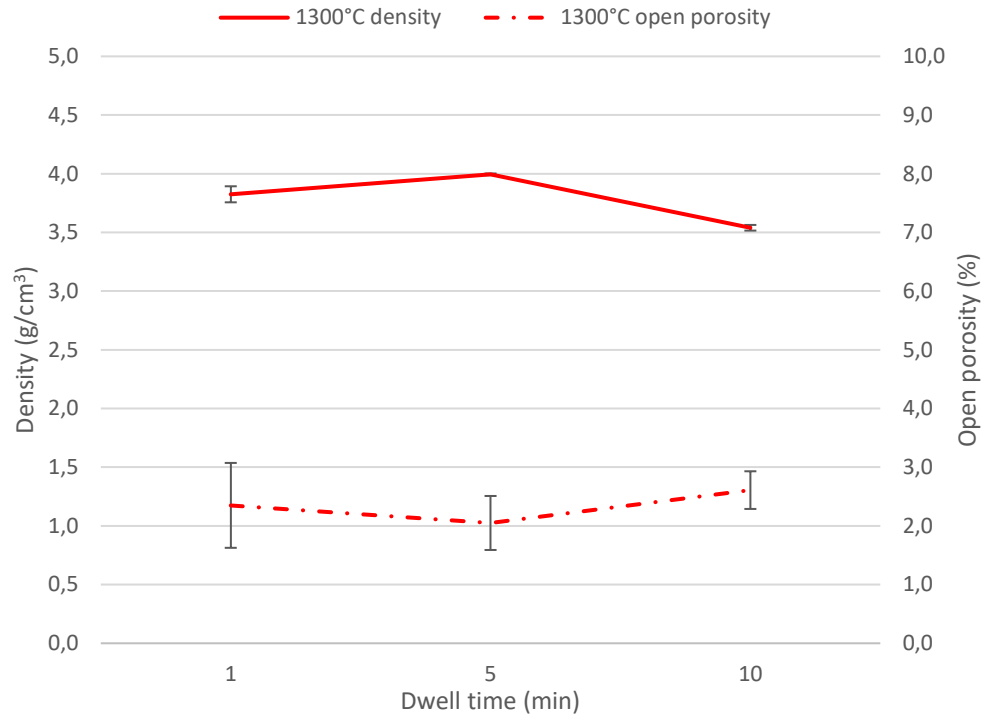


Figure 13: Densities and open porosities of $\text{Ti}_3\text{AlC}_2\text{-cBN}$ (20 vol.%, 100 μm) samples sintered at different temperatures for different dwell time.

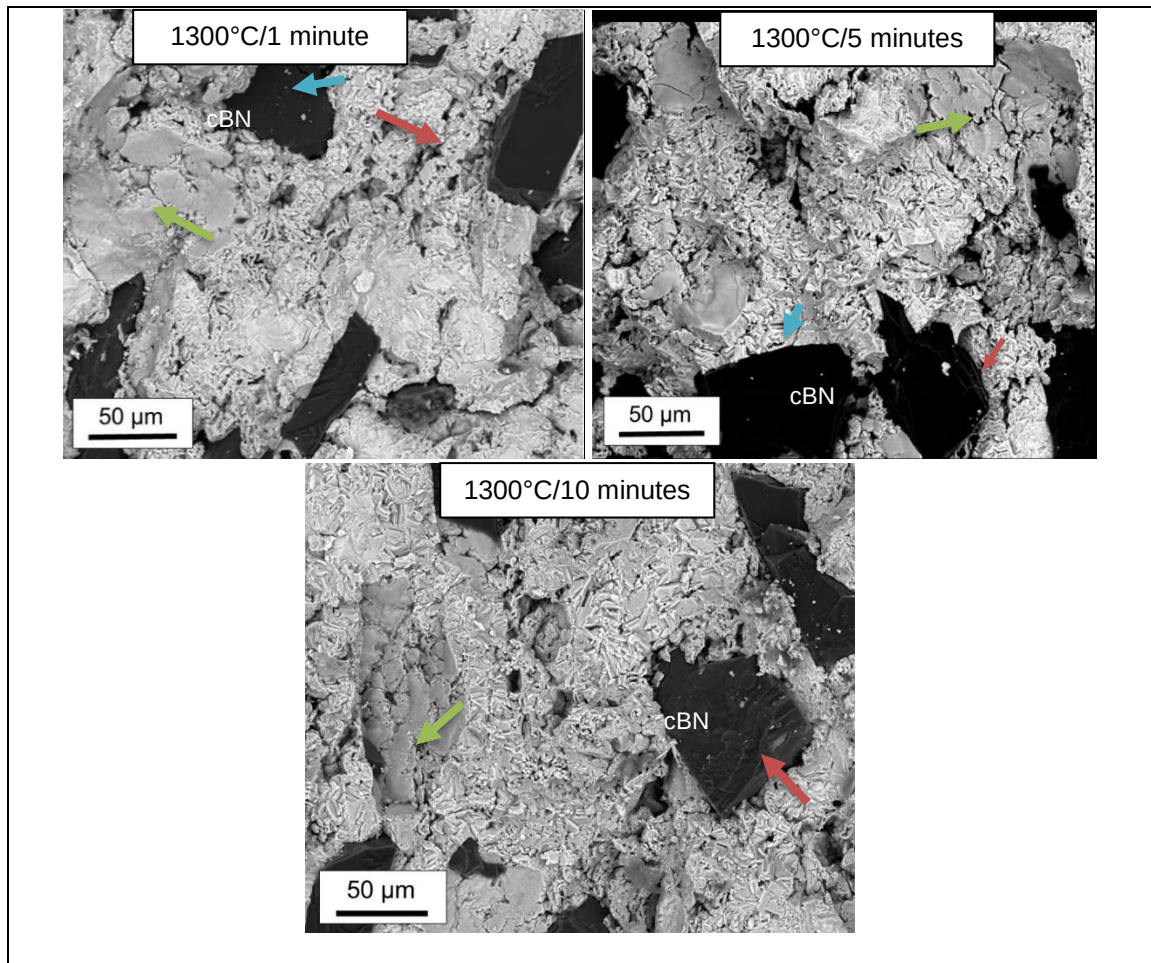
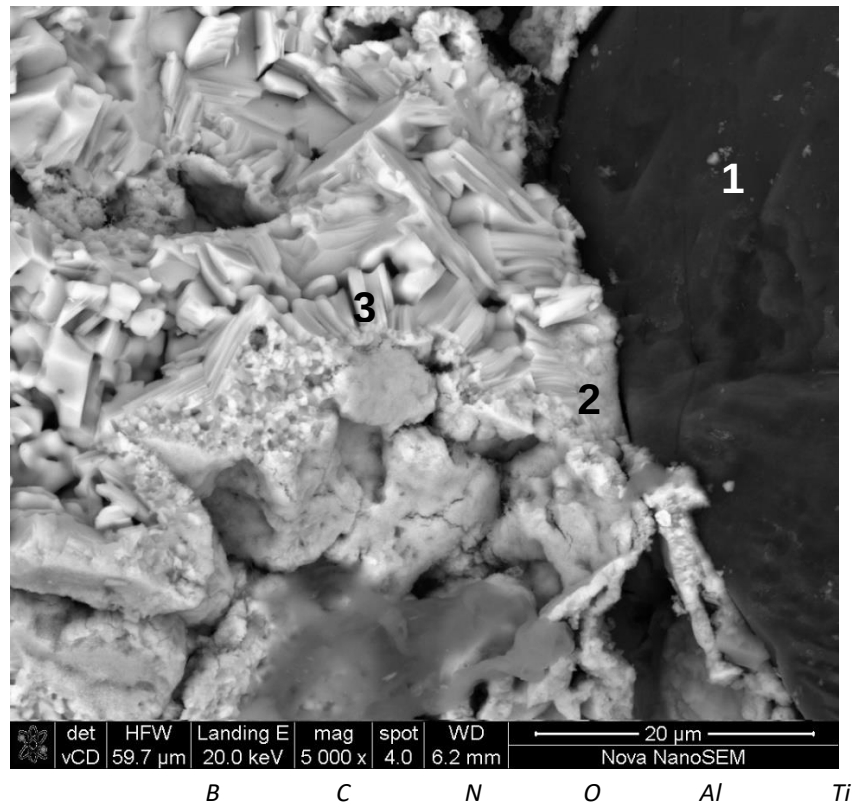


Figure 14: SEM (BSE) images of Ti_3AlC_2 -cBN (20 vol.%, 100 μm) samples sintered for different times at 1300°C. Blue arrows indicate crack propagation between cBN and matrix indicating strong bond between cBN and matrix, red arrows indicate crack propagating through the cBN and Green arrows indicate possible cBN pull-out.



		atomic %						Total
		B	C	N	O	Al	Ti	
site 1	average	54,3	0,0	43,5	2,2	0,0	0,2	101,5
	std deviation	1,7	0,0	3,9	2,1	0,0	0,2	7,8
site 2	average	0,0	53,8	0,0	0,0	2,0	44,2	100,0
	std deviation	0,0	10,3	0,0	0,0	3,1	10,3	23,8
site 3	average	0,0	30,5	0,0	0,0	22,6	46,9	100,0
	std deviation	0,0	6,8	0,0	0,0	4,7	2,9	14,3

Figure 15: SEM (BSE) and EDX analysis of Ti_3AlC_2 -cBN (20 vol.%, 100 μm) samples sintered at 30 MPa 1300°C 10 minutes.

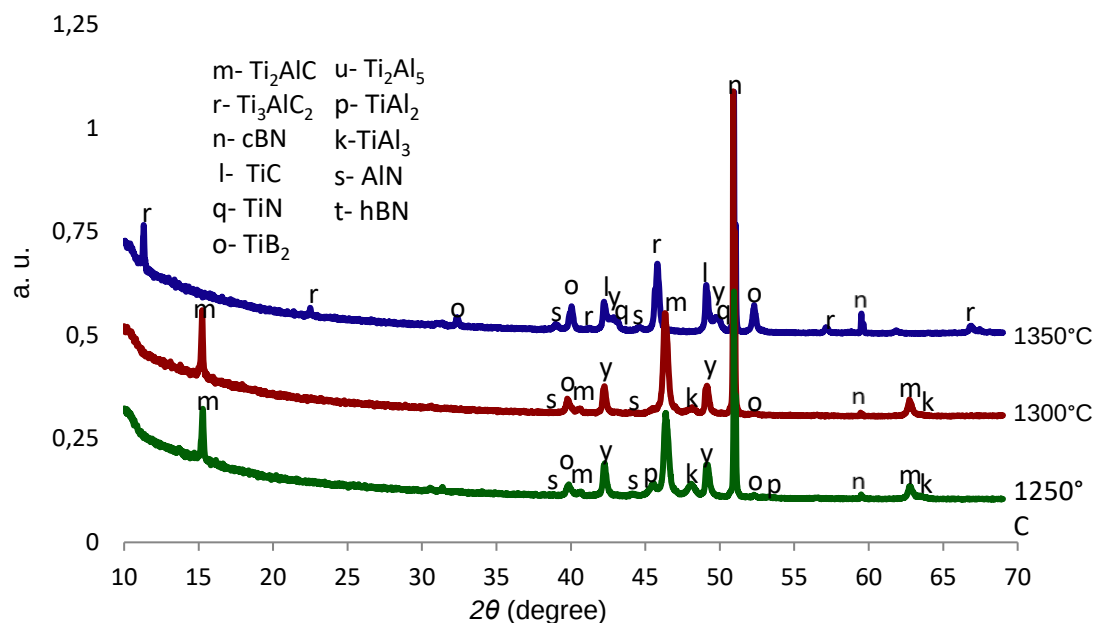


Figure 16: XRD traces of Ti_3AlC_2 -cBN (40 vol%, 100 μm) samples sintered at 30 MPa, 10 minutes and different temperatures.

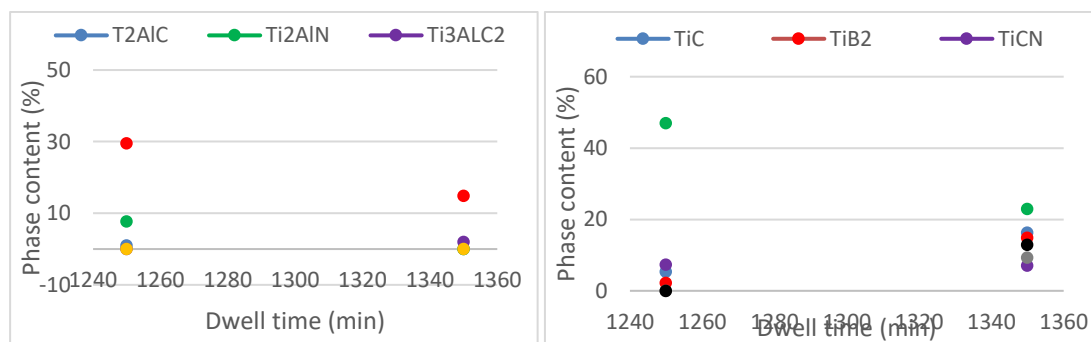


Figure 17: Phase quantities, determined by Rietveld analysis, of Ti_3AlC_2 -cBN (40 vol.%, 100 μm) samples sintered for 5 minutes at different temperatures.

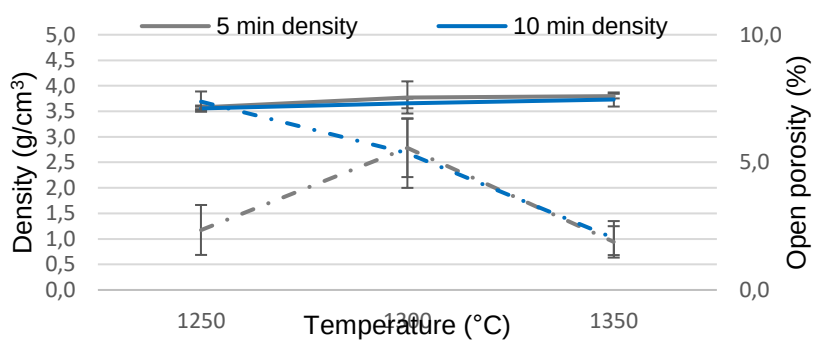


Figure 18: Densities and open porosities of Ti_3AlC_2 -cBN (40 vol.%, 100 μm) samples sintered at different temperatures and dwell time.

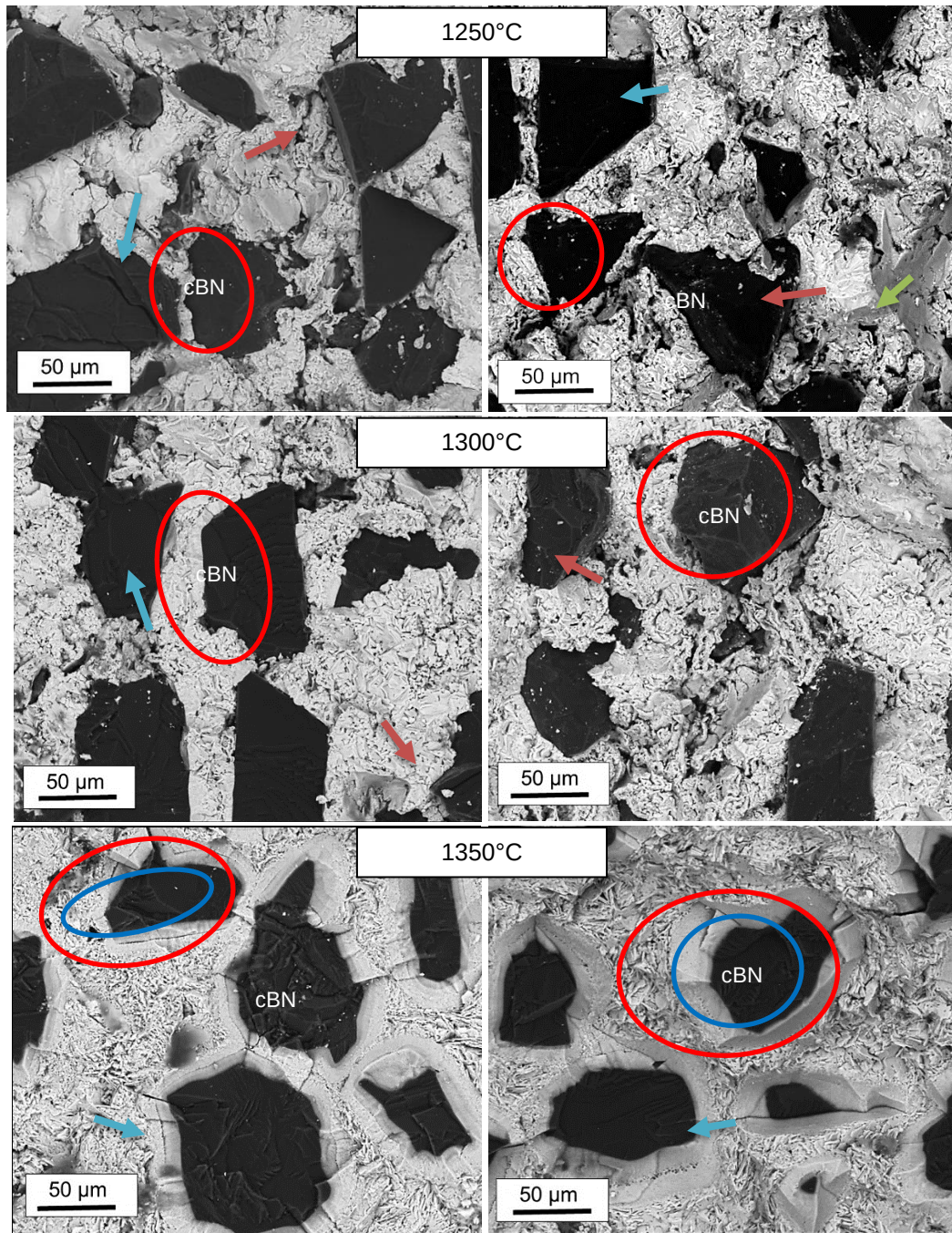
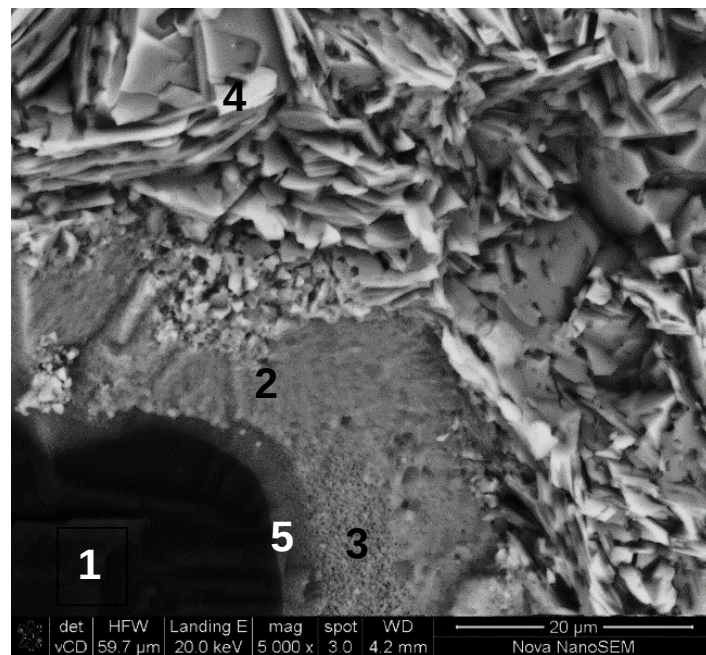


Figure 19: SEM (BSE) of Ti_3AlC_2 -cBN (40vol.%, 100 μm) samples sintered at 30 MPa and different temperatures for 5 minutes (left) and 10 minutes (right).



		B	C	N	Al	Ti	Total
		atomic %					
site 1	average	50,0	16,8	32,9	0,0	0,3	100,0
	std deviation	4,7	14,1	15,0	0,0	0,5	
site 2	average	56,2	20,3	10,4	1,3	11,8	100,0
	std deviation	6,3	13,3	11,6	0,6	3,4	
site 3	average	62,2	22,1	3,0	1,2	11,5	100,0
	std deviation	5,2	5,2	7,3	0,5	2,2	
site 4	average	51,1	33,3	0,0	3,1	12,5	100,0
	std deviation	4,0	4,7	0,0	1,5	1,8	
site 5	average	62,6	24,3	3,0	0,6	9,6	100,0
	std deviation	4,6	11,6	6,7	0,6	6,0	

Figure 20: SEM (BSE) and EDX analysis of Ti_3AlC_2 -cBN (40vol.%, 100 μm) samples sintered at 30 MPa, 1350°C for 5 minutes.

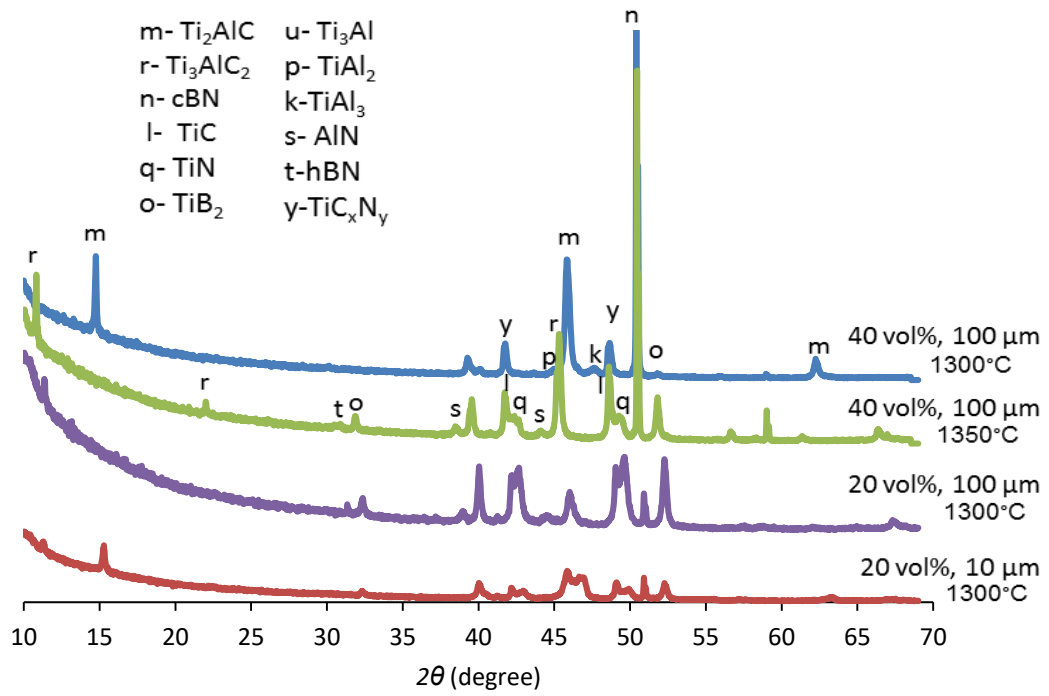


Figure 21: XRD traces of Ti_3AlC_2 -cBN samples sintered at 1300°C for 10 minutes, showing different volume fraction (20 or 40 vol%) and different size (10 and 100 μm) cBN, also included is the successful sample at the 40 vol% cBN sample sintered at 1350°C for 5 minutes.