

MICROSTRUCTURE AND PROPERTIES OF SELECTED WC-CEMENTED CARBIDES MANUFACTURED BY SPS METHOD

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‘A thesis submitted to the Faculty of Engineering and the Built Environment, University of the Witwatersrand, Johannesburg, in fulfilment of the requirements for the degree of Doctor of Philosophy.’

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DECLARATION

I, Rodney Michael Genga, declare that this thesis is my own unaided work. It is being submitted to the Degree of Doctor of Philosophy to the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination to any other university.

.....

Signature

.....day of..... Year.....

ABSTRACT

The effects of spark plasma sintering (SPS), WC starting particle size (0.1-0.8 μm), NbC, TiC and Mo_2C additions on the microstructure and mechanical properties of WC-Co and WC-Ni alloys were investigated. Spark plasma sintering has the main advantage of very high degrees of densification obtainable at low temperatures within short sintering times, preventing Ostwald ripening. Spark plasma sintered WC-0.5 Cr_3C_2 -10Co (wt%) and WC-9.3Ni (wt%) samples had finer WC grains with poorly distributed binder pools than similar liquid phase sintered (LPS) samples, resulting in higher hardness, lower fracture toughness (K_{1C}) and transverse rupture strength (TRS). Although the SPS samples had smaller WC grains than the LPS samples, WC grains of up to 1 μm occurred in the nano and ultrafine grades, due to coalescence of fine particles. High NbC additions (≥ 20 wt%) to WC-10Co (wt%) reduced the WC grain size, hardness, K_{1C} , TRS and modulus of elasticity in all grades. The poor mechanical properties were attributed to the reduction of WC volume fraction, formation of the (Nb,W) solid solution and poor wetting of NbC by Co. Additions of 6.25 wt% TiC and 0.5-5 wt% Mo_2C to the WC-9.3Ni (wt%) nano and ultrafine samples gave the finest WC grain sizes, due to good grain growth inhibition. Molybdenum carbide also improved the Ni binder distribution due to better wetting of WC by the Ni. The refined microstructure and improved Ni binder distribution, together with reduced binder amount (7 wt%) gave >20 GPa hardness, slight reduction in K_{1C} , good modulus of elasticity and lower TRS.

The abrasion wear resistance increased with reduced WC grain size and binder amount, explaining the significantly higher abrasion resistance of the SPS WC-5 Mo_2C -6.25TiC-7Ni (wt%) ultrafine and nano grades than the LPS samples. The LPS WC-9.3Ni sample, had higher abrasion wear resistance than the LPS WC-0.5 Cr_3C_2 -10Co (wt%) sample, because of the slightly lower binder content and the Ni binder's better wear properties. The LPS samples had the highest thermal shock and impact resistance (higher TRS and K_{1C}). The WC-0.5 Cr_3C_2 -5NbC-10Co (wt%) sample had a good hardness, from SPS and the addition of NbC and Cr_3C_2 grain growth inhibitors, as well as good K_{1C} and TRS, from its high binder amount and good wetting of WC by Co. These resulted in a good combination of abrasion wear, thermal shock and impact resistance in the WC-0.5 Cr_3C_2 -5NbC-10Co (wt%) sample. The WC-5 Mo_2C -6.25TiC-7Ni (wt%) ultrafine grade sample had the lowest thermal shock and impact resistance because of its poor K_{1C} and TRS.

DEDICATION

I would like to dedicate this work to God, without whom all this would not have been possible,

and my beloved parents, Mrs Florence Auma Genga and Professor Riewa Onyango Genga, who are the pillars and foundation of life, thank you for always believing in me.

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TABLE OF CONTENTS

DECLARATION	i
ABSTRACT.....	ii
DEDICATION.....	iii
ACKNOWLEDGMENTS	iv
TABLE OF CONTENTS.....	v
LIST OF FIGURES	ix
LIST OF TABLES	xix
Chapter 1: Introduction	1
1.1 Hypothesis.....	3
1.2 Overview	3
Chapter 2: Literature Review	4
2.1 WC-cemented carbides background	4
2.2 Production of cemented carbides	6
2.2.1 Powder production	7
2.2.2 Consolidation of powders	17
2.2.3 Sintering.....	27
2.3 Mechanical properties of sintered cemented carbides	39
2.3.1 Density	42
2.3.2 Hardness.....	42
2.3.3 Fracture toughness (K_{IC}).....	43
2.3.4 Transverse rupture strength (TRS).....	44
2.3.5 Wear resistance	44
2.3.6 Magnetic properties	49
2.3.7 Thermal shock resistance	51
2.3.8 Modulus of elasticity (Young's modulus)	51
2.4 Manipulation of WC-cemented carbides to achieve improved mechanical properties	51
2.4.1 Alteration of fractional compositions of the hard and the binder phase	51
2.4.2 Partial substitution of WC-phase	52
2.4.3 Control of WC grain size	52
2.4.4 Alteration of binder-phase	55
2.4.5 Control of sintering temperature and time	58

2.5 NbC addition to WC-Co	58
2.6 WC-Ni bonded cemented carbides	59
2.7 Mechanical properties for machining titanium	60
2.8 Approach of study	61
Chapter 3: Experimental procedure	62
3.1 Starting powders	62
3.1.1 Particle size analysis	62
3.1.2 Powder morphology	64
3.1.3 Powder crystal structure	64
3.1.4 Powder impurities	65
3.1.5 Powder oxygen analysis	65
3.2 Consolidation of powders	66
3.2.1 Powder Milling	66
3.2.2 Drying and sieving of the powders	68
3.3 Sintering	69
3.3.1 Spark plasma sintering	69
3.3.2 Liquid phase sintering	69
3.4 Characterisation of sintered samples	71
3.4.1 Density measurements	71
3.4.2 Magnetic properties	72
3.4.3 Cutting of sintered samples	73
3.4.4 Sample mounting	73
3.4.5 Sample grinding and polishing	73
3.4.6 Microstructure analysis	74
3.4.7 Phase analysis	75
3.4.8 Mechanical properties	75
Chapter 4: Optimisation of Milling and Sintering	83
4.1 Starting powder characterisation	83
4.1.1 Powder particle size	83
4.1.2 Powder morphology	87
4.1.3 Powder crystal structure	91
4.2 Optimisation of Milling	93
4.2.1 Determining milling media and milling time	93

4.2.2 Production of ultra-fine (0.4 μm) and submicron (0.8 μm) WC powders	95
4.3 Optimisation of spark plasma sintering process	98
4.3.1 Sintering temperature.....	98
4.3.2 Sintering pressure.....	100
4.3.3. Effect of sintering time on densification.....	102
4.3.4 Addition of NbC to WC-0.5Cr ₃ C ₂ -10Co (wt%)	103
4.3.5 Sintering WC-Ni	105
4.3.6 Addition of TiC and Mo ₂ C to WC-0.5Cr ₃ C ₂ -Ni (wt%).....	106
4.3.7 Overall sintering conditions	108
4.3.8 Density of sintered samples	111
Chapter 5: Microstructure, constituent phases and mechanical properties.....	115
5.1 Microstructure.....	115
5.1.1 Microstructures of WC-NbC-Co cemented carbides.....	115
5.1.2 Microstructures of WC-Mo ₂ C-TiC-Ni cemented carbides	124
5.2 Constituent phases	135
5.2.1 Phases present in the WC-NbC-Co compositions.	135
5.2.2 Phases present in the WC-Mo ₂ C-TiC-Ni compositions.....	137
5.3 Mechanical Properties:.....	138
5.3.1 Hardness.....	138
5.3.2 Fracture toughness (K _{1C}).....	141
5.3.3 Elastic modulus.....	144
5.3.4 Magnetic saturation.....	145
5.3.5 Transverse rupture strength (TRS).....	146
Chapter 6: Sliding wear, thermal shock and impact resistance results	147
6.1 Sliding wear	147
6.1.1 Sliding wear due to 100 Cr6 steel ball	147
6.1.2 Sliding wear from silicon nitride (Si ₃ N ₄) balls	156
6.2 Thermal shock and impact resistance	163
6.2.1 Optical images of insert cutting edges	163
6.2.2 Microstructure of fractured cutting edges.....	165
6.2.3 Flank wear rate, thermal shock and impact force measurements	168
Chapter 7: Discussion	178
7.1 Characterisation of starting powders	178

7.2 Optimisation of milling.....	179
7.3 Optimisation of Sintering.....	180
7.3.1 Addition of NbC to WC-0.5Cr ₃ C ₂ -10Co (wt%)	181
7.3.2 Sintering WC-Ni	182
7.3.3 Addition of TiC and Mo ₂ C to WC-0.5Cr ₃ C ₂ -Ni (wt%).....	182
7.4 Microstructure of WC cemented carbides	183
7.4.1 Microstructure of WC-NbC-Co cemented carbides	183
7.4.2 Microstructure of WC-Mo ₂ C-TiC-Ni cemented carbides.....	184
7.5 Constituent phases	187
7.5.1 Phases present in the WC-NbC-Co compositions	187
7.5.2 Phases present in the WC-Mo ₂ C-TiC-Co compositions.....	188
7.6 Mechanical Properties.....	188
7.6.1 Hardness.....	188
7.6.2 Fracture toughness (K _{1C}).....	192
7.7 Elastic modulus	195
7.7.1 Elastic modulus of WC-NbC-Co compositions.....	195
7.8 Magnetic saturation.....	196
7.9 Transverse rupture strength.....	197
7.10 Sliding wear resistance	198
7.10.1 Samples sliding wear due to 100 Cr 6 steel ball	198
7.10.2. Wear on 100 Cr6 steel balls	200
7.10.3. Sample wear due to silicon nitride (Si ₃ N ₄) balls.....	203
7.10.4 Wear on silicon nitride (Si ₃ N ₄) balls.....	204
7.11 Thermal shock and impact resistance	206
Chapter 8: Conclusions and Recommendations	212
8.1 Conclusions.....	212
8.2 Recommendations	214
REFERENCES	216
APPENDIX: OUTPUTS FROM THIS WORK	239
PUBLICATIONS.....	239
PRESENTATIONS AND CONFERENCES	240
AWARDS	240

LIST OF FIGURES

Figure 2.1. Production of APT from wolframite ore [1998Upa].	8
Figure 2.2. SEM-SE image of APT [1998Upa].	8
Figure 2.3. SEM-SE image of tungsten oxide (WO_3) [1998Upa].	9
Figure 2.4. SEM-SE image of tungsten powder [1998Upa].	10
Figure 2.5. Production of cobalt powders and granules [1998Upa].	11
Figure 2.6. Flow sheet of cemented carbide production [1998Upa].	18
Figure 2.7. Schematic drawing of tumbler ball mill [1996Koc].	19
Figure 2.8. Powder particles becoming trapped between the balls during milling [1996Koc].	20
Figure 2.9. Effect of milling time on WC particle size reduction [1970Lar].	22
Figure 2.10. Schematic drawing of an attritor mill [1996Koc].	23
Figure 2.11. Schematic representation of single action compaction and double action compaction [1997Luy].	26
Figure 2.12. Loss of wax (lubricant) with variation of temperature and time [1970Spi].	27
Figure 2.13. Basic phenomena occurring during sintering driven by $\Delta(\gamma A)$ [2005Kan].	28
Figure 2.14. Comparison between densification and sintering parameters [2005Kan], where T is temperature, P is pressure and L is particle size.	32
Figure 2.15. Schematic diagram showing the microstructure changes during conventional sintering, starting from mixed powders to fully dense sintered compact [2009Ger].	35
Figure 2.16. Schematic diagram of a SPS machine [2002Mam].	37
Figure 2.17. Schematic diagram of the flow of pulse discharge current during SPS, with (1) through the powders, (2) through the punches, and (3) through the die [2011Bas1].	37
Figure 2.18. Schematic diagram of pulse current flowing through powder particles [1999Tok].	38
Figure 2.19. Neck growth at a particle contact point due to enhanced diffusion, from high localised temperatures and applied pressure [2011Bas1].	38
Figure 2.20. Effect of grain size and Co content on the abrasion resistance of WC-Co [1998Upa].	50
Figure 2.21. Effect of temperature on grains size of nano WC during sintering [2008Wan].	54
Figure 2.22. Contrast of wetting behaviour for a liquid on a horizontal plane, showing how a low contact angle supports wetting, while a high angle resists wetting [1956Par, 2009Ger].	57

Figure 3.1. Schematic diagram showing the Microtrac S3500 tri-laser system for particle size analysis [2007Mac].	63
Figure 3.2. Stainless steel milling pot (Pilot tools (Pty) Ltd.).	68
Figure 3.3. SPS profile for production of WC-10Co (wt%), total time 23 minutes.	70
Figure 3.4. LPS temperature profile for WC-10Co (wt%), total time 24 h and 42 minutes.	71
Figure 3.5. Hardness indentation on the surface of the specimen [Element Six S.O.P].	75
Figure 3.6. Difference in indenter penetration depth during Rockwell hardness testing [1996URL].	76
Figure 3.7. Schematic diagram showing arrangement of the sample and balls for a B3B TRS test [2004Bör2].	78
Figure 3.8. Schematic diagram showing arrangement of the sample, ball and experimental parameters during the abrasion wear test [1999Jac].	79
Figure 3.9. Schematic diagram of cutting tool inserts showing the shape and dimensions.	82
Figure 4.1. Particle size analysis of as-received micron-WC powder.	84
Figure 4.2. Particle size analysis of as-received submicron-WC powder doped with 0.5 wt% Cr ₃ C ₂ .	84
Figure 4.3. Particle size analysis of as-received nano-WC powder.	84
Figure 4.4. Particle size analysis of as-received Co powder.	85
Figure 4.5. Particle size analysis of as-received micron Ni powder.	85
Figure 4.6. Particle size analysis of as-received ultra-fine Ni powder.	85
Figure 4.7. Particle size analysis of as-received NbC powder.	86
Figure 4.8. Particle size analysis of as-received TiC powder.	86
Figure 4.9. Particle size analysis of as-received Mo ₂ C powder.	86
Figure 4.10. SEM-BSE image of as-received micron WC powder, showing mainly spherical particles of different sizes.	87
Figure 4.11. SEM-BSE image of as-received submicron WC-0.5Cr ₃ C ₂ (wt%) powder, showing rounded particles.	88
Figure 4.12. SEM-BSE image of as-received nano WC powder, showing angular particles and particle agglomerates between ~0.3-0.5 µm.	88
Figure 4.13. SEM-BSE image of as-received Co powder, showing agglomerates of irregular particles.	89
Figure 4.14. SEM-BSE image of as-received micron Ni powder, showing chains of agglomerate angular particles.	89

Figure 4.15. SEM-BSE image of as-received ultra-fine Ni powder, showing spherical particles of different sizes.	89
Figure 4.16. SEM-BSE image of as-received TiC powder, showing angular particles.....	90
Figure 4.17. SEM-BSE image of as-received NbC powder, showing angular particles of different sizes.	90
Figure 4.18. SEM-BSE image of as-received Mo ₂ C powder, showing irregular particles that agglomerated with mainly smooth surfaces.....	90
Figure 4.19. X-ray diffraction patterns for as-received 1, 0.8 and 0.1 μm WC powders.	91
Figure 4.20. X-ray diffraction pattern for as-received Co powder.	91
Figure 4.21. X-ray diffraction patterns for as-received 0.2μm and 2.5μm Ni powders.	92
Figure 4.22. X-ray diffraction pattern for as-received TiC powder.....	92
Figure 4.23. X-ray diffraction pattern for as-received NbC powder.	92
Figure 4.24. X-ray diffraction pattern for as-received Mo ₂ C powder.	93
Figure 4.25. Comparison between WC-10Co (wt%) and steel milling balls.....	94
Figure 4.26. WC-0.5Cr ₃ C ₂ -9.3Ni (wt%) milling curve using WC-10Co (wt%) milling balls.	94
Figure 4.27. Comparison between 6:1 and 3:1 ball-to-powder ratios during milling of nano WC-9.3Ni (wt%).....	95
Figure 4.28. Particle size reduction of WC powder from 1 μm to 0.8 μm using a 10:1 ball-to-powder ratio.	95
Figure 4.29. Particle size reduction of WC powder from 1 μm to 0.4 μm using a 15:1 ball-to-powder ratio.	96
Figure 4.30. SEM-BSE image of as-received 0.8 μm WC powder, showing angular grains..	97
Figure 4.31. SEM-BSE image of as-received 0.4 μm WC powder, showing angular particle and particle agglomerates.	97
Figure 4.32. X-ray diffraction patterns showing micron WC starting powders, submicron and ultra-fine WC powders.....	98
Figure 4.33. Images of the rams (a) before, and (b) after SPS WC-0.5Cr ₃ C ₂ -10Co (wt%) at 1240°C, a silver shiny coating was present on the rams after sintering.....	99
Figure 4.34. SEM-BSE images of WC-0.5Cr ₃ C ₂ -10Co (wt%): sintered at (a) 1050°C, (b) 1140°C, (c) 1190°C, (d) 1220°C and (e) 1240°C, WC (light), Co (medium) and pores (dark).	101

Figure 4.35. SEM-BSE images of WC-0.5Cr ₃ C ₂ -10Co (wt%): (a) Sample 2.1, (b) Sample 2.2, and (c) Sample 2.3, WC (light), Co (medium) and pores (dark).	102
Figure 4.36. Variation in compact shrinkage (densification) due addition of NbC to WC-0.5Cr ₃ C ₂ -10Co (wt%).	104
Figure 4.37. Effect of sintering temperature and time on densification of WC-0.5Cr ₃ C ₂ -1NbC-10Co (wt%).	104
Figure 4.38. Comparison of shrinkage between 1 and 10 NbC (wt%) additions to WC-0.5Cr ₃ C ₂ -10Co (wt%), sintered at 1260°C, 60 MPa for 5 minutes.	105
Figure 4.39. SEM-BSE images of WC-0.5Cr ₃ C ₂ -1NbC-10Co (wt%): (a) sintered at 1220°C, 50MPa for 2 minutes, and (b) sintered at 1260°C, 60MPa for 5 minutes; WC (light), Co (medium light), NbC (medium dark), pores (dark).	105
Figure 4.40. SEM-BSE images of WC-0.5Cr ₃ C ₂ -10NbC-10Co (wt%): (a) sintered at 1220°C, 50MPa for 2 minutes, and (b) sintered at 1260°C, 60MPa for 5 minutes; WC (light), Co (medium light), NbC (medium dark), pores (dark).	106
Figure 4.41. Variation in densification due to addition of 6.25 TiC (wt%) and 3.5 Mo ₂ C (wt%) to WC-0.5Cr ₃ C ₂ -9.3Ni (wt%).	107
Figure 4.42. Improved densification of WC-0.5Cr ₃ C ₂ -6.25TiC-9.3Ni (wt%) because of increased sintering pressure from 60-70MPa.	107
Figure 4.43. Comparison between densification curves of WC-0.5Cr ₃ C ₂ -3.5Mo ₂ C-6.25TiC-9.3Ni (wt%) sintered at 1280°C and 1310°C.	108
Figure 5.1. SEM-BSE images of WC-0.5Cr ₃ C ₂ -10Co (wt%) sintered by: (a) LPS and (b) SPS, showing WC (light), and Co (dark).	116
Figure 5.2. SEM-BSE images of WC-0.5Cr ₃ C ₂ -10Co (wt%), with: (a) 0.5, (b) 1, (c) 2, (d) 3, and (e) 5 NbC (wt%) additions: WC (light), NbC (medium) and Co (dark).	117
Figure 5.3. SEM-BSE images of WC-0.5Cr ₃ C ₂ -10Co (wt%), with: (a) 10, (b) 20, (c) 30, (d) 50, and (e) 80 NbC (wt%) additions: WC (light), NbC (medium) and Co (dark).	118
Figure 5.4. SEM-BSE images of WC-0.5Cr ₃ C ₂ -10Co (wt%) with: (a) 5, (b) 10, (c) 20, and (d) 80 NbC (wt%) additions., showing rounding of WC grains and difference in contrast between NbC and Co: WC (light), NbC (medium) and Co (dark).	119
Figure 5.5. HAADF-STEM mapping images of WC-0.5Cr ₃ C ₂ -20NbC-10Co (wt%), showing C (purple), Nb (blue), Cr (yellow), W (green) and Co (red).	119
Figure 5.6. HAADF-STEM EDX mapping images of WC-0.5Cr ₃ C ₂ -20NbC-10Co (wt%), showing C (purple), Nb (blue), Cr (yellow), W (green) and Co (red).	120

Figure 5.7. SEM-BSE images of WC-10Co (wt%), with: (a) 0, (b) 1, (c) 3, (d) 5, and (e and f) 20 wt% NbC additions: WC (light), NbC (medium) and Co (dark).	122
Figure 5.8. SEM-BSE images of WC-10Co (wt%), with: (a) 0, (b) 1, (c) 3, (d) 5, and (e) 20 NbC (wt%) additions: WC (light), NbC (medium) and Co (dark).	123
Figure 5.9. SEM-BSE images of (a) WC-0.5Cr ₃ C ₂ -9.3Ni (wt%), with WC (light), and Ni (dark), and (b) WC-0.5Cr ₃ C ₂ -10Co (wt%), with WC (light) and Co (dark).	124
Figure 5.10. SEM-BSE images of WC-0.5Cr ₃ C ₂ -6.25TiC-9.3Ni (wt%) with: (a) 0, (b) 0.5, (c) 1, (d) 2, (e) 3.5, and (f) 5 Mo ₂ C (wt%), showing decreased Ni pool size: WC (light), Ni (medium) and TiC (dark).	126
Figure 5.11. SEM-BSE images of WC-0.5Cr ₃ C ₂ -3.5Mo ₂ C-6.25TiC-9.3Ni (wt%) sintered at: (a) 1280°C, and (b) 1310°C; showing different Ni pool sizes: WC (light), Ni (medium) and TiC (dark).	127
Figure 5.12. SEM-BSE images of WC-9.3Ni (wt%) sintered by: (a) LPS at 1430°C, (b) 1510°C, and (c) SPS at 1240°C, produced from nano WC powder: WC (light) and Ni (dark).	128
Figure 5.13. SEM-BSE images of: (a) WC-6.25TiC-9.3Ni (wt%), with (b) 0.5, (c) 1, (d) 2, (e) 3.5, and (f) 5 Mo ₂ C (wt%), produced from nano WC powder, showing reduction in WC grain size with additions of Mo ₂ C: WC (light), Ni (medium) and TiC (dark).	129
Figure 5.14. HAADF-STEM EDX mapping images of WC-6.25TiC-5Mo ₂ C-9.3Ni (wt%), showing C (purple), Mo (blue), W (green), Ni (red) and Ti (yellow).	130
Figure 5.15. HAADF-STEM EDX mapping images of WC-5Mo ₂ C-6.25TiC-9.3Ni (wt%), showing C (purple), Mo (blue), W (green), Ni (red) and Ti (yellow).	130
Figure 5.16. (a) HAADF-STEM EDX mapping image of WC-5Mo ₂ C-6.25TiC-9.3Ni (wt%), showing overlap between W and Mo, and (b) BF-STEM image, showing a WC grain (dark) under Mo ₂ C (light).	131
Figure 5.17. HR-STEM image of the WC-Ni interface of WC-5Mo ₂ C-6.25TiC-9.3Ni (wt%); the inset shows a STEM-EELS elemental map of (left to right) W (orange), C (red), Ti (green) and Ni (blue).	131
Figure 5.18. SEM-BSE images of WC-Ni (wt%) produced from nano WC powder: (a) 10 wt%, (b) 9.3 wt%, (c) 8 wt%, (d) 7 wt%, and (e) 6 with Ni, with WC (light), Ni (dark).	132
Figure 5.19. SEM-BSE images of: (a) WC-9.3Ni (wt%), (b) WC-6.25TiC-9.3Ni (wt%), with (c) 1 wt%, (d) 3.5 wt%, and (e) 5 wt% Mo ₂ C, produced from ultrafine WC powder: WC (light), Ni (medium) and TiC (dark).	133

Figure 5.20. HAADF-STEM EDX mapping images of WC-5Mo ₂ C-6.25TiC-9.3Ni (wt%), showing C (purple), Ni (red), W (green), Mo (blue) and Ti (yellow).	134
Figure 5.21. SEM-BSE images of WC-6.25TiC-9.3Ni (wt%) produced from submicron WC powder, with (a) WC-9.3Ni (wt%), (b) 0 wt%, (c) 3.5 wt%, and (d) 5 wt% Mo ₂ C: WC (light), Ni (medium) and TiC (dark).	135
Figure 5.22. X-ray diffraction patterns for the WC-0.5Cr ₃ C ₂ -10Co (wt%), produced by LPS and SPS.	136
Figure 5.23. X-ray diffraction patterns for the WC-0.5Cr ₃ C ₂ -10Co (wt%), with 1-80 wt% NbC additions.	136
Figure 5.24. X-ray diffraction patterns for the WC-10Co (wt%) produced from nano WC, with 1-20 wt% NbC additions.....	137
Figure 5.25. X-ray diffraction patterns of the WC-0.5Cr ₃ C ₂ -9.3Ni (wt%), with 6.25 wt% TiC and 1-5 wt% Mo ₂ C additions.	137
Figure 5.26. X-ray diffraction patterns of the WC-9.3Ni (wt%) produced from nano WC starting powders, with 6.25 wt% TiC and 1-5 wt% Mo ₂ C additions.....	138
Figure 6.1. Optical images of wear tracks of: (a) 10Co (1430) produced by LPS, (b) 5N-Cr, and (c) 5M-7Ni-u produced by SPS.....	147
Figure 6.2. Laser confocal 3D topographic maps and wear track profiles of the wear tracks for: (a) 10Co (1430), and (b) 9.3Ni (1430) samples produced by LPS.	148
Figure 6.3. Laser confocal 3D topographic maps and wear track profiles of the wear tracks for: (a) 9.3Ni-n, (b) 0M-n, (c) 5N-Cr, and (d) 5M-7Ni-n samples.	149
Figure 6.4. Laser confocal 3D topographic maps and wear track profiles of the wear tracks for: (a) 9.3Ni-u, (b) 0M-u, and (c) 5M-7Ni-u samples.....	150
Figure 6.5. Laser confocal 3D topographic maps and wear track profiles of the wear tracks for: (a) 9.3Ni-s, (b) 0M-s, and (c) 5M-s samples.....	151
Figure 6.6. Optical images of the 100 Cr6 steel balls wear scars from the: (a) 10Co (1430), (b) 5N-Cr, and (c) 5M-7Ni-u samples.	152
Figure 6.7. SEM-BSE images of the wear tracks of: (a) 10Co (1430), showing WC (light), and Co (dark), (b) 5N-Cr, showing WC (light), NbC (medium light), Co (medium dark) and debris (dark), and (c) 5M-7Ni-u, showing WC (light), Ni (medium light), debris (medium dark) and TiC (dark).	153

Figure 6.8. SEM-BSE image and X-ray maps of the 5N-Cr sample wear track, showing WC (light), NbC (medium light), Co (medium dark) and iron oxide (dark) on the sample surface.	153
Figure 6.9. SEM-BSE image of the PCD sample wear track, C (dark) and debris (light grey).	154
Figure 6.10. SEM-BSE image and X-ray maps of the PCD sample wear track, showing C (red), Fe (green) and O ₂ (yellow).	154
Figure 6.11. Coefficient of friction curves for the 10Co (1430), 5N-Cr, 5M-7Ni-u and PCD samples.	156
Figure 6.12. Optical images of wear tracks of: (a) 10Co (1430), (b) 5N-Cr, and (c) 5M-7Ni-u from the Si ₃ N ₄ ball.	157
Figure 6.13. Laser confocal 3D maps and wear track profiles of wear tracks for: (a) 10Co (1430), and (b) 9.3Ni (1430).	158
Figure 6. 14. Laser confocal 3D maps and wear track profiles of wear tracks for: (a) 9.3Ni-n, (b) 5N-Cr, (c) 5M-7Ni-n, and (d) 5M-7Ni-u samples.	159
Figure 6.15. Optical images of the Si ₃ N ₄ ball wear scars from: (a) 10Co (1430), (b) 5N-Cr, and (c) 5M-7Ni-u samples.	160
Figure 6.16. SEM images of 10Co-(1430) of the wear track in (a) BSE mode, and (b) SE mode, showing depressions and fragmentation of WC grains: WC (light), and Co (dark)...	161
Figure 6.17. SEM images of 5N-Cr of the wear track in BSE ((a) and (c)) mode and SE ((b) and (d)), showing scratches and fragmentation of WC grains (arrows): WC (light), NbC (medium) and Co (dark).	161
Figure 6.18. SEM images of 5M-7Ni-u of the wear track in BSE ((a) and (c)) and SE ((b) and (d)) modes, showing scratches and transgranular crack propagation (arrows): WC (light), Ni (medium) and TiC (dark).	162
Figure 6.19. Coefficient of friction curves for 10Co (1430), 5N-Cr and 5M-7Ni-u samples.	162
Figure 6.20. Flank wear on: (a) 10Co (1430), (b) 5N-Cr, and (c) 5M-7Ni-u cutting tool insets after a 40 m/minute v_c and 1 mm a_p	163
Figure 6.21. Flank wear on: (a) 10Co (1430), (b) 5N-Cr, and (c) 5M-7Ni-u cutting tool insets after a 60 m/minute v_c and 1 mm a_p	164
Figure 6.22. Flank wear on: (a) 10Co (1430), (b) 5N-Cr, and (c) 5M-7Ni-u cutting tool insets after a 75 m/minute v_c and 2 mm a_p	164

Figure 6.23. Flank wear on: (a) 10Co (1430), (b) 9.3Ni (1430) cutting tool insets after a 75 m/minute v_c and 2 mm a_p	165
Figure 6.24. Showing (a) Un-used PCD cutting edge and flank wear after cutting speeds of: (b) 60 m/minute, and (c) 150 m/minute and 0.5 mm a_p	166
Figure 6.25. SEM BSE and SE images of the fractured cutting edge of the 5M-7Ni-u cutting tool insert after 40 m/minute v_c and an 1 mm a_p , showing: (a) and (b) Ti-6Al-4V debris (dark grey), (c) and (d) carbon debris (dark), and (f) interconnected microvoids (arrows): WC (light), Ni (medium), TiC (dark).	167
Figure 6.26. SEM images of the fractured cutting edge of the 5N-Cr cutting tool insert after a 60 m/minute v_c and an 1 mm a_p	168
Figure 6.27. SEM images of the fractured cutting edge of the 10Co (1430) cutting tool insert after a 75 m/minute v_c and an 1 mm a_p , showing cracks parallel to the cutting edge (arrows).	169
Figure 6.28. Variation of resultant force with time of the 5M-7Ni-u insert with a 40 m/minute v_c and 1 mm a_p	171
Figure 6.29. Variation of resultant force with time of the 5N-Cr insert with a 40 m/minute v_c and 1 mm a_p	171
Figure 6.30. Variation of resultant force with time of the 10Co (1430) insert with a 40 m/minute v_c and 1 mm a_p	172
Figure 6.31. Comparison of the variation resultant force with time for the 10 Co (1430), 5N-Cr and 5M-7Ni-u cutting tool inserts with a 40 m/minute v_c and 1 mm a_p	172
Figure 6.32. Comparison between sample thermal variations per second and average resultant cutting forces.	173
Figure 6.33. Variation of resultant force with time of the 5M-7Ni-u insert with a 60 m/minute v_c and 1 mm a_p	173
Figure 6.34. Variation of resultant force with time of the 5N-Cr insert with a 60 m/minute v_c and 1 mm a_p	174
Figure 6.35. Variation of resultant force with time of the 10Co (1430) insert with a 60 m/minute v_c and 1 mm a_p	174
Figure 6.36. Variation of resultant force with time of the 10Co (1430) insert with a 75 m/minute v_c and 2 mm a_p	175
Figure 6.37. Variation of resultant force with time of the 9.3Ni (1430) insert with a 75 m/minute v_c and 2 mm a_p	175

Figure 6.38. Variation of resultant force with time of the PCD insert with a 60 m/minute v_c and 0.5 mm a_p .	176
Figure 6.39. Variation of resultant force with time of the PCD insert with a 150 m/minute and 0.5 mm a_p .	177
Figure 7.1. Effect of WC grain size on hardness for WC-0.5Cr ₃ C ₂ -NbC-10Co (wt%) samples.	189
Figure 7.2. Effect of WC volume fraction on Vickers hardness for WC-0.5Cr ₃ C ₂ -NbC-10Co (wt%) samples.	189
Figure 7.3. Effect of binder mean pool size on Vickers hardness.	191
Figure 7.4. Effect of WC grain size on the Vickers hardness for nano and ultrafine WC-Mo ₂ C-TiC-Ni samples.	191
Figure 7.5. Relationship of Vickers hardness and fracture toughness in WC-NbC-Co samples.	193
Figure 7.6. Effect of WC volume fraction on fracture toughness in WC-NbC-Co samples.	193
Figure 7.7. Relationship of fracture toughness and Vickers hardness with Ni binder amounts in nano grade WC-Ni samples.	194
Figure 7.8. Relationship between Vickers hardness and fracture toughness in nano grade WC-Ni samples.	194
Figure 7.9. Effect of WC volume fraction on elastic modulus in WC-NbC-Co samples.	196
Figure 7.10. Effect of densification on elastic modulus for WC-0.5Cr ₃ C ₂ -9.3Ni (wt%), with TiC and Mo ₂ C additions.	196
Figure 7.11. Relationship between Vickers hardness and transverse rupture strength.	198
Figure 7.12. Relationship between transverse rupture strength and fracture toughness.	198
Figure 7.13. Variation of sample wear rate with Vickers hardness from the 100 Cr6 steel balls.	200
Figure 7.14. Comparison between the steel ball wear rate and the samples' Vickers hardness.	202
Figure 7.15. Variation of coefficient of friction with ball worn volume.	202
Figure 7.16. Variation of sample wear rate with sample Vickers hardness from the Si ₃ N ₄ balls.	204
Figure 7.17. Variation in Si ₃ N ₄ ball wear rate with sample hardness.	205
Figure 7.18. Variation of coefficient of friction from the Si ₃ N ₄ balls with sample Vickers hardness.	206

Figure 7.19. Comparison of sample wear rates from 100 Cr6 steel (Steel) and Si ₃ N ₄ (SN) balls and their variations with Vickers hardness.....	207
Figure 7.20. Comparison between insert flank wear rate and fracture toughness.	210
Figure 7.21. Comparison between insert flank wear rate and transverse rupture strength....	211

LIST OF TABLES

Table 2.1. Typical sintering temperatures for WC for hard-metal grades in hydrogen atmosphere [1975Bro].	31
Table 2.2. Comparison of mechanical and physical properties between WC and NbC [2008Hua1, 2008Hua2].	60
Table 3. 1. Consumables and chemicals used in the production and testing	62
Table 3.2. Specifications of starting powders.	63
Table 3.3. WC-Co cemented carbide compositions.	66
Table 3.4. WC-Ni cemented carbide compositions.	67
Table 3.5. Sample grinding and polishing procedure.	74
Table 3.6. Milling conditions for the WC cemented carbide insets.	82
Table 3.7. Milling conditions for the PCD inserts.	82
Table 4.1. Comparison between expected and measured particle size distributions	87
Table 4.2. Particle size distribution of submicron and ultra-fine powders.	96
Table 4.3. XRF results for 1, 0.8 and 0.4 μm WC powders.	97
Table 4.4. Oxygen analysis of 1, 0.8 and 0.4 μm WC powders.	98
Table 4.5. Variation of sintering temperature criteria.	99
Table 4.6. Variation in densification due to variation in sintering temperature.	99
Table 4.7. Variation of magnetic properties with sintering temperature.	100
Table 4.8. Variation of sintering pressures.	100
Table 4.9. Densification due to variation in pressures as shown in Table 4.8.	102
Table 4.10. Variation in densification due to difference in sintering time.	103
Table 4.11. Change in densification with NbC addition.	103
Table 4.12. Variation in densification with sintering temperature and time.	104
Table 4.13. Change in densification of WC-0.5Cr ₃ C ₂ -9.3Ni (wt%) due to varying sintering conditions.	106
Table 4.14. Densification due to addition of 6.25 TiC (wt%) and 3.5 Mo ₂ C (wt%) to WC-0.5Cr ₃ C ₂ -9.3Ni (wt%).	107
Table 4.15. Densification of WC-0.5Cr ₃ C ₂ -3.5Mo ₂ C-6.25TiC-9.3Ni (wt%) with increased sintering temperature.	108
Table 4.16. Sintering conditions for WC-0.5Cr ₃ C ₂ -10Co (wt%) with NbC addition.	109
Table 4.17. Sintering conditions for WC-10Co (wt%) with different NbC additions, using nano and ultra-fine WC starting powders.	109

Table 4.18. Sintering conditions for WC-0.5Cr ₃ C ₂ -9.3Ni (wt%) with different TiC and Mo ₂ C additions.	110
Table 4.19. Liquid phase sintering conditions.	110
Table 4.20. Sintering conditions for WC-Ni with different TiC and Mo ₂ C additions, using nano, ultra-fine and submicron WC starting powders.	111
Table 4.21. Density and open porosity of WC-10Co (wt%) with 0-20 NbC (wt%) additions, produced from ultra-fine (u) WC starting powders.	111
Table 4.22. Density and open porosity of WC-0.5Cr ₃ C ₂ -10Co (wt%) with 0-80 NbC (wt%) additions.	112
Table 4.23. Density and open porosity of WC-10Co (wt%) with 0-20 NbC (wt%) additions, produced from nano (n) WC starting powders.	112
Table 4.24. Density and open porosity of WC-0.5Cr ₃ C ₂ -9.3Ni (wt%) with 6.25 TiC (wt%) and 0-5 Mo ₂ C (wt%) additions.	112
Table 4.25. Density and open porosity of WC-9.3Ni (wt%) with 6.25 TiC (wt%) and 0-5 Mo ₂ C (wt%) additions, using submicron (s) WC starting powders.	113
Table 4.26. Density and open porosity of WC-9.3Ni (wt%) with 6.25 TiC (wt%) and 0-5 Mo ₂ C (wt%) additions, using ultra-fine (u) WC starting powders.	113
Table 4.27. Density and open porosity of the liquid phase sintered samples.	113
Table 4.28. Density and open porosity of WC-9.3Ni (wt%) with 6.25 TiC (wt%) and 0-5 Mo ₂ C (wt%) additions, using nano (n) WC starting powders.	114
Table 5. 1. Sintered WC grain sizes in WC-NbC-Co samples.	116
Table 5.2. EDX analyses of WC-0.5Cr ₃ C ₂ -10Co (wt%) with 5 and 20 NbC (wt%) additions.	116
Table 5.3. EDX analyses of WC-0.5Cr ₃ C ₂ -10Co (wt%) with 5 and 20 wt% NbC addition.	121
Table 5.4. Image analysis results of WC-0.5Cr ₃ C ₂ -9.3Ni (wt%) with TiC and Mo ₂ C additions (Figures 5.9, 5.10 and 5.11).	124
Table 5.5. EDX analyses of WC-0.5Cr ₃ C ₂ -9.3Ni (wt%) with TiC and Mo ₂ C additions.	125
Table 5.6. Effect of WC starting size, TiC and Mo ₂ C on WC sintered grain size.	127
Table 5.7. EDX analyses of WC-9.3Ni (wt%) with TiC and Mo ₂ C additions with TiC and Mo ₂ C additions.	128
Table 5.8. Effect of WC starting grain size on the Vickers hardness (HV ₃₀) of WC-NbC-10Co (wt%).	139

Table 5.9. Effect of WC starting grain size on the Vickers hardness (HV ₁₀) of WC-NbC-10Co (wt%).....	139
Table 5.10. Effect of WC starting grain size on the Rockwell-A hardness of WC-NbC-10Co (wt%).....	140
Table 5.11. Effect of WC starting grain size on the Vickers hardness (HV ₃₀) of WC-Mo ₂ C-6.25TiC-9.3Ni (wt%).....	140
Table 5.12. Effect of WC starting grain size on the Vickers hardness (HV ₁₀) of WC-Mo ₂ C-6.25TiC-9.3Ni (wt%).....	141
Table 5.13. Effect of WC starting grain size on the Rockwell-A hardness of WC-Mo ₂ C-6.25TiC-9.3Ni (wt%).....	141
Table 5.14. Effect of WC starting grain size on the fracture toughness with HV ₃₀ indentation load on WC-NbC-10Co (wt%).	142
Table 5.15. Effect of WC starting grain size on the fracture toughness with HV ₁₀ indentation load on WC-NbC-10Co (wt%).	143
Table 5.16. Effect of WC starting grain size on the fracture toughness with HV ₃₀ indentation load on WC-Mo ₂ C-6.25TiC-9.3Ni (wt%).	143
Table 5.17. Effect of WC starting grain size on the fracture toughness with HV ₁₀ indentation load on WC-Mo ₂ C-6.25TiC-9.3Ni (wt%).	144
Table 5.18. Elastic modulus of WC-NbC-10Co (wt%) cemented carbides.	144
Table 5.19. Elastic modulus of WC-9.3Ni (wt%), with 6.25 TiC (wt%) and 1-5 Mo ₂ C (wt%).	145
Table 5.20. Magnetic saturation of WC-0.5Cr ₃ C ₂ -10Co (wt%), with 0.5-80 NbC (wt%) additions.....	145
Table 5.21. Transverse rupture strength of WC-Co and WC-Ni cemented carbides.	146
Table 6.1. Sliding wear results from 100 Cr6 steel balls.....	151
Table 6. 2. 100 Cr6 steel ball sliding wear analysis.....	155
Table 6.3. Sample sliding wear properties from the of Si ₃ N ₄ ball.	157
Table 6.4. Silicon nitride ball sliding wear results.....	160
Table 6.5. Comparison of insert properties due to variation of milling conditions.	170
Table 6.6. Comparison of PDC insert properties due to variation of milling conditions.	176

Chapter 1: Introduction

Cemented carbides or hardmetals are types of cermets that consist of carbide (WC) grains embedded in a ductile metallic (Co, Ni and/or Fe) binder matrix. Due to their good combination of high hardness, heat stability, fracture toughness, strength and wear resistance [1975Bro, 1997Cho, 1998Upa, 1999Are], they are employed in several different tribological applications such as cutting tools, metal forming, mining, drilling, machining and even in the aerospace domain [2008Bon]. All of these properties are important to ensure a high performance and long life of the components. To further extend the applications and operating life of WC-cemented carbide tools, higher values hardness, wear resistance and fracture toughness are required [1975Bro, 2008Bon]. However, generally increased hardness results in a reduction in fracture toughness [1998Upa, 2008Hau1]. Thus, an optimum compromise between these two contradictory properties should be achieved. This compromise is possible through the reduction in WC starting particle size, manipulation of the sintering time and temperature, alteration of composition and microstructure modifications [1998Upa].

Tungsten carbide grain size refinement from micron particle sizes to the nanometric scale increases the hardness and improves wear resistance due to a final finer grained microstructure, as well as strengthening of the binder phase by the increased W solubility [2003Seo, 2008Wan]. However, compared to micron-sized cemented carbides, sintering of nano-sized powders has the additional challenge of retaining the nano-scaled grain size upon achieving full density, because of rapid grain coarsening [2008Wan]. This grain growth increases with increased sintering temperature and time [2008Wan]. Therefore, new rapid sintering methods such as spark plasma sintering (SPS) offer an advantage [1999Tok, 2003Cha, 2008Hau1], since the high heating rates combined with high compressive pressure are used to consolidate powder compacts to a high density in a short time and at low temperatures [1999Tok, 2006Son], preventing grain coarsening. The hardness, strength and toughness can also be improved by optimizing the amount of metal binder [1998Upa, 2008Bon].

Another route to obtain high hardness, wear resistance and fracture toughness is to incorporate suitable additives, such as Cr_3C_2 and NbC that are effective grain growth inhibitors for tungsten carbide based cemented carbides [2008Hau1, 2002Wit]. Small

additions of up to 0.45wt% NbC and 0.5wt% Cr₃C₂ to WC-Co have been reported to improve mechanical properties and corrosion resistance [2008Hau1, 2008Hau2]. Partial substitution of WC with NbC in the WC-Co cemented carbides increases the resistance to chemical wear during cutting [2008Hau2].

Cobalt has been the preferred binder for WC, due to its good properties, such as low temperature carbide solubility and high wettability with WC [1998Upa]. However, because of unstable market prices, health hazards for plant maintenance personnel and limited corrosion resistance, nickel has been studied as an alternative binder [1987Pen, 1986Reo]. In comparison to Co, Ni retains its ductile fcc structure at all temperatures, has higher hot hardness and better wear performance in corrosive environments [2008Guo1, 2008Guo2]. However, due to its poor wetting of WC and higher plasticity, Ni bound WC-hardmetals have lower hardness than Co binder hardmetals [1987Pen, 1986Reo]. The hardness can be improved by rapid sintering techniques (e.g. SPS) and addition of grain growth inhibitors, such as Cr₃C₂, TiC and Mo₂C [1986Reo, 1995Ban, 2008Guo2]. The addition of Mo or Mo₂C also improves the wettability between WC and Ni [1986Reo, 2008Guo2].

Titanium and its alloys are widely used in the aerospace industry due to their good combination of strength to weight ratio at elevated temperatures, fracture toughness and corrosion resistance [1955Sie]. They are also used in the medical industry as surgical implants because of their exceptional mechanical biocompatibility [1984Mye, 2008Nii]. Despite these good properties, Ti and its alloys are very expensive because of poor machinability, which is caused by high chemical reactivity, low thermal conductivity and high strength at elevated temperatures [1955Sie, 1984Bom, 1986Dea]. However, plain WC-Co cutting tools have the best performance in almost all machining processes of Ti alloys, while CVD coated carbides and ceramics perform poorly, due to the reactivity with Ti, low fracture toughness and poor thermal conductivity [1997Ezu]. Hence, improvement of the mechanical properties such as hot hardness, wear resistance, fracture toughness, thermal shock and corrosion resistance of WC-cemented carbides would further improve their Ti machining performance, lowering the Ti production cost.

The outputs of this work are given in the Appendix.

1.1 Hypothesis

A finer microstructure with an optimized binder amount and the introduction of alloying additions which can improve the hot hardness and wear resistance would give better properties and improve WC-cemented carbide cutting tool performance.

1.2 Overview

In this study, an attempt was made to improve the microstructure and mechanical properties of WC-Co cemented carbides through varying the WC starting particle size (micron to nano), optimisation of milling, using SPS, and the addition of Cr_3C_2 and NbC grain growth inhibitors. Niobium carbide was also added in large amounts (up to 80 wt%) as a WC substitute, with the aim of improving high temperature applications. An attempt was also made to prepare WC-Ni cemented carbides by SPS, varying the starting WC powder size (submicron to nano), optimizing Ni content (6-10wt%) and using alloying additions (TiC , Cr_3C_2 and Mo_2C), with the aim of achieving mechanical properties comparable to commercially manufactured WC-Co based cemented carbides. Mechanical properties such as hardness, fracture toughness, wear resistance, modulus of elasticity, thermal shock, impact resistance and transverse rupture strength were studied.

Chapter 2 gives a detailed literature review on WC-cemented carbides, powder metallurgy used for their processing, different sintering techniques, effects of grain size, alternative binders, and the effect of the type and amount of carbide additives on the microstructure and mechanical properties.

Chapter 3 gives a detailed description of all the experimental procedures and equipment used.

Chapter 4 describes the powders used, optimization of milling and sintering processes, and their effects on density.

Chapter 5 contains the results on microstructures, phase identification and mechanical properties.

Chapter 6 comprises the results on wear, thermal shock and impact behavior of promising compositions.

Chapter 7 contains a detailed overall discussion of the results.

Chapter 8 is the final conclusions and recommendations for future work.

Chapter 2: Literature Review

2.1 WC-cemented carbides background

Cemented carbides or hard-metals are commercially one of the oldest and most successful powder metallurgy composites [1934Sch, 1975Bro]. They primarily consist of tungsten carbide bonded within a ductile cobalt matrix [1975Bro, 1997Luy, 1998Upa]. Their properties are derived from the constituents, i.e. hard, wear resistant and brittle carbides and tougher, more ductile metal binders (cobalt, nickel or iron) [1934Sch]. They were initially developed between 1923 and 1925, by Schroter for the Osram electrical lighting, to replace the costly diamond wire drawing dies for tungsten filaments [1925Sch]. They initially consisted of 6wt% Co bonded WC, and due to their good hardness and wear resistance, cemented carbides were further developed into cutting tools, wear parts and machine components by Krupp in Germany [1998Upa]. Introduction of TiC and TaC to WC-Co in the 1930s greatly improved the cutting performance during metal cutting [1991Jen, 1998Upa]. Shwartzkopf found [1948Sch] that partial substitution of WC with other carbides such as TiC, TaC, NbC and VC resulted in the formation of solid solutions with better mechanical properties than plain WC-Co. This started the development of multcarbide cutting tools for high speed machining of steel [1991Jen, 1998Upa]. The hardness and wear resistance of WC-cemented carbides were further improved through the introduction of submicron WC ($<1\ \mu\text{m}$) in 1946.

As a result of successful partial substitution of WC with other carbides and concerns over the continued availability of WC raw material, attention was focused towards a tungsten-free alloy (TiC based cemented carbide) around 1960 [1998Bro]. A titanium carbide nickel-molybdenum binder cemented carbide was developed, but was only used for specific applications, unlike WC-Co alloys that were used for several different applications [1998Upa]. Other carbides were also investigated, but WC-cemented carbides had better performance over a wide range of applications [1998Bro, 1998Upa].

The introduction of chemical vapor deposition (CVD) of TiC over WC-Co from 1965-1978 significantly improved the cutting speeds and life the cutting tool inserts, leading to expansion in their applications [1991Jen, 1998Bro, 1998Upa]. Physical vapor deposition (PVD) and modified CVD coating processes were introduced in the 1980s. From 1992-1995, the positive attributes of the CVD and PVD processes were then combined to develop Plasma

CVD using diamond or a “diamond like” amorphous coating. This diamond coating performed well for several applications, even though the adhesion between coating and WC tool was not satisfactory [1975Bro, 1998Upa].

Nano-scaled WC powders were introduced in the early 1990s with the aim of improving the mechanical properties, since reduction in WC grain size increases the hardness and wear resistance [1975Bro], but the additional challenge of retraining the nano-structure after sintering limited their applications [1993Fan]. The increase in grain size of nano-powders is because of the long sintering times and high sintering temperature during conventional liquid phase sintering, enabling continuous Ostwald ripening and coalescence [1993Fan], resulting in grain growth. Through new rapid sintering methods such as spark plasma sintering (SPS) and optimization of grain growth inhibitors, reduction of the WC grain growth was possible [2003Zhu, 2011Par], improving the hardness and wear resistance. Therefore, to promote development of efficient and industrially relevant WC cemented carbides, recent research has been focused on refinement of WC grains, improvement of high temperature stability, corrosion and oxidation resistance, and improvement of WC tool surface coatings. Refinement of WC grain size can be achieved through use of grain growth inhibitors [1966Exn, 1972Hay, 1991Jen, 2002Wit], use of fine starting powders (nano and ultra-fine) [1993Fan, 1998Upa], rapid sintering (spark plasma sintering) [1999Tok, 2002Mam, 2006Son] and carbon control [1978Exn]. Increased high temperature stability can be achieved through addition of carbides such as TiC, NbC, TaC [1982Suz, 1982Sar] and Cr₃C₂ [1986Cha]. The corrosion and oxidation resistance can be improved through partial or complete substitution of Co with Ni [1996Hum, 1997Hum] and addition of Cr₃C₂ [1987Pen]. Tungsten carbide tool surface coatings can be improved by using diamond and TiN [2003Seo, 2008Bon]. The drive to continuously improve WC cemented carbides is because, although the availability of other materials for cutting has increased, the demand for hard WC cemented carbides is still as high as it was when they were first developed in the 1920s [2003Seo].

2.2 Production of cemented carbides

Before 1945, tungsten monocarbide WC (generally termed tungsten carbide) was produced by melting tungsten metal, carbon black and metal oxides at 2000°C, although the tools manufactured by this process were too brittle for industrial use [1975Bro]. Today, WC-cemented carbides are produced using powder metallurgy [1975Bro, 1991Jen, 1997Luy]. Powder metallurgy is a process by which metals, alloys and ceramics, in the form of a mass of dry particles (usually <150 µm in diameter), are mixed, pressed and heated to form useful engineering components of predetermined shape [1991Jen]. In powder metallurgy, the particle properties, microstructure, sintered material properties and applications are interrelated. This allows for compositional and microstructure control during the production process to achieve the desired properties in the finished products [1991Jen].

Power metallurgy is used to produce WC-cemented carbides over other production methods such as casting due to the following advantages [1997Luy]:

- The component materials retain their original properties,
- Tungsten carbide decomposes before melting, hence methods which require melting such as casting are not appropriate for WC cemented carbide production,
- Large volumes of small parts requiring close tolerance with minimum finishing operations can be economically produced, and
- There are lower stresses on the finished product, improving the shock resistance.

Limitations of powder metallurgy:

- The powders, phases and grain sizes must be homogenously distributed before sintering, or else the density will not be uniform, and
- Need high stress capacity.

Generally, powder metallurgy involves three main steps:

- Production of powders,
- Consolidation of powders (mixing, milling and pressing), and
- Heating of pre-form (sintering).

2.2.1 Powder production

2.2.1.1 Tungsten powder

Tungsten carbide is obtained by carburization of tungsten powders that are prepared by hydrogen reduction of tungsten oxide, WO_3 [1991Jen, 1998Upy]. Tungsten is found in nature mainly as Scheelite, CaWO_4 , and Wolframite, $(\text{Fe,Mn})\text{WO}_4$ [1979Yih]. Since it had an extremely high melting point ($3423 \pm 15^\circ\text{C}$) [1999Las], its extraction is done by hydrometallurgy instead of pyrometallurgy [1998Upa]. In nearly all tungsten metal extraction processes, ammonium paratungstate (APT), $5(\text{NH}_4)_2\text{O} \cdot 12\text{WO}_3 \cdot 5\text{H}_2\text{O}$, is an intermediate product [1991Jen, 1997Luy]. With recent improvement in processing techniques, APT can be made to almost any desired purity and granular size [1991Jen]. Due to these reasons, APT has largely replaced ore concentrates as the main source from which production begins [1991Jen].

Ammonium paratungstate can be produced from Scheelite, CaWO_4 , and Wolframite, $(\text{Fe,Mn})\text{WO}_4$. Scheelite, CaWO_4 , concentrates are decomposed by leaching with hot HCl to remove Ca and to precipitate tungstic acid, H_2WO_4 . The acid is then dissolved in ammonia and crystallized as ammonium tungstate, $(\text{NH}_4)_2\text{WO}_4$. Ammonium tungstate is then evaporated by boiling to give ammonium paratungstate, $5(\text{NH}_4)_2\text{O} \cdot 12\text{WO}_3 \cdot 5\text{H}_2\text{O}$. The APT granule size increases with increased crystallisation temperature [1975Bro, 1991Jen, 1997Luy].

In the case of production from Wolframite, $(\text{Fe,Mn})\text{WO}_4$, the ore is usually treated with sodium hydroxide under high pressure to produce sodium tungstate solution as shown in Figure 2.1 [1998Upa]. Calcium chloride is then added to the sodium tungstate to produce calcium tungstate, CaWO_4 , known as “artificial Scheelite”, which is then fed into the Scheelite production line to attain APT [1991Jen, 1998Upy]. A typical scanning electron microscope (SEM) image of APT is shown in Figure 2.2 [1998Upa].

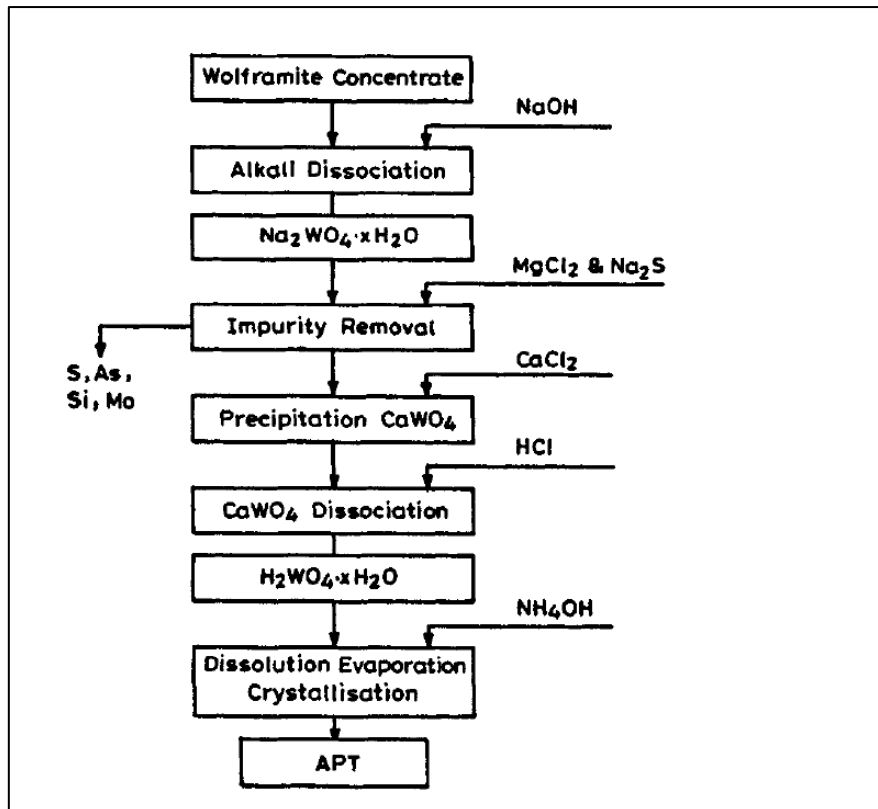


Figure 2.1. Production of APT from wolframite ore [1998Upa].

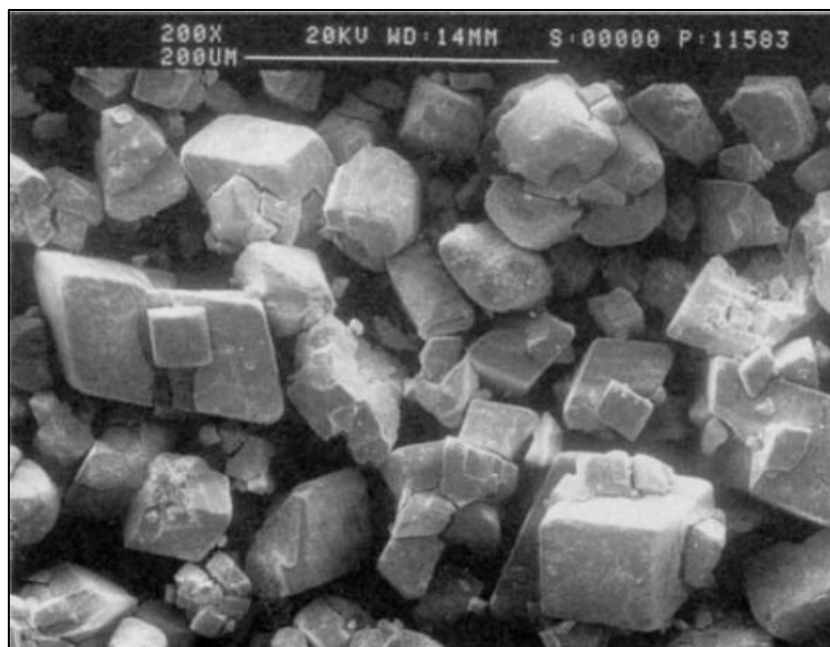


Figure 2.2. SEM-SE image of APT [1998Upa].

Ammonium paratungstate is converted into tungsten oxide, WO_3 , through a calcination process. Calcination is done in an oxygen-bearing environment between 560°C to 850°C [1998Upa]. If the calcination temperature is low, fine WO_3 are produced and vice versa for high temperatures. Figure 2.3 shows a typical SEM-SE image of tungsten oxide.

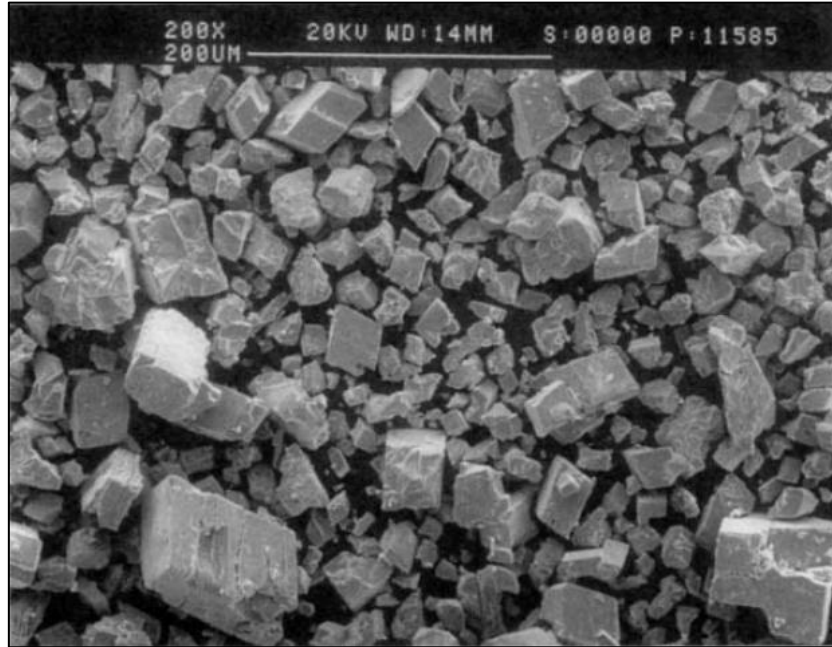


Figure 2.3. SEM-SE image of tungsten oxide (WO_3) [1998Upa].

Tungsten oxide is reduced in hydrogen to obtain W metal. The reaction involves removal of oxygen from WO_3 by hydrogen, because it forms a more stable compound with hydrogen (H_2O) than WO_3 as shown in Equation 2.1 [1975Bro, 1997Luy]:



The final grain size of tungsten powders is dependent on starting WO_3 size and reduction temperature. Fine starting WO_3 powders produced fine W powders [1991Jen, 1998Bro]. High reduction temperatures decrease the stability of H_2O and the driving force for the reaction, making nucleation of new W particles more difficult than growth of the pre-existing particles, leading to large grain growth [1997Luy]. A typical SEM image of tungsten powder after reduction is shown in Figure 2.4 [1998Upa].

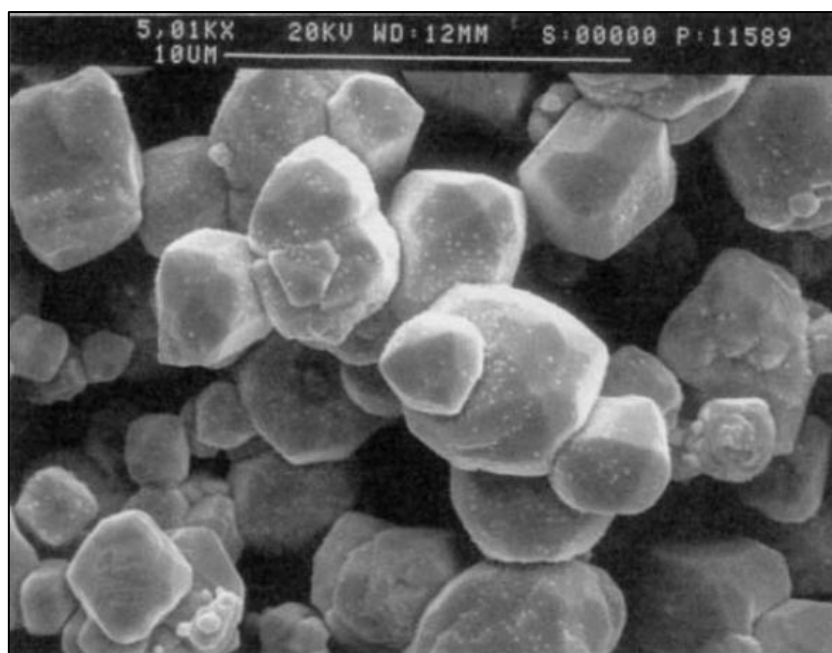


Figure 2.4. SEM-SE image of tungsten powder [1998Upa].

2.2.1.2 Carbon Powder

The carbon used to produce WC is usually obtained from high purity pressed carbon lampblack, with low ash and sulphur contents. The ash content should not exceed 0.2% [1997Luy, 1998Upa]. Sulphur is a common impurity in carbon lampblack, and its presence can affect the grain size of WC. The accepted amount of sulphur is less than 0.01% [1998Upa].

2.2.1.3 Cobalt Powder

Cobalt is found in ores of other metals in the earth's crust [1987Pen], but for economic exploitation, the mineral is found in sulphides, arsenides, oxides and hydroxides [1998Upa]. Initially, cobalt was produced through the reduction of cobalt oxide in hydrogen at temperatures from 600°C to 700°C, as shown in Equation 2.2 [1997Luy]:



However, from the above process Co powders greater 2µm in particle size were obtained, and if finer grains are required, an additional milling step had to be added to the production [1998Upa]. Thus, new methods have been developed for production of spherical and non-agglomerated cobalt powders of both micron and submicron sizes [1998Upa]. The process involves reduction of cobaltous hydroxide, $\text{Co}(\text{OH})_2$, by a mixture of ethylene-glycol and diethylene-glycol, as shown in Figure 2.5. Micron sized powders are produced through

homogeneous nucleation and growth from the $\text{Co}(\text{OH})_2$ solution. The submicron powders are obtained either by seeding the reactive medium with foreign metal nuclei (silver or palladium) to induce heterogeneous nucleation, or by raising the reaction temperature [1998Upa].

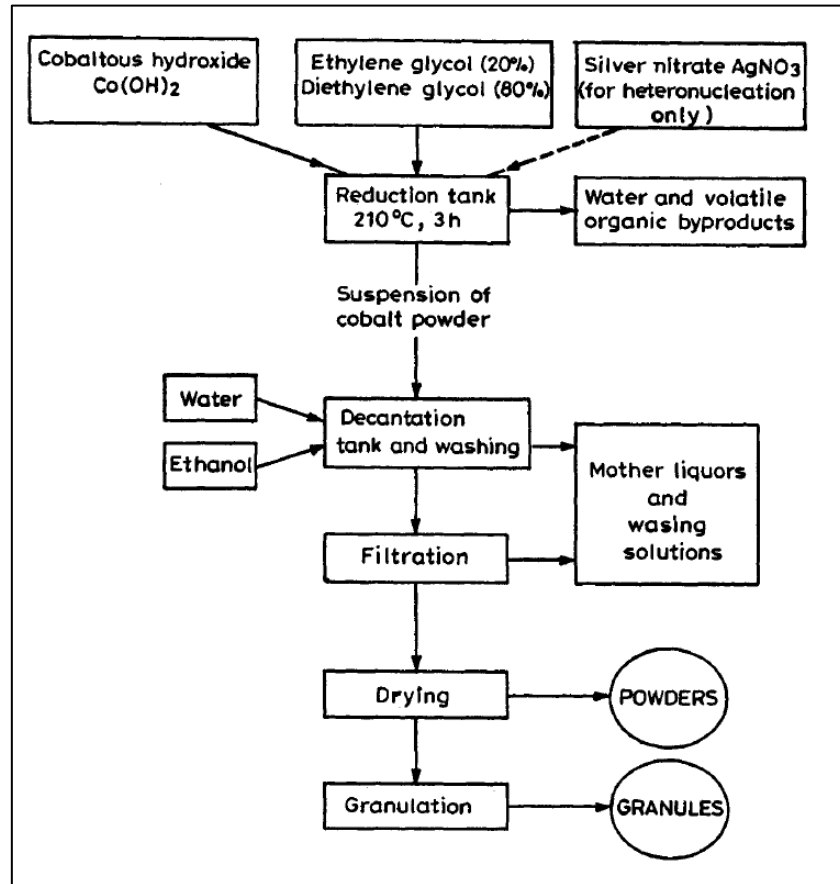


Figure 2.5. Production of cobalt powders and granules [1998Upa].

Cobalt exists as two allotropes; below $\sim 400^\circ\text{C}$, it has a stable hexagonal close packed structure (hcp), ϵ -Co, and above $\sim 400^\circ\text{C}$, it has a stable face centered cubic (fcc), α -Co. The temperature of the allotropic change depends on the purity and the rate of temperature change. For the highest purity Co ($\sim 99.998\%$) and slow temperature changes, the transformation temperature ranges between 417 - 421.5°C [1952Hes, 1982Bet]. The hcp Co allotrope is harder and more brittle [1998Upa]. Generally, a mixture of roughly the same amount of the both allotropes exists in cobalt powders, but during milling, the amount of hcp (ϵ -Co) increases by up to 100% [1996Hua]. However, after sintering, the cobalt binder has a fcc structure which cannot be transformed by annealing [1998Upa]. This is due to dissolved tungsten and carbon stabilizing the high temperature fcc allotrope, by reducing the transformation temperature [1983Ake]. Carbon is more effective than tungsten in stabilizing

the fcc allotrope. Cobalt has a melting temperature of 1495°C, theoretical density of 8.9g/cc, Young's modulus of 207 GPa, thermal expansion of 16µm/m.K [1992Scu] and hardness of ~1.043 GPa [1968Sam].

2.2.1.4 Conventional synthesis of tungsten carbide powder (WC)

Tungsten carbide is made by reacting tungsten powders with carbon black (carburization) in a hydrogen atmosphere at temperatures 1400-1800°C [1975Bro, 1991Jen, 1997Luy]. Prior to carburization, mixing of the tungsten and carbon powders is done to attain homogeneous distribution [1998Upa]. Simple blending of the powders does not serve the purpose because of their extreme differences in densities [1998Bro]. Effective mixing is achieved either by dry ball milling or using a V-type blender with high revolutions per minute amplifiers [1998Upa]. The temperature during carburizing must be high enough to enable carburization within an acceptable period of time and to volatilize most of the residual impurities, but not too high, else unacceptable grain growth would be induced [1991Jen]. Coarse WC powders (>2µm) are obtained from coarse tungsten powders carburized at relatively high temperatures (1600°C and above). Fine WC powders (<1µm) are produced from submicron tungsten powders at temperatures as low as 1400°C [1991Jen].

The carburization process can be expressed by Equation 2.3:



The C is picked up by the W from the carbon powders via the gaseous hydrocarbons formed with the hydrogen [1997Luy]. Initially, W₂C (eta phase) nuclei form, and with further additional C pick-up WC particles are formed [1997Luy]. The amount of carbon added to tungsten is calculated using Equation 2.4. The atomic ratio W:C is 1:1, the atomic weight of W is 184 amu, the atomic weight of C is 12 amu.

$$\text{Therefore, the amount of C in WC is given by} = \frac{C}{W + C} \quad (\text{Equation 2.4})$$

$$= \frac{12}{184 + 12} = 6.122 \text{ wt\%}$$

Accurate carbon control is important to ensure good mechanical properties [1991Jen, 1997Luy]. A slight deficiency in the amount of carbon results in formation of the extremely brittle eta phase (W₂C), while excess carbon results in formation of fine flakes of free graphite. These lower the wear resistance and weaken the cemented carbide [1998Upa].

Tungsten carbide has a simple hexagonal structure, which is not observed for the pure metal (bcc structure) and is as a result of the introduction of planes of carbon atoms [1998Upa]. It should be noted that the reaction in Equation 2.5 is primarily is due to redistribution of hexagonal planes [1967Kra]. Segregation of carbon atoms during the change from WC to W_2C transforms the simple hexagonal structure to a close packed structure:



Tungsten carbide has a melting point of 2800°C, theoretical density of 15.68g/cc [1992Scu, 1997Luy], a hardness 22-27 GPa depending on the sintering method [2007Kim, 2008Hua2, 2008Hua3] and an indentation fracture toughness of $\sim 4.38 \text{ MPa.m}^{1/2}$ [2008Hua3]. Additionally, it has a Young's modulus between 519-714 GPa [2011Nin] and a coefficient of thermal expansion of 5.2 $\mu\text{m/m.K}$ [1992Scu].

2.2.1.5 Modern synthesis of tungsten carbide powder (WC)

In modern tungsten conversion plants, scheelite and wolframite ores, as well as hard and soft tungsten carbide scrap, are used as raw materials [2005She]. Scheelite and wolframite ores may be leached, calcined, roasted and/or ground into smaller particles before the processing into ATP is carried out [1999Las]. Hard scrap refers to the used cemented tungsten from the hardmetal industry such as cutting, mining, drilling and turning tools [1996Jan, 2005Kim]. A large number of machine shops and manufacturers that use WC cemented carbide products collect their used inserts and other parts, and sell them to scrap processors who then sort, clean and repackage the scrap for sale [2005She]. Hard scrap can be treated in two ways, by being fused in the presence of an oxidising agent and a diluent, then cooled, crushed and dissolved in water, or by electrolysis [1999Las]. During electrolysis, the hard scrap is the anode in a solution of sodium hydroxide or sodium carbonate. Soft scrap consists of corrosion and wear resistant tungsten alloys, heavy metal alloys, speciality steels, super alloys and other tungsten bearing alloys, such as W-Ni-Fe and W-Ni-Cu alloys used for military applications [1996Jan, 2005She]. Soft scrap is treated by heating in air or oxygen-enriched air to oxidize the tungsten to the hexavalent state, so that it can easily dissolve in an alkaline solution [2005She]. The recycling of soft and hard tungsten scrap has become increasing popular in recent years, due to increased cost of tungsten powder produced from scheelite and wolframite ores, as well as continuous availability of tungsten scrap from used tungsten cemented carbides and tungsten alloys [1996Jan, 2005She]. After treatment of the scheelite and wolframite ores, as well as the hard and soft scrap, the remaining processing

steps are for the production of APT, which is then calcined under a reducing agent to form tungsten blue oxide [2005She]. Tungsten blue oxide is then reduced to form tungsten powder, which is carburized to produce tungsten carbide.

2.2.1.5.1 Processing of tungsten scrap

Tungsten scrap can be processed in several different ways which can be classified into four main recycling methods; hydrometallurgy, melting metallurgy, direct recycling and semi-direct recycling [1999Las, 2005She]. In hydrometallurgy recycling, tungsten is reclaimed from the scrap using chemical methods, and is used as a substitute of tungsten ore [1999Las]. Tungsten produced from hydrometallurgy recycling is indistinguishable from that produced from tungsten ores [1999Las, 2005She]. During melting metallurgy, the different melting temperatures of the elements in the scrap are used to separate them, and the reclaimed tungsten is mainly used in production of alloys, such as steels, stellites, menstruum tungsten, ferrotungsten and tungsten melting materials [1999Las, 2005She]. In direct recycling, the scrap is disaggregated into a powder by chemical and/or physical means without changing the original composition. While during semi-direct recycling, one of the components of the scrap is dissolved chemically, allowing for the rest of the scrap to be broken down by physical means [2005She]. Generally, chemical processes have the advantages of been able to treat all types of scrap and produce tungsten with highest amount of purity, but they are expensive, require higher energy consumption and result in low yields. Thus, an optimum balance between chemical and physical processing of scrap is advised [2005She].

2.2.1.5.2 Production of Nano tungsten carbide powders

High energy milling was initially used for the production of nano ($\leq 0.1 \mu\text{m}$) WC powders; the process involves high energy collision between the large WC starting powders ($>1 \mu\text{m}$) and the milling balls (milling media) [2014Cao1]. This can be carried out in different types of mills, such as horizontal ball mills, attritor mills and planetary ball mills. The principle of operation of all these mills is the same (collision between the balls and powders), and the milling energy can be significantly increased by increasing the milling speed, optimising the powder to ball weight ratio and increasing the density of the milling media [1996Koc]. Although high energy milling can be used to produce nano WC, limitations such as contamination from the milling media and ambient gases (O_2 and N_2), long processing time, no control of particle morphology and retained residual stress [2010Won, 2014Cao1], encouraged the introduction of alternative production methods. These methods include

chemical vapour condensation (CVC) [2004Kim] and spray conversion processes [1994McC, 2010Won].

2.2.1.5.2.1 Chemical vapour condensation (CVC)

Chemical vapour condensation, also known as chemical vapour synthesis involves placing of vapour phased precursors in hot-walled reactors under conditions that favour nucleation of particles in the vapour phase, rather than deposition of a film on the wall [2004Cao2]. The CVC process has the key advantage of producing a wide range of materials, as long as the starting compositions are in the form of solid, liquid or gas precursors [2004Cao2]. To produce WC nano powders, a carrier gas of high purity carbon monoxide is fed through an evaporator containing solid tungsten hexacarbonyl ($W(CO)_6$) precursor [2004Kim]. The solid $W(CO)_6$ precursor is vaporised at $120^\circ C$, and the resulting vapour is passed through a heated reaction furnace (reactor). In the reactor, the vapour is decomposed and reacted, after which it is condensed into nano powders in the collection chamber [2004Kim]. The CVC process produces nano sized powders with high purity and no agglomeration, and can produce powders of a grain size $<0.03\ \mu m$ [2004Kim].

2.2.1.5.2.2 Spray conversion process

Spray conversion can be used to produce nano WC and WC-Co mixed powders in three production steps [1994McC, 2010Won]. The first step involves preparation of a homogenous aqueous solution from a W source (tungstic acid (H_2WO_4)), and a Co source (cobaltous chloride ($CoCl_2$)) for production of nano WC-Co powders [1994McC]. The second step involves rapid precipitation of the solute from the prepared solution to form chemically homogenous precursors by atomised droplet drying methods (i.e. spray drying, calcining and roasting) [1994McC, 2010Won]. In the final step, reduction of the precursor powders is carried out, followed by carburisation with carbon containing gases (Co/Co_2) to form nano WC or WC-Co mixed powders [2010Won]. Particle morphology and distribution can be controlled by optimising the drying rate in the second production step and the final size of the powders can be reduced by minimising the conversion time at the reactive temperature during the third production step [1994McC].

2.2.1.6 Modern synthesis of cobalt powder

Cobalt is primarily extracted from its concentrates and ores [1987Pen], using processes such as hydrometallurgy, pyrometallurgy and electrochemical methods [1998Haw, 2004Gur1]. The world supply of Co has been reducing over the last few decades [1987Pen], leading to unstable market prices [2008Guo1, 2008Guo2], thus alternative sources such as recycling of WC-Co scrap processes have been developed [2004Gur1]. Cobalt production from recycling of WC-Co scrap (secondary Co) has been very successful, resulting in about a third of the Co consumption in the cemented carbide industry arising from recycled Co [2013Alt]. Two main recycling processes can be used for the production of secondary Co, the zinc melt method (ZMM) [2013Alt] and selective cobalt leaching method (SCLM) [2004Gur2].

2.2.1.6.1 Zinc melt method (ZMM)

The zinc melt method involves immersing the WC-Co scrap in molten zinc in an electrical furnace, at 1 atmosphere of an inert gas at 650-800°C [2013Alt], to distil the zinc at 700-950°C [2007Mai]. Optimum conditions for the process depend on the Co content and the Zn to Co ratio [2013Alt]. When the scrap is dipped into the molten Zn bath, the Zn penetrates between the WC grains dissolving the Co. The dissolution of the Co results in separation of the WC particles which float on the molten Zn-Co alloy solution [2013Alt]. Since Zn has a high vapour pressure, it is easily removed by evaporation under vacuum conditions. As the Zn evaporates, the Co content in the molten solution increases and Co precipitates on the surface of the floating WC particles, forming WC-Co powders with same chemistry as the original starting powders before sintering [2013Alt].

2.2.1.6.2 Selective cobalt leaching method (SCLM)

The selective cobalt leaching method allows for separate recovery Co and WC powders from WC-Co scrap in four steps; acid leaching, precipitation, calcination and H₂-reduction [2004Gur2]. Leaching of Co from the cemented carbide scrap is done in nitric acid (HNO₃), leading to formation of cobalt nitrate (Co(NO₃)₂) solution [2004Gur1, 2004Gur2]. The Co(NO₃)₂ solution is separated from the solid WC particles by filtration. Precipitation is carried out at 25°C in the presence of 2 M sodium hydroxide (NaOH) solution which is slowly added to the Co(NO₃)₂ solution until the desired equilibrium pH is achieved [2004Gur2]. Sodium hydroxide is a strong alkaline solution that reacts with the Co(NO₃)₂ solution, forming cobalt hydroxide (Co(OH)₂) precipitates. The precipitates are then separated from the remaining solution by filtration [2004Gur2]. After precipitation, the

Co(OH)₂ solution undergoes calcination at 300°C in argon for 30 minutes, followed by hydrogen reduction at 800°C for 90 minutes, leading to the production of submicron Co powders [2004Gur2].

2.2.2 Consolidation of powders

Consolidation of cemented carbides involves three main steps: milling, pressing and dewaxing, all of which are important in ensuring high quality production [1975Bro, 1997Luy]. A general flow sheet highlighting the consolidation processes during cemented carbide powder metallurgy production is shown in Figure 2.6 [1998Upa]. The starting powders normally consist of WC and Co powders, but depending on the application, WC can be partially substituted by carbides of Ti, Ta, V, Cr and Mo. The Co binder may at times be partially or completely substituted by Ni or Fe [1934Sch, 1987Pen].

2.2.2.1 Milling

The primary objectives of milling are to achieve uniform distribution between WC and Co by ensuring that every WC particle is coated by Co and particle size reduction (comminution) [1997Luy, 1998Bro]. Milling can be done in the presence of a liquid (wet milling), or without a liquid (dry milling). Wet milling is preferred because it prevents oxidation of the very active new surfaces produced during particle breakdown (oxygen results in the eventual loss of carbon) [1997Luy, 1998Bro, 1998Upa]. Although water results in the best milling comminution, organic liquids such as ethanol, hexane and acetone are preferred, because they are better at preventing oxidation [1997Luy, 1998Upa]. The milling liquid also aids in heat dissipation, as well as to facilitate dispersion of WC and Co powders [1975Bro]. After milling, the liquid has to be removed, and this can be achieved by decantation, followed by vacuum filtration. More modern techniques such as use of rota-evaporators and spray drying are much faster and more efficient [1998Upa]. Organic liquids have the additional advantage of lower boiling points than water during drying, making them easier to remove from the powders [1997Luy, 1998Upa].

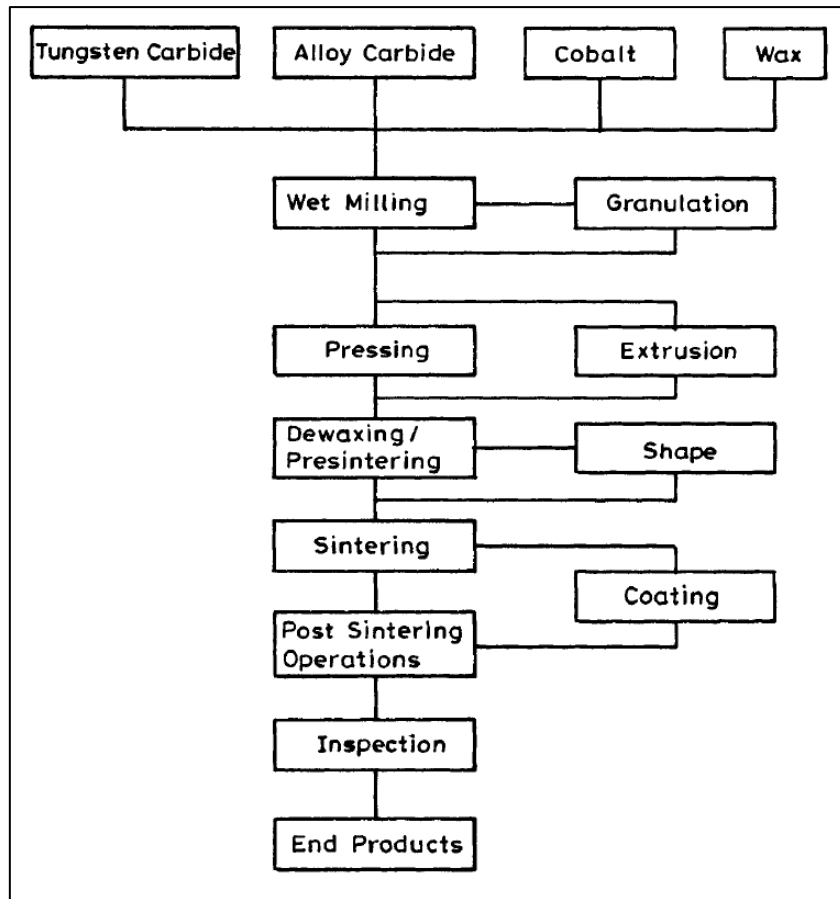


Figure 2.6. Flow sheet of cemented carbide production [1998Upa].

Milling can be done using mainly three types of mills:

- Ball mills,
- Attritor mills, and
- Vibrator mills.

2.2.2.1.1 Ball milling

Ball milling is the most commonly used comminution method in cemented carbides, and also results in uniform mixing of carbide particles with the metallic binder and milling lubricants (wax), such as polyethylene glycol (PEG) [1998Upa]. Polyethylene glycol is normally added to prevent loss of compaction energy during pressing, due to friction between adjacent particles and between the particles and the die walls [1975Bro, 1997Luy]. Reducing friction allows for greater pressure to be applied to the powders for a given load and minimises the difficulties in ejection after pressing the powders into a green compact [1975Bro]. The maximum amount of PEG that can be added is 2wt% of the total powder weight, which is generally about 25% of the total volume. Good mixing during milling should be achieved to

ensure uniform distribution of PEG [1997Luy]. The best mixing is achieved by ball milling [1997Luy, 1998Bro]. The mechanical properties and elimination of porosity in the sintered products are largely dependent on the uniformity of mixing during milling. In ball milling, the active processes are impact, abrasion and compression [1997Luy]. Basically, mechanical alloying between the hard phase and the binder matrix, as well as particle size reduction are achieved through mechanical attrition, brought about by the impact between the balls and the powders resulting in compression and abrasion of the powders [1996Koc]. The movement of the balls and the powder during ball milling is shown in (Figure 2.7) [1996Koc].

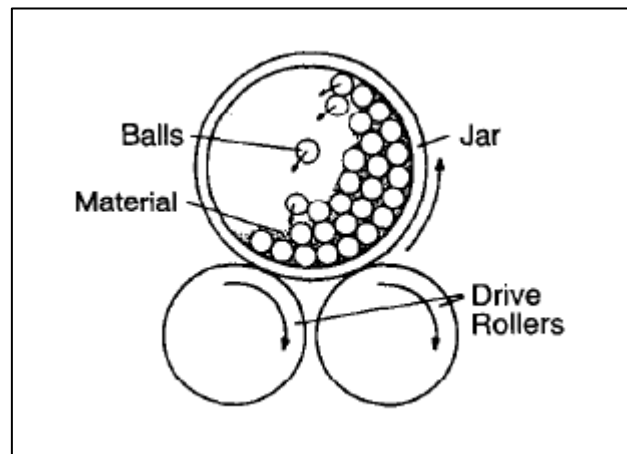


Figure 2.7. Schematic drawing of tumbler ball mill [1996Koc].

The main event during WC and Co powder mixing and breakdown is the ball and powder collision [1996Koc]. The powder particles get trapped between the balls during milling, as shown in Figure 2.8, and undergo deformation and/or fracture processes which define the structure of the mixed powder. The process depends on the mechanical behaviour, phase equilibria and stress states of the individual powders [1996Koc]. Different morphologies during milling can be obtained, depending on whether the powders are both ductile, both brittle, or one is ductile and the other is brittle. When both powders are ductile, they exhibit flattening and cold welding into lamellar structures, which after sufficient repeated fractures and re-welding form homogeneous equiaxed particles. If powders are both brittle, the powders will only fracture into smaller segments, resulting in a morphology that does not assume a lamellar structure, but instead forms an equiaxed “popcorn” ball structure. In the case of a ductile-brittle powder mixture, the brittle particles fracture and get trapped at the weld interface between the ductile particles. Continued fracture and cold welding leads to coating of the fractured brittle particles by the ductile particles, resulting in uniform distribution of the two powders [1996Koc].

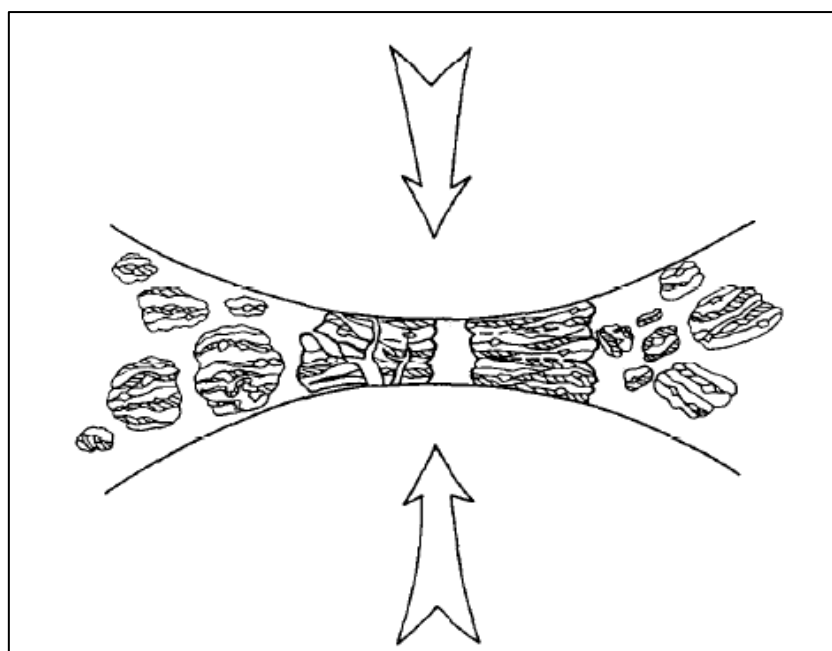


Figure 2.8. Powder particles becoming trapped between the balls during milling [1996Koc].

The mill energy and the nature of powers are important in determining the kinetics of a milling process, and in some cases, its feasibility. Generally, high energy mills produce end products more rapidly [1996Koc]. The energy of the mill depends on the kinetic energy of the milling media (milling balls). The kinetic energy of the balls is a function of speed of rotation of the mill, as well as their density, size and size distribution [1996Koc, 1998Upya]. The rotation speed should not be too fast, otherwise the centrifugal forces will be higher than gravitational forces, resulting in pressing of the balls on the walls of the milling pot. This prevents collision between the powders and the balls [1997Luy, 1998Upa]. If the speed is too slow, there will be very little movement, lowering the force of impact between the balls and the powders [1997Luy]. The ideal speed is that which results in some of the powder and balls been lifted up to the top of the milling pot and subsequently dropping down on the remaining material, resulting in mixing and comminution [1997Luy]. This ideal speed can be calculated using Equation 2.6 [1998Upa]:

$$n_{\text{crit}} = \frac{42.3}{D} \quad (\text{Equation 2.6})$$

where n is the speed in rpm and D = diameter of the milling pot in meters. At the critical speed n_{crit} , the powders and ball are at equilibrium between centrifugal force and gravitational

force. Milling above this speed results in poor milling due to higher centrifugal force than gravitational force. An optimum speed of about 70-80% n_{crit} is recommended [1998Upa].

Milling balls made from dense materials such as tungsten carbide and steel provide more energy than lighter materials such as ceramics [1996Koc]. The ball size and size distribution should be optimised depending on the mill. If the balls are too densely packed, the mean free path for ball motion is reduced, while if they are loosely packed, the collision frequency is reduced [1996Koc]. A ball-to-powder weight ratio of 3:1 is normally used [1998Upa], but higher ratios can be used, depending on the size of the mill and desired particle size of the powders after milling. For effective milling, the mill should be 1/3-1/2 filled with balls [1997Luy]. Higher ball to powder ratios are used for very fine powders (nano and ultrafine) because the achieving of good mixing of fine powders is difficult [2003Kim], hence higher milling energy is required. Milling energy can be increased by either increasing the milling speed and/or ball-to-powder ratio [1996Koc].

Milling time is another important variable during milling, as it affects the particle size and homogeneity of the powders [1997Luy, 1998Upa]. Prolonged milling reduces the porosity of the sintered product, because it helps to achieve a homogeneous distribution of the metal binder, and shrinkage during sintering is dependent on the binder distribution. Faster sintering shrinkage rates at lower temperatures can be achieved through increasing the milling times [1997Luy]. However, milling is often carried out for unnecessarily long periods of time, for example, the difference in results between milling for 24 and 96 h is much greater than for 96 and 200h [1997Luy]. Reduction in particle size increases with increased milling time as shown in Equation 2.7 [1965Fis], but this does not continue indefinitely [1997Luy]:

$$S = Kt^{1/2} \quad \text{(Equation 2.7)}$$

where S is the particle size, t is the milling time and K is a constant dependent on the type of mill and milling conditions. Lardner *et al.* [1970Lar] studied the effect of milling time, milling liquids and size of the balls on the milled carbide grain size, and showed for a particular mill and mill charge combination, there is a limiting grain size beyond which no further reduction takes place (Figure 2.9). Once the limiting size is reached and milling is continued, particles undergo substantial mechanical cold bonding (agglomeration), which is then broken down by the milling media [1980Hill].

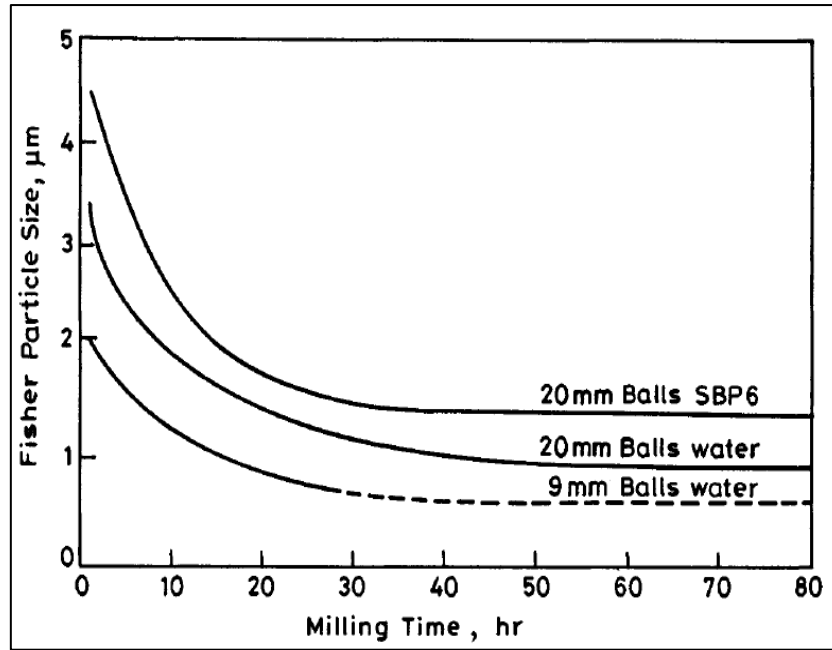


Figure 2.9. Effect of milling time on WC particle size reduction [1970Lar].

2.2.2.1.2 Attritor milling

Attritor milling is achieved through violent movement of the balls around the milling pot by fast rotating impellers arms [1998Bro]. The active processes during attritor milling are abrasion and compression [1997Luy]. A schematic of attritor mill is shown in Figure 2.10 [1996Koc]. In comparison to ball milling, attritor milling action is much faster with an estimated grinding rate of about 10 times faster than that of ball milling [1998Upa]. Due to their high rotating speeds and grinding rates, they are the most effective mills for breakdown of powders, but unlike ball milling, they result in the poorest mixing [1997Luy, 1998Bro]. Additionally, the variation in particle size of milled powder is large because they work mainly on impact, producing a typical Gaussian distribution of grain sizes [1998Bro]. Conversely, ball milling preferentially breaks up the largest grains trapped between the balls, and has very little effect on the small grains. This results in a narrow grain size distribution of the milled powder [1998Bro].

The critical parameter in ensuring repeatability of milling results during attritor milling is the energy (E) spent [1997Luy], which is given by Equation 2.8 [1997Luy]:

$$E = T \cdot v \cdot t \quad (\text{Equation 2.8})$$

where T is the torque applied to the rotating balls, v is the velocity at which the balls are rotating and t is the milling time. The values of T, v and t can be changed, but as long as their

product is the same, the results of the milling process will be the same. It is possible to relate the resulting median WC particle size to the milling energy by applying Charles' equation (Equation 2.9) [1989Mas]:

$$E = A (d^{-\alpha} - d_0^{-\alpha}) \quad (\text{Equation 2.9})$$

where E is the energy, d is the final average particle size, d_0 is the initial average particle size. The values of A and α change, depending on the size of the mill, as well as variation in binder content, because level of energy lost to the deformation during milling is dependent on the ductility of the binder [1989Mas].

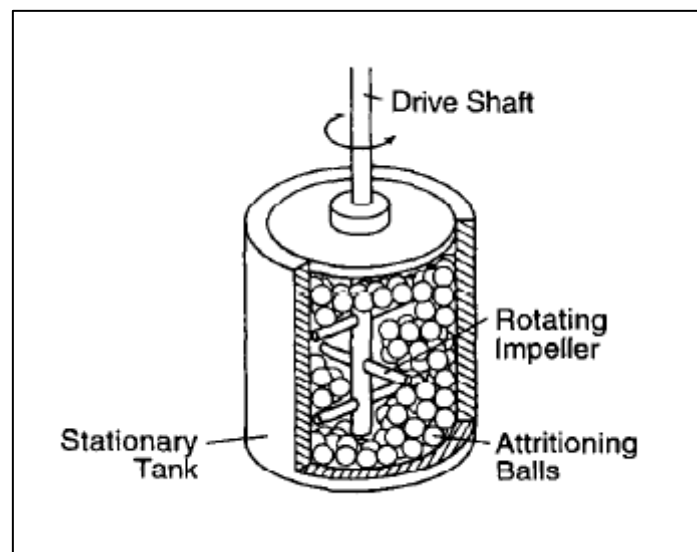


Figure 2.10. Schematic drawing of an attritor mill [1996Koc].

2.2.2.1.3 Vibrator milling

In vibrator milling, the main process involved is compression [1997Luy]. These mills have no limiting speed, and the balls rotate individually and in unison, making the milling process very efficient [1998Upa]. For example, 48 hours of high energy vibrator milling can be more effective than 7 days of simple rotational ball milling [1983Bro].

During large scale milling, achieving uniform distribution is difficult, because the mixture consists of a small amount of binder phase and a large amount of carbide phase. Thus, mixing is initially done manually in small separate batches, before being poured into the large mill [1997Luy]. To minimise contamination, ball and attritor mills are lined with carbide and loaded with carbide balls and/or carbide cylebs (cylinders with hemispherical ends) [1975Bro]. Attritor impeller arms should have carbide covers, to reduce contamination, as

well as increase application life. Stainless steel mills with steel balls have been successfully used to mill cemented carbides [1975Bro]. Generally, care must be taken to avoid the pick-up of impurities, particularly oxides [1998Bro].

After milling, the powders are dried to remove the milling liquid. This can be done by decantation, filtration, heating in a vacuum, or by centrifugal action in the heating medium [1997Luy, 1998Upa]. The drying temperature must not be higher than the boiling point of the milling liquids to avoid oxidation of the powders. All the liquid should be removed to prevent porosity and oxides in the sintered product [1997Luy, 1998Upa]. The dried powders are then sieved to break up the large cakes of powder that form during drying, and to remove any large impurities that may have been picked up during milling or drying [1997Luy]. The sieving is done using vibrating sieves.

2.2.2.1.4 Precursor mixing

Ball milling can be used to achieve uniform distribution of micron, submicron (0.9-0.5 μm) and ultrafine (0.5-0.2 μm) WC-Co cemented carbides. However, it is very difficult with nano powders ($\leq 0.1 \mu\text{m}$) [1992McC, 2003Kim, 2014Xia], because of their agglomeration, due to their high surface energy [2008Wan]. Thus, chemical processes such as precursor mixing techniques have been developed [1992McC, 2014Xia]. Precursor mixing involves dissolving solid precursor chemicals, W source ammonium metatungstate (AMT) $((\text{NH}_4)_6(\text{H}_2\text{W}_{12}\text{O}_{40}) \cdot 4\text{H}_2\text{O})$, Co source cobalt nitrate $(\text{Co}(\text{NO}_3)_2)$ and C source polyvinyl alcohol (PVA) $((\text{C}_2\text{H}_4\text{O})_x)$ into distilled water, with a solid to water weight ratio 2:1 [2014Xia]. The resulting solution is stirred vigorously to ensure that the solids are completely dissolved, then fed to a spray drier to produce a powder-like precursor [2014Xia]. The spray-dried precursor is then placed in a belt furnace to remove residual moisture and crystalline water, facilitate dissociation of C-H (into C and H) and N-H groups (into N and H), and to convert the precursor into a W-C-Co-O complex structure (pre-composite powder) [2014Xia]. This process takes place between 500-600°C. The pre-composite powder is then converted to nanosize WC-Co powder (0.03-0.1 μm) in a rotary furnace [2014Xia].

2.2.2.2 Pressing

Pressing is done to form green compacts from the loose powders through the use of external pressure [1998Upa]. The main reasons for compaction are to consolidate the powders into the desired shape and impart adequate green strength to facilitate handling [1975Bro, 1997Luy, 1998Upa]. Two types of powder compaction techniques can be used: die compaction and

isostatic compaction [1975Bro, 1997Luy, 1998Upa]. Die compaction is carried out in two ways, single action compaction (SAC) and double action compaction (DAC). In SAC, the upper punch can move, while the lower punch is stationary. Conversely, in DAC, the powder is compressed simultaneously by both the upper and lower dies (Figure 2.11). Isostatic compaction involves hydrostatic pressure applied simultaneously and equally in all directions. The powder is placed within a tightly sealed rubber container immersed in a fluid bath within a pressure vessel [1980Mak, 1997Luy]. Standard parts such as cutting inserts are produced using die compaction, while larger sized parts are produced using isostatic compaction [1998Upa].

After compaction, a green density of 60-65% theoretical density is normally attained [1991Jen, 1997Luy]. The green density is a measure of the effectiveness of compaction and has an impact on the sintering behaviour of the compact [1991Jen]. For example, when the compact's green density is less than 60% theoretical density, the shrinkage is high, affecting the final dimensions of the sintered compact [1998Upa]. Green density increases with increased compaction pressure, increased particle size, decreased compaction speed and decreased hardness and strength of particles [1997Luy]. After compaction, variation in density occurs in different parts of the compact, due to friction forces between the particles and the die walls. Friction forces limit the particle movement and the deformation of the compact [1997Luy]. The effect of friction can be related to the length to diameter (L/D) ratio of the compact as shown in Figure 2.11 [1997Luy]. If the L/D ratio is small, then variation in density is reduced and vice versa for high L/D ratio. Addition of wax, such as PEG (polyethylene glycol), reduces the effect of friction during pressing [1998Bro, 1998Upa]. Minimising the variation in density prevents distortion of sintered compacts due to the more rapid shrinkage from regions with lower densities [1997Luy, 1998Upa].

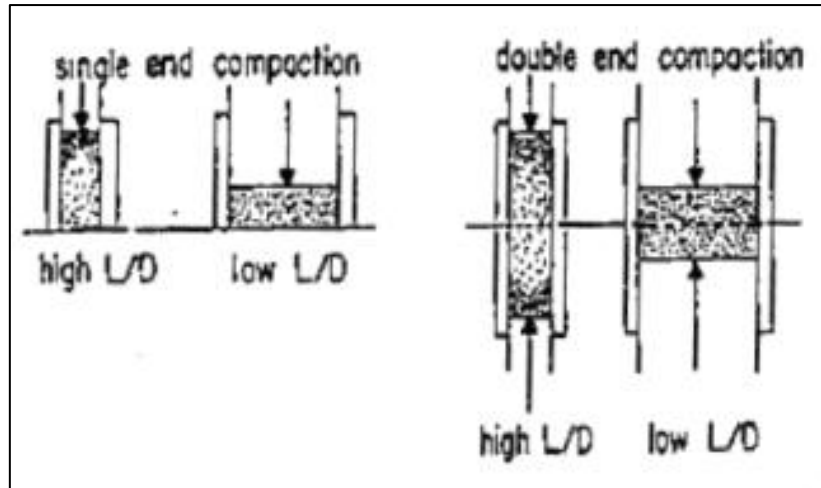


Figure 2.11. Schematic representation of single action compaction and double action compaction [1997Luy].

2.2.2.3 Dewaxing

After pressing, the milling wax (lubricant) should be completely removed before sintering because its presence will result in porosity [1975Bro]. The usual process is to volatilize the wax in hydrogen or in a vacuum at temperatures just below 400°C [1975Bro, 1997Luy, 1998Upa]. Dewaxing begins at about 150°C, but temperatures of 250-300°C are used to ensure all the wax is removed. [1970Spi]. Wax removal rate increases with increased temperature (Figure 2.12) and the reaction is more dependent on temperature than time [1970Spi]. During heating, wax vaporization occurs from the exposed surfaces of the compact. As the wax is lost, more diffuse to the surface from the inner parts of the compact and this process continues until all the wax is removed [1998Upa].

Dewaxing is generally followed by heating of the compact in hydrogen at temperatures ranging from 700-1000°C and this process is known as presintering [1997Luy, 1998Bro]. Presintering is done to facilitate solid-state welding of the particles, resulting in the compact having sufficient mechanical strength for machining. The green compacts are produced in simple shapes such as rectangular and circular blanks which are then machined by techniques such as milling, turning and grinding [1998Upa]. The presintered compacts have about the same dimensions as the pressed compact, but much higher strength, enabling machining operations to be carried out without breaking the fragile compact [1997Luy, 1998Upa]. During presintering, the compacts are normally packed in carbon, to minimize carbon loss from reactions between WC and hydrogen and/or water vapour, as shown in Equations 2.10 and 2.11 [1997Luy].

At about 600°C the following reaction occurs:



and above 825°C:



The presence of W metal is undesirable, as it may lead to formation of eta phase.

2.2.3 Sintering

Sintering involves heating of the green compact at temperatures below the melting point of the main constituent, at a predetermined pressure and time, with aim of increasing surface contact between particles [1960Kin]. Since the particles are very active at these temperatures, surface contact is enhanced through mechanisms such as coalescence and Ostwald ripening, leading to compaction [1897Ost, 1961Lif]. The impetus for sintering is the decrease in the total interfacial energy of particles in the green compact [1960Kin]. The total interfacial energy can be expressed as γA , where γ is the specific interface energy and the A is the total interface area of the compact.

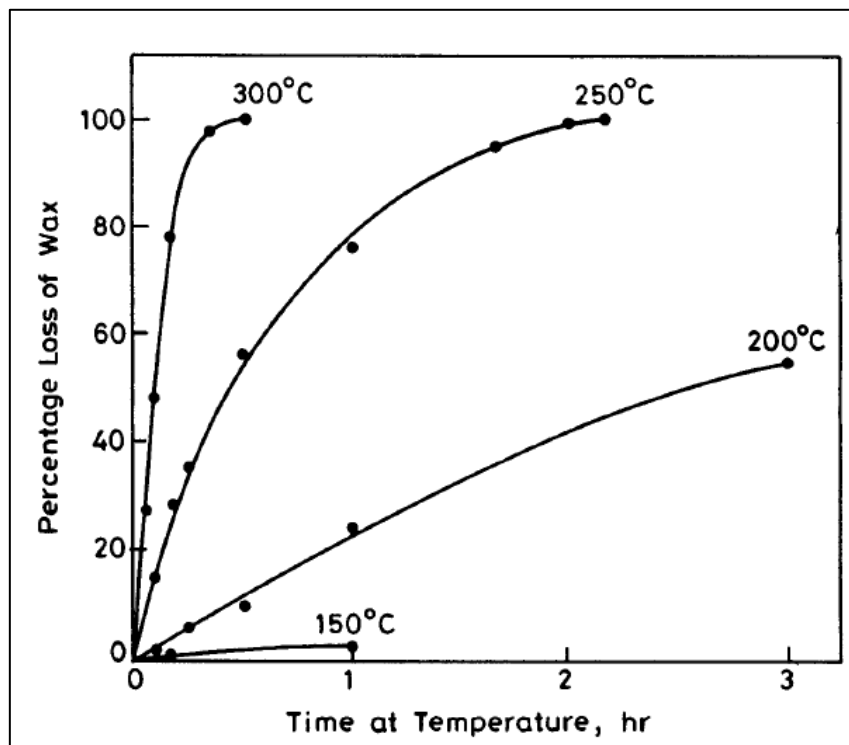


Figure 2.12. Loss of wax (lubricant) with variation of temperature and time [1970Spi].

The reduction in total interface energy can be expressed as Equation 2.12 [1960Kin, 2005Kan]:

$$\Delta(\gamma A) = \Delta\gamma A + \gamma \Delta A \quad (\text{Equation 2.12})$$

During sintering, the change in interfacial energy ($\Delta\gamma$) is because of densification (pore shrinkage), while the change in interfacial area (ΔA) is due to grain coarsening, as shown in Figure 2.13 [2005Kan]. For solid state sintering, $\Delta\gamma$ is as a result of the replacement of solid/vapour interfaces (surface energy Γ_{sv}) by solid/solid interfaces (surface energy Γ_{ss}), since $\Gamma_{ss} < \Gamma_{sv}$ [1960Kin, 2005Kan].

As shown in Figure 2.13, during sintering, densification occurs via the elimination of porosity between the particles, since if the amount of porosity is high, then the amount of surface area is large, increasing the total surface energy (γA). Thus, sintering tends to reduce the total surface area by decreasing the number and size of pores (densification) [1960Kin, 1997Luy]. The shrinkage in pore size is due to particle coarsening (ΔA) resulting from widening of contact between particles [1960Kin, 1997Luy].

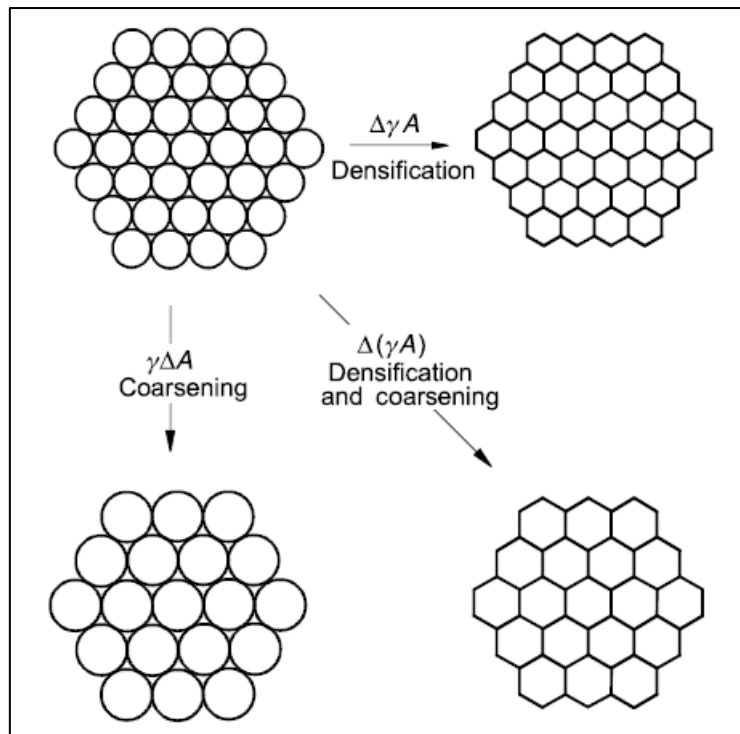


Figure 2.13. Basic phenomena occurring during sintering driven by $\Delta(\gamma A)$ [2005Kan].

During sintering, the compact reduces in volume compared to the green compact because of the densification, thus volume shrinkage is used as an indication of densification [1938Pri].

Densification takes place in four main stages: particle bonding, neck growth, pore channel closure and pore shrinkage [1960Kin, 1969Bro]. Bonding between particles initially takes place due to diffusion between particles in intimate contact. Transport of material to the region of contact results in the formation of solid material bridges called necks [1960Kin, 1985Ger]. Neck growth is achieved through the transport of atoms to the contact region by grain boundary diffusion, volume diffusion and surface diffusion [1960Kin]. Necking accounts for about 2-3% volume shrinkage (58-68% densification) [1960Kin, 2005Kan]. Necking leads to the formation of interconnected particles, with interconnected pores between them. Due to increased densification and increased grain size, the interconnected pores become unstable and separate into isolated closed pores, at this point the densification of the compact is 91-95% [1969Bro]. The pores then become more rounded and shrink completely, due to movement of material into the porosity and movement of any gas to the external surface, leading to full densification [1960Kin].

2.2.3.1 Sintering variables

The variables that determine sinterability and the microstructure of the sintered powder compact can be divided into two: sintered material variables and sintering process variables [1975Bro, 2005Kan]. The sintered material variables include chemical composition of compact, powder size, powder size distribution, powder shape and degree of powder agglomeration [1975Bro, 2005Kan]. These variables affect the compressibility and sinterability (densification and grain growth) of the powders. For compacts containing more than one kind of powder (e.g. cemented carbides), homogeneity is of prime importance. Homogeneity of sintered compacts consisting of a mixture of two or more powders is significantly improved through effective mixing during milling [1975Bro]. Sintering process variables include sintering temperature, time, pressure, atmosphere, heating and cooling rate [1985Ger, 2005Kan].

Sintering of WC-Co is carried out in a vacuum or hydrogen atmosphere at a temperature above the W-Co-C eutectic temperature ($\sim 1320^{\circ}\text{C}$) [1976Fro]. By the time the sintering temperature is reached, the Co is no longer pure, but contains some W and C which diffuse into it [1998Upa]. Pure Co melts at about 1490°C , but with the solution of W and C, it starts to melt at temperatures between 1280°C and 1320°C , depending on the amount of dissolved W and C [1976Fro]. The amount of available C affects the W solubility in Co [1998Upa, 2002Wit]; in carbon-rich WC-Co compositions, the W content in the Co is as low as about 4 wt%, but in carbon-deficient compositions, the W content can be as high as 16wt%

[1997Luy]. Sintering of WC-Co takes place in the presence of a liquid phase, hence the name liquid phases sintering (also known as conventional sintering). During sintering of WC-cemented carbides, the most important sintering variables are sintering atmosphere, temperature and time.

2.2.3.1.1 Sintering Atmosphere

Tungsten carbide-cobalt hard-metals are sintered at high temperatures ranging between 1350-1650°C, depending on the composition. At these high temperatures, chemical reactions between the powders and the surrounding atmosphere are possible. Additionally, the surface areas of the compacts are extremely high, especially when sintering fine powders (0.5-0.8µm), and this makes them susceptible to reaction with the sintering atmosphere [1998Upa]. In most cases, the reactions involve carbon, and slight deviations from the stoichiometric carbon content results in the formation of either eta phase or free graphite, both reduce the mechanical properties [1975Bro].

Sintering of WC-cemented carbides can be done in a hydrogen or vacuum atmosphere. Hydrogen has the advantage of reducing any absorbed oxygen in the compact into water vapour which is then carried away. This prevents the reaction of carbon and oxygen to form CO and CO₂ [1998Bro]. However, in some cases, the hydrogen reacts with carbon to form CH₄, resulting in a loss of carbon. This can be corrected by passing CH₄ with hydrogen during sintering [1998Upa]. Sintering in a vacuum (unlike in hydrogen) prevents the loss of carbon through formation of CH₄. However, retained or absorbed oxygen is free to react with carbon, leading to carbon deficiency through the formation of CO and CO₂ [1975Bro, 1998Upa]. Thus, during sintering in a vacuum, carbon black is initially added to compensate for loss of carbon [1975Bro, 1998Upa].

2.2.3.1.2 Sintering Temperature and Time

The sintering temperature is primarily dependent on the composition of the WC-cemented carbide, as shown in Table 2.1 [1975Bro]. Factors such as solubility of WC in binder, wetting of WC by the binder and diffusion increase with increased sintering temperature, favouring rapid densification [1998Upa]. Sintering temperature also varies with the amount of binder [1975Bro 1997Luy, 1998Upa], with low temperatures of 1350°C for 30 wt% Co and high temperatures of 1650°C for 3 wt% Co [1997Luy]. Sintering time can be reduced by increasing the temperature due to faster diffusion and higher volumes of the liquid phase

[1998Upa]. However, high temperature sintering results in WC grain coarsening, as well as distortion of the compact [1998Upa]. The sintering time is also dependent on the thickness of the compact, with thicker compacts requiring longer times to sinter [1997Luy]. Therefore, an optimum compromise between temperature and time should be achieved.

2.2.3.2 Conventional sintering

Conventional or liquid phase sintering (LPS) is commonly used because the presence of the liquid phase enhances diffusion, facilitating material transport and complete densification without external pressure [1960Kin]. However, part of the densification during LPS of WC-Co takes place in the solid state. Thus, conventional sintering takes place in two main steps, solid state sintering and liquid phase sintering.

Table 2.1. Typical sintering temperatures for WC for hard-metal grades in hydrogen atmosphere [1975Bro].

Composition weight %					Sintering temperature (°C)
WC	TiC	Ta(Nb)C	Cr ₃ C ₂	Co	
94	-	-	-	6	1540
91	-	-	-	9	1480
89	-	-	-	11	1460
87	-	-	-	13	1450
80	-	-	-	20	1400
75	-	-	-	25	1380
70	-	-	-	30	1350
96.5	-	-	0.5	3	1640
95	-	-	0.5	4.5	1620
93.5	-	-	0.5	6	1560
90.5	-	-	0.5	9	1500
85.5	7	3.5	-	4	1640
81.5	7	3.5	-	8	1560
80	14	-	-	6	1620
84	10	-	-	6	1600
87	7	-	-	6	1590
87	5	-	-	8	1560
66	25	-	-	9	1620

Other factors, such as pressure and particle size, also affect densification. Increased pressure and decreased particle size result in an increased densification rate as shown in Figure 2.14 [2005Kan].

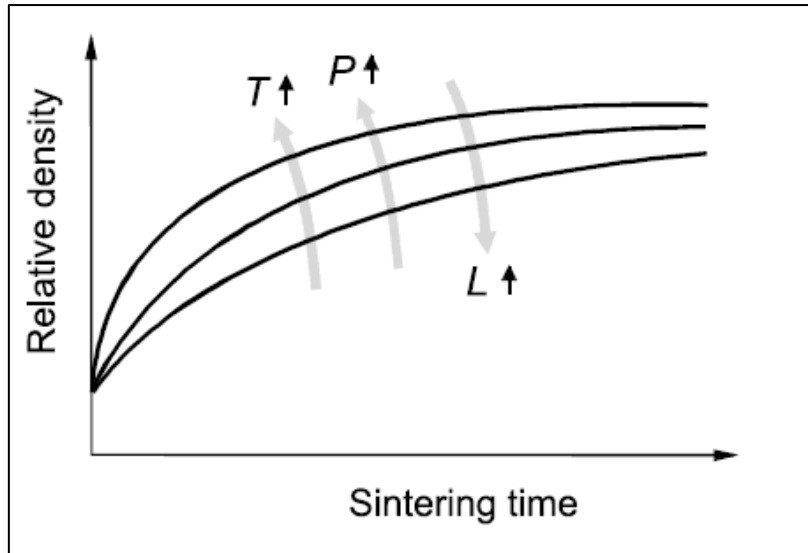


Figure 2.14. Comparison between densification and sintering parameters [2005Kan], where T is temperature, P is pressure and L is particle size.

2.2.3.2.1 Solid state sintering

More than 50% of the densification is achieved before the eutectic temperature during sintering of WC-Co [1983Bro]. Solid state densification is highly dependent the solubility relationship between the binder and the hard phase [1998Upa]. At around 400°C, ϵ -Co (hcp) begins to transform into α -Co (fcc) [1984Kir], and at about 800°C, WC particles start to sinter independently from the Co, forming a WC skeleton [1997Luy]. Cobalt diffuses onto the WC surfaces at temperatures as low as 800-1000°C, forming WC-Co agglomerates and resulting in initial densification [1998Upa, 2007Pet]. The size of these agglomerates depends on the size and distribution of Co. The good low temperature solubility of WC in Co helps in surface smoothing of the particles, leading to enhanced close packing of particles [1953Edw]. At about 1100°C, pore reduction begins and the smaller carbide particles dissolve into Co, forming a (Co) binder which is alloyed with W and C. Further increased temperature to about 1200°C leads to WC grain coarsening. The WC contiguity increases with increased temperature, 1100-1250°C, resulting in a WC skeleton with (Co) and pores between [1996Uhr].

2.2.3.2.2 Liquid phase sintering

The minimum criteria for successful reduction of interface energy during liquid phase sintering are: low sintering temperature, solubility of the solid phase in the liquid phase, and good wetting of solid phase by liquid [1952Gur]. In the WC-Co cemented carbides, the liquid

phase satisfies all these conditions [1976Fro]. The LPS stage takes place in three main steps [1953Can]:

- Primary rearrangement,
- Secondary rearrangement, and
- Coarsening.

2.2.3.2.2.1 Primary re-arrangement

Rapid initial densification is observed in the primary re-arrangement stage due to movement of particles in the direction of the just-formed wetting liquid phase by capillarity force [1981Smo]. The particle re-arrangement is as a result of the capillarity force, leading to closer packing of the particles. Solubility of the WC particles in the liquid phase binder further improves the re-arrangement for closer packing, increasing the densification [1981Smo]. Simultaneously, pore elimination occurs due to the drive to minimise the total interface energy of the system [1959Kin, 1960Kin], as shown in Figure 2.14 [2009Ger]. Most of the densification is achieved during primary re-arrangement, because of the formation of the liquid phase that fills up most of the voids [1981Smo].

2.2.3.2.2.2 Secondary re-arrangement

Secondary rearrangement is mainly due to solution reprecipitation (Ostwald ripening) [1897Ost, 1959Kin]. In this step, densification occurs simultaneously with grain growth and shape accommodation of WC [1959Kin]. After primary re-arrangement, the newly-formed liquid phase spreads between WC particles, forming liquid films between them. The surface tension forces create excess pressure in the liquid films. This leads to high chemical potential for solubility of the solid phase in contact with the liquid, which then dissolves, while material is deposited out of the liquid [1959Kin]. The smaller WC grains dissolve due to their higher dissolution potential (increased chemical potential) [1897Ost, 1961Lif, 2006Her] and the larger grains grow by material reprecipitation (Ostwald ripening). The large grains undergo shape accommodation because of precipitate material from the dissolved smaller grains, leading to availability of liquid phase for filling the pores [1959Kin], as shown in Figure 2.15. The amount and size of pores reduce with increase in grain size.

Grain growth due to Ostwald ripening can be described by Equation 2.13 [2008Wan]:

$$G^n - G_0^n = k(t - t_0) \quad (\text{Equation 2.13})$$

where G_0 grain size before sintering (t_0) and G is the grain size at end of sintering (t), K is a material constant dependent on temperature (Equation 2.14) [2008Wan], while n is equal to 2 for interface reaction-controlled Ostwald ripening and 3 for diffusion-controlled Ostwald ripening [2008Wan]:

$$k = k_0 \exp(-Q/RT) \quad (\text{Equation 2.14})$$

where Q is the activation energy for grain growth, R is the gas constant and T is absolute temperature. Thus, grain growth due to Ostwald ripening is dependent on activation energy for grain growth, time and temperature.

2.2.3.2.2.3 Coarsening

During LPS, densification occurs at the same time as grain coarsening, but in the final stage, grain growth is dominant [1959Kin, 1998Upa]. Grain growth in the final stage is due to interface reaction-controlled Ostwald ripening [1998Upa]. After secondary rearrangement, the WC-Co hard-metals are fully, or almost completely dense, hence this final sintering stage affects the microstructure in terms of grain size, distribution and shape, as well as binder phase distribution. The changes in the microstructure affect mechanical properties, such as hardness, strength, wear resistance and fracture toughness [1955Gur].

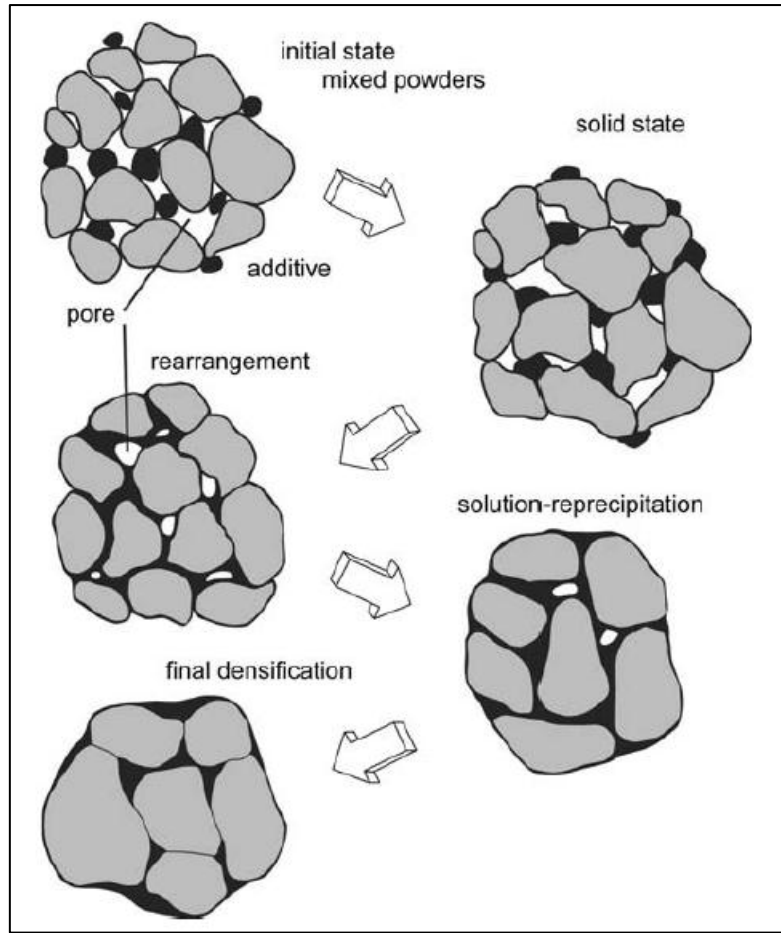


Figure 2.15. Schematic diagram showing the microstructure changes during conventional sintering, starting from mixed powders to fully dense sintered compact [2009Ger].

2.2.3.3 Spark plasma sintering (SPS)

Liquid phase sintering is the most commonly used method for consolidation of tungsten carbide hard-metals [1975Bro, 1991Jen]. However, due to limitations such as long sintering times and WC grain growth [2008Hua1], new rapid sintering methods such as spark plasma sintering (SPS) offer advantages over LPS [1999Tok, 2008Hua1]. Spark plasma sintering, also known as a pulse electric current sintering (PECS), employs high heating rates combined with high compressive pressures to consolidate powder compacts to a high density in a short time and at low temperatures [1999Tok, 2002Mam]. The initial idea of using an electrical field to facilitate sintering began in 1933 [1933Tay], and the addition of external pressure while current passed through the powders was introduced in 1955 [1955Len]. Achieving sustainable activation of powders via repeated electrical discharge was possible by 1971, resulting in full densification in shorter sintering times [1971Goe]. From the mid-1980s to the early 1990s, research in electric field activated sintering lead to development of plasma

activated sintering machines that had a generated current limit of 800A [2002Mam]. Spark plasma sintering machines were then developed in Japan, as improvement on plasma activated sintering machines, and they had direct current pulse generators of over 20,000A [2002Mam]. Spark plasma sintering has the main advantage of achieving very high degrees of densification at low temperatures within a short period of time, compared to conventional sintering, hot pressing (HP) and hot isostatic pressing (HIP) [1999Tok, 2006Son].

2.2.3.3.1 Principles of SPS

Spark plasma sintering uses a pulsed electric current combined with rapid heating and pressure to achieve full density at low temperatures and in short time periods [1999Tok, 2002Mam, 2006Son]. A schematic representation of a SPS machine set-up is shown in Figure 2.16 [2002Mam]. The mixed powders are loaded directly into the graphite dies, and are sintered in a vacuum or argon environment [2002Mam]. The process begins by applying pulsed current discharge, achieved by a voltage of about 30V and a current of 600-1000A [2002Mam]. The duration of each pulse may be varied from 1 to 300ms.

Normally, for conductive powders, the heating is due to the Joule effect and heat transfer from the graphite dies and punches, which are as a result of current flow through paths 1, 2 and 3 on Figure 2.17 [2011Bas1]. Heating of non-conductive powders is by heat transfer from the dies (path 2) and the punches (path 3). The heating of the dies and punches is due to their resistance to current.

During SPS, the on-off direct current (DC) pulse voltage and current from the pulse generator are applied to the loose powders. The current is forced to choose the path of least resistance, and this is normally through points of contact between particles as shown in Figure 2.18 [1999Tok]. This is because there is generally an electrical potential difference between two contacting particles, thus the local current will flow from the higher electrical potential particle to the lower electrical potential particle [2006Son].

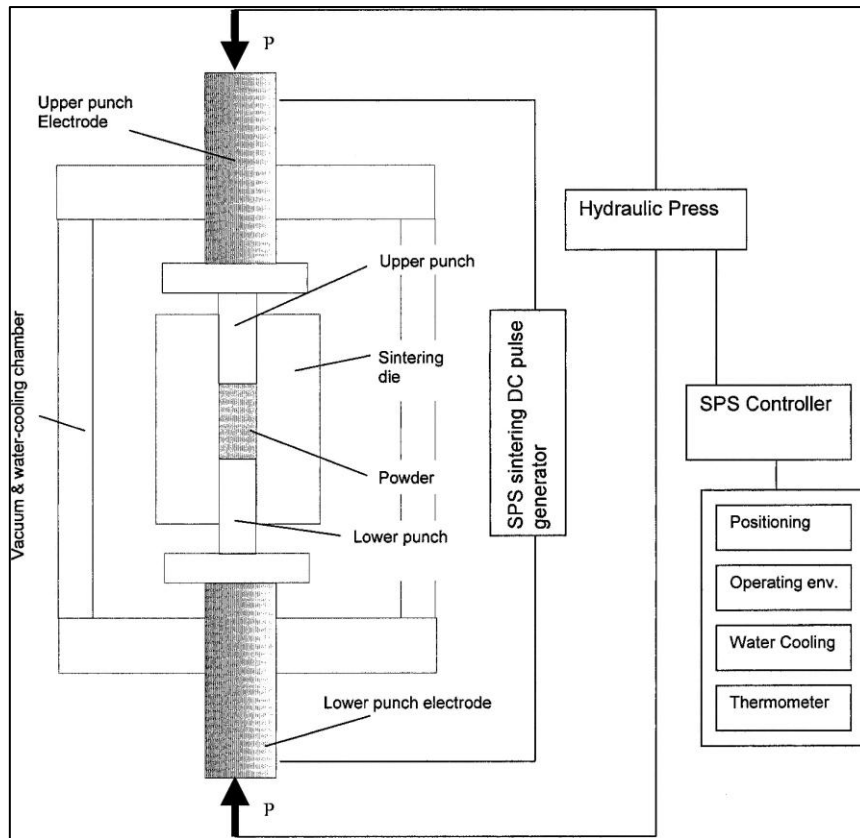


Figure 2.16. Schematic diagram of a SPS machine [2002Mam].

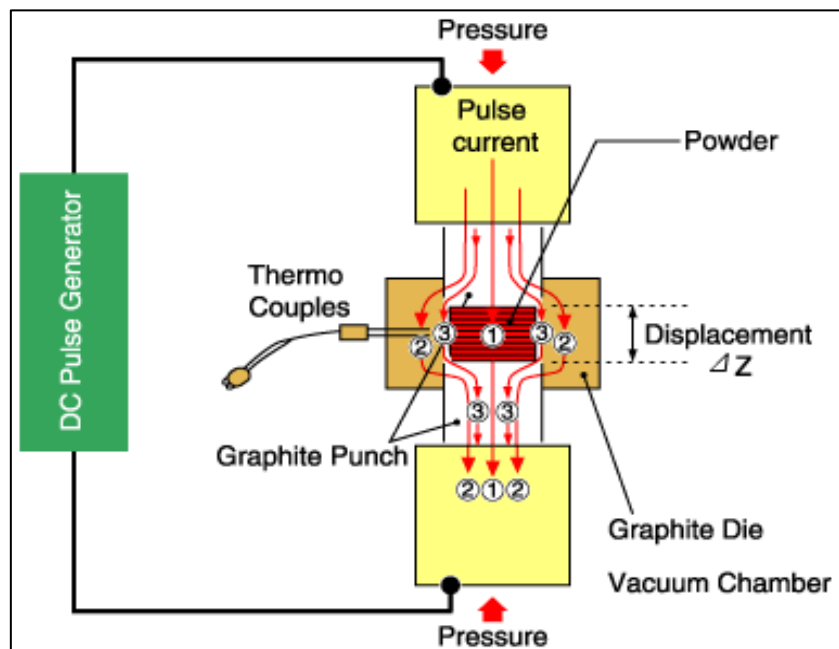


Figure 2.17. Schematic diagram of the flow of pulse discharge current during SPS, with (1) through the powders, (2) through the punches, and (3) through the die [2011Bas1].

Small capacitor banks form across the particle contact points, resulting in generation of electrical discharge across the capacitors. The electrical discharge generates sparks that lead

to localised heating of the particle surfaces [1999Tok]. This results in melting, and in some cases vaporisation, of the particle surface, followed by rapid solidification, initiating the formation of necks between the contacting powders [1999Tok, 2002Mam, 2006Son]. The necks grow rapidly due to the enhanced diffusion because of the high localised temperatures (Joule effect and electrical discharge), merging the particles together (Figure 2.19). Additionally, application of external pressure further improves the compaction, leading to complete densification in a few minutes [1999Tok, 2002Mam, 2006Son]. Due to the short sintering time and lower sintering temperature, SPS does not allow for continuous Ostwald ripening, preventing grain growth in the sintered compacts [1999Tok, 2008Hua].

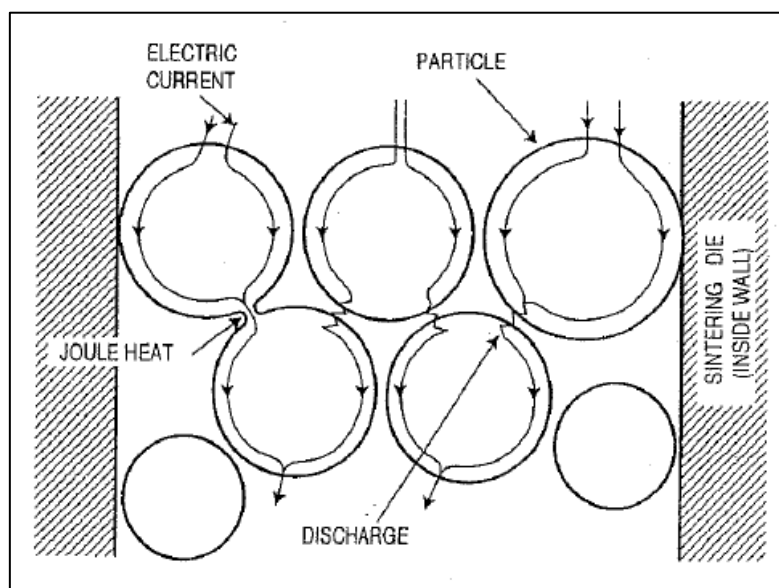


Figure 2.18. Schematic diagram of pulse current flowing through powder particles [1999Tok].

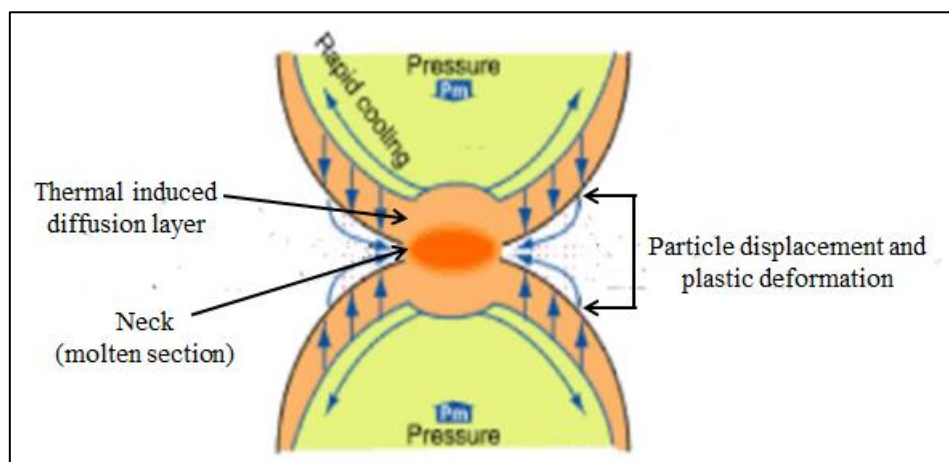


Figure 2.19. Neck growth at a particle contact point due to enhanced diffusion, from high localised temperatures and applied pressure [2011Bas1].

2.2.3.4 Other sintering methods

2.2.3.4.1 Hot isostatic pressing (HIP)

During hot isostatic pressing (HIP), the mixed powders are compacted in a die (as in cold isostatic pressing), dewaxed and conventionally sintered in a vacuum furnace. Then sintered products are placed in a HIP machine and an isostatic pressure of typically 35 MPa is initially applied, the pressure is then increase to the required HIP temperature (typically between 1360°C and 1420°C) and pressure increased to >70MPa [1998Upa]. Increased temperature and pressure ensures that the once the binder melts, it is forced into the all the voids in the material. Hot isostatic pressing's main advantage is to significantly reduce porosity, particularly where porosity is detrimental for the finished parts (reduces the toughness and strength) [1998Upa]. However, HIP has the main disadvantage of producing cemented carbides with inhomogeneous microstructures, due to the formation of cobalt lakes [1998Upa].

2.2.3.4.2 Sinter-HIP

The sinter-HIP process is similar to HIP, but the conventional sintering and hot isostatic pressing takes place in one cycle at lower pressures (6-10 MPa), lowering the procurement and operation costs. During the sinter-HIP process the three consolidation steps (dewaxing, conventional sintering and hot isostatic pressing) take place in one furnace. Prevention of oxygen pick-up and carbon control is done effectively, since these steps are carried out in one furnace [1998Upa].

2.2.3.4.3 Microwave sintering (MS)

Microwave energy is a form of electromagnetic energy with a frequency between 300 MHz and 300 GHz, and has been used for over three decades in several different applications, such as food processing, wood drying, rubber vulcanization, medical therapy and polymers manufacture [2010Ogh]. Using microwave technology in material science and processing is not new; it has been applied in process control, decomposition of gaseous species by microwave plasma, calcination, drying of ceramic sanitary wares, powder synthesis and sintering [1996Cla, 2006Agr]. Microwave processing of materials was mostly limited to ceramics, semiconductors, inorganic and polymeric materials until 2000 [2010Org]. There was a misconception that all metals reflect microwaves or cause plasma formation, and hence cannot be heated, except for exhibiting surface heating, due to limited penetration of the

microwave radiation [2010Org]. However, this phenomenon is valid only for sintered or bulk metals at room temperature, and not for powdered metals [2006Arg]. Now it is realised that microwave sintering can also be applied to powdered metals and ceramics [2010Org].

During conventional sintering (LPS), heating is achieved through mechanisms such as conduction, convection and radiation, while during microwave sintering (MS), heating is a process in which the materials couple with microwaves, volumetrically absorb the electromagnetic energy and transform it into heat [2010Ogh]. In conventional heating, the material surface is heated first, followed by the heat moving inward [2005Bre, 2010Ogh], creating a temperature gradient from the surface to the inside [2010Ogh]. The thermal conductivity of WC (~63 W/mK) is similar to Co (~69.2 W/mK) [2005Bre], and consequently both contribute equally to thermal conduction during conventional sintering. In MS of WC-Co, the source of heat is oscillation of free electrons at high frequency microwaves (2.45 GHz) in the components [2005Bre]. Although the Co Curie point (temperature below which it is ferromagnetic) is ~1131°C, the contribution of heat from oscillations of magnetic domains is very small because of its small hysteresis [2005Bre]. Volumetric heating during MS is initiated throughout the sample instantaneously as a result of the high frequency microwave energy interaction with both WC and Co [2005Bre]. Heat during MS is generated from within the material first, working outwards at very high heating rates, leading to complete densification within a few minutes, unlike during LPS [2005Bre, 2010Ogh]. Other advantages of MS include enhanced diffusion, lower sintering temperatures, reduced energy consumption [2010Ogh] and no geometrical limitations [2012Shi].

There are two critical components of the microwave furnace which ensure effective heating during sintering; the insulation box and susceptors [2012Shi]. The insulation box consists of a small chamber fabricated from low density rigid insulation board. Low density and very low dielectric loss are necessary to ensure that the box will allow microwaves to pass through with little interaction, allowing the material to heat up in the furnace [2012Shi]. Thus, the box acts as an oven which allows microwaves to pass through, but contains the heat generated by its contents [2012Shi]. The susceptors are made of a material which absorbs microwaves at room temperature and acts as heating elements, which “boost” the temperature until the dielectric loss in the material is high enough that it couples directly with the field. For example, when MS zirconia powder using silicon carbide susceptors, the powder will heat primarily by radiation from the SiC, until it reaches approximately 600°C, then the zirconia couples preferentially with the electromagnetic field and heats volumetrically [2012Shi].

2.2.3.4.4 High frequency induction heat sintering (HFIHS)

High frequency induction heat sintering (HFIHS) is a recent technique capable of consolidating ceramics and metallic powders to near theoretical density [2006Kim2, 2012Shi, 2013Zak]. The HFIHS technique is a rapid sintering process (dwell time of 1-2 minutes) [2006Kim2], normally used for production nanostructured cemented carbides and ceramics [2013Zak]. It is similar to hot pressing, which is carried out in a graphite die, but heating is accomplished by a source of high frequency electricity which drives a large alternating current through a coil (also known as the work coil) [2012Shi]. The current passed through the coil generates an intense and rapidly changing magnetic field within the work coil. Thus, the coil acts as a heating source for the sample [2012Shi]. The alternating magnetic field can also induce current flow in the sample as a secondary source of heat, if it is conductive [2012Shi], resulting in the sample being heated from both the outside and inside. The arrangement of the work coil and the sample can be thought of as an electrical transformer. The work coil is like the primary, where electrical energy is input, and the sample acts as the single turn secondary which is short-circuited [2014URL]. This causes large currents to flow (eddy currents) through the conductive sample. Additionally, the high frequency used in induction heating applications gives rise to a phenomenon called the skin effect [2014URL], which forces the alternating current to flow in a thin layer towards the sample surface, increasing the effective resistance of the sample to the passage of the large current. The increased resistance significantly increases the heating effect caused by the current induced in the sample [2014URL].

Induction frequency heat sintering has several advantages over convection sintering, such as being a non-contact technique, which provides localized heating through custom-designed coils [2006Kim2, 2012Shi]. The heat is transferred to the material through electromagnetic waves, and the heating process does not contaminate the material while being heated [2012Shi]. The process is energy efficient, converting up to 80% of the expended energy into useful heat to save costs [2012Shi]. It allows the right amount of heat to be applied exactly where it is needed for an exact period of time, ensuring rapid and controlled sintering [2013Zak], accurate performance, increased production and reduced distortion [2012Shi].

2.3 Mechanical properties of sintered cemented carbides

Each step during powder metallurgy of WC-cemented carbides has a significant effect on the mechanical properties of the final product. Thus, mechanical properties are used as quality control measurements for the cemented carbide manufacturing process [1975Bro].

2.3.1 Density

Densification is achieved via the elimination of porosity during sintering, and can be used as an indication of the effectiveness of the sintering process. The density of a correctly sintered sample will be close to the theoretical density (the density that the sample would have if no voids were present) [1991Jen].

2.3.2 Hardness

Hardness is the resistance to plastic deformation [1932AST]. It is one of the most critical requirements for cemented carbides applications [1975Bro]. Hardness gives an indication of the nature of the composition and microstructure of the WC-cemented carbide, since it varies with amount and distribution of the binder, WC grain size and degree of porosity [1975Bro]. Poor densification lowers the hardness of the cemented carbides [1995Ban]. Lee and Gurland [1978Lee] related the hardness of WC-cemented carbides to the microstructure by developing a model that took account of the volume fraction of constituents, binder mean free path, WC grain size and degree of contact between carbide grains. They proposed Equation 2.15:

$$H_{cc} = H_{wc}V_{wc}C + H_b(1-V_{wc}C) \quad (\text{Equation 2.15})$$

where H_{cc} is the hardness of the cemented carbide, H_{wc} is the hardness of the WC phase, V_{wc} is the volume fraction of the WC phase, C is the WC contiguity and H_b is the hardness of the binder phase. Contiguity is the ratio of carbide/carbide interface area to the total interface area, and hence is a measure of the degree of contact between WC grains in the microstructure [1966Suz]. The hardness of the WC phase (H_{wc}) and binder phase (H_b) are dependent on WC grain size (d) and binder mean free path (λ), as shown in Equations 2.16 and 2.17 [1978Lee]:

$$H_{wc} = 1382 + \frac{23.1}{\sqrt{d}} \quad (\text{Equation 2.16})$$

$$H_b = 304 + \frac{12.7}{\sqrt{\lambda}} \quad (\text{Equation 2.17})$$

Mean free path is the arithmetic mean of the distance from one carbide-binder interface to another, measured across the binder phase [1978Lee]. Hardness of WC-cemented carbides decreases with increased temperature above approximately 600°C [1967Wes]. The ability of WC-cemented carbide to retain its hardness at elevated temperatures is known as hot hardness [1967Wes], and hardness increases with reduction in both WC grain size and binder content. Additions of TiC, TaC and NbC improve the resistance to plastic deformation and rate of strength loss with increased temperature [1982Suz]. When added, these cubic carbides do not exist as individual mono-carbides, but as complex solid solutions, i.e. (W,Ti)C, (W,Ta,Nb)C or (W,Ta,Nb,Ti)C, that significantly increase the hot hardness [1982Suz]. These complex solid solutions are not wetted by Co as well as WC, resulting in the formation a chain-like structure, and this morphology is believed to retard WC grain boundary slipping during high temperature deformation [1982Suz]. Due to this, WC-cemented carbide cutting tools with multi-carbides have higher resistance to cutting edge deformation during cutting operations [1982Sar]. Addition of Cr₃C₂ grain growth inhibitor also improves the hot hardness [1986Cha].

2.3.3 Fracture toughness (K_{1C})

Fracture toughness is the resistance of the material to crack propagation and is independent of specimen size, geometry and finish [1977BS]. The term K_{1C} is used to represent fracture toughness, and it refers to the plain strain fracture toughness [1977BS]. It is the critical value of stress intensity factor (K_C) at a crack tip required to produce catastrophic failure under simple uniaxial loading (mode 1) [1977BS, 2005Sha]. Fracture toughness is generally inversely related to hardness, and increases with increased binder mean free path (λ) [1979Pet]. The mean free path increases with increased binder amount and carbide grain size [1976Che, 1979Pet]. Poor densification lowers the K_{1C} , since pores act as crack initiation and/or crack propagation sites [1974Ram, 1976Che].

At elevated temperatures, K_{1C} does not vary significantly until about 600°C, at which it increases [1984War]. However, in the case of additions of TiC, TaC and NbC, the increase in K_{1C} begins at about 700°C [1984War]. The increased K_{1C} is due to increased local plasticity at the crack tip, due to decreased hot hardness around the same temperature, as well as crack healing and blunting at the high temperatures [1984War]. In the case of WC-Co, an additional reason for increased toughness is the hexagonal to cubic phase transformation of the Co at the crack tip at elevated temperatures, increasing the ductility [1998Upa].

2.3.4 Transverse rapture strength (TRS)

Transverse rapture strength is a measure of the ultimate strength property and is used as a standard in cemented carbides. It is a combination of shear strength, compressive strength and tensile strength, and hence is used a general measure of the toughness of WC-cemented carbides [1963Gur, 1997Luy]. Toughness is a measure of the maximum energy a material can absorb before actual fracture or failure takes place [1963Gur]. Transverse rapture strength is also useful for detecting defects such as porosity [1975Luy], since WC-cemented carbides are intrinsically very strong, but the theoretical strength is not always achieved in practice, due to surface and internal defects [1975Bro, 1975Luy]. These defects act as stress concentration points when the material is loaded, resulting in premature failure, because of local plastic deformation at the defects, while the average applied stress on the rest of the material is well below the critical value [1975Luy]. Hence, TRS fracture load is dependent on the intrinsic strength of the cemented carbide, as well as the nature and distribution of defects. Generally, fracture starts from crack-like defects (e.g. inclusions, pores and other microstructure imperfections) [2010AST, 2013Cia], and the size of the largest crack determines the strength [2005Dez]. Since the size of the largest defect in different samples of the same composition varies, a large scatter of TRS values is normally obtained [2005Dez]. The probability of failure depends on the applied load and the sample volume, since different volumes will have different amounts and sizes of defects [2013Cia, 2005Dez]. Although the TRS is normally taken as the average of the scattered values [ISO2009], the actual strength is not a single value, but should be described by a suitable distribution function that accounts for the effects of the applied load and volume of sample [2005Dez]. Weibull distribution [1951Wei] is used in most cases, because of its accurate failure analysis and risk predictions [2004Cia, 2005Dez, 2013Cia]. The transverse rapture strength (TRS) can be determined by the “ball-on-three-ball” (B3B) method. The B3B test is a biaxial strength test that is applicable to specimens with different shapes (discs, plates etc.) and sizes [2002Bör]. Biaxial strength testing gives a more realistic indication of the material strength than uniaxial test methods, such as bending tests [1999Mor]. Additionally, the B3B test has the advantages of minimum variation in results due to small geometric inaccuracies of the specimen or test assembly, low influence of friction, and edge defects are not relevant [2004Bör1].

2.3.5 Wear resistance

Cemented carbides are widely used for tribological applications such as cutting, mining, drilling and metal forming, due to their high hardness and wears resistance [1988Gur,

1996Bha, 2006Kim]. Wear resistance generally increases with increased hardness [2004Luy], although not always. As machining tools, WC-cemented carbides fail due to plastic deformation, fracture and wear. During the machining process, the tool cutting edge is subjected to substantial compressive and shear stresses, high temperatures (close to 1000°C) and very steep temperature gradients in the order of 1°C/μm. These result in various wear processes [1976Lar], and the three main types of wear mechanism normally responsible for tool wear are abrasive wear, attrition wear and diffusion/chemical wear.

2.3.5.1 Abrasive wear

Abrasive wear occurs when a hard particle is rubbed across a surface resulting in formation of craters and grooves due to material pull-out from the surface [1976Lar]. Abrasive wear is closely related to the hardness of the cemented carbide and is affected by composition and microstructure [1973Lar, 2004Luy]. Abrasive wear depends on two main factors, the hardness of the abrasive material relative to the hardness of the WC-cemented carbide [1979Lar] and the mean free path of the WC-cemented carbide [1973Lar].

Generally, abrasion occurs by pushing hard asperities into a softer material [2011Bas3]. The most common type is when hard asperities slide over a softer surface, damaging the contact surface by plastic deformation. The hard particles could be hard inclusions and/or reaction products between the wear debris (formed during sliding) and the atmosphere [1998Gat, 1999Bhu, 2011Bas3]. These harder asperities deform the softer material and cause scratches in the surface. When the wear debris form chip-like shapes, the physical mechanism is referred to as the cutting mode, but when asperities do not form wear debris, and instead leave grooves on the surface [1987Gah], this is known as ploughing [2011Bas3]. During ploughing, some material is trapped at the edges of the grooves, and eventually forms new wear debris after more sliding passes. The debris undergoes plastic deformation and strain hardening, then becomes another source of abrasive debris. These two forms of abrasion (cutting mode and ploughing) are typically observed in non-brittle materials, such as most metals [2011Bas3].

Abrasive wear in brittle materials occurs due to the lack of plastic deformation, leading to cracking [2011Bas3]. Depending on the severity of the contact, the cracks can go deep into the subsurface and form small local cracks oriented in various directions, leading to large wear losses. Abrasion in multiphase materials with a soft matrix embedding hard grains (e.g. cemented carbides) occurs when a hard asperity sliding over a surface can interlock with one

of the hard and/or large grains [1998Upa, 2011Bas3]. If the strength of the hard asperity is large enough, it can pull out the grains, leaving large pits on the surface. These pits act as stress concentrators and form potential sites for progression of surface damage during sliding. Abrasive wear of cemented carbides depends on two main factors, the hardness of the abrasive material relative to the hardness of the WC-cemented carbide [1979Lar] and the mean free path of the WC-cemented carbide [1973Lar]. If the abrasive material is harder than the WC cemented carbide, it acts like a cutting tool, forming craters or grooves on the cemented carbide surface. The material is removed by gross plastic deformation, leading to extensive WC grain fragmentation on the surface and on the extruded material [1976Lar]. However, if the abrasive material is relatively soft compared to the WC cemented carbide, it cannot indent the surface; instead it slides on the surface under considerable load and high frictional forces [1973Lar, 1976Lar, 1998Upa]. This leads to slight displacement of the carbide grains, resulting in gradual extrusion of the softer binder phase. As the binder is preferentially pulled out, the compressive stresses in the WC grains brought about by the difference in contraction between the carbide grains and the binder during cooling after sintering are gradually relaxed, facilitating carbide grain fragmentation [1973Lar]. Increased mean free path reduces the abrasive wear resistance, due to the increased number of hard abrasive particles of a size capable of direct contact with the binder, resulting in increased binder pull-out [1973Lar]. The binder mean free path increases with increased binder content [1976Che, 1979Pet]. Therefore, abrasion resistance can be increased through reduction in WC grain size (higher hardness) [1951Hal, 1953Pet] and reduction in binder content (smaller binder mean free paths) as shown in Figure 2.20 [1973Lar].

Several topographical features are observed on the wear track due to abrasion, and these include scratches and grooves, cracks, wear debris and tribochemical layers (oxide layers) [2008Kum, 2011Bas]. Scratches and grooves form as a result of fragmentation and pull-out of WC grains, displacement of the ductile binder [1998Upa, 2011Bas] and break up of asperities that are trapped between the sample and the abrasive body, and rub against the sample surface [1999Bhu, 2011Bas]. Cracks occur due to high localized stress from Herzian pressure (contact pressure at the sample/abrasive body interface) [1988Las, 2004Pir], which leads to intergranular and transgranular fracture, particularly for the WC cemented carbides with low fracture toughness [1990Spi]. Wear debris forms from the breaking up of asperities at contacting surfaces and fragmentation of WC grains [2011Bas]. High Hertzian pressures result in increased friction-induced contact temperatures ($\sim 500^{\circ}\text{C}$) and compaction of wear

debris, leading to the formation of a tribochemical layer [2008Kum]. The tribochemical layer mainly contains oxides such as WO_3 from the cemented carbide debris [2011Bas] and/or SiO_2 [2003Jon] or Fe_2O_3 [2008Kum] in the case of Si_3N_4 and Fe abrasive bodies, respectively. The tribochemical layer normally reduces the friction, giving lower wear rates, particularly in humid environments [2003Jon, 2008Kum, 2011Bas]. The wear depth is also an important parameter of the wear track topography, and it increases with increased Hertzian pressure, and decreases with increased cemented carbide hardness [2011Bas].

For abrasive damage to occur, one material must be substantially harder than the other; at least a 20% difference in hardness is required for effective abrasion [2011Bas]. However, if the difference is larger, the abrasive wear mechanism will change into complete plastic deformation and no debris will be formed. Hence, there will be no material loss (no wear), although significant surface damage will occur [2011Bas]. Abrasive wear can be classified as two-body and three-body wear [1998Gat, 1999Bhu]. When only two bodies are in relative motion and one is substantially harder, such abrasive damage is referred to as two-body abrasion. This takes place during mechanical operations, such as grinding, cutting and machining [2011Bas3]. In three-body abrasion, hard abrasive particles trapped between the two moving bodies act as an interfacial third body and are responsible for wear on both of the surfaces [1998Gat, 1999Bhu]. Three-body abrasion occurs in abrasive-free lapping and polishing [2011Bas]. Wear in three-body abrasion is about one to two orders of magnitude smaller than in two-body abrasion [2011Bas], because the third body acts on the minimum energy principle, and tends to find the “easier” way between the two contacting surfaces [2011Bas]. The hardness, shape and contact angle of the asperities with the sample surface are also critical parameters in abrasion [2011Bas]. For a given hardness, the sharpness of the contact angle will determine the mode of deformation, e.g. cutting, wedge formation or ploughing [2011Bas]. The toughness or brittleness of the WC cemented carbide will also affect the extent of the deformation and the shape of the scratches or grooves [2011Bas].

2.3.5.2 Attrition wear

Attrition wear is also known as adhesive wear, is the process in which micron-sized particles are detached from the tool surface and carried away by streams of workpiece material during cutting [1976Lar, 1979Tre]. It is as a result of cold welding (adhesion) of the workpiece onto the cutting tool surface, and mainly occurs during metal cutting, particularly at low cutting speeds [1979Tre]. Due to the high pressures generated at the interface between the cutting edge and the workpiece, intermittent welding between the tip and chips takes

place. Eventually, the chips break from the workpiece, carrying away the particles from the cutting tip with them [1979Tre]. This wear occurs mainly by plucking away of complete WC grains. Attrition wear rate decreases with reduction in grain size [1979Tre].

The adhesion is caused by surface interactions and welding of asperity junctions at the sliding contact interface [2011Bas]. This interfacial adhesion may be by covalent, ionic, metallic and/or van der Waal bonds [2011Bas]. If the bonds at the weld junctions are stronger than in the workpiece bulk material, a part of the weaker bonded material will detach from the bulk and become attached to the sliding counter-body [2011Bas]. This results in the formation of irregularities and pits on the surface that loses material, while the counter-body gains a transfer film. The sliding interface of these two bodies becomes rough and the components (e.g. cutting insert and workpiece) lose their dimensional accuracy and tolerances [2011Bas]. The transfer films may grow depending on the length of the sliding period and can be eventually removed as wear particles; they often work harden and also result in abrasive action [2011Bas].

Adhesion during attrition wear is stronger in contacts with chemically similar materials and those with good solubility, where atoms of the two bodies can easily interact [2011Bas]. Toughness is another factor which strongly affects attrition wear [2011Bas]. Materials that tend to deform easily will attach to each other, leading to the generation of a larger contact surface where the bonds which need to be broken during sliding will form. This known as junction growth [2011Bas]. Metals, particularly those with weak contaminant layers (oxides) or those that do not form oxides, have also been reported to experience strong adhesive wear [2011Bas].

2.3.5.3 Diffusion/Chemical wear

In diffusion/chemical wear, the tool shape at the cutting edge is changed due to diffusion between workpiece and the cutting tool [1979Tre]. It results in dissolution of the cutting tool surface by the chip material flowing over it. Diffusion wear is dependent on the solubility between the workpiece and the cutting tool, as well as the interface temperature during cutting. The interface temperature is proportional to the cutting speed, thus diffusion wear is a major factor limiting the cutting speeds within the carbide industry [1985Kra]. Addition of TiC to WC-Co improves the diffusion wear resistance, since it results in the formation of a (W,Ti)C solid solution which has a much higher chemical stability than WC [1979Tre].

Diffusion wear is much higher during high speed machining (HSM) (500-5000 m/min) compared to classical machining (≤ 300 m/min), and this is due to the way the heat is generated and distributed between the insert, chips and the workpiece [2008Cal]. Generally during HSM, because of the adiabatic nature of the cutting process, i.e. occurring at speeds and feeds exceeding the speed of propagation of heat through the workpiece, most of the heat is not dispersed into the depth of workpiece, but is instead retained in the chip/cutting edge interface [2008Cal, 2009Zha]. This heat significantly increases when machining a workpiece with low thermal conductivity, e.g. Ti and its alloys, and temperatures as high as 1000°C have been reported [2008Zha]. The high temperatures generated facilitate diffusion between the cutting edge and the workpiece [1998Upa, 2008Abd]. During HSM of steel by WC-cemented carbides, the WC grains dissolve into the workpiece blunting the cutting edge [1998Upa, 2008Hua2]. Chemical wear is also observed during machining of Al and its alloys, and this is enhanced by the good solubility of Al in fcc Co [2008Cal]. During machining, when the cutting edge/chip interface temperature is $\sim 300^\circ\text{C}$ and higher, Co undergoes a phase transformation from hcp to fcc [1998Upa], and the fcc allotrope has a higher Al solubility [2008Cal]. This solid solution is brittle and when it precipitates, it causes disintegration of the cutting edge [2008Cal].

2.3.6 Magnetic properties

The ferromagnetic properties of the binder phases (cobalt, nickel and iron) in the WC-cemented carbides make it possible to perform quick non-destructive quality control tests such as coercivity and magnetic saturation tests [1975Bro]. The coercivity and magnetic saturation tests give information about the effectiveness of the sintering process and some information about the microstructure [1944Ker, 1975Bro].

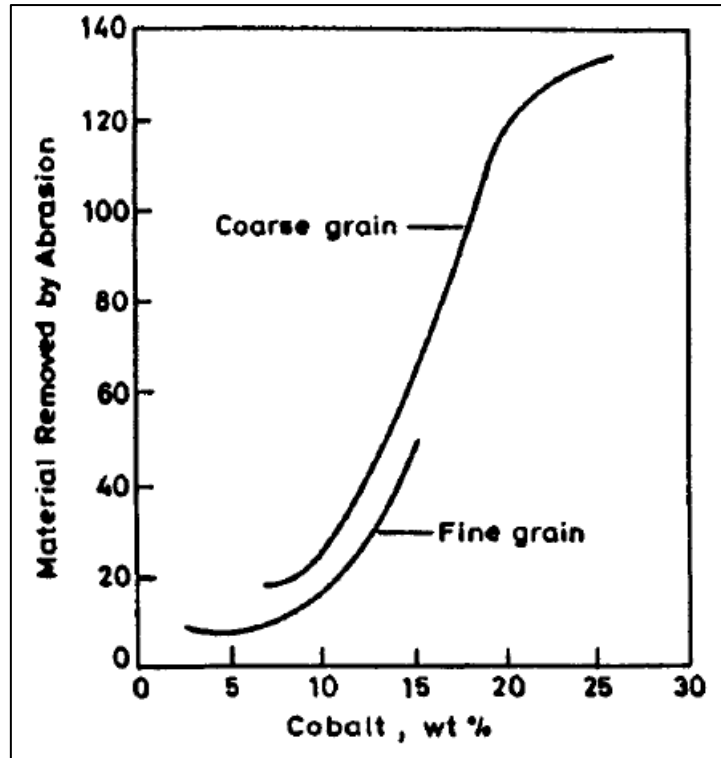


Figure 2.20. Effect of grain size and Co content on the abrasion resistance of WC-Co [1998Upa].

2.3.6.1 Coercivity (H_c)

Coercivity is the magnetic field required to demagnetize a material after it has been magnetized up to saturation [1975Bro, 1997Luy]. Coercivity increases with decreased binder mean free path, and hence is used as an indirect measure of the degree of sintering, amount of binder, binder distribution and WC grain size [1979Roe]. Generally, larger WC grains have thicker binder mean free paths between them, and vice versa for finer WC grain [1979Roe]. Therefore, for WC-Co, coercivity is high when the Co content is low and/or WC grain size is fine, and low when the Co content is high and/or the WC grain size is coarse [1979Roe, 1997Luy]. Free carbon, which also leads to increased WC grain growth [2002Wit], also reduces the coercivity.

2.3.6.2 Magnetic saturation

Magnetic saturation is the maximum magnetization that can be induced in a material by a strong magnetic field [1975Bro]. For WC-Co, the maximum magnetization induced in Co decreases linearly with increased W solubility, and is not affected by the amount of C in the solution. However, the solubility of W in the Co is dependent on the amount of C in the (Co) [1975Bro, 1997Luy]. The lower the total C content in the WC-Co cemented carbide, the higher the W solubility in (Co), reducing the magnetic saturation value [1975Bro, 1997Luy].

Very low magnetic saturation values are associated with eta phase in the microstructure. Thus, magnetic saturation is an indirect measure of the C content in the cemented carbide.

2.3.7 Thermal shock resistance

Thermal shock resistance is the resistance to fracture when a material subjected to sudden transient changes in temperature [1955Kin]. It increases with increased fracture toughness and with reduced hardness [1968Kre]. Hence, it is dependent on the microstructure of the cemented carbide. Increased binder amount and binder mean paths increases resistance to thermal cracking [1968Kre, 1998Upa].

2.3.8 Modulus of elasticity (Young's modulus)

Modulus of elasticity is a measure of the stiffness and can be used as an indirect indicator of the bonding in the material [1977Pag]. The modulus of elasticity decreases with decreased densification and reduced wetting of the WC grains by the binder [1995Ban, 1998Upa].

2.4 Manipulation of WC-cemented carbides to achieve improved mechanical properties

The desired mechanical properties of the end-product are dependent on the application. Therefore, through powder metallurgy, manipulation of WC-cemented carbides to achieve the desired properties is possible by [1975Bro]:

- Alteration of fractional compositions of the hard and the binder phase,
- Partial substitution of WC-phase,
- Control of WC grain size,
- Alteration of binder-phase, and
- Control of sintering temperature and time.

2.4.1 Alteration of fractional compositions of the hard and the binder phase

Reduced binder content with increased WC fraction generally yields high hardness due to increased fraction of the harder phase [1975Bro, 2004Luy]. Higher fracture toughness is achieved with increased binder fraction, as the binder provides the ductile matrix [1975Bro, 2007Pet]. Thus, by simple manipulation of the two constituent phases, different mechanical properties can be achieved.

2.4.2 Partial substitution of WC-phase

To improve the hardness WC-cemented carbides at elevated temperatures, partial substitution of WC is done with different carbides such as TaC, TiC and NbC. These carbides form complex solutions with WC that inhibit WC-grain boundary sliding, preventing deformation. Carbides like TiC can also be added as secondary hardening phases, since its hardness is higher than WC by about 5 GPa [1983Bro, 2007Kim]. Titanium carbide is also added to WC-cemented carbides because it improves the chemical stability of WC, limiting diffusion wear during application [1979Tre]. However, although these carbide additives have some beneficial effects on the mechanical properties, their addition should be kept as low as possible, since they lower the strength of the hard metal [1975Bro, 1994Bha].

2.4.3 Control of WC grain size

The WC grain size is the most carefully controlled variable besides carbon control in the production of cemented carbides. From ore processing to the final sintering, each step has an influence on the carbide grain size [1975Bro]. Up until milling, the grain size can be effectively controlled, although during sintering, grain growth occurs due to the driving force for the reduction of interfacial energy [1960Kin].

Generally, WC-Co based cemented carbides contain 3-30wt% binder content and the WC grain size ranges from submicron level to a few microns [1975Bro]. Recent advances in the technology for synthesis of nano-sized particles has led to the development of nano WC and Co powders [1992McC, 1993Fan, 2003Zha], resulting in higher hardness and improved wear resistance, due to finer WC grains and Co binder strengthening from increased W dissolution [1988Alm, 2003Seo, 2008Bon]. Furthermore, reduction in hardness with increased binder content is reduced in cemented carbides with finer sized WC than micron-sized WC [1999Mil, 2003Seo]. Compared to micron-sized cemented carbides, sintering of nano-sized powders has an additional problem of retaining the nano-scaled grain size upon achieving full density because of rapid grain coarsening [1993Fan, 1995Sur, 1996Mal], which increases with increased sintering temperature and time. Additionally, cemented carbides are consolidated by LPS, typically at high sintering temperatures ($\sim 1400^{\circ}\text{C}$) and for long sintering dwell times (~ 75 minutes), resulting in increased grain growth of nano powders [1996Gro]. Grain growth during sintering is mainly attributed to two main mechanisms, solution-precipitation and coalescence [1959Kin, 1960Kin, 1995Sch, 1998Lau].

2.4.3.1 Grain growth due to solution-precipitation

As the sintering temperature is reached (above the Co-W-C eutectic temperature), continuous solution of the finer WC grains into the liquid phase takes place, because of their high surface energies, and at the same time, deposition by reprecipitation on the existing larger grains occurs, as discussed in Section 2.2.3.2.2. This leads to WC grain growth, and the grain size increases with increased sintering temperature and time (Equations 2.13 and 2.14). Once this stage is over, the grain size is more uniform, and further grain growth is slower, since most of the fine grains have already dissolved and been reprecipitated on the large grains [1998Upa, 2006Her]. Hence, cemented carbides with large grain size variation are more sensitive to this process, because of the higher surface energies of the fine grains and the presence of large grains on which reprecipitation occurs [1998Upa]. Compositions with large WC grains ($>3\mu\text{m}$) with uniform size show negligible change in grain size after LPS [1998Upa].

The amount of C and Co in the cemented carbide also affects solution-precipitation grain growth. Increased C content lowers the eutectic temperatures [1978Exn], increasing the amount of liquid phase required for solution-precipitation at lower temperatures, resulting in increased grain growth [1970Lar]. Grain growth is strongly dependent on the amount of liquid phase available to enable transfer of material from fine to coarse grains. At low binder contents, uniform binder distribution is difficult to achieve, resulting in grain growth mainly around the binder pools in the microstructure. This leads to non-uniform grain growth [1998Upa].

2.4.3.2 Coalescence

Solid state grain growth takes place via the coalescence mechanism. It involves the merging of two neighbouring grains by the formation of contacts between grains (necking) and subsequent elimination of the continuous boundaries by movement of grain boundaries [1959Kin, 1977San]. Generally, grain growth takes place either by amplification or by multiplication processes [2008Wan]. Amplification is the steady outward growth of a crystal by deposition of new atoms on its surface, while multiplication involves stacking up or merging of grains. Therefore, solution-precipitation (Ostwald ripening) is an amplification process, while coalescence is a multiplication process [2008Wan].

The rapid grain growth of fine WC powders (ultra-fine and nano) has been reported to occur in the early stages of sintering (solid state), before the liquid phase is formed [1977San, 1995Fan, 2005Fan], and this is due to coalescence. Grain growth as a result of coalescence

increases with increased temperature (Figure 2.21) and time, with temperature being more dominant [2008Wan].

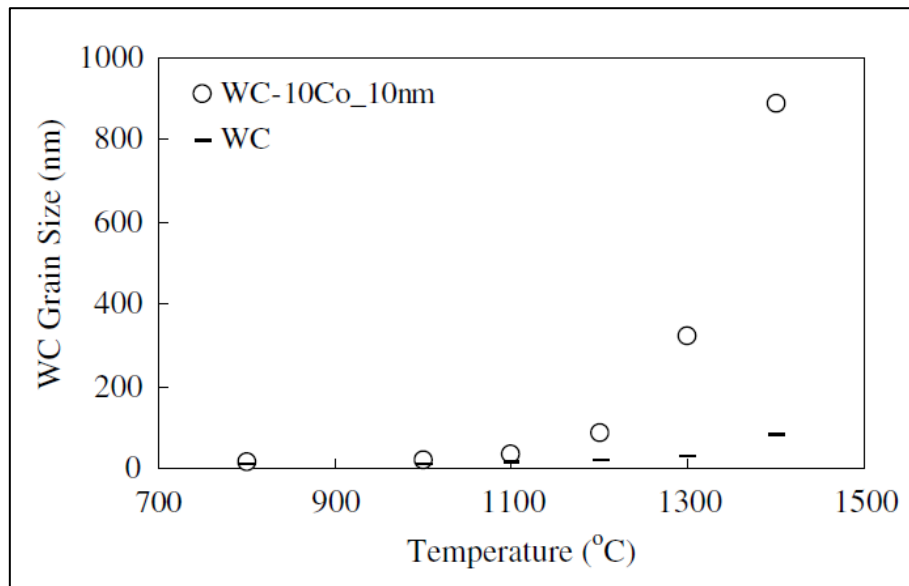


Figure 2.21. Effect of temperature on grains size of nano WC during sintering [2008Wan].

2.4.3.3 Grain growth inhibitors

Reduction in carbide grain size can be achieved in different ways, one of which is via the introduction of a grain growth inhibitor. The grain growth inhibition can be attributed to several different mechanisms. Two key possible mechanisms are:

- Reduction of pore size and grain boundary mobility, and
- Reduction of interface energy between the WC/WC and WC/binder phase.

2.4.3.3.1 Reduction of pore size and grain boundary mobility

During the later stages of sintering, at about 94% densification, the interconnected pores become unstable and break up into isolated pores [1991Jen]. If these pores are either too small to “hold on” the grain boundaries (gbs) or too large to move along with the grain boundaries, they separate from the gbs and become trapped inside the grains. Pores shrink at a much slower rate inside the grains than at the grain boundaries, because bulk diffusivity is much slower than grain boundary diffusivity. These trapped large pores result in larger grains. When additives are introduced, they enhance the transport of vacancies from the pores inside the grains to the grain boundaries (by enhancing bulk diffusivity), thus reducing the size of the pores. The additives also reduce the mobility of the gbs, allowing the pores to stay

in the gbs, leading to faster pore shrinkage rate. This results in the formation of smaller grains [1991Jen].

2.4.3.3.2 Reduction of interface energy between the WC/WC and WC/binder phase

The difference in the interface energy at the WC/WC and WC/binder interfaces is the driving force for grain growth, as it determines the rate of grain growth [1966Exn], and if reduced, the carbide grain size can also be reduced. Grain growth inhibitors (GGIs) segregate at the WC/WC and WC/binder interfaces during sintering, altering the interface energies by interfering with the interfacial dissolution-nucleation-reprecipitation process [1966Exn]. The GGI precipitate or form bonds with carbon, tungsten or even the binder at the WC/WC and WC/binder interfaces, which reduces interface energy for solution re-precipitation of the WC grains, resulting in smaller WC grains [1966Exn, 2002Wit, 2005Mor].

Different grain growth mechanisms have been suggested to explain how GGIs work. These include face-oriented deposition (interface alloying), which involves blocking of active grain growth centres of the crystals at the interface [1995Sch], as well as face-specific absorption that results in decreased interfacial energies. Retardation of grain growth is also achieved through the presence of GGIs in the binder, reducing the W flux through the binder, and limiting the amount of W available for Ostwald ripening [1998Oka].

For WC-cemented carbides, the following additives have been reported [1972Hay, 1975Bro, 2007Sun] to have good grain growth inhibition: VC, Cr₃C₂, TaC, NbC, TiC and ZrC. The choice of the inhibitor is based on the overall effectiveness, which has been shown to be VC > Cr₃C₂ > NbC > TaC > TiC > ZrC [1972Hay, 1998Upa, 2002Wit]. Addition of up to 1wt%VC results in superior hardness and wear resistance than WC-Co [1972Hay, 1998Luy, 2005Mac]. Furthermore, large additions of TiC and TaC also resulted in increased hardness and wear resistance [1998Upa, 2007Has].

2.4.4 Alteration of binder-phase

Cobalt has been the preferred binder since the inception of WC-cemented carbides in 1923 [1987Pen]. It is present in the microstructure as a continuous thin film separating the carbide grains, improving the toughness of the cemented carbide [1988Roe]. Cobalt is the most used metal binder because of its very good solubility of WC at low and high temperatures, and good wettability of WC [1987Pen]. Additionally, Co has very good comminution characteristics, giving better distribution during milling, and subsequent homogenous

distribution in the microstructure [1955Daw]. However, because of unstable market prices due to short supply, health hazards for plant maintenance personnel and limited corrosion resistance, alternative binders have been investigated [1987Pen, 2008Bon]. Alternatives to Co can be grouped into three categories: complete substitution, partial substitution and additives [1987Pen].

2.4.4.1 Complete substitution

Complete replacement of cobalt is possible by nickel and iron [1934Sch, 1987Pen, 1988Alm].

2.4.4.1.1 Nickel

Nickel does not undergo any phase transformations, and hence retains its ductile face centred cubic (fcc) structure at all temperatures [1962God, 1977Mos, 1987Pen]. Nickel also shows better resistance to chemical attack than cobalt in wet environments [1996Hum, 1997Hum, 1999Eng, 2000Eng1]. Furthermore, due to its more ductile fcc structure, Ni reduces loss of WC grains by extruding outwards to replace the eroded binder between the WC grains, improving the wear resistance [1987Pen]. However, conventionally sintered Ni binder cemented carbides have lower hardness than Co binder cemented carbides [1955Daw, 1985Vas, 1992Che], due to poor wetting of WC [1962Wha], higher plasticity and absence of the β - α phase transition [1962God, 1977Mos, 1985Vas, 1987Pen]. Complete densification of Ni bonded WC cemented carbides in conventional sintering is difficult, due to poor comminution during milling and poor wetting of WC [1955Daw]. The Ni fcc structure is more ductile and has a low work-hardening coefficient, and thus absorbs less energy in during milling than Co which consists of 40-60% hcp structure (and is more brittle). This lowers nickel's ability to be broken down and evenly distributed in the WC during milling, affecting the even distribution of the Ni-liquid phase required for densification during sintering [1995Sha]. The poor wetting of WC by Ni also affects the distribution of the liquid phase required for densification. The wettability of WC by the liquid phase is defined by the contact angle, θ , (ability of the liquid to spread on the surface) [1956Par]. Densification requires a low contact angle to ensure that the grains are pulled together [1956Par, 2009Ger]. The good wetting of WC by Co is due to the contact angle of 0° [1956Par, 2006Cha], while the poor wetting of WC by Ni is due to a large contact angle as shown in Figure 2.22. The contact angle can be altered by factors that affect solubility or surface chemistry. For

example, TiC has poor solubility in Ni, but the addition of Mo improves the solubility and hence reduces the contact angle from 30° to 0° [1956Par, 1998Bol, 2003Liu, 2009Ger].

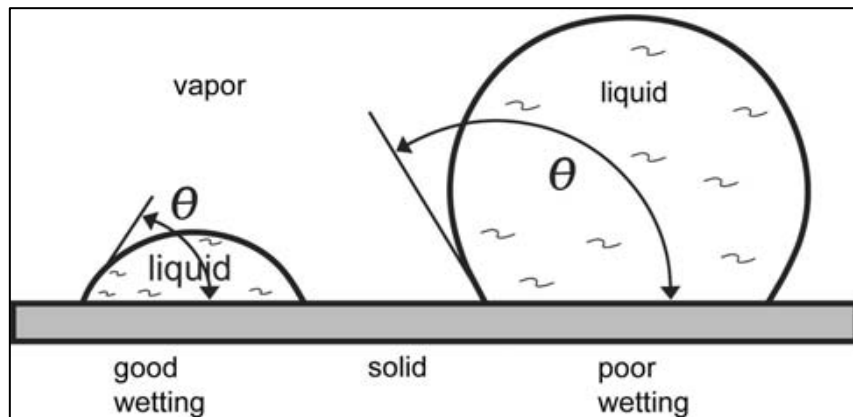


Figure 2.22. Contrast of wetting behaviour for a liquid on a horizontal plane, showing how a low contact angle supports wetting, while a high angle resists wetting [1956Par, 2009Ger].

2.4.4.1.2 Iron

Iron as a binder results in WC grain growth inhibition due to its high affinity for carbon during sintering, promoting increased hardness [1987Pen, 2002Wit]. Iron's high affinity for carbon results in the formation of stable metal-carbon bonds, impeding carbon transport and precipitation by increasing the activation energy for nucleation and growth of WC [2002Wit]. This increases the resistance to grain growth. The high affinity for carbon also promotes the formation of eta phase [1987Pen, 2002Wit]. The ease of oxidation of Fe in the atmosphere limits its applications as a binder [2002Wit, 2008Guo1].

2.4.4.2 Partial substitution

Partial substitution of Co can be done by addition of Ni or a combination of Ni and Fe.

2.4.4.2.1 Nickel with cobalt

Nickel addition to Co stabilizes the ductile fcc phase by reducing the fcc to hcp transformation temperature [1987Pen, 1998Upa]. Both thermal and stress induced transformation is suppressed during plastic deformation. This improves the toughness of the cemented carbide, resulting in longer service life [1955Daw].

2.4.4.2.2 Nickel-iron with cobalt

Partial substitution of Co with Ni and Fe improves the hardness and toughness of the binder phase [1987Pen]. The good mechanical properties of WC-(Fe-Co-Ni) cemented carbides are

brought about by the formation of a martensitic structure in the binder, with strength with high ductility [1987Pen]. Control of carbon content is critical, due to the presence Fe in the binder [1987Pen].

2.4.4.3 Additives

Addition of elements such as ruthenium and chromium improves the properties of the Co-binder. Ruthenium additions raise the fcc to hcp transformation temperature from 420°C to as high as 1050°C, effectively stabilising the harder hcp phase [1987Pen]. This improves the overall hardness of WC-Co cemented carbide. Addition of chromium improves the oxidation and corrosion resistance [1995Dan, 1998Upa], as well as increases the hardness and work hardening rate of Co [1987Pen, 1995Dan, 1998Upa]. Higher binder hardness results in improved abrasion wear resistance [1987Pen].

2.4.5 Control of sintering temperature and time

Factors that favour rapid densification such as rate of diffusion, solubility of WC in the binder, wetting of WC by the binder and amount of liquid phase present for secondary rearrangement of WC particles are dependent on the sintering temperature [1959Kin]. Thus, rapid densification in a short sintering time can be achieved by sintering at high temperatures due to the increase of the above factors. However, increased sintering temperatures results in coarsening of WC grains due to Ostwald ripening (solution reprecipitation) as shown in Equation 2.14 and coalescence as shown in Figure 2.21. Compared to LPS, during SPS, shorter sintering times and lower temperatures are used, resulting in finer grained microstructures with smaller and poorly distributed binder pools, increasing the hardness and lowering the fracture toughness [2008Hua1]. Depending on the desired mechanical properties, manipulation of sintering parameters can be done.

2.5 NbC addition to WC-Co

Niobium carbide has similar hardness and thermal expansion to WC [1992Suc], but has a significantly higher melting temperature (good for high temperature applications) and lower density [2008Hua1, 2008Hua2], as shown in Table 2.2. Small additions of up to 0.45wt% NbC to WC-Co effectively inhibit grain growth, increasing the hardness by up to 2GPa [2008Hua1, 2008Hua2]. It also increases the high temperature hardness, improving the deformation resistance of WC-based cutting tools [1982Suz], as well as reducing the coefficient of friction between the cutting edge and workpiece [1998Upa]. Additionally, NbC

improves the chemical stability of the WC-cemented carbide for applications where good chemical wear resistance is required [1985Kra]. However, Huang *et al.* [2007Hua1, 2007Hua2] showed that, compared to similar LPS WC-Co cemented carbides, NbC-Co cemented carbides had lower hardness and fracture toughness. The lower hardness was attributed to excessive coarsening of the NbC grains, due to the high sintering temperature (1360°C) and long sintering dwell time (60 minutes) during LPS.

This grain growth can be reduced through the use of SPS and addition of grain growth inhibitors such as Cr_3C_2 . Addition of Cr_3C_2 lowers the Co-W-C eutectic temperature [1999Car], reducing the densification temperatures, and thus minimising grain growth due to high temperatures. Chromium carbide also improves the hot hardness [1986Cha], abrasion and corrosion resistance. The lower fracture toughness was attributed to poor wetting of NbC by Co. Thus, good toughness can be maintained by partial substitution of WC with NbC, instead of complete substitution, retaining a considerable volume fraction of tougher WC-Co in the cemented carbide [2008Hua1].

2.6 WC-Ni bonded cemented carbides

Nickel has been studied as a potential replacement for cobalt due to its good properties (Section 2.4.4.1.1). However, because of its drawbacks such as poor wetting of WC, lower WC solubility and lower hardness because of its higher plasticity compared to Co, use of Ni bonded WC hard-metals still remains a challenge.

Poor wetting of WC by Ni lowers both the hardness and fracture toughness of the cemented carbide [1956Par, 1962Wha, 2008Guo1]. Poor wettability during liquid phase sintering lowers the capillarity force required for rearrangement of particles during densification. During secondary rearrangement, because of poor wetting, fewer WC particles dissolve into the binder, resulting in an inhomogeneous microstructure with large and poorly distributed (Ni) pools between a continuous WC skeleton [1956Hum].

This lowers both the hardness and fracture toughness [1956Par, 1962Wha, 2011Gen, 2013Gen]. Addition of Mo or Mo_2C improves the wetting of WC by Ni [1986Roe, 1998Upa], leading to better distribution of Ni in the microstructure and good mechanical properties. Molybdenum partitioning at the WC/Ni interface has been reported to promote a stronger carbide/binder interface [1986Roe], improving the hardness and fracture toughness. Molybdenum carbide is also a good grain growth inhibitor [1999Yao], increasing the

hardness of WC-Ni cemented carbides. The lower solubility of WC in Ni, and slightly higher sintering temperatures than for WC-Co can be used to achieve good densification [1988Alm].

Table 2.2. Comparison of mechanical and physical properties between WC and NbC [2008Hua1, 2008Hua2].

Properties	Carbide	
	WC	NbC
Hardness (GPa)	22.5	19.6
Elastic modulus (GPa)	696	340-580
Density (g/cm ³)	15.7	7.8
Melting temperature (°C)	2800	3600
Coefficient of thermal expansion (µm/m.K)	5.2	6.7

2.7 Mechanical properties for machining titanium

Titanium and its alloys are widely used in the aerospace industry due to their good combination of strength-to-weight ratio at elevated temperatures, fracture toughness and corrosion resistance [1955Sie]. They are also used in the medical industry as surgical implants, because of exceptional mechanical biocompatibility [1984Mye, 2008Nii]. Despite these good properties, production of Ti and its alloys is very expensive, due to poor machinability, originating from high chemical reactivity, low thermal conductivity and high strength at elevated temperatures [1955Sie, 1984Bom, 1986Dea]. Titanium is very chemically reactive and tends to weld on to the cutting tool during machining, resulting in chipping and premature tool failure [1997Ezu]. Since Ti has low thermal conductivity, up to about 80% of the heat generated at the tool/workpiece interface is conducted to the tool cutting edge, adversely lowering the tool life [1986Dea]. Due to the low thermal conductivity, low cutting speeds are used for machining Ti and its alloys, especially during milling, because of poor thermal shock resistance [1997Ezu, 2009Gin]. The higher temperature strength of Ti and its alloys results in high mechanical stresses at the cutting edge, due to resistance to deformation at high temperatures, leading to failure through mechanism such as abrasion [1997Ezu].

However, plain WC-Co cutting tools have been reported to have the best performance in almost all machining process of Ti alloys, while CVD coated carbides and ceramics perform poorly due to reactivity with Ti, low fracture toughness and poor thermal conductivity

[1997Ezu]. Thus, improvement of the mechanical properties such as hot hardness, abrasion and chemical wear resistance, fracture toughness and thermal cracking resistance of WC-cemented carbides would further improve their Ti machining performance, and lower the Ti production cost.

Therefore, mechanical properties for machining of Ti and its alloys can be improved by refinement of sintered WC grain size through use of fine WC starting powders, SPS and addition of GGIs, resulting in increased hot hardness and abrasion wear resistance. Addition of TiC and NbC improves WC chemical stability, and substituting the Co binder with Ni improves the hot hardness, thermal shock, impact and chemical resistance.

2.8 Approach of study

Using the information from the literature survey, the first part of this study was to investigate NbC content varying from 0 to 10 wt%, to attain compositions with optimum values of hardness and toughness, and to investigate NbC as a major carbide phase in WC-Co cemented carbides by varying the content from 20 wt% to 80 wt% NbC. Furthermore, through use of fine starting powders (submicron, ultrafine and nano), SPS and addition of Cr_3C_2 grain growth inhibitor, good mechanical properties were targeted.

The second part of the study involved development of WC-Ni cemented carbides with aim of attaining mechanical properties similar to WC-Co cemented carbides. This can be achieved by improvement of the hardness through use of fine starting WC powders (submicron, ultrafine and nano) and addition of grain growth inhibitors such as TiC, Cr_3C_2 and Mo_2C . Titanium carbide has a higher hardness than WC, and hence acts as a secondary hardening phase. Additionally, by SPS and optimising the amount of Ni binder, the (lower) hardness can be significantly increased, while maintaining good fracture toughness.

The third part of the study was to identify promising compositions from the WC-Co and WC-Ni cemented carbides and test their abrasion wear, thermal shock and impact resistance properties under aggressive conditions. These results were compared to LPS WC-10Co (wt%) and WC-9.3Ni (wt%) samples tested under the same milling conditions.

Chapter 3: Experimental procedure

In this chapter, the procedures used to produce the investigated WC-cemented carbides and the methods used to characterise their properties are described. The characterisation measurements included analysis from the starting powders to the finished sintered products. The consumables used for the production and testing of the investigated compositions are given in Table 3.1.

Table 3.1. Consumables and chemicals used in the production and testing.

Chemical/consumable	Source
99% pure Ethanol	MK LABS, South Africa
Poly ethylene glycol (PEG)	BASF, Germany.
5 mm Ø steel milling media	BMG, South Africa
7 mm Ø WC milling media	Pilot tools (Pty) Ltd., South Africa
SPS graphite punches and dies	SGL Carbon, South Africa
SPS graphite foils	SGL Carbon, South Africa
SPS carbon protective cloth	FCT, Germany
Diamond coated cutting wheel	Struers, USA
Mounting Polyfast	Struers, USA
Grinding wheels and polishing cloths	AKASEL, Denmark
Polishing lubricant and diamond suspensions	AKASEL, Denmark
Edge honing white fused Alumina-F60	Wester Mineralien, South Africa

3.1 Starting powders

The characteristics and sources of the starting powders are shown in Table 3.2. Characterisation of starting powders involved the particle size, morphology and crystal structure.

3.1.1 Particle size analysis

A Microtac S3500 particle size analyser (Pilot tools (Pty) Ltd.) was used to determine the particle size of the starting powders. Particle size was measured by detection of diffracted light by the particles as the laser light passed through them while they were suspended in water. The diffracted light is detected by a photo-detection system that relates the nature of diffraction to a particle size [2007Mac]. Unlike most light diffraction methods used for particle size analysis that use one laser source, the Microtac S3500 utilizes three-lasers simultaneously (Figure 3.1). The tri-laser system provides more accurate, reliable and

repeatable measurements [2007Mac]. The information from the resultant scattered light from the three lasers was combined to generate particle size distributions [1999ISO].

Table 3.2. Specifications of starting powders.

Materials	Particle size (μm)	Crystal Structure	Purity (wt%)	Source
WC	1.0	Hexagonal	>99.00	H.C. Starck, Germany
WC doped with 0.5.wt% Cr_3C_2	0.8	Hexagonal	>99.00	H.C. Starck, Germany
WC	0.1	Hexagonal	>99.95	Dong Yang (HK) Int’L Group, China
Co	0.9	hcp	>99.80	OMG Americas, USA
Ni	2.5	fcc	>99.50	Speciality Metals, South
Ni	0.2	fcc	>99.80	Dong Yang (HK) Int’L Group, China
TiC	1.5	Cubic	>99.00	Treibacher, Austria
NbC	1.2	Cubic	>99.00	Treibacher, Austria
Mo_2C	1.7	Cubic	>99.00	Treibacher, Austria

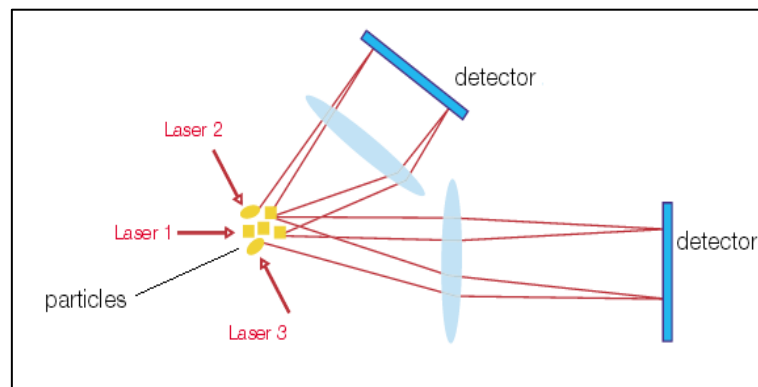


Figure 3.1. Schematic diagram showing the Microtrac S3500 tri-laser system for particle size analysis [2007Mac].

The powders were dispersed in distilled water containing a dispersant (sodium hexametaphosphate), and mixed using an ultrasonic probe for about 2 minutes. The ultrasonic probe was also used to break up powders agglomerates. A few drops of the mixture were poured into the particle size analyser for measurements. The very fine powders ($0.1\mu\text{m}$ WC and $0.2\mu\text{m}$ Ni) formed large agglomerates due to the high surface energies, thus these

powders were mixed with water and sodium hexametaphosphate and milled for 2 h in the 100g mill before particle size analysis.

3.1.2 Powder morphology

The powder morphology was determined using a JEOL, JSM-7500F scanning electron microscope (SEM) (Element Six). The powders were stuck on to aluminium sample holders using conductive double-sided carbon tape, to prevent them from been displaced while moving the stage during the SEM analysis. The conductive tape was also used to prevent charging of the powders, in case any of the powders were non-conductive.

Scanning electron microscopy can be used in in backscattered electron (BSE) or secondary electron (SE) detection modes to produce images. When an incident beam of electrons collides with the sample (e.g. powders), some of the electrons from the beam interact with the specimen, and emit backscattered electrons. These backscattered electrons can be used to form an image of the sample. The number of backscattered electrons increases with increased atomic number of the specimen [1980Pos]. This results in formation of a bright image for high atomic number samples, because they produce more backscattered electrons [1980Pos]. Secondary electrons are formed when the electrons from the incident beam collide with the sample, resulting in the ionisation of atoms in the sample. Due to this ionisation, electrons are emitted from the sample (secondary electrons) and they can be used to form an image of the sample. Secondary electrons have low energy when compared to the incident beam, making it necessary to collect the electrons with a positively biased collector in order to form an image [1980Pos]. The bright areas on the image correspond to parts of the sample where large quantities of secondary electrons were emitted relative to other areas of the sample. Using this, the secondary electron mode can be used for topographic imaging of the sample surface [1980Pos].

The SEM images of the powders were taken using the backscattered detector. The SEM images were also be used to confirm the particle size of the powders.

3.1.3 Powder crystal structure

The crystal structure of the powders was determined by X-ray diffraction (XRD) using a Bruker D2 Phaser (School of Chemistry, Wits University). The XRD technique is based on the fact that crystalline materials are made up of repeating unit cells that have a particular crystal structure. This particular crystal structure diffracts incident X-rays at particular angles

according to Bragg's law (Equation 3.1) [1912Bra]. Hence, a unique pattern of X-ray intensity versus the diffracted angle can be plotted for the material based on its crystal structure. The diffraction method is based on generation of X-rays by a cathode ray tube; the X-rays are then directed to the sample and are diffracted at an angle of 2θ depending on the crystal structure. These diffracted X-rays are then collected, processed and used to produce a pattern of X-ray intensity versus 2θ unique to crystalline material [1912Bra]:

$$n\lambda = 2d\sin \theta \quad \text{(Equation 3.1)}$$

where d is the inter-planer spacing, θ is the angle of incidence to the planes, λ is the wave length of the X-ray source and n is an integral number.

The powders' XRD measurements were done using 2θ values ranging from 20° - 100° and a step size of 0.02° - 0.2° per second. The phases present on the powders XRD patterns were identified using X'Pert Highscore®, Philips database.

3.1.4 Powder impurities

Impurities present in the powder in amounts that were too small to be detected by the XRD analysis, were detected by X-ray fluorescence using a Philips, PW2510 XRF machine (Element Six).

X-ray fluorescence is based on emission of characteristic secondary (or fluorescent) X-rays by atoms of a material that have been excited through bombarding with high-energy X-rays (photons) [1983Ani, 2007Ver]. This results in absorption of X-rays by the powder atoms, leading to ejection of electrons from the atoms inner shell, forming photoelectrons [1983Ani, 2007Ver]. This movement leaves the atoms in an excited state due to absences in the inner shell, thus, electrons from the outer shells fall into the absences, and in the process, emit X-rays with energy equal to the difference between the two states. Since each element has its own unique set of energy levels, each element emits a specific pattern of X-rays that can be used to identify it [1983Ani, 2007Ver]. The emitted X-rays are collected by an XRF detector and used to identify the elements present in the powders. About 10g of powder was required for each analysis.

3.1.5 Powder oxygen analysis

The amount of oxygen present in the powder was determined using an ELTRA ON-900 Oxygen-Nitrogen analyser (Element Six) in a helium atmosphere. Firstly, a graphite crucible

was placed in the instrument, and was out-gassed to ensure there was no oxygen present. About 20 mg of powder was weighed and placed in the loading head and once the instrument was closed, the powders were dropped into the crucible. The crucible was heated to 200°C at a pressure of 1.5 bar for 15 minutes. The contents were then analysed to determine the amount of oxygen present in the powder [Element Six S.O.P].

3.2 Consolidation of powders

Depending on the desired mechanical properties, different types and amounts of carbides were added to the WC-Co and WC-Ni cemented carbides. The investigated compositions are listed in Tables 3.3 and 3.4. Before mixing each composition, the individual powders were weighed using a Mettler Toledo PB303-S weighing balance (School of Chemical and Metallurgical Engineering, Wits University).

Table 3.3. WC-Co cemented carbide compositions.

Composition (wt%)	Submicron WC-0.5 wt%Cr₂C₃(s)	Ultrafine WC (u)	Nano WC (n)
WC-10Co	✓	✓	✓
WC-0.5NbC-10Co	✓	-	-
WC-1NbC-10Co	✓	✓	✓
WC-2NbC-10Co	✓	✓	✓
WC-3NbC-10Co	✓	-	-
WC-5NbC-10Co	✓	✓	✓
WC-10NbC-10Co	✓	-	-
WC-20NbC-10Co	✓	-	✓
WC-30NbC-10Co	✓	-	-
WC-50NbC-10Co	✓	-	-
WC-80NbC-10Co	✓	-	-

(s) 0.8 µm starting size, (u) 0.4 µm starting size, (n) 0.1 µm starting size.

3.2.1 Powder Milling

The investigated compositions were wet milled in a 70 mm diameter x 80mm long stainless steel pot (Figure 3.2), using a portable 100g capacity ball mill (borrowed from Pilot Tools (Pty) Ltd.). The milling was done using 99% pure ethanol milling liquid, as well as WC-10Co (wt%) and steel milling balls. The powders placed in the 100 g capacity mill were already in the required size range (submicron, ultrafine and nano), thus the main purpose of milling was

to facilitate mixing of the powders and break powder agglomerates, rather than powder particle size reduction. A ball-to-powder ratio of 3:1 was used for the submicron WC compositions and 6:1 for the ultrafine and nano WC compositions. An ethanol-to-powder ratio of 0.3:1 was used.

Table 3.4. WC-Ni cemented carbide compositions.

Composition (wt%)	Submicron WC-0.5 wt%Cr₂C₃(s)	Submicron WC (s)	Ultrafine WC (u)	Nano WC (n)
WC-9.3Ni	✓	✓	✓	✓
WC-6.25TiC-9.3Ni	✓	✓	✓	✓
WC-6.25TiC-0.5Mo ₂ C-9.3Ni	✓	✓	✓	✓
WC-6.25TiC-1Mo ₂ C-9.3Ni	✓	✓	✓	✓
WC-6.25TiC-2Mo ₂ C-9.3Ni	✓	-	-	✓
WC-6.25TiC-3.5Mo ₂ C-9.3Ni	✓	✓	✓	✓
WC-6.25TiC-5Mo ₂ C-9.3Ni	✓	✓	✓	✓
WC-6.25TiC-3.5Mo ₂ C-7Ni	-	-	✓	✓
WC-6.25TiC-5Mo ₂ C-7Ni	-	-	✓	✓
WC-10Ni	-	-	-	✓
WC-8Ni	-	-	-	✓
WC-7Ni	-	-	-	✓
WC-6Ni	-	-	-	✓

(s) 0.8 µm starting size, (u) 0.4 µm starting size, (n) 0.1 µm starting size.

The milling period was optimised depending on the composition and the starting powder particle size. For the powders compositions that were to be produced by liquid phase sintering (LPS), 0.2 wt% of the of polyethylene glycol (PEG) was added to the powder, ethanol and ball mixture before milling.

Submicron (0.8 µm) and ultrafine (0.4 µm) WC powders were produced by aggressive wet milling of the 1 µm WC powder in 99% pure ethanol, using WC-10Co (wt%) milling balls in a 1kg capacity steel milling pot, lined with a WC-Co inner protective layer. The 1 µm WC powder was milled for 19 h using a ball to powder weight ratio of 10:1 to produce the submicron (0.8 µm) WC powder, and for 30 h using a ball to powder weight ratio of 15:1 to produce the ultrafine (0.4 µm) WC powder.

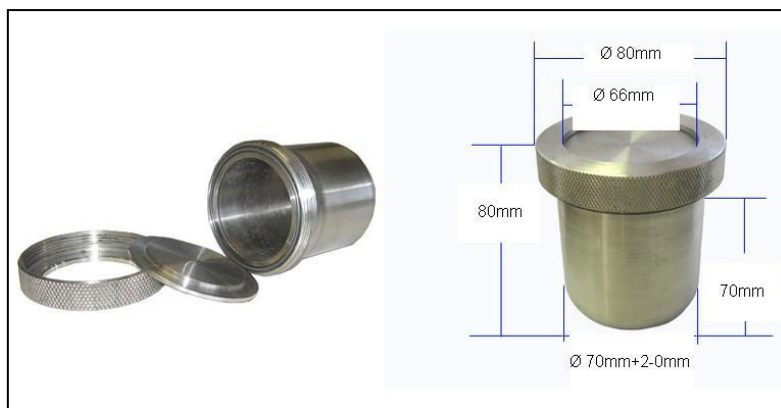


Figure 3.2. Stainless steel milling pot (Pilot tools (Pty) Ltd.).

A milling speed of 66 rpm was used for production of both powders. Particle size analysis was done every 1 h to monitor the break-down of the powders. After milling, the powders were characterised using XRD, XRF and oxygen analysis, to check for contamination of the powders that might have taken place during the aggressive milling process.

3.2.2 Drying and sieving of the powders

Drying of the milled powders was done using a Heidolph Laborator 4010 Digital rota evaporator (School of Chemical and Metallurgical Engineering, Wits University) at 60°C and 80 rpm for 1 h, to remove the ethanol, so as to avoid formation of oxides in the composition during sintering. Since pure ethanol has a boiling point of about 78.3°C [1968Gal], drying was done at a lower temperature (60°C) to avoid oxidation of powders. The dried powders were then sieved using 150 µm and 90 µm sieves to break down the powder cakes that formed during drying and to eliminate any large impurities (>100 µm) that might have been picked up during milling and drying. In the case of the powders that were to be liquid phase sintered, pressing into a green compact of 25mm diameter by 6mm thick shapes was done before sintering.

3.3 Sintering

3.3.1 Spark plasma sintering

The milled composite powders were consolidated in a HP D5 FCT Systeme spark plasma sintering furnace (School of Chemical and Metallurgical Engineering, Wits University). The powder was poured into cylindrical graphite dies with inner and outer diameters of 20.9 mm and 40 mm respectively, and 48 mm height. The composite powder assemblies were loaded in graphite dies and heated in a vacuum (2 hPa).

Taking WC-10Co (wt%) as an example, the powders were first heated to 1050°C at a rate of 200°C/minute and subsequently to 1240°C at a heating rate of 100°C/minute, the temperature was held at 1240°C for 5 minutes during sintering. A cooling rate of 200°C/minute was then administered. The applied pressure was adjusted within 30 seconds from 16 MPa to 30 MPa at 1050°C, and from 30 MPa to 50 MPa at 1240°C. The pressure was then held constant at 50MPa throughout the rapid sintering cycle. This sintering profile is shown in Figure 3.3. Horizontal and vertical graphite papers were used to separate the powders from the die and punch set-up. Hexagonal boron nitride was placed on the graphite paper to prevent carbon diffusion from the graphite paper to the powders during sintering. The graphite die was wrapped in a carbon cloth to minimise the heat loss from the die surface. The temperature was controlled by an optical pyrometer focused on a central borehole on the upper punch, 1mm above the top surface of the sample, for accurate estimation of the sample temperature [2008Hua1]. The compaction of the composite powders in the axial direction was monitored by measuring the distance moved by pistons. The relative piston movement during powder compaction is a measure of the shrinkage, and hence was used as an indication of the degree densification during sintering. Different sintering profiles depending on the powder composition were used to achieve good densification. The sintering dwell times were varied between 2-5 minutes, pressures between 50-70 MPa and temperatures between 1220-1380°C to attain full densification.

3.3.2 Liquid phase sintering

After the pressing the milled powder composition into a green compacts, the compacts were sintered using an ULTAR-TEMP Sinter-HIP furnace (Pilot Tools (Pty) Ltd.). The compacts were placed in the furnace heating chamber and heated in vacuum (0.04MPa) at an initial heating rate of 2.4°C/minute to 270°C. The temperature was held constant for 65 minutes, as the vacuum pump was turned off to allow for flow of hydrogen into the heating chamber for

dewaxing. Dewaxing was then carried out in four steps, using a series of heating rates and dwell times from 270°C to 450°C (Figure 3.4), to ensure that all the PEG was eliminated. After dewaxing, the temperature was held at 450°C for an additional 20 minutes, during which the vacuum pump was switched on to remove the hydrogen. A heating rate of 4.2°C/minute was then administered from 450°C to 1000°C, at which the temperature was held for 5 minutes, with the vacuum pump turned off to allow flow of methane and hydrogen for carbon correction. Carbon correction was done to ensure the carbon lost during dewaxing was replaced [1975Bro]. Carbon control was done for 90 minutes, after which the vacuum pump was switched on to remove the methane and hydrogen. A heating rate of 3.3°C/minute was used from 1000°C to 1200°C. At 1200°C, cobalt loss protection (CLP) was carried out by the addition of argon gas at a pressure of 0.37 MPa. The CLP was done using a heating rate 3.5°C/minute up to 1430°C. The temperature was held constant for 75 minutes, and for the last 20 minutes, hot isostatic pressing (HIP) was done at 4.4 MPa to eliminate all the surface porosity [1975Bro]. The furnace was then water cooled at a rate of 3.5°C/minute.

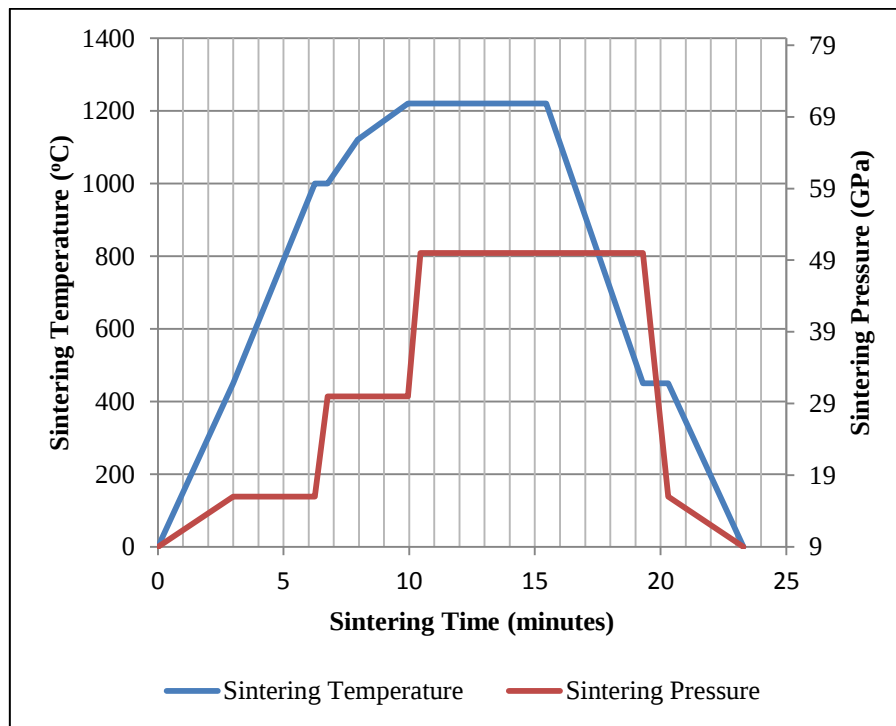


Figure 3.3. SPS profile for production of WC-10Co (wt%), total time 23 minutes.

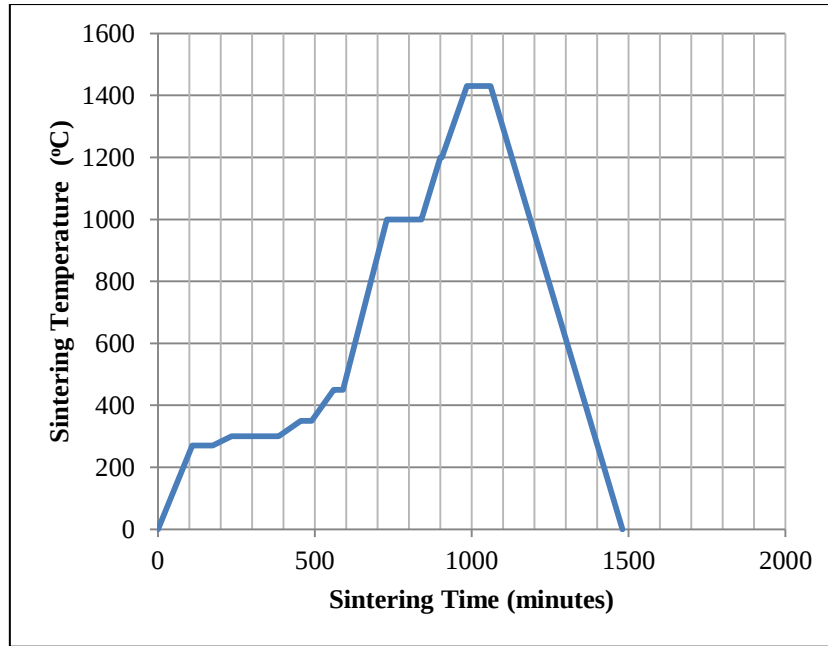


Figure 3.4. LPS temperature profile for WC-10Co (wt%), total time 24 h and 42 minutes.

3.4 Characterisation of sintered samples

3.4.1 Density measurements

The density and open porosity of the samples were determined by Archimedes' principle using a Sartorius ED224S density measuring machine. After sintering, the samples were initially cleaned to remove the hexagonal boron nitride and graphite paper from the sample surface. The samples were then boiled in distilled water for 5 h to fill surface pores and eliminate bubbles on the sample surface, so as to accurately measure the density and open porosity. After boiling, the samples were weighed in air to attain the wet mass (W_2), and then weighed in distilled water to attain the suspended mass (W_3). The samples were then dried in a Labotec INC-O-MAT (School of Chemical and Metallurgical Engineering, Wits University) oven at 80°C for 24 h, and then weighed in air to attain dry mass (W_1) [1955AST].

The true density and open porosity of samples were determined using Equations 3.2-3.7 [1955AST].

$$\text{True volume of sample} = \frac{W_1 - W_3}{\rho_w} \quad (\text{Equation 3.2})$$

where ρ_w is the density of distilled water at room temperature.

$$\text{True density of sample} = \frac{W_1 \rho_w}{W_1 - W_3} \quad (\text{Equation 3.3})$$

$$\text{Percentage densification} = \frac{\text{True sample density}}{\text{Theoretical density}} \times 100\% \quad (\text{Equation 3.4})$$

The theoretical density is dependent on the density and mass % of the individual constituents of the compositions (Equation 3.4), e.g. for WC-10Co (wt%), the density of WC is 15.7 g/cm³ and Co is 8.9 g/cm³ [1992Scu].

$$\text{Theoretical density (g/cm}^3\text{)} = 100 \text{ wt.\%} \times \left(\frac{90 \text{ wt \%}}{15.7 \text{ g/cm}^3} + \frac{10 \text{ wt \%}}{8.9 \text{ g/cm}^3} \right)^{-1} \quad (\text{Equation 3.5})$$

$$\text{Volume of open porosity} = \frac{W_2 - W_1}{\rho_w} \quad (\text{Equation 3.6})$$

$$\text{Volume percentage open porosity} = \frac{W_2 - W_1}{W_2 - W_3} \times 100\% \quad (\text{Equation 3.7})$$

3.4.2 Magnetic properties

3.4.2.1 Magnetic Saturation (CoM)

Maximum magnetisation of the samples was induced using a Setaram Sigmameter Magnetic analyser (Pilot Tools (Pty) Ltd.). The binder magnetic saturation (CoM) is a measure of the amount of the magnetic material in the cemented carbide, and was determined by its magnetic pull (force) when placed in a homogenous magnetic field of sufficient strength to saturate the sample.

A sample containing 1 wt% Co is equal to 2.02 $\mu\text{Tm}^3/\text{kg}$ [1997Luy], if the Co is pure (no W in solution). Equation 3.8 [1997Luy] was used to calculate theoretical value of CoM once the starting Co wt% in the cemented carbide was known. If the CoM value was less than the theoretical value, then W solubility took place during sintering. The mass of the each sample was measured before testing.

$$\text{Theoretical CoM } (\mu\text{Tm}^3/\text{kg}) = (2.02 \times \text{wt\%Co}) \quad (\text{Equation 3.8})$$

3.4.2.2 Coercivity (H_c)

The coercivity was measured using a Forster-Koerzimat 1.095 instrument (Pilot Tools (Pty) Ltd.). This instrument consisted of two sections, a magnetic field generator and a magnetic field measuring unit. The samples were attached to a wooden sample holder and placed between the magnetic coils in the magnetic field generator. A strong magnetic field was used to magnetise the samples, after which a coercive magnetic field was then used to demagnetise the samples. The magnetic field required to demagnetise (coercivity) the samples was measured by the magnetic field measuring unit.

3.4.3 Cutting of sintered samples

The samples were cut to attain a cross-section area from the outer surfaces to the centre, for representative characterisation. This enabled testing of the sample from many different regions (from all edges to the centre) to ensure that the properties were uniform throughout. Cutting was done in a Struers Secotom-10 precision cutting machine (School of Chemical and Metallurgical Engineering, Wits University), using a 12 cm diameter Struers diamond coated wheel. A wheel cutting speed of 3500 rpm and feed rate of 0.02 mm/s was used to achieve a finished cut in 22 minutes. Water was used as a coolant throughout the cutting process.

3.4.4 Sample mounting

Mounting of the samples was done for support of the sample during polishing of the exposed cross-section area after cutting, and to make them easier to hold. One half of the sample was mounted in Struers polyfast using a Struers Cito-Press 10 (School of Chemical and Metallurgical Engineering, Wits University) at 250 bar and 180°C. Water was used as a coolant during the process.

3.4.5 Sample grinding and polishing

Grinding and polishing were done to eliminate surface damage during cutting and to produce a smooth surface finish for microstructure analysis and mechanical testing. A Struers LaboPol-5 machine (Pilot Tools (Pty) Ltd.) was used for grinding and polishing. Piatto 220 and 1200 wheels were used for grinding, while AKASEL 9 μm , 3 μm and 1 μm cloths with Diamaxx diamond slurries were used for polishing. The parameters and lubricants are shown in Table 3.5.

3.4.6 Microstructure analysis

Microstructures of the cemented carbides were examined by scanning electron microscopy in the backscattered electron mode using a JEOL JSM-7500F (Element Six), with an Inca Penta FETx3 energy dispersive X-ray spectroscopy system (EDX) and a Philips XL ESEM-FEG (Element Six), with an EDAX EDS detector. The SEMs were run at 15 kV acceleration voltage, at working distances between 10-12mm. Both EDX point and area analyses were done to identify phases. The SEM micrographs were used to analyse the homogeneity of the phase distribution, WC grain size, binder mean free path and WC contiguity. Image analysis of the SEM micrographs was done on using ImagJ and SIS-pro software and calculations were done using MathConnex 2000 with MathCad 2000 Professional (Element Six). Mapping of the SEM microstructures was done using EDAX Genesis software (Element Six).

Table 3.5. Sample grinding and polishing procedure.

Process	Step	Wheel/Cloth	Lubricant	Speed (rpm)	Load (N)	Time (minutes)
Grinding	1	Piatto-220	Water	350	35	15
	2	Piatto-1200	Water	350	35	10
Polishing	1	Plaran-9 μ m	Diamaxx-9 μ m	300	30	10
	2	Daran-3 μ m	Diamaxx-3 μ m	250	20	6
	3	Napal-1 μ m	Diamaxx-1 μ m	250	20	3

High angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) using a JEOL 2100 (Centre for High Resolution Transmission Electron Microscopy, Nelson Mandela Metropolitan University), with a LAB6 filament was used to plot EDX maps of the distribution of the elements in the microstructure. This was used for samples with microstructures that were too fine ($\sim 0.6\mu\text{m}$ WC grain size) for accurate SEM-EDX analysis due to the detector limit of $\sim 2\mu\text{m}$. High resolution transmission electron microscopy (HRTEM) using a JEOL ARM-200F (Centre for High Resolution Transmission Electron Microscopy, Nelson Mandela Metropolitan University) was done to analyse the grain interfaces at an atomic level to better understand the variations within the microstructures, as a result of specific additives. The samples for STEM and HRTEM were prepared using a FEI, Helios Nanolab FIB-SEM (Centre for High Resolution Transmission Electron Microscopy, Nelson Mandela Metropolitan University).

3.4.7 Phase analysis

X-ray diffraction was done to using a Bruker D2 Phaser (School of Chemistry, Wits University) to identify the phases present, as well as confirm the findings from SEM-EDX and STEM-EDX phase analyses. The XRD measurements were done using 2θ values ranging from 20° - 100° and a step size of 0.02° - 0.2° per second. The phase present on the powders XRD patterns were identified using Philips X'Pert Highscore® database.

3.4.8 Mechanical properties

3.4.8.1 Hardness

Hardness was determined by Vickers hardness and Rockwell hardness tests. Both tests were carried out on the polished surfaces of the samples.

3.4.8.1.1 Vickers hardness

Vickers hardness was measured using a Mitutoyo AVK-Co (Pilot Tools (Pty) Ltd.) hardness indenter, applying loads of 10Kg (HV_{10}) and 30Kg (HV_{30}) with a diamond indenter for 10 seconds. Five indentations at different regions on each sample were carried out, and the average calculated. An example of the indentations is shown in Figure 3.5 and the calculations of hardness from the indentations are given as Equations 3.8-3.10 [1922Smi].

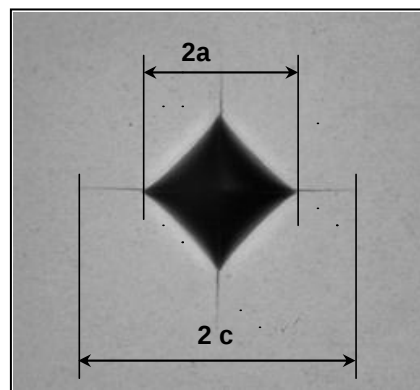


Figure 3.5. Hardness indentation on the surface of the specimen [Element Six S.O.P].

The applied force F in Newtons (Equation 3.9) and length of diagonals ($D = 2a$) were used to calculate the Vickers hardness (HV) (Equation 3.10):

$$F = \text{applied force} = M \times g \quad (\text{Equation 3.9})$$

where M is the applied load, i.e. 30 kg for case of HV_{30} , and g is gravitational acceleration (9.82 m/s^2).

$$HV = F/A = F (0.1891)/ D^2 \quad (\text{Equation 3.10})$$

Therefore substituting for Equation 3.10,

$$HV_{30} = (30 \times 9.82 \times 0.1891)/ D^2$$

The HV_{30} is then converted into hardness in GPa using Equation 3.11:

$$H \text{ (GPa)} = HV_{30} \times 0.009807 \quad (\text{Equation 3.11})$$

3.4.8.1.2 Rockwell Hardness (HR)

Rockwell hardness tests were done using a Mitutoyo AKR-600 Rockwell-A tester (Pilot Tools (Pty) Ltd), applying a load of 60Kg with a diamond indenter for 10 seconds. The test involves applying a minor load (F_0) and when equilibrium has been reached, an indicating device which follows the movement of the indenter, responds to the change in indenter penetration depth, and sets a zero reference position, (Figure 3.6). An additional major load (F_1) is then applied for 10 seconds and released leaving the minor load applied at the new depth of penetration. The difference in depth of penetration between the initial minor load position and the major load position is automatically measured by the machine and converted into a Rockwell hardness number (HR) (Equation 3.12) [1922Roc, 1932AST]:

$$HR = E - e \quad (\text{Equation 3.12})$$

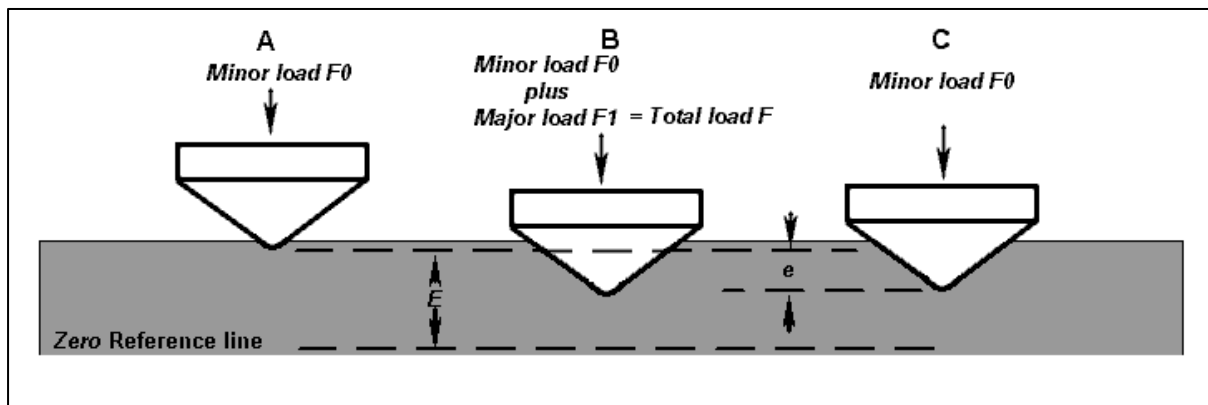


Figure 3.6. Difference in indenter penetration depth during Rockwell hardness testing [1996URL].

3.4.8.2 Fracture toughness (K_{1C})

Fracture toughness was measured using the Mitutoyo AVK-Co hardness indenter (Pilot Tools (Pty) Ltd). Due to the stress induced by the diamond indenter and the brittle nature of the samples, radial cracks were generated at the edges of the indentations (Figure 3.5). The

criteria for the accurate computation of fracture toughness (K_{1C}) using Shetty's equation (Equation 3.13) were satisfied [1985She, 1990Spi]: $1.25 \leq c/a \leq 2.25$ and $0.25 \leq I/a \leq 2.5$, where c is the crack length from the centre of indentation to the crack tip, a is half diagonal length of indentation and I is the difference between c and a . Shetty's equation is [1985She, 1990Spi]:

$$K_{1C} = 0.0889H^{0.5} \times (F/4I)^{0.5} \quad (\text{Equation 3.13})$$

where H is the hardness (GPa), F is the applied force (Newtons) and I is average crack length (mm) given by Equation 3.14.

$$I = (2c-2a)/2 \quad (\text{Equation 3.14})$$

The fracture toughness was attained in $\text{MPa.m}^{1/2}$ units.

3.4.8.3 Modulus of Elasticity

The modulus of elasticity was determined using Krautkramer-Branson USIP 12 ultrasonic equipment (Element Six) by measuring the samples' transverse (v_T) and longitudinal velocity (v_L). The samples were ground to a thickness of 3 mm and polished on opposite sides to ensure they were smooth and flat as per the requirements for the test [2010Ult]. The transverse (v_T) and longitudinal velocity (v_L) values were then used to calculate the Poison's ratio (ν) using Equation. 3.15 [2010Ult]:

$$\nu = \frac{v_L^2 - 2v_T^2}{2(v_L^2 - v_T^2)} \quad (\text{Equation 3.15})$$

The transverse velocity (v_T) and the density (ρ) of the cemented carbide were used to calculate the shear modulus (G) using Equation. 3.16 [2010Ult]:

$$G = \rho v_T^2 \quad (\text{Equation 3.16})$$

The Young's modulus (E) was calculated using both the Poison's ratio and the shear modulus using Equation. 3.17 [2010Ult]:

$$E = 2G(1+\nu) \quad (\text{Equation 3.17})$$

3.4.8.4 Transverse rapture strength (TRS)

The transverse rapture strength (TRS) was determined by the “ball-on-three-ball” (B3B) method using an Instron 5500R Universal tester (Element Six). The samples were cut to 16 mm diameter by 1.5 mm thick discs using a Fanuk Robocut α -O1A Electro-discharge machine (EDM) wire cutter (Element Six). They were polished before the test. Six samples from each composition were used for the test. The sample and the balls were set up in a jig as shown in Figure 3.7 [2004Bör2], and 12 mm diameter balls were used. The sample was placed over a loading ball (1) that was centrally positioned on the stamp. Balls 2, 3 and 4 were then placed on the sample. The sample and the balls were held in exact passion by the guide. Once the set up was ready, a pre-load of 200 N was applied and the guide was pushed down, so that the sample was only supported by the balls. The sample was held in position by friction with the balls because of the applied load. The load was then increased until failure, using a 100 KN load cell at a test speed of 0.9 mm/minute. The fracture load, number of pieces the sample broke into and time taken to break were recorded.

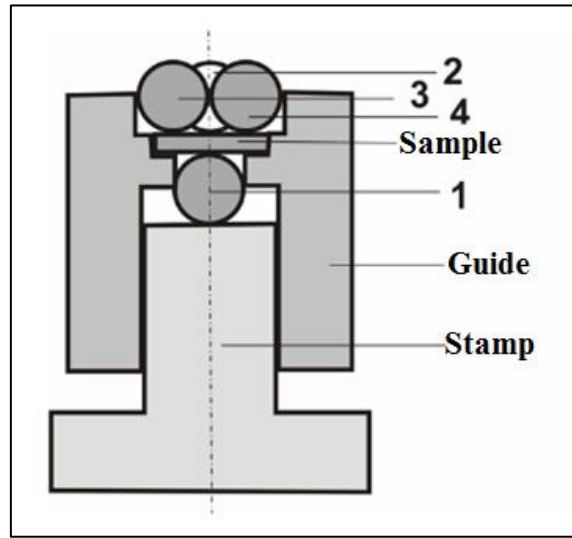


Figure 3.7. Schematic diagram showing arrangement of the sample and balls for a B3B TRS test [2004Bör2].

The TRS (σ_{TRS}) of the sample was calculated using Equation 3.18 [2002Bör]:

$$\sigma_{\text{TRS}} = f F / t^2 \quad (\text{Equation 3.18})$$

where F is the maximum load at fracture, t is the sample thickness and f is a dimensionless factor that is dependent on the sample geometry (radius and thickness), Poisson's ratio of the

sample and load transfer from the jig to the sample. The value of f was calculated using Equation 3.19 [Element Six S.O.P]:

$$f = \frac{(2.21793 + 0.00085238 F + 6.6489 \times 10^{-9} \times F^2 - 0.344302t)}{(1 + 0.00058215 F)} \quad (\text{Equation 3.19})$$

3.4.8.5 Sliding wear test

A sliding wear test was used to test the sliding wear resistance of the samples using a CSM pin-on-disk tribometer (School of Chemical and Metallurgical Engineering, Wits University) with a ball configuration on the samples' polished surfaces. Two samples per composition were used for the test that was done at room temperature of $23.5 \pm 0.81^\circ\text{C}$ and humidity that ranged between $47.6 \pm 1.4 - 53.8 \pm 1.7 \%$. A load of 10N was applied on 6 mm diameter 100 Cr6 steel and silicon nitride balls as the abrasive materials, for a wear sliding distance of 300m at a speed of 0.21m/s (Figure 3.8). The test was done in open air with no lubricant. InstrumX Tribbox software was used to determine the static and dynamic friction coefficients, as well as the Hertzian pressure from the test. Characterisation of the wear track was done using a Motic optical microscope (School of Chemical and Metallurgical Engineering, Wits University) with a Moticam 2300 camera, SEM-EDX for identifying the elements and phases present on the track and Zeiss Laser confocal LSM-5-PASCAL (Council for Science and Industrial Research, CSIR) using Zen 2008 software for 3D mapping of the wear track and measuring the worn track cross section area (S). A 10 μm interval height for Z-stacking was used to generate the wear track 3D maps.

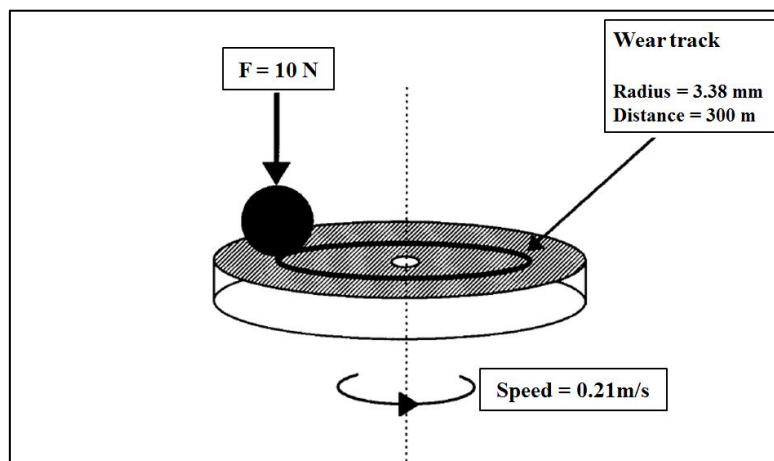


Figure 3.8. Schematic diagram showing arrangement of the sample, ball and experimental parameters during the abrasion wear test [1999Jac].

The worn volume (ΔV_S) of the samples was calculated according to the Japanese industrial standard (JISR1613), using Equation 3.20 [2003Jon]:

$$\Delta V_S = (\pi R(S_1 + S_2 + S_3 + S_4))/2 \quad (\text{Equation 3.20})$$

where R is the sliding radius and S is the worn track cross section area.

The sample wear rate (k_S) was calculated using Equation 3.21 [1967Lan]:

$$K_S = \Delta V_S / F.s \quad (\text{Equation 3.21})$$

where ΔV_S is the sample worn volume (mm^3), F is the applied load (N) on the ball and s is the sliding distance (m).

The ball volume loss (ΔV_B) was also calculated using the Equations 3.22 and 3.23 [2002AST]:

$$\text{Ball volume loss } (\Delta V_B) = (\pi h/6) \times (3d^2/4 + h^2) \quad (\text{Equation 3.22})$$

where h is the height of material removed (mm), d is the ball wear scar diameter (mm) and r is the ball radius (mm). The height of material removed is given by Equation 3.23:

$$h = (r^2 - d^2/4)^{0.5} \quad (\text{Equation 3.23})$$

The ball wear rate (K_B) was calculated using Equation 3.24:

$$K_B = \Delta V_B / F.s \quad (\text{Equation 3.24})$$

3.4.8.6 Thermal shock and impact resistance

In order to mimic the thermal shock and impact that cutting tools experience during operation, an actual milling test was designed. Cutting tool inserts of the shape shown in Figure 3.9 were made from the 20 mm diameter by 5 mm thick bulk samples, by initially cutting 13.2 mm by 13.2 mm by 3.5 mm square shapes using a Fanuk Robocut α -O1A Electro-discharge machine (EDM) wire cutter (Element Six). The squares were then lapped to the required thickness using a Peter-Walters 3R-1200 (Element Six), and edge rounded, face and end ground to the final dimensions using an Ewag RS12 Edge profile grinder (Element Six). The final step in the tool insert shaping was edge honing to eliminate the sharp edges between faces after grinding, and this was done to prevent premature failure due to high stress concentration at the cutting edge. The tool inserts were edge honed to a radius of 20 μm using an AUER SAN 1000 S1S machine (Pilot Tools (Pty) Ltd.), in which a mixture of

aluminium oxide grit and water was sprayed at the edges at a pressure of 0.28 MPa and at controlled angles to ensure uniform honing. The honed edges were measured at regular intervals to ensure uniformity using a GF Messtechnik optical microscope with Mikro CAD^{pico} software.

The inserts were locked onto a MD Tools BT40-22-45V cutting tool holder that was attached to a GX1000 CNC machine (School of Mechanical, Industrial and Aeronautical Engineering, Wits University) with a Fanuc oi-MC controller, which was used to face mill Ti-6Al-4V workpieces. The cutting tool holder had a radial depth of cut (a_r) of 45mm and one insert was used per milling run, while the workpiece cutting surface had a width of 40 mm. This ensured interrupted face milling, because during every cut, the insert cutting edge would detach from the workpiece at the end of the cut, due to the extra 5mm, and then engage the workpiece at the beginning of the next cut. This interruption allowed for rapid heating and subsequent cooling of the insert cutting surface, as well as impact between the cutting edge and the workpiece with every cut. The cutting speed (v_c) and depth of cut (a_p) were varied as shown in Tables 3.6 and 3.7. The temperature variation at the insert cutting edge was measured using a Nikon D5000 high speed thermal camera (School of Mechanical, Industrial and Aeronautical Engineering, Wits University) with FLIR Tool software. For accurate temperature readings, the emissivity of the workpiece had to be determined. This was done by heating the workpiece in a Labotec INC-O-MAT (School of Mechanical, Industrial and Aeronautical Engineering, Wits University) oven to 250°C, then simultaneously measuring the temperature using a FLUKE 52II thermometer (School of Mechanical, Industrial and Aeronautical Engineering, Wits University) and the thermal camera. The temperature was determined using the thermometer, and thermal camera temperature was calibrated to the thermometer reading. The emissivity value on the thermal camera that corresponded to the actual temperature was the correct emissivity of the workpiece. The emissivity of the Ti-6Al-4V workpiece was found to be 0.29 when the surface was oxidised, and 0.21 when the oxide layer was removed. The impact forces during milling were measured by Kistler Multicomponent Force Link 9366CC0 force gauges (School of Mechanical, Industrial and Aeronautical Engineering, Wits University) attached to the workpiece clamping vice. DynoWare Version 2.5.3.8 software was used to compute and record the force variations.

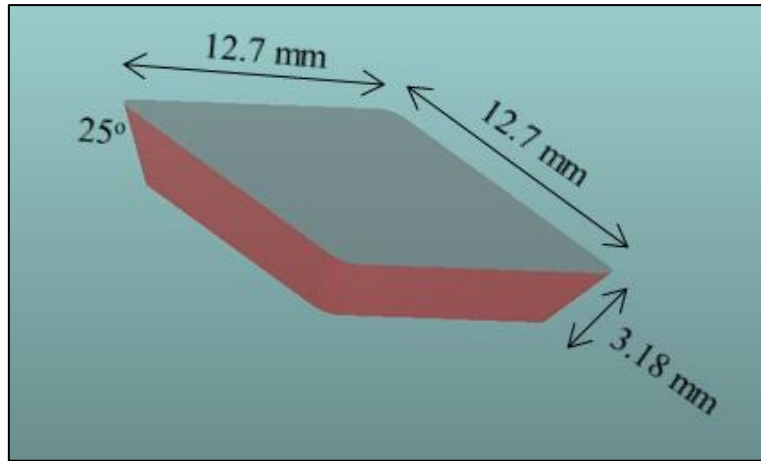


Figure 3.9. Schematic diagram of cutting tool inserts showing the shape and dimensions.

The spindle (n) speed and feed rate (V_f) are given by Equations 3.25 and 3.26, respectively [1965Boo]:

$$n = v_c / \pi a_r \quad (\text{Equation 3.25})$$

where a_r is the radial depth of cut.

$$V_f = n \times f_z \times z \quad (\text{Equation 3.26})$$

where n is the spindle speed, f_z is the feed per tooth and z is the number of teeth (inserts).

Table 3.6. Milling conditions for the WC cemented carbide insets.

Milling test variables			CNC parameters	
Axial Depth of cut (mm)	Cutting speed (m/minute)	Feed per tooth (mm/tooth)	Spindle speed (rpm)	Feed rate (mm/minute)
1	40	0.10	283	28.3
1	60	0.10	424	42.4
2	75	0.10	530	53.0

Table 3.7. Milling conditions for the PCD inserts.

Milling test variables			CNC parameters	
Axial Depth of cut (mm)	Cutting speed (m/minute)	Feed per tooth (mm/tooth)	Spindle speed (rpm)	Feed rate (mm/minute)
0.5	60	0.10	424	42.4
0.5	150	0.10	1060	106.0

Chapter 4: Optimisation of Milling and Sintering

In this chapter, the characteristics, mixing and particle size break-down, as well as consolidation of the starting powders were studied. These factors affect the microstructure and in turn the mechanical properties of the cemented carbide. Thus, by optimising the milling and sintering process, mechanical properties of the sintered product can be improved.

4.1 Starting powder characterisation

4.1.1 Powder particle size

The D_{10} , D_{50} , D_{90} and mean values for all the starting powders are shown in Figures 4.1-4.9 were used to describe the particles size distribution of the powders [1999ISO]. The width of the curves increased with increased variation of the particle size distribution. Although the submicron WC-0.5Cr₃C₂ powders had a smaller D_{50} and mean particle size than the 1 μm WC powder (WC-m), it had a wider particle size distribution curve (PSDC) (Figures 4.1 and 4.2 and Table 4.1). The PSDCs for the WC-0.5Cr₃C₂ and WC-m powders had almost two distributions, the former was wider before the D_{50} peak (Figure 4.1), while the latter was steeper before the D_{50} peak and had wider distribution towards the larger particle sizes (Figure 4.2). The nano WC powders PSDC (Figure 4.3) had a narrow high D_{50} peak, followed by a long distribution at larger particle sizes. The Co powder PSDC had a near uniform distribution on both sides (Figure 4.4). The 3 μm Ni powder PSDC (Figure 4.5) had slightly wider distribution before the D_{50} peak than larger particle sizes, while the ultrafine Ni powder PSDC (Figure 4.6) was steeper before and just after the D_{50} peak, followed by significantly smaller but wide distribution of larger particle sizes. Both the NbC and TiC PSDCs were similar (Figures 4.7 and 4.8); they were almost bimodal with a slightly wider distribution before the D_{50} peak, followed by a steep decrease after the D_{50} , then a wider taper at larger particle sizes. Molybdenum carbides PSDC (Figure 4.9) was bimodal, and had wider distribution before the D_{50} peak, followed by steep decrease at larger particle sizes.

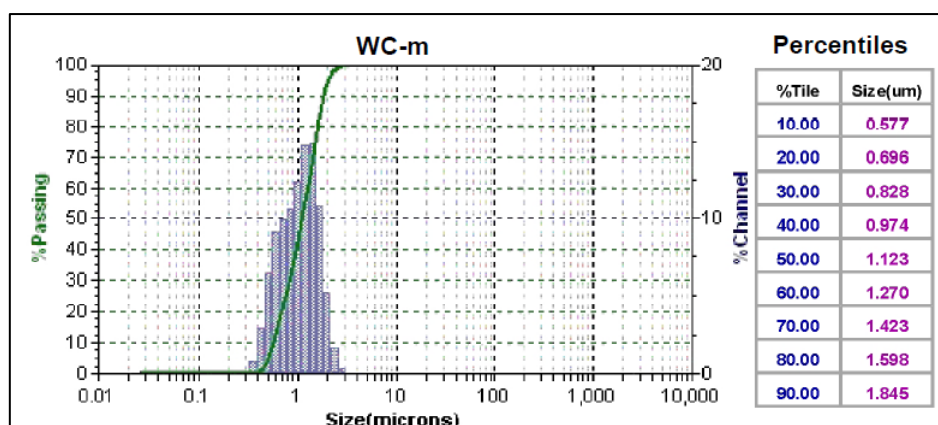


Figure 4.1. Particle size analysis of as-received micron-WC powder.

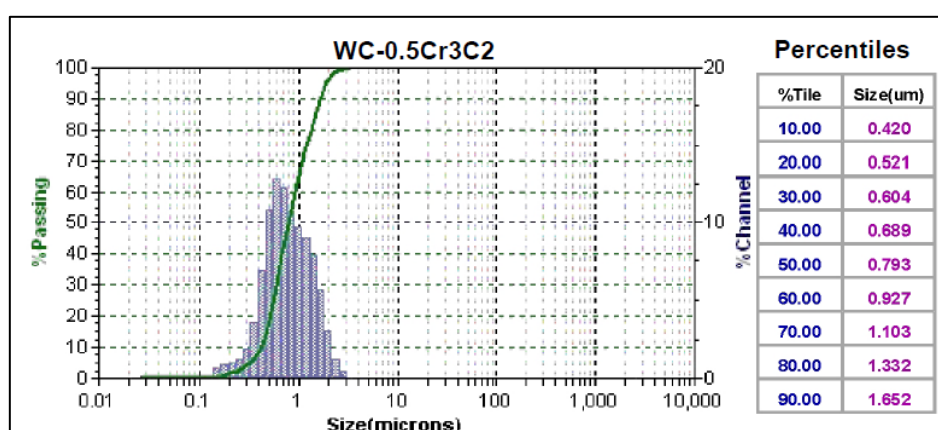


Figure 4.2. Particle size analysis of as-received submicron-WC powder doped with 0.5 wt% Cr₃C₂.

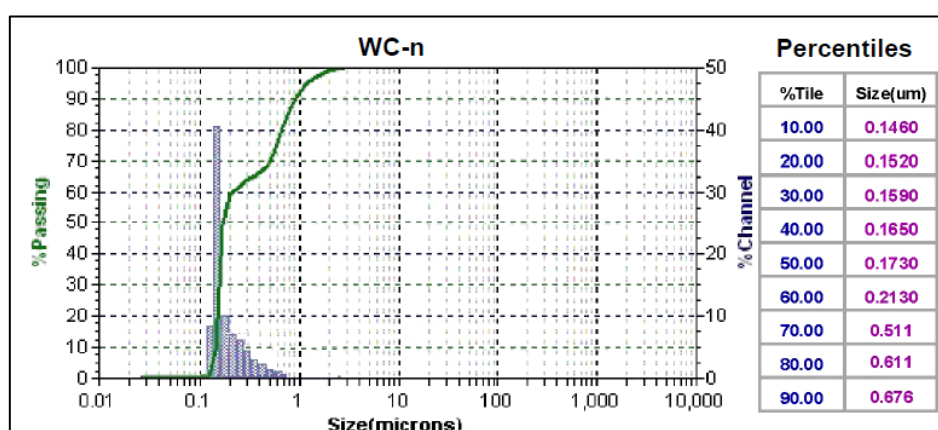


Figure 4.3. Particle size analysis of as-received nano-WC powder.

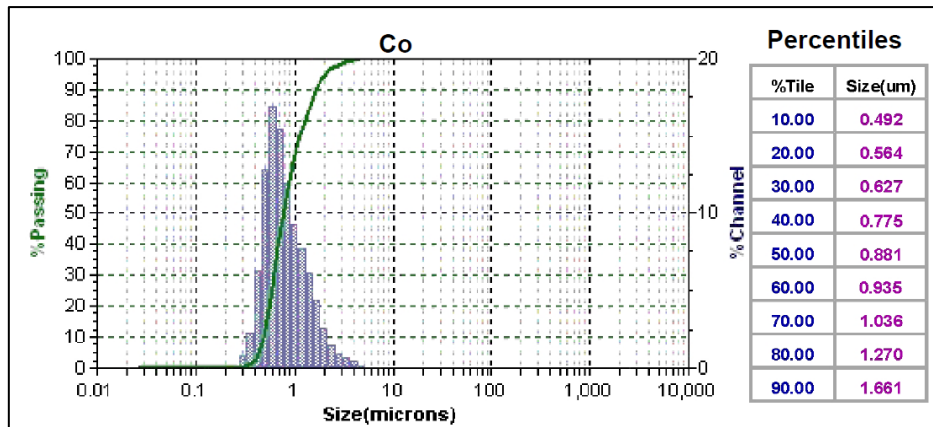


Figure 4.4. Particle size analysis of as-received Co powder.

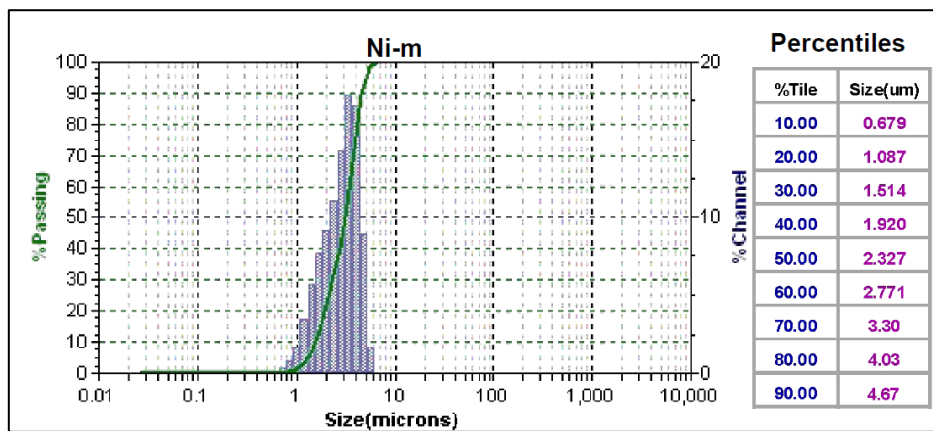


Figure 4.5. Particle size analysis of as-received micron Ni powder.

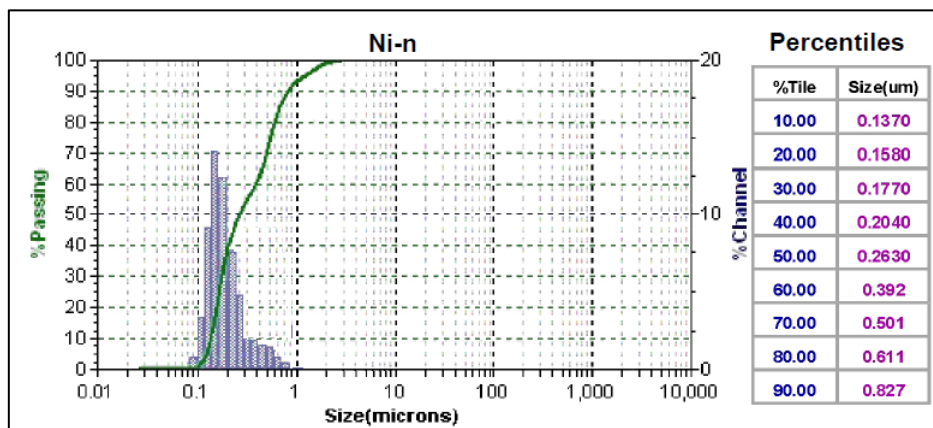


Figure 4.6. Particle size analysis of as-received ultra-fine Ni powder.

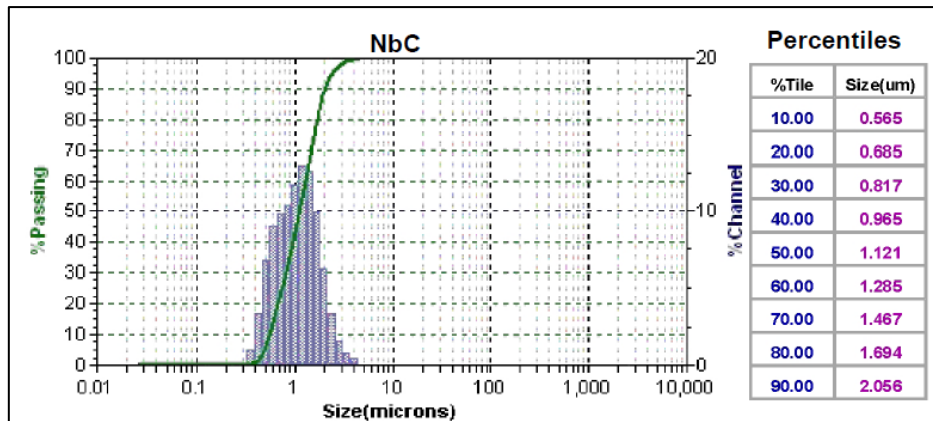


Figure 4.7. Particle size analysis of as-received NbC powder.

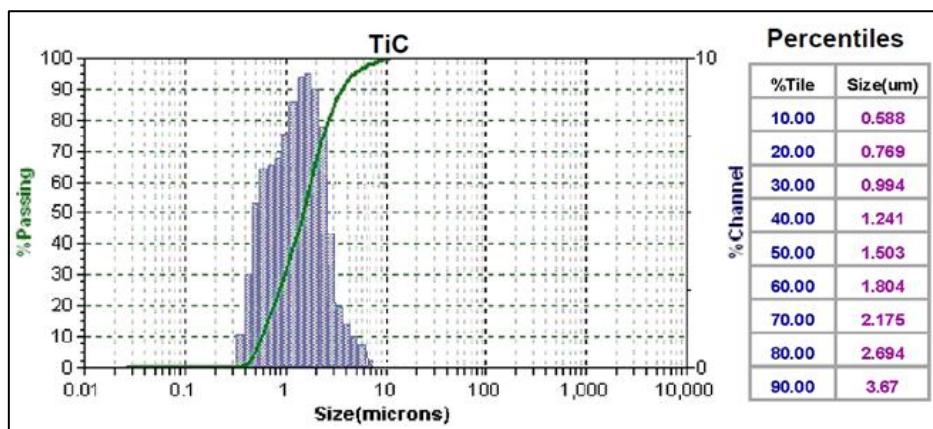


Figure 4.8. Particle size analysis of as-received TiC powder.

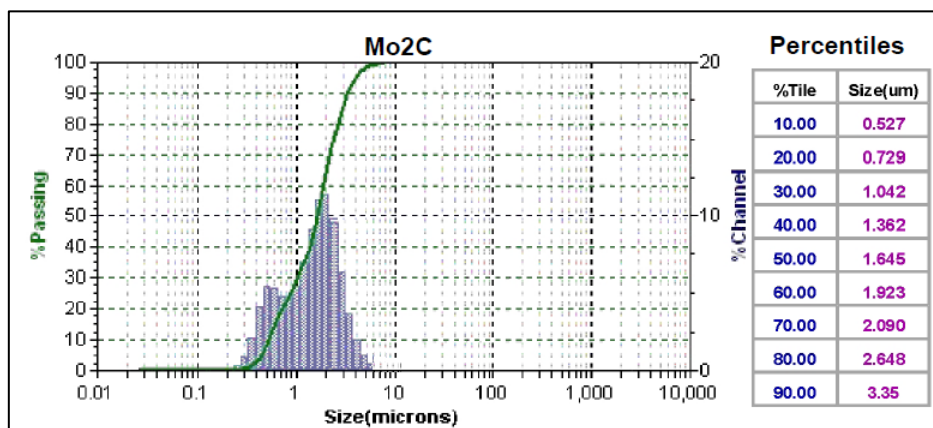


Figure 4.9. Particle size analysis of as-received Mo₂C powder.

Table 4.1. Comparison between expected and measured particle size distributions.

Powder	Expected size (μm)	D ₁₀ (μm)	D ₅₀ (μm)	D ₉₀ (μm)	Mean (μm)
WC-m	1.0	0.577	1.123	1.857	1.174
WC-0.5 Cr ₃ C ₂	0.8	0.420	0.793	1.652	0.827
WC-n	0.1	0.146	0.173	0.676	0.192
Co	0.9	0.492	0.881	1.661	0.924
Ni-m	2.5	0.679	2.327	4.67	2.540
Ni-n	0.2	0.137	0.263	0.827	0.284
TiC	1.5	0.588	1.503	2.694	1.524
NbC	1.2	0.565	1.121	2.058	1.240
Mo ₂ C	1.7	0.527	1.645	3.350	1.827

4.1.2 Powder morphology

The morphology of the powders was determined from SEM images of the powders in backscattered electron (BSE) mode. The micrographs were also used to confirm the particle size analysis results. The micrographs of the starting powders are shown in Figures 4.10-4.18. The as-received micron WC powder was spherical with a wide size distribution (Figure 4.10), while the as-received WC-0.5Cr₃C₂ (wt%) powder had rounded particles (Figure 4.11), and Cr₃C₂ was not detected by EDX. As-received nano WC powders had angular-shaped particles with agglomerates between ~0.3-0.5 μm (Figure 4.12). The as-received Co powder had agglomerates of irregular powder shapes (Figure 4.13).

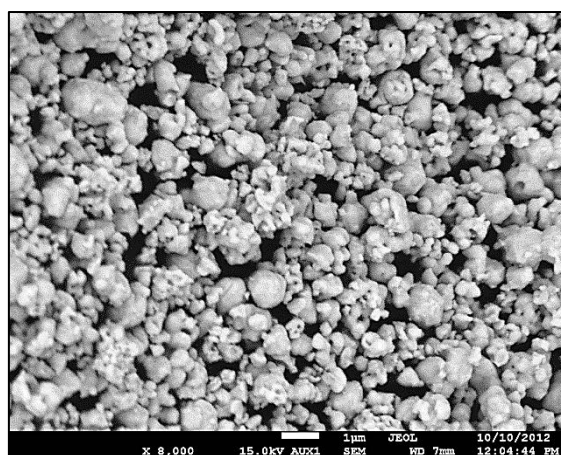


Figure 4.10. SEM-BSE image of as-received micron WC powder, showing mainly spherical particles of different sizes.

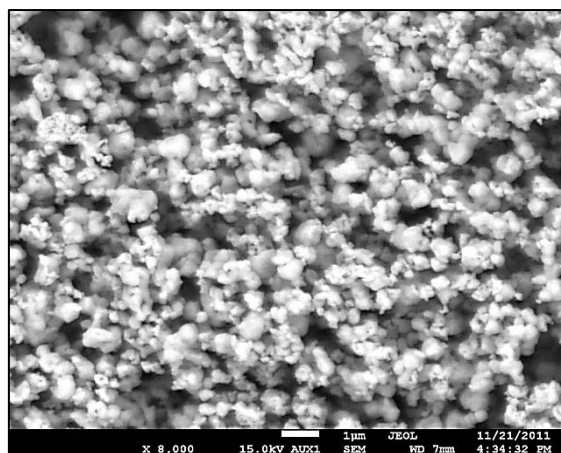


Figure 4.11. SEM-BSE image of as-received submicron WC-0.5Cr₃C₂ (wt%) powder, showing rounded particles.

The as-received micron Ni powder had chains of agglomerated angular particles (Figure 4.14), while the as-received ultra-fine Ni powder had spherical particles of different sizes (Figure 4.15). As-received TiC powder had angular particles (Figure 4.16), while the as-received NbC powder also had angular particles, but of different sizes (Figure 4.17). As-received Mo₂C powders had irregular shaped particles that agglomerated with mainly smooth surfaces (Figure 4.18).

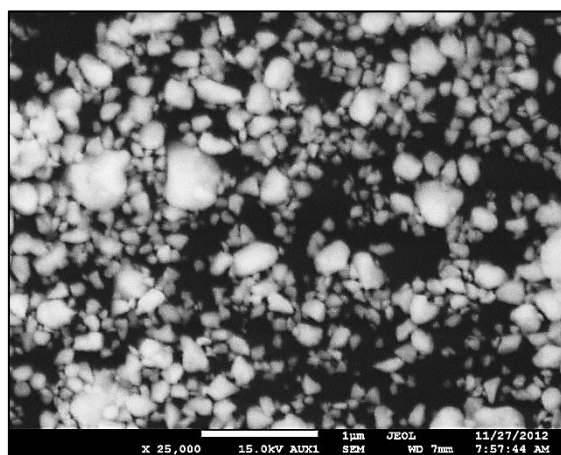


Figure 4.12. SEM-BSE image of as-received nano WC powder, showing angular particles and particle agglomerates between ~0.3-0.5 μm.

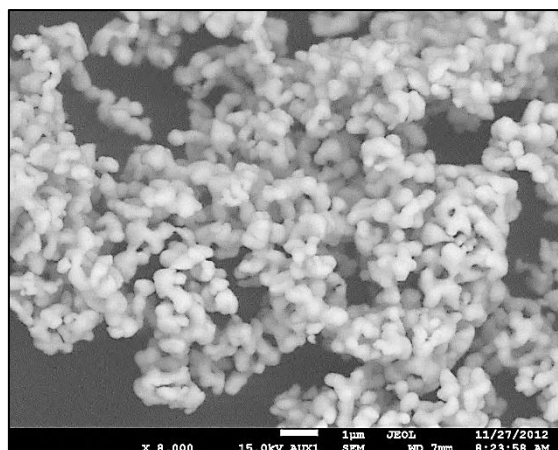


Figure 4.13. SEM-BSE image of as-received Co powder, showing agglomerates of irregular particles.

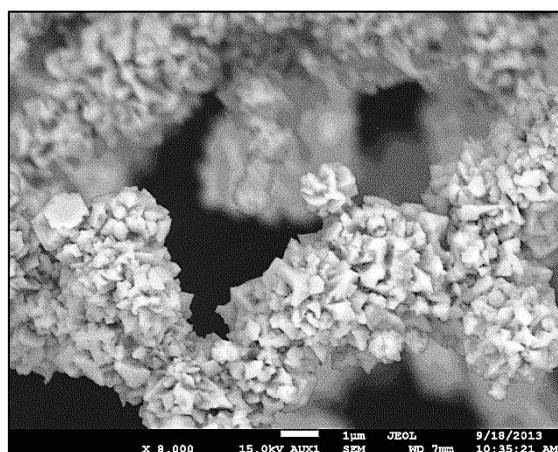


Figure 4.14. SEM-BSE image of as-received micron Ni powder, showing chains of agglomerate angular particles.

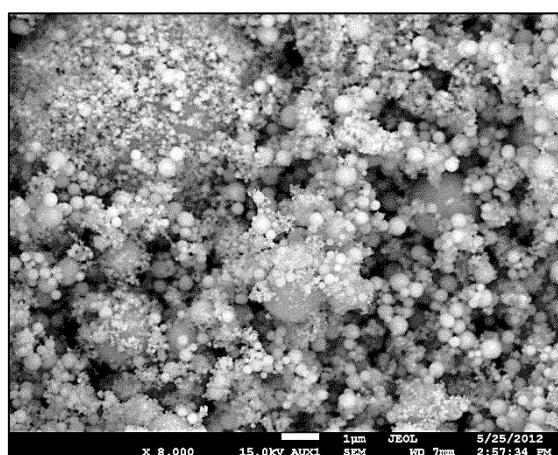


Figure 4.15. SEM-BSE image of as-received ultra-fine Ni powder, showing spherical particles of different sizes.

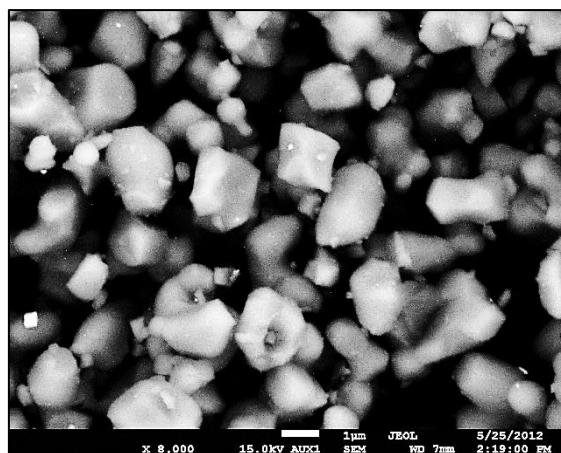


Figure 4.16. SEM-BSE image of as-received TiC powder, showing angular particles.

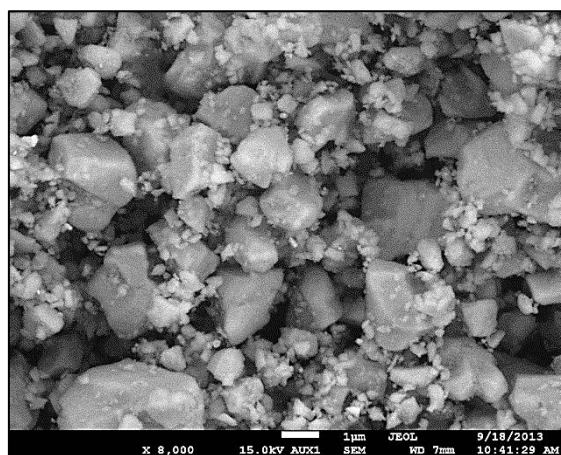


Figure 4.17. SEM-BSE image of as-received NbC powder, showing angular particles of different sizes.

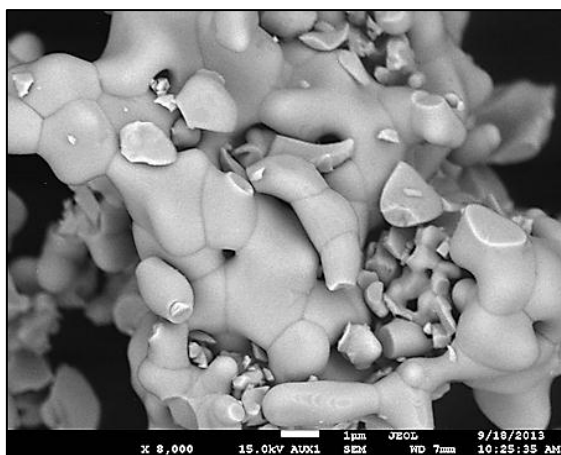


Figure 4.18. SEM-BSE image of as-received Mo₂C powder, showing irregular particles which aggregated with mainly smooth surfaces.

4.1.3 Powder crystal structure

The crystal structures of the as-received powders were determined using XRD analysis. The powder XRD patterns are shown in Figures 4.19-4.24. Chromium carbide was not detected in the WC-0.5Cr₃C₂ powder XRD analysis, although 0.71 wt% Cr was detected in the powder by XRF analysis.

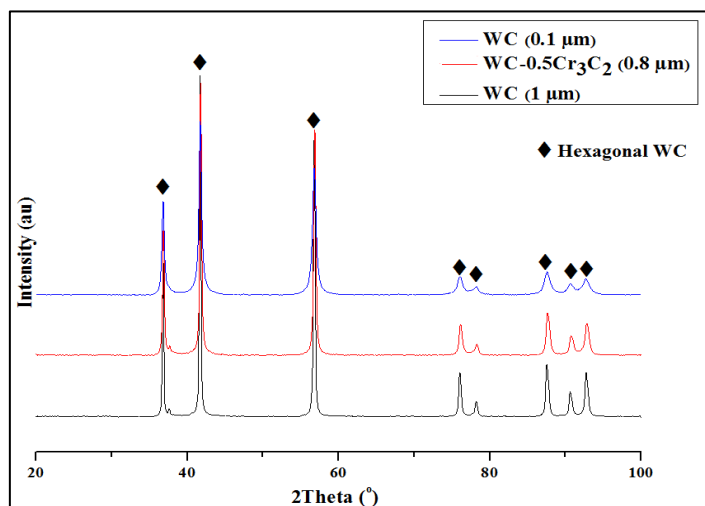


Figure 4.19. X-ray diffraction patterns for as-received 1, 0.8 and 0.1 μm WC powders.

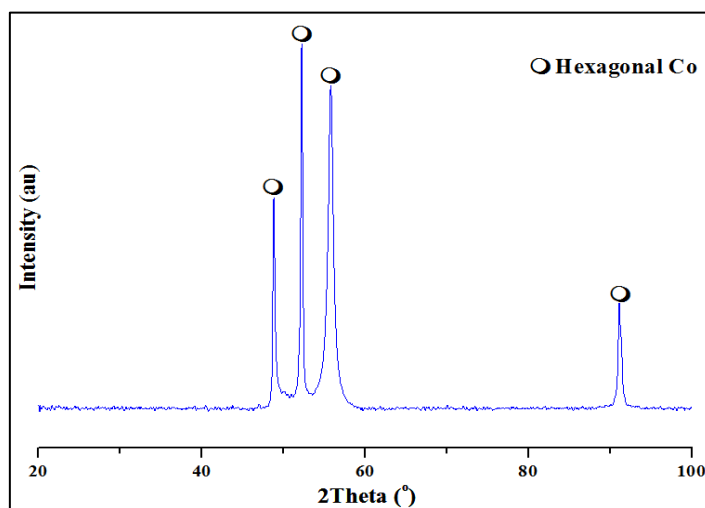


Figure 4.20. X-ray diffraction pattern for as-received Co powder.

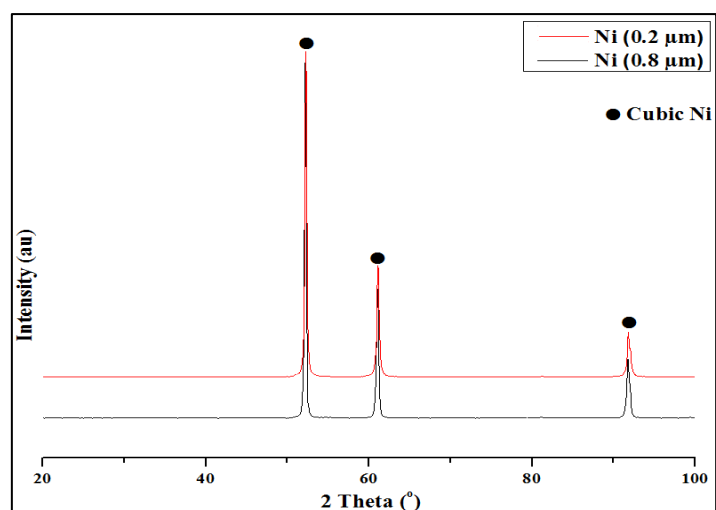


Figure 4.21. X-ray diffraction patterns for as-received 0.2µm and 2.5µm Ni powders.

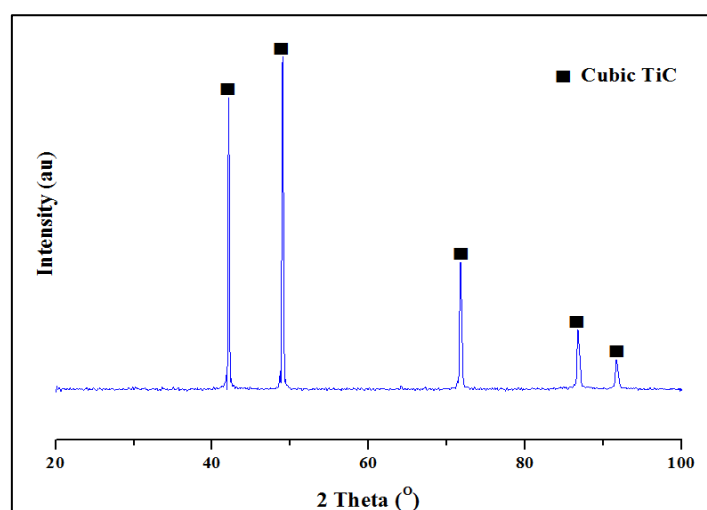


Figure 4.22. X-ray diffraction pattern for as-received TiC powder.

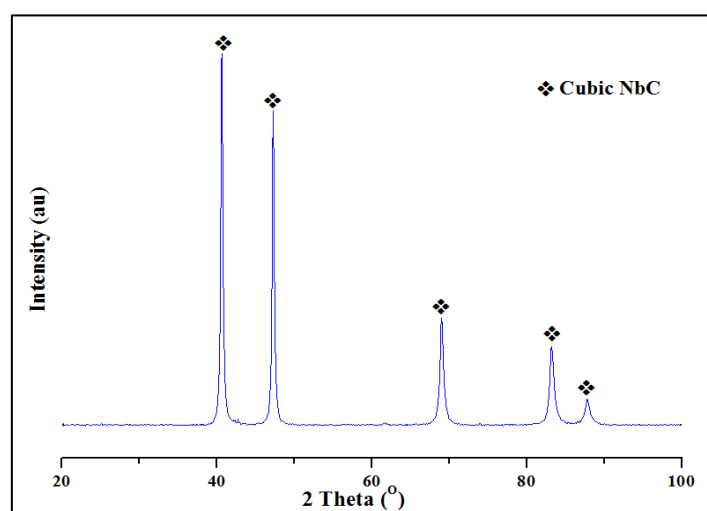


Figure 4.23. X-ray diffraction pattern for as-received NbC powder.

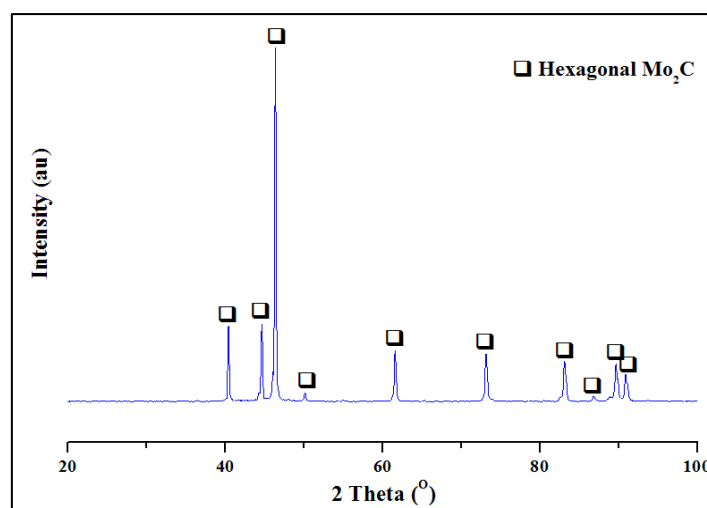


Figure 4.24. X-ray diffraction pattern for as-received Mo₂C powder.

4.2 Optimisation of Milling

4.2.1 Determining milling media and milling time

Most of the starting powders, apart from the ultra-fine WC (0.4 µm) and submicron WC (0.8 µm), were the required size range, thus milling was done to achieve good mixing and breakdown powder agglomerates which prevent uniform distribution of powders. Optimisation of milling to improve the mechanical properties was done through the determination of most effective dense milling media between WC-10Co (wt%) and steel balls, the best ball to powder ratio, and the best milling time.

A composition consisting of WC-0.5Cr₃C₂-10Co (wt%) was milled in the 100g capacity mill, using WC-10Co (wt%) and steel balls. This information was used to plot Figure 4.25, and since the starting particle sizes of WC-0.5Cr₃C₂ was 0.8 µm and Co was 0.9 µm (Table 4.1), a D₅₀ of about 0.8 µm was used as the indication of effective agglomerate breakdown. After about 9 h milling using the WC-10Co (wt%) balls, a D₅₀ particle size of 0.816 µm was attained, beyond which no further significant reduction in particle size took place. However, after 20 h milling with steel balls, a D₅₀ of about 0.95 µm was attained, indicating WC-10Co (wt%) balls were effective in agglomerate breakdown.

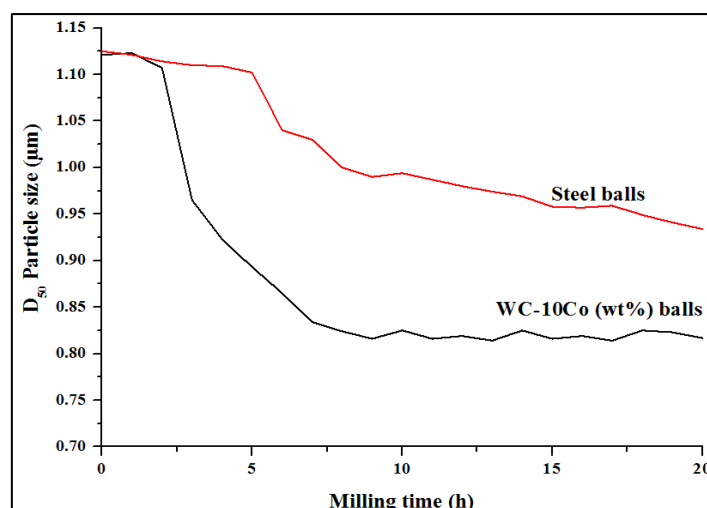


Figure 4.25. Comparison between WC-10Co (wt%) and steel milling balls.

In the case of WC-0.5Cr₃C₂-9.3Ni (wt%), milling was done using WC-10Co (wt%) balls. After milling for about 10 h, a D₅₀ particle size of 0.804 μm was attained, below which no significant reduction was observed (Figure 4.26). Hence, the WC-0.5Cr₃C₂-X-9.3Ni (wt%) compositions were milled using a WC-10Co (wt%) ball to powder ratio of 3:1 for 10 h.

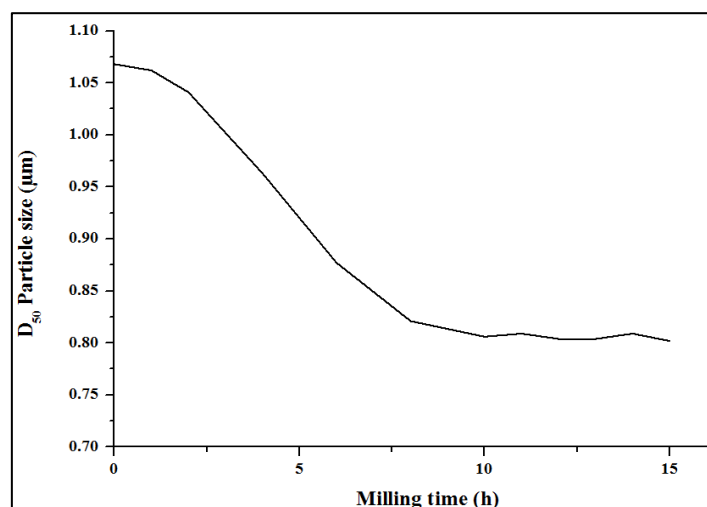


Figure 4.26. WC-0.5Cr₃C₂-9.3Ni (wt%) milling curve using WC-10Co (wt%) milling balls.

During milling of the very fine powders WC (0.1 μm) and Ni (0.2 μm) compositions, higher milling energies were required to break up the aggregates formed. This was achieved by increasing the WC-10Co (wt%) ball-to-powder ratio from 3:1 to 6:1. A comparison between these two ratios is shown in Figure 4.27. After about 12 h milling using the 6:1 ratio, a D₅₀ particle size of <0.2 μm was attained, beyond which no further significant reduction was

observed. Milling for 20 h using the 3:1 ratio resulted in a particle size $>0.3 \mu\text{m}$. Thus, the nano and ultra-fine compositions were milled using WC-10Co (wt%) ball to powder ratio of 6:1 for 15 h.

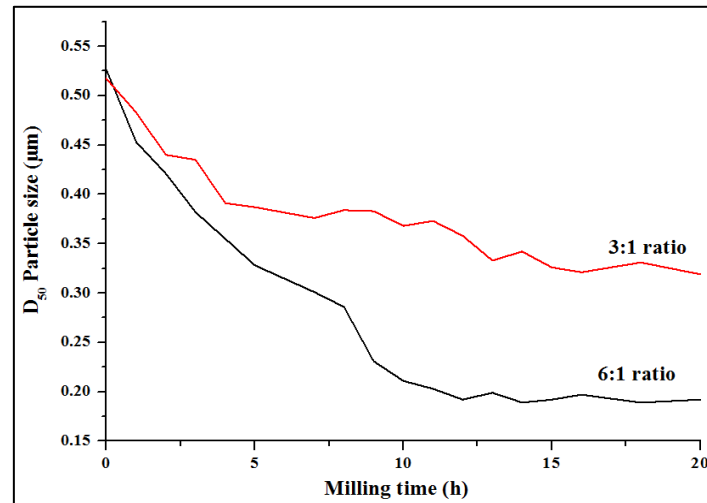


Figure 4.27. Comparison between 6:1 and 3:1 ball-to-powder ratios during milling of nano WC-9.3Ni (wt%).

4.2.2 Production of ultra-fine (0.4 μm) and submicron (0.8 μm) WC powders

Submicron and ultra-fine WC powders were produced through high energy milling of 1 μm WC starting powders in a 1 kg capacity mill. Submicron powder was produced using a ball-to-powder ratio of 10:1 at a speed of 66 rpm. After milling for about 19 h (Figure 4.28), a D₅₀ particle size of 0.802 μm and a mean size of 0.824 μm were attained (Table 4.2).

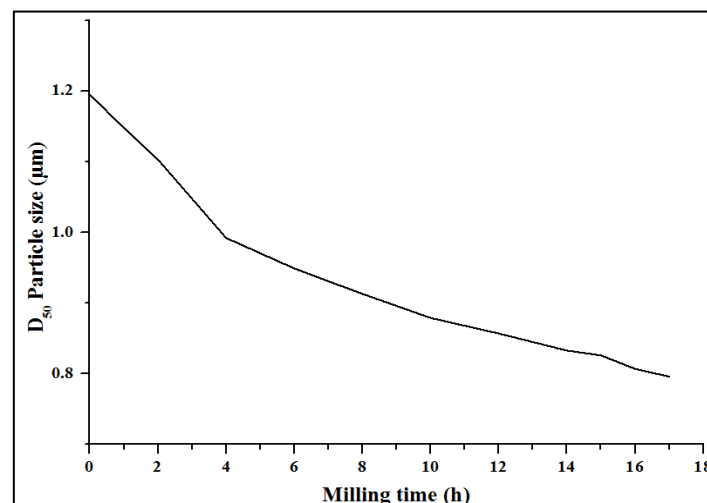


Figure 4.28. Particle size reduction of WC powder from 1 μm to 0.8 μm using a 10:1 ball-to-powder ratio.

Table 4.2. Particle size distribution of submicron and ultra-fine powders.

Powder	Expected size (μm)	D₁₀ (μm)	D₅₀ (μm)	D₉₀ (μm)	Mean (μm)
Submicron	0.8	0.492	0.802	1.661	0.824
Ultra-fine	0.4	0.156	0.391	0.953	0.420

The ultra-fine powders were produced using a ball-to-powder ratio of 15:1 at a speed of 66 rpm. After about 30 h milling (Figure 4.29), a D₅₀ particle size of 0.391 μm and a mean size of 0.420 μm were obtained (Table 4.2).

The microstructures of the submicron and ultra-fine powders are shown in Figures 4.30 and 4.31. Both powders had angular-shaped particles, but the ultra-fine powders also had powder agglomerates. X-ray diffraction analysis was done to check for Co and Fe impurities and indicated the hexagonal WC phase only (Figure 4.32). Trace amounts of Ga and Nb were detected by XRF analysis, and these impurities were present in the 1 μm WC starting powders (Table 4.3). Oxygen analysis was also done and compared to the starting powders to ensure that no oxides were formed during the high energy milling. From Table 4.4, a negligible increase in oxygen amount was observed in both milled powders.

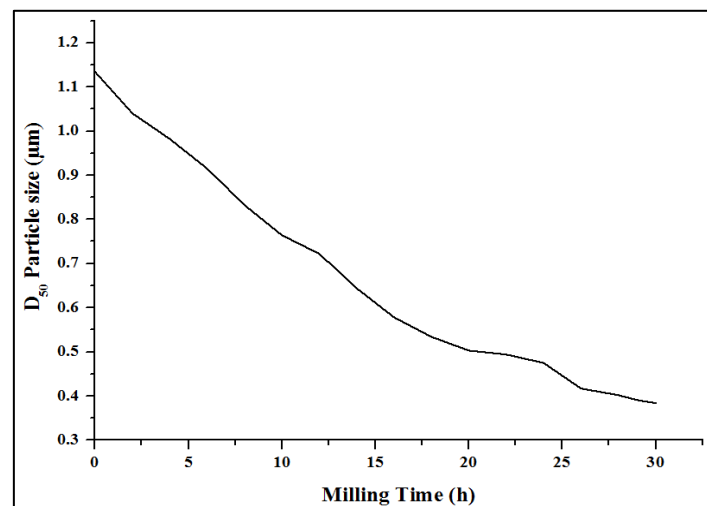


Figure 4.29. Particle size reduction of WC powder from 1 μm to 0.4 μm using a 15:1 ball-to-powder ratio.

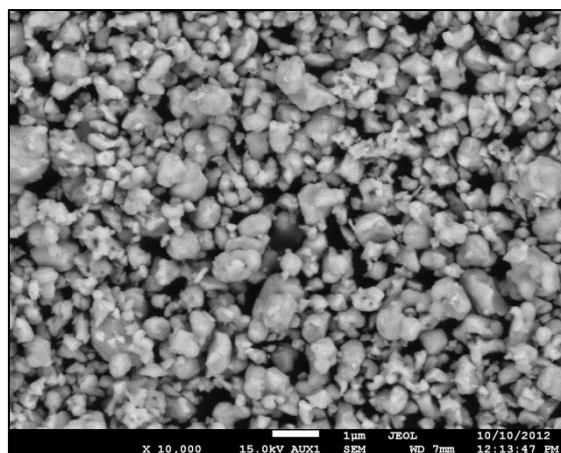


Figure 4.30. SEM-BSE image of as-received 0.8 μm WC powder, showing angular grains.

Table 4.3. XRF results for 1, 0.8 and 0.4 μm WC powders.

WC particle size (μm)	Elements (wt%)		
	W	Ga	Nb
1.0	99.19	0.65	0.16
0.8	99.21	0.63	0.16
0.4	99.23	0.62	0.15

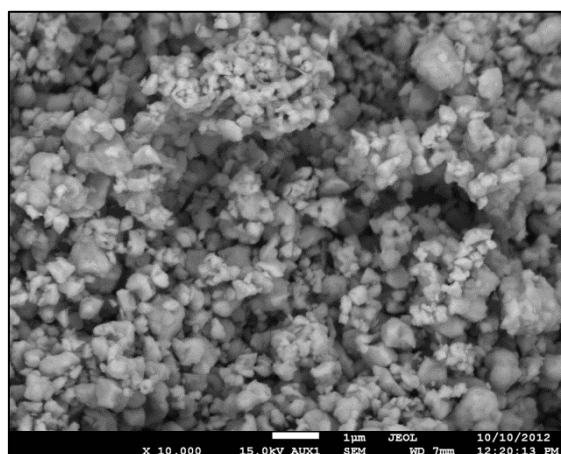


Figure 4.31. SEM-BSE image of as-received 0.4 μm WC powder, showing angular particle and particle agglomerates.

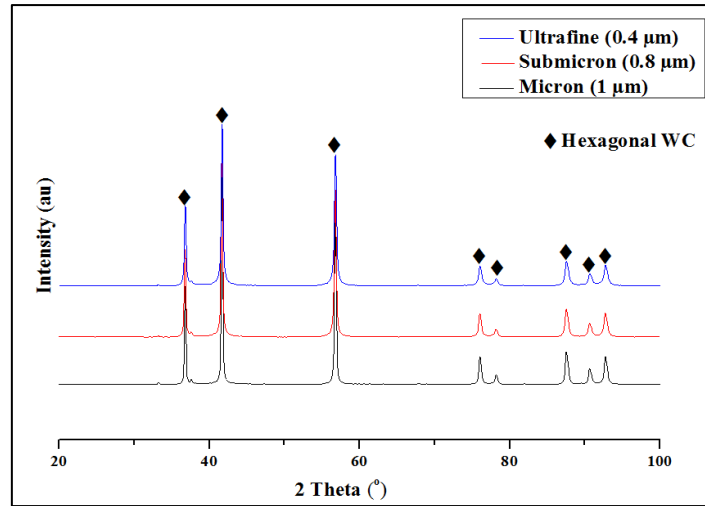


Figure 4.32. X-ray diffraction patterns showing micron WC starting powders, submicron and ultra-fine WC powders.

Table 4.4. Oxygen analysis of 1, 0.8 and 0.4 μm WC powders.

Particle size of WC	Amount of oxygen (wt%)
1.0	0.39 ± 0.06
0.8	0.41 ± 0.02
0.4	0.42 ± 0.05

4.3 Optimisation of spark plasma sintering process

4.3.1 Sintering temperature

Sintering temperature was varied from 1050°C-1240°C for sintering WC-0.5Cr₃C₂-10Co (wt%) (Table 4.5). A cooling rate of 200°C/min was used for all sintering profiles.

4.3.1.1 Densification

The densities attained after sintering using the profiles in Table 4.5 are shown in Table 4.6. Samples 1.1-1.3 had poor densification with high amounts of open porosity. Densification increased with increased temperature, and above 1220°C (Sample 1.4), a calculated density higher than 100% was attained (Sample 1.5). Cobalt (lower density phase) was squeezed out of the sample and onto the rams (as a silver shiny coating) (Figure 4.33 (b)) during sintering of Sample 1.5.

Table 4.5. Variation of sintering temperature criteria.

Sample	Temperature (°C)	Pressure (MPa)
1.1	200°C/minute to 600°C	50
	then 100°C/minute to 1050°C	
	held at 1050°C for 5 minutes	
1.2	200°C/minute to 700°C	50
	then 100°C/minute to 1140°C	
	held at 1140°C for 5 minutes	
1.3	200°C/minute to 700°C	50
	then 100°C/minute to 1190°C	
	held at 1190°C for 5 minutes	
1.4	200°C/minute to 1050°C	50
	then 100°C/minute to 1220°C	
	held at 1220°C for 5 minutes	
1.5	200°C/minute to 1050°C	50
	then 100°C/minute to 1240°C	
	held at 1240°C for 5 minutes	

Table 4.6. Variation in densification due to variation in sintering temperature.

Sample	Temperature (°C)	Densification (%)	Open porosity volume(%)
1.1	1050	77.41 ± 0.65	9.33 ± 0.34
1.2	1140	84.12 ± 1.21	8.95 ± 1.05
1.3	1190	92.65 ± 0.43	7.81 ± 0.94
1.4	1220	98.12 ± 0.72	0.75 ± 0.13
1.5	1240	101.34 ± 0.04	0.00 ± 0.00

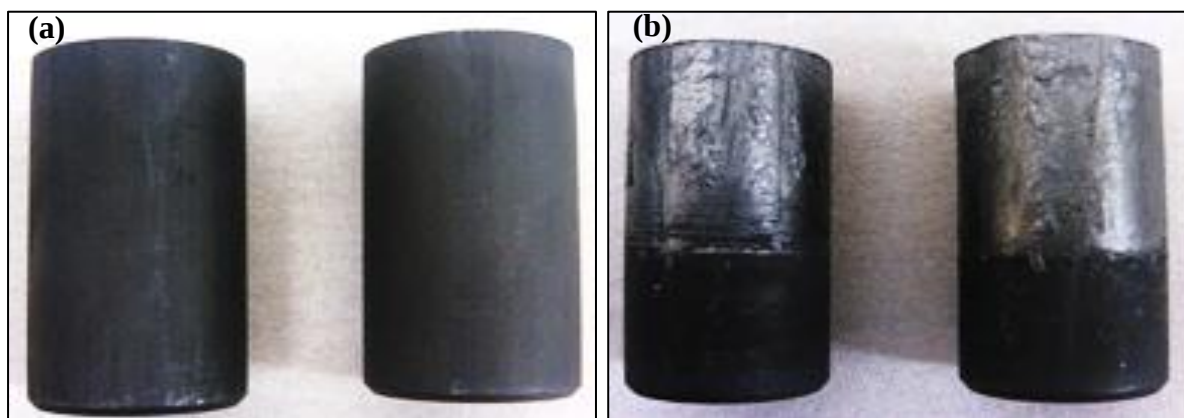


Figure 4.33. Images of the rams (a) before, and (b) after SPS WC-0.5Cr₃C₂-10Co (wt%) at 1240°C, a silver shiny coating was present on the rams after sintering.

4.3.1.2 Microstructure

The microstructures of Samples 1.1-1.5 are shown in Figure 4.34. Sample 1.1 had the highest amount of porosity followed by Sample 1.2. Sample 1.3 had a few large pores, while no porosity was observed in the microstructures of Samples 1.4 and 1.5. Sample 1.5 (Figure 4.34 (e)) had the smallest Co pools, which were sparsely distributed.

4.3.1.3 Magnetic properties

Magnetic saturation decreased, while coersivity increased with increased sintering temperature (Table 4.7). Sample 1.5 had a much lower magnetic saturation and significantly higher coersivity.

Table 4.7. Variation of magnetic properties with sintering temperature.

Sample	Temperature (°C)	Magnetic saturation ($\mu\text{Tm}^3/\text{kg}$)	Coersivity (KA/m)
1.1	1050	19.3 ± 0.3	20.28 ± 0.04
1.2	1140	18.8 ± 0.2	22.57 ± 0.13
1.3	1190	18.2 ± 0.1	22.69 ± 0.21
1.4	1220	17.9 ± 0.1	23.07 ± 0.05
1.5	1240	13.8 ± 0.2	27.84 ± 0.17

4.3.2 Sintering pressure

Sintering pressure application was varied as shown in Table 4.8; all samples were sintered using the heating profile for Sample 1.4.

Table 4.8. Variation of sintering pressures.

Sample	Temperature (°C)	Pressure (MPa)
2.1	200°C/minute to 1050°C	50
	then 100°C/minute to 1220°C	
	held at 1050°C for 5 minutes	
2.2	200°C/minute to 1050°C	16-50 at 4MPa/minute
	then 100°C/minute to 1220°C	
	held at 1050°C for 5 minutes	
2.3	200°C/minute to 1050°C	16
	then 100°C/minute to 1220°C	30
	held at 1050°C for 5 minutes	50

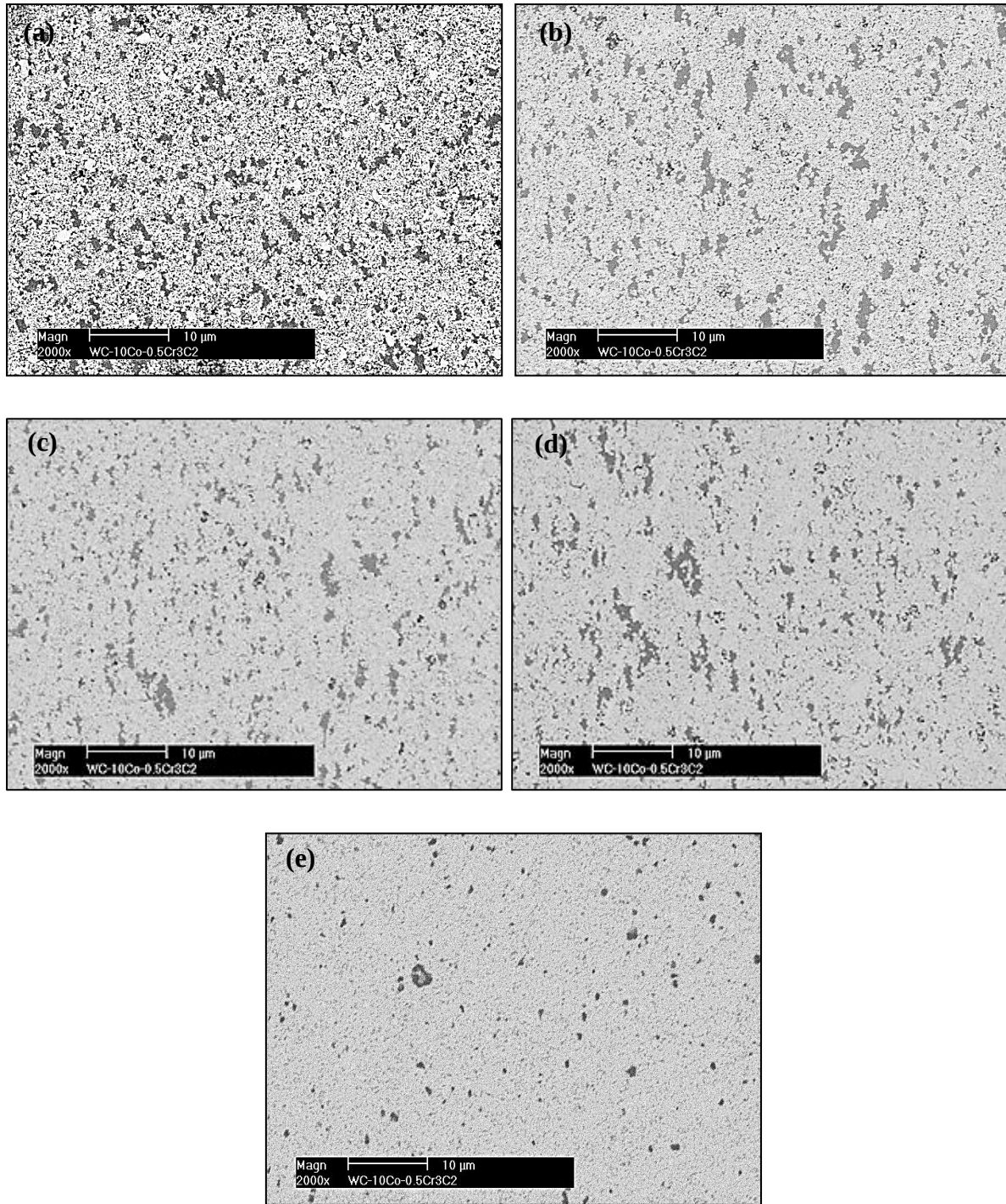


Figure 4.34. SEM-BSE images of WC-0.5Cr₃C₂-10Co (wt%): sintered at (a) 1050°C, (b) 1140°C, (c) 1190°C, (d) 1220°C, and (e) 1240°C: WC (light), Co (medium) and pores (dark).

4.3.3.1 Densification

Densification of samples is shown in Table 4.9, and Sample 2.3 had the highest densification and negligible open porosity, while Sample 2.2 had the lowest densification and highest open porosity.

Table 4.9. Densification due to variation in pressures as shown in Table 4.8.

Sample	Densification (%)	Open porosity volume(%)
2.1	98.12 ± 0.72	0.75 ± 0.13
2.2	89.20 ± 1.33	8.11 ± 0.79
2.3	99.22 ± 0.46	0.08 ± 0.03

4.3.3.2 Microstructure

Representative micrographs of Samples 2.1, 2.2 and 2.3 are shown in Figure 4.35. Sample 2.2 (Figure 4.35 (b)) had highest porosity, while Sample 2.3 had smaller Co pools in comparison to Sample 2.1.

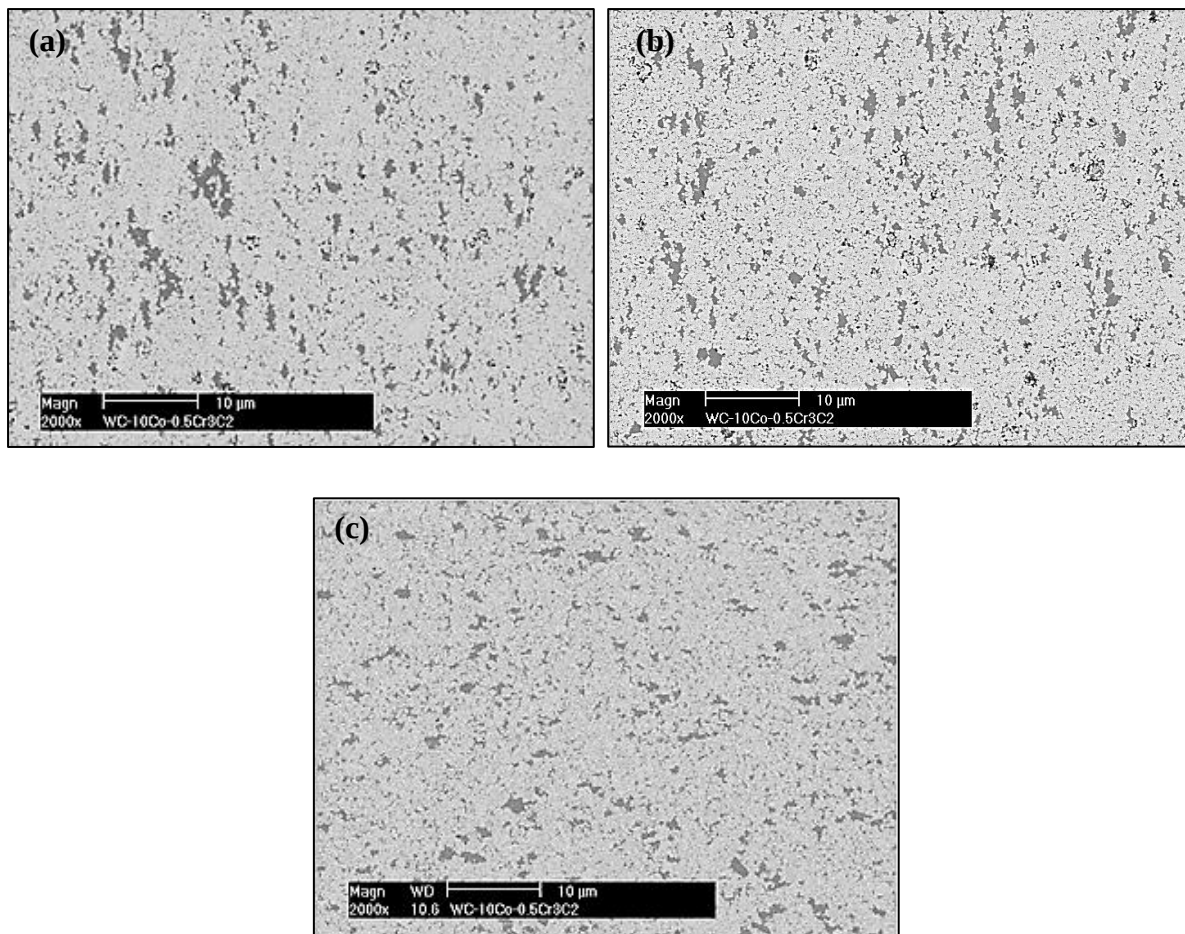


Figure 4.35. SEM-BSE images of WC-0.5Cr₃C₂-10Co (wt%): (a) Sample 2.1, (b) Sample 2.2, and (c) Sample 2.3: WC (light), Co (medium) and pores (dark).

4.3.3. Effect of sintering time on densification

Densification due to variation in sintering dwell time is shown in Table 4.10, and all the samples were sintered using the profile for Sample 2.3. Sample 3.1 had the lowest

densification, while Samples 3.2–3.5 had densification >99%; all samples had negligible open porosities. Thus, a sintering time of 2 minutes was used WC-0.5Cr₃C₂-10Co (wt%).

Table 4.10. Variation in densification due to difference in sintering time.

Sample	Time (minutes)	Densification (%)	Open porosity volume (%)
3.1	1	98.39 ± 0.76	0.07 ± 0.03
3.2	2	99.17 ± 0.51	0.09 ± 0.05
3.3	3	99.21 ± 0.96	0.09 ± 0.04
3.4	4	99.19 ± 0.73	0.06 ± 0.09
3.5	5	99.22 ± 0.46	0.08 ± 0.03

4.3.4 Addition of NbC to WC-0.5Cr₃C₂-10Co (wt%)

Addition of 0.5wt% NbC did not affect the densification temperature of WC-0.5Cr₃C₂-10Co, although additions ≥1 wt% inhibited densification (Figure 4.36). A comparison between the relative piston movement for WC-0.5Cr₃C₂-10Co, WC-0.5Cr₃C₂-1NbC-10Co and WC-0.5Cr₃C₂-10NbC-10Co (wt%) during sintering is shown in Figure 4.36. The WC-0.5Cr₃C₂-10Co (wt%) composition had the highest piston travel (shrinkage), due to complete densification at 1220°C (Figure 4.36 and Table 4.11). Although the 1 and 10 NbC (wt%) samples achieved lower shrinkage, their densification was still increasing throughout the sintering dwell time, indicating incomplete sintering at 1220°C for 2 minutes.

Table 4.11. Change in densification with NbC addition.

Sample	Densification (%)	Open porosity volume(%)
0 NbC	99.17 ± 0.51	0.09 ± 0.05
1 NbC	89.94 ± 0.17	8.38 ± 1.24
10 NbC	87.75 ± 0.23	9.06 ± 0.91

To increase the densification, the sintering temperature, pressure and time were increased during sintering of the 1 NbC (wt%) sample (Table 4.12). A pressure of 60MPa was used for all samples.

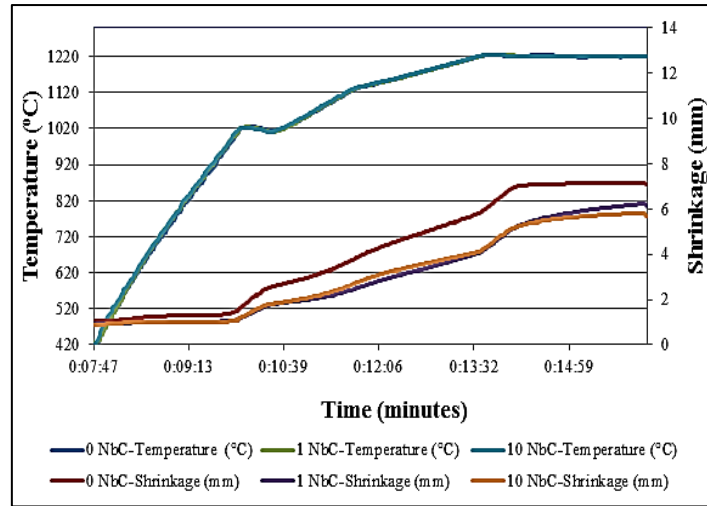


Figure 4.36. Variation in compact shrinkage (densification) due addition of NbC to WC-0.5Cr₃C₂-10Co (wt%).

Table 4.12. Variation in densification with sintering temperature and time.

Sample	Temperature (°C)	Time (minutes)	Densification (%)	Open porosity volume (%)
4.1	1250	2	97.72 ± 0.72	0.18 ± 0.04
4.2	1250	5	98.45 ± 0.51	0.09 ± 0.03
4.3	1260	5	99.23 ± 0.45	0.07 ± 0.02

From Figure 4.37 and Table 4.12, Sample 4.2 had higher densification than Sample 4.1, because of increased sintering time, while Sample 4.3 had the highest densification.

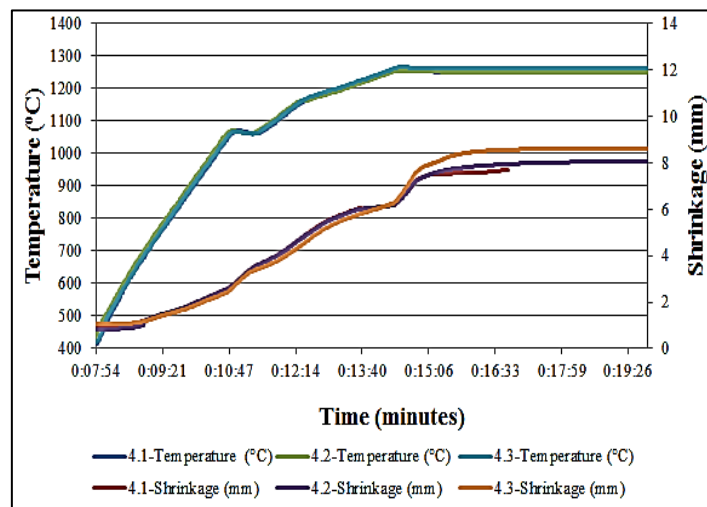


Figure 4.37. Effect of sintering temperature and time on densification of WC-0.5Cr₃C₂-1NbC-10Co (wt%).

The sintering profile for Sample 4.3 was applied to 10 wt% NbC (Figure. 4.38) and a good densification of >99 % was attained. Elimination of porosity in the 1 and 10 wt% NbC samples was confirmed by SEM-BSE images (Figures 4.39 and 4.40). This sintering profile was used for additions of 1-80 wt% NbC to WC-0.5Cr₃C₂-10Co (wt%).

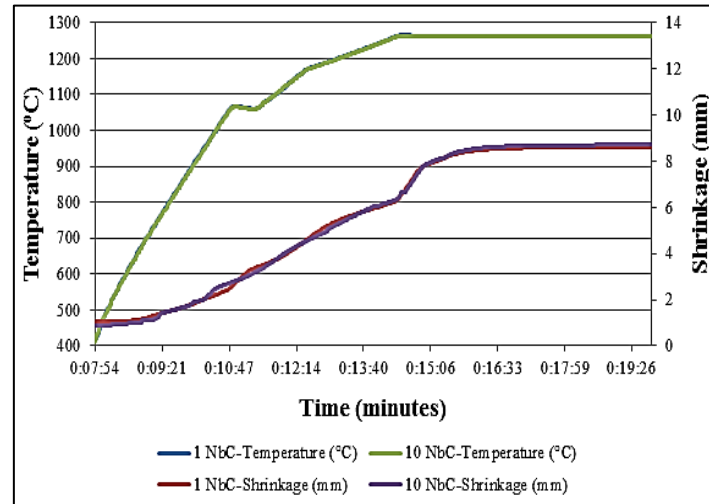


Figure 4.38. Comparison of shrinkage between 1 and 10 NbC (wt%) additions to WC-0.5Cr₃C₂-10Co (wt%), sintered at 1260°C, 60 MPa for 5 minutes.

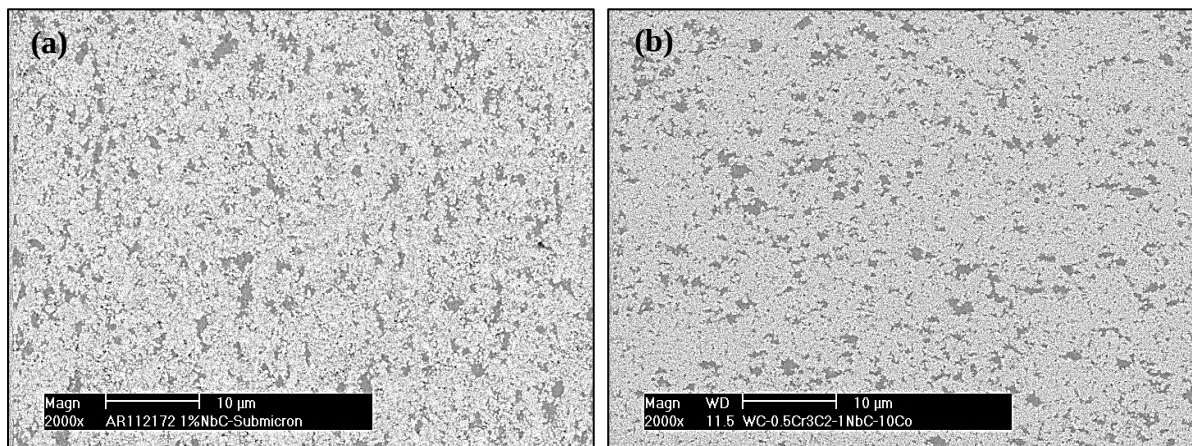


Figure 4.39. SEM-BSE images of WC-0.5Cr₃C₂-1NbC-10Co (wt%): (a) sintered at 1220°C, 50MPa for 2 minutes, and (b) sintered at 1260°C, 60MPa for 5 minutes: WC (light), Co (medium light), NbC (medium dark), pores (dark).

4.3.5 Sintering WC-Ni

The sintering temperature for WC-0.5Cr₃C₂-9.3Ni (wt%) was varied from 1140°C to 1300°C and pressure increased from 50 MPa to 60 MPa, as shown in Table 4.13. A dwell time of 5 minutes was used for all samples.

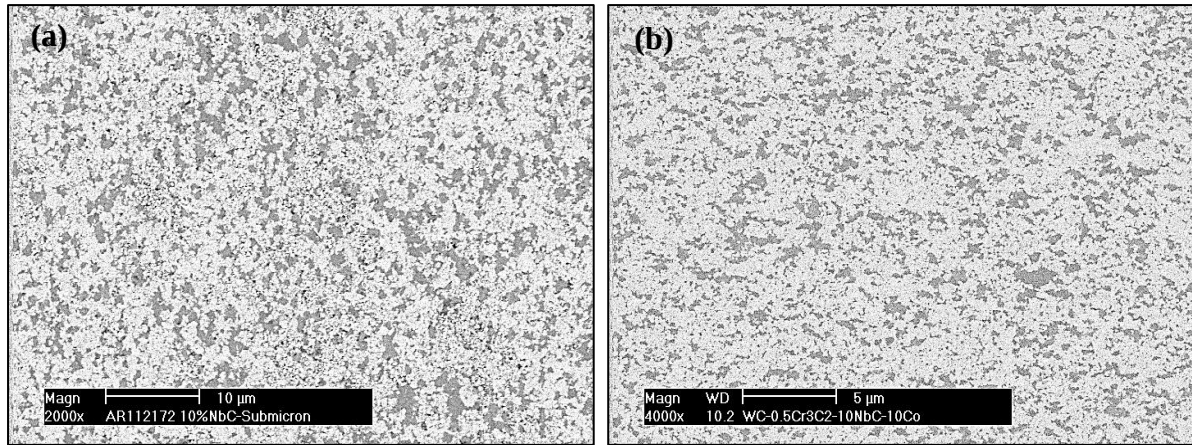


Figure 4.40. SEM-BSE images of WC-0.5Cr₃C₂-10NbC-10Co (wt%): (a) sintered at 1220°C, 50MPa for 2 minutes, and (b) sintered at 1260°C, 60MPa for 5 minutes; WC (light), Co (medium light), NbC (medium dark), pores (dark).

Increased sintering temperature and pressure improved the densification (Table 4.13), with 1280°C (Sample 5.4) having the best densification. Sample 5.5 had a calculated density of $101.42 \pm 0.35\%$ and Ni squeezed onto the rams during sintering. A sintering temperature of 1280°C, pressure of 60 MPa and dwell time of 5 minutes were used to achieve full density of WC-0.5Cr₃C₂-9.3Ni (wt%), compared to WC-0.5Cr₃C₂-Co (wt%) of 1220°C, 50 MPa and 2 minutes.

Table 4.13. Change in densification of WC-0.5Cr₃C₂-9.3Ni (wt%) due to varying sintering conditions.

Sample	Temperature (°C)	Pressure (MPa)	Densification (%)	Open porosity volume (%)
5.1	1140	50	93.11 ± 0.71	6.57 ± 0.98
5.2	1220	50	95.83 ± 0.24	4.83 ± 1.26
5.3	1260	60	98.02 ± 0.67	0.57 ± 0.04
5.4	1280	60	99.30 ± 0.32	0.04 ± 0.02
5.5	1300	60	101.42 ± 0.35	0.00 ± 0.00

4.3.6 Addition of TiC and Mo₂C to WC-0.5Cr₃C₂-Ni (wt%)

Addition TiC and Mo₂C inhibited densification of WC-0.5Cr₃C₂-9.3Ni (wt%) at 1280°C, 60MPa for 5 minutes as shown in Figure 4.41 and Table 4.14, compared to WC-0.5Cr₃C₂-9.3Ni “9.3Ni”, WC-0.5Cr₃C₂-6.25TiC-9.3Ni “0Mo₂C” and WC-0.5Cr₃C₂-6.25TiC-3.5 Mo₂C - 9.3Ni (wt%) “3.5Mo₂C”. The densification of the 0 Mo₂C was improved by increasing pressure from 60-70 MPa (Figure. 4.42), resulting in $99.11 \pm 0.09\%$ densification.

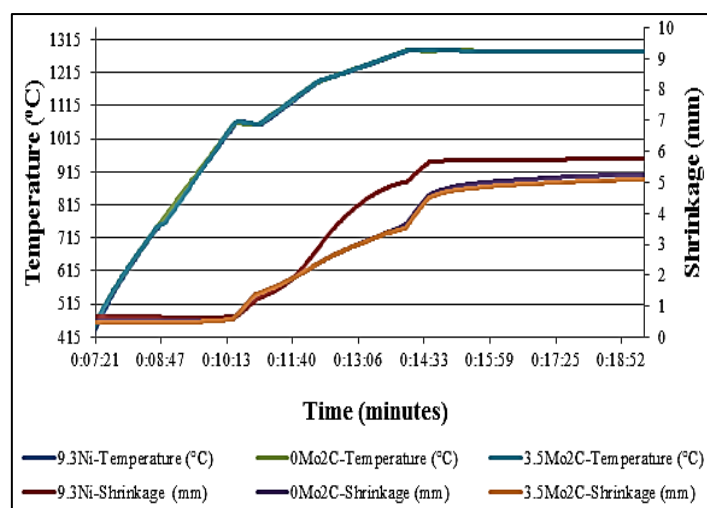


Figure 4.41. Variation in densification due to addition of 6.25 TiC (wt%) and 3.5 Mo₂C (wt%) to WC-0.5Cr₃C₂-9.3Ni (wt%).

Table 4.14. Densification due to addition of 6.25 TiC (wt%) and 3.5 Mo₂C (wt%) to WC-0.5Cr₃C₂-9.3Ni (wt%).

Sample	Densification (%)	Open porosity volume (%)
9.3 Ni	99.30 ± 0.32	0.04 ± 0.02
0 Mo ₂ C	98.23 ± 0.17	0.81 ± 0.11
3.5 Mo ₂ C	96.65 ± 1.46	6.52 ± 1.23

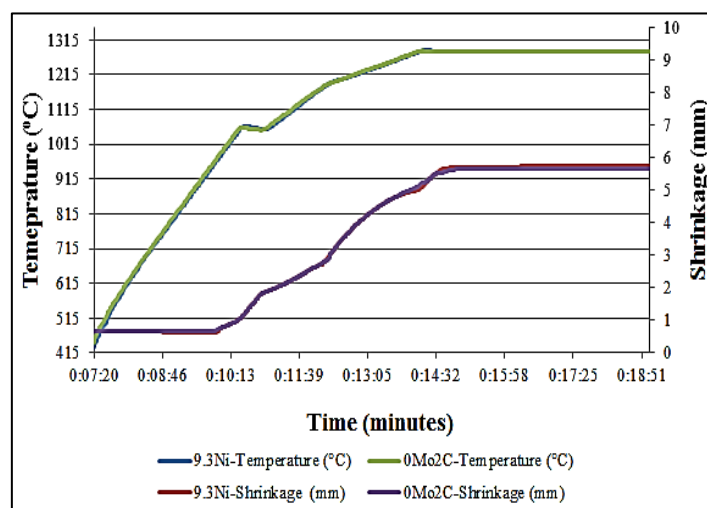


Figure 4.42. Improved densification of WC-0.5Cr₃C₂-6.25TiC-9.3Ni (wt%) because of increased sintering pressure from 60-70MPa.

To improve the densification of the 3.5 Mo₂C sample, higher sintering temperatures were used as shown in Table 4.13. A dwell time of 5 minutes and pressure of 70 MPa were used

for all samples. Higher sintering temperatures increased densification, with 1310°C (Sample 6.2) having the best densification (Table 4.15 and Figure 4.43), above which a calculated density of $100.94 \pm 0.04\%$ and loss of Ni content was observed (Sample 6.3). The same approach was applied for all the Mo₂C addition samples (0.5-5 Mo₂C (wt%)) to attain >99% densification.

Table 4.15. Densification of WC-0.5Cr₃C₂-3.5Mo₂C-6.25TiC-9.3Ni (wt%) with increased sintering temperature.

Sample	Temperature (°C)	Densification (%)	Open porosity volume (%)
6.1	1300	98.47 ± 0.27	0.16 ± 0.02
6.2	1310	99.20 ± 0.29	0.03 ± 0.04
6.3	1320	100.94 ± 0.34	0.00 ± 0.00

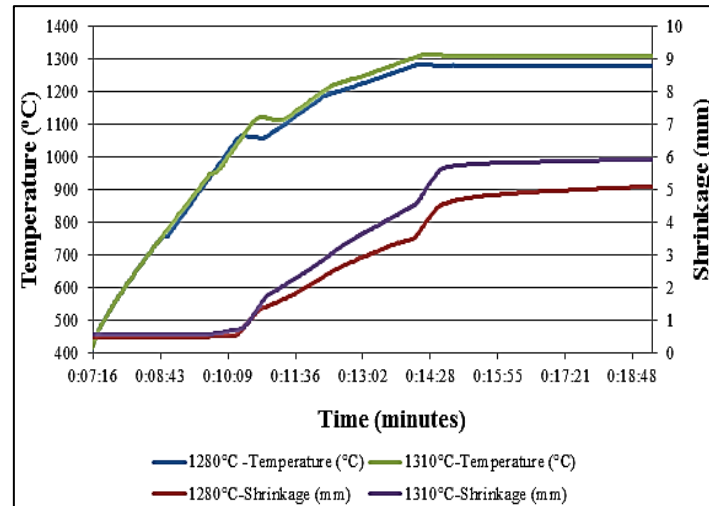


Figure 4.43. Comparison between densification curves of WC-0.5Cr₃C₂-3.5Mo₂C-6.25TiC-9.3Ni (wt%) sintered at 1280°C and 1310°C.

4.3.7 Overall sintering conditions

The sintering conditions used for WC-0.5Cr₃C₂-10Co (wt%) with 0-80 wt% NbC additions are shown in Table 4.16 and for WC-0.5Cr₃C₂-9.3Ni (wt%) with 6.25 TiC (wt%) and 0-5 Mo₂C (wt%) are shown in Table 4.17.

4.3.7.1 Sintering conditions for WC-XNbC-10Co (wt%) produced from nano and ultra-fine WC powders

Similar compositions to those in Table 4.16 were produced from nano and ultra-fine WC powders that were not doped with Cr₃C₂. Slightly higher sintering temperatures were used for

nano and ultra-fine WC compositions (Table 4.18) than for WC-0.5Cr₃C₂ compositions to achieve good densification.

Table 4.16. Sintering conditions for WC-0.5Cr₃C₂-10Co (wt%) with NbC addition.

Sample (wt%)	Temperature (°C)	Pressure (MPa)
WC-0.5Cr ₃ C ₂ -10Co	200°C/minute to 1000°C	16
	then 100°C/minute to 1220°C	30
	held at 1220°C for 5 minutes	50
WC-0.5Cr ₃ C ₂ -0.5NbC-10Co	200°C/minute to 1000°C	16
	then 100°C/minute to 1220°C	30
	held at 1220°C for 5 minutes	60
WC-0.5Cr ₃ C ₂ -1NbC-10Co WC-0.5Cr ₃ C ₂ -2NbC-10Co WC-0.5Cr ₃ C ₂ -3NbC-10Co WC-0.5Cr ₃ C ₂ -5NbC-10Co WC-0.5Cr ₃ C ₂ -10NbC-10Co WC-0.5Cr ₃ C ₂ -20NbC-10Co WC-0.5Cr ₃ C ₂ -30NbC-10Co WC-0.5Cr ₃ C ₂ -50NbC-10Co WC-0.5Cr ₃ C ₂ -80NbC-10Co	200°C/minute to 1050°C then 100°C/minute to 1260°C held at 1260°C for 5 minutes	16 30 60

Table 4.17. Sintering conditions for WC-10Co (wt%) with different NbC additions, using nano and ultra-fine WC starting powders.

Sample (wt%)	Temperature (°C)	Pressure (MPa)
WC-10Co	200°C/minute to 1050°C	16
	then 100°C/minute to 1240°C	30
	held at 1240°C for 5 minutes	50
WC-1NbC-10Co WC-2NbC-10Co WC-5NbC-10Co WC-20NbC-10Co	200°C/minute to 1050°C then 100°C/minute to 1290°C held at 1290°C for 5 minutes	16 30 60

Table 4.18. Sintering conditions for WC-0.5Cr₃C₂-9.3Ni (wt%) with different TiC and Mo₂C additions.

Sample (wt%)	Temperature (°C)	Pressure (MPa)
WC-0.5Cr ₃ C ₂ -9.3Ni	200°C/minute to 1050°C	16
	then 100°C/minute to 1280°C	30
	held at 1280°C for 5 minutes	60
WC-0.5Cr ₃ C ₂ -6.25TiC-9.3Ni WC-0.5Cr ₃ C ₂ -0.5Mo ₂ C-6.25TiC-	200°C/minute to 1050°C	16
	then 100°C/minute to 1280°C	40
	held at 1280°C for 5 minutes	70
WC-0.5Cr ₃ C ₂ -1Mo ₂ C-6.25TiC-9.3Ni	200°C/minute to 1100°C	16
	then 100°C/minute to 1300°C	40
	held at 1300°C for 5 minutes	70
WC-0.5Cr ₃ C ₂ -2Mo ₂ C-6.25TiC-9.3Ni WC-0.5Cr ₃ C ₂ -3.5Mo ₂ C-6.25TiC- 9.3Ni	200°C/minute to 1100°C	16
	then 100°C/minute to 1310°C	40
	held at 1310°C for 5 minutes	70
WC-0.5Cr ₃ C ₂ -5Mo ₂ C-6.25TiC-9.3Ni	200°C/minute to 1100°C	16
	then 100°C/minute to 1320°C	40
	held at 1320°C for 5 minutes	70

4.3.7.2 Liquid phase sintered samples

Liquid phase sintering (LPS) was carried out using the conditions in Table 4.19. Higher sintering temperatures and longer sintering times were used than for SPS.

Table 4.19. Liquid phase sintering conditions.

Sample (wt%)	Sintering temperature (°C)	Sintering dwell time (minutes)
WC-0.5Cr ₃ C ₂ -10Co	1430	75
WC-9.3Ni-n	1430	75
WC-9.3Ni-n	1510	75

n: nano WC starting powders.

4.3.7.3 Sintering conditions for WC-XMo₂C-6.25TiC-10Co (wt%) produced from nano ultra-fine and submicron WC powders

Compositions similar to those in Table 4.17 were produced using nano, ultra-fine and submicron WC starting powders. Slightly higher sintering temperatures were used for the 1-5 wt% Mo₂C (Table 4.20) compared to the compositions produced using WC-0.5Cr₃C₂ starting powders.

Table 4.20. Sintering conditions for WC-Ni with different TiC and Mo₂C additions with WC starting powders.

Sample (wt%)	Temperature (°C)	Pressure (MPa)
WC-10Ni	200°C/minute to 1050°C	16
WC-9.3Ni		
WC-8Ni	100°C/minute to 1280°C	40
WC-7Ni		
WC-6Ni	held at 1280°C for 5 minutes	60
WC-6.25TiC-9.3Ni	200°C/minute to 1050°C	16
	100°C/minute to 1280°C	40
	held at 1280°C for 5 minutes	70
WC-1Mo ₂ C-6.25TiC-9.3Ni	200°C/minute to 1050°C	16
	100°C/minute to 1290°C	40
	held at 1290°C for 5 minutes	70
WC-3.5Mo ₂ C-6.25TiC-9.3Ni	200°C/minute to 1100°C	16
	100°C/minute to 1320°C	40
	held at 1320°C for 5 minutes	70
WC-5Mo ₂ C-6.25TiC-9.3Ni	200°C/minute to 1100°C	16
	100°C/minute to 1330°C	40
	held at 1330°C for 5 minutes	70
WC-3.5Mo ₂ C-6.25TiC-7Ni	200°C/minute to 1400°C	16
	100°C/minute to 1380°C	40
	held at 1380°C for 5 minutes	70
WC-5Mo ₂ C-6.25TiC-7Ni	200°C/minute to 1400°C	16
	100°C/minute to 1380°C	40
	held at 1380°C for 5 minutes	70

4.3.8 Density of sintered samples

The densities of all the sintered samples are shown in Tables 4.21-4.28.

Table 4.21. Density and open porosity of WC-10Co (wt%) with 0-20 NbC (wt%) additions, produced from ultra-fine (u) WC starting powders.

Sample (wt%)	Sample abbreviation	Densification (%)	Open porosity volume (%)
WC-10Co	10Co-u	99.45 ± 0.43	0.06 ± 0.02
WC-1NbC-10Co	1N-u	99.35 ± 0.67	0.09 ± 0.04
WC-2NbC-10Co	2N-u	99.52 ± 0.23	0.07 ± 0.01
WC-5NbC-10Co	5N-u	99.42 ± 0.72	0.08 ± 0.03
WC-20NbC-10Co	20N-u	99.34 ± 0.23	0.05 ± 0.01

Table 4.22. Density and open porosity of WC-0.5Cr₃C₂-10Co (wt%) with 0-80 NbC (wt%) additions.

Sample (wt%)	Sample abbreviation	Densification (%)	Open porosity volume (%)
WC-0.5Cr ₃ C ₂ -10Co (LPS)	10Co-Cr (LPS)	99.93 ± 0.95	0.00 ± 0.00
WC-0.5Cr ₃ C ₂ -10Co	10Co-Cr	99.17 ± 0.51	0.09 ± 0.05
WC-0.5Cr ₃ C ₂ -0.5NbC-10Co	0.5N-Cr	99.53 ± 0.72	0.06 ± 0.03
WC-0.5Cr ₃ C ₂ -1NbC-10Co	1N-Cr	99.23 ± 0.45	0.07 ± 0.02
WC-0.5Cr ₃ C ₂ -2NbC-10Co	2N-Cr	99.42 ± 0.34	0.05 ± 0.02
WC-0.5Cr ₃ C ₂ -3NbC-10Co	3N-Cr	99.02 ± 0.10	0.07 ± 0.04
WC-0.5Cr ₃ C ₂ -5NbC-10Co	5N-Cr	99.63 ± 0.41	0.05 ± 0.01
WC-0.5Cr ₃ C ₂ -10NbC-10Co	10N-Cr	99.27 ± 0.63	0.04 ± 0.02
WC-0.5Cr ₃ C ₂ -20NbC-10Co	20N-Cr	99.20 ± 0.35	0.09 ± 0.01
WC-0.5Cr ₃ C ₂ -30NbC-10Co	30N-Cr	99.72 ± 0.21	0.04 ± 0.01
WC-0.5Cr ₃ C ₂ -50NbC-10Co	50N-Cr	99.82 ± 0.73	0.05 ± 0.02
WC-0.5Cr ₃ C ₂ -80NbC-10Co	80N-Cr	99.30 ± 0.29	0.03 ± 0.01

Table 4.23. Density and open porosity of WC-10Co (wt%) with 0-20 NbC (wt%) additions, produced from nano (n) WC starting powders.

Sample (wt%)	Sample abbreviation	Densification (%)	Open porosity volume (%)
WC-10Co	10Co-n	99.72 ± 0.15	0.03 ± 0.01
WC-1NbC-10Co	1N-n	99.25 ± 0.32	0.08 ± 0.03
WC-2NbC-10Co	2N-n	99.67 ± 0.21	0.06 ± 0.02
WC-5NbC-10Co	5N-n	99.33 ± 0.11	0.04 ± 0.01
WC-20NbC-10Co	20N-n	99.14 ± 0.42	0.09 ± 0.04

Table 4.24. Density and open porosity of WC-0.5Cr₃C₂-9.3Ni (wt%) with 6.25 TiC (wt%) and 0-5 Mo₂C (wt%) additions.

Sample (wt%)	Sample abbreviation	Densification (%)	Open porosity volume (%)
WC-0.5wt%Cr ₃ C ₂ -9.3Ni	9.3Ni-Cr	99.30 ± 0.89	0.04 ± 0.02
WC-0.5Cr ₃ C ₂ -6.25TiC-9.3Ni	0M-Cr	99.11 ± 0.09	0.06 ± 0.01
WC-0.5Cr ₃ C ₂ -0.5Mo ₂ C-6.25TiC-9.3Ni	0.5M-Cr	99.02 ± 0.69	0.02 ± 0.04
WC-0.5Cr ₃ C ₂ -1Mo ₂ C-6.25TiC-9.3Ni	1M-Cr	99.11 ± 0.76	0.05 ± 0.01
WC-0.5Cr ₃ C ₂ -2Mo ₂ C-6.25TiC-9.3Ni	2M-Cr	99.58 ± 0.26	0.06 ± 0.04
WC-0.5Cr ₃ C ₂ -3.5Mo ₂ C-6.25TiC-9.3Ni	3.5M-Cr (1280)	96.65 ± 1.46	6.52 ± 1.23
WC-0.5Cr ₃ C ₂ -3.5Mo ₂ C-6.25TiC-9.3Ni	3.5M-Cr	99.20 ± 0.29	0.03 ± 0.04
WC-0.5Cr ₃ C ₂ -5Mo ₂ C-6.25TiC-9.3Ni	5M-Cr	99.56 ± 0.32	0.01 ± 0.01

Table 4.25. Density and open porosity of WC-9.3Ni (wt%) with 6.25 TiC (wt%) and 0-5 Mo₂C (wt%) additions, using submicron (s) WC starting powders.

Sample (wt%)	Sample abbreviation	Densification (%)	Open porosity volume (%)
WC -9.3Ni	9.3Ni-s	99.21 ± 0.08	0.07 ± 0.03
WC-6.25TiC-9.3Ni	0M-s	99.35 ± 0.10	0.04 ± 0.01
WC-1Mo ₂ C 6.25TiC-9.3Ni	1M-s	99.23 ± 0.31	0.06 ± 0.02
WC-2Mo ₂ C -6.25TiC-9.3Ni	2M-s	99.24 ± 0.18	0.08 ± 0.02
WC-3.5Mo ₂ C -6.25TiC-9.3Ni	3.5M-s	99.36 ± 0.04	0.02 ± 0.01
WC-5Mo ₂ C -6.25TiC-9.3Ni	5M-s	99.61 ± 0.12	0.08 ± 0.03

Table 4.26. Density and open porosity of WC-9.3Ni (wt%) with 6.25 TiC (wt%) and 0-5 Mo₂C (wt%) additions, using ultra-fine (u) WC starting powders.

Sample (wt%)	Sample abbreviation	Densification (%)	Open porosity volume (%)
WC -9.3Ni	9.3Ni-u	99.24 ± 0.17	0.07 ± 0.03
WC-6.25TiC-9.3Ni	0M-u	99.27 ± 0.05	0.04 ± 0.01
WC-1Mo ₂ C 6.25TiC-9.3Ni	1M-u	99.25 ± 0.07	0.06 ± 0.02
WC-2Mo ₂ C -6.25TiC-9.3Ni	2M-u	99.36 ± 0.76	0.08 ± 0.02
WC-3.5Mo ₂ C -6.25TiC-9.3Ni	3.5M-u	99.21 ± 0.10	0.02 ± 0.01
WC-5Mo ₂ C -6.25TiC-9.3Ni	5M-u	99.42 ± 0.23	0.08 ± 0.03
WC-3.5Mo ₂ C-6.25TiC-7Ni	3.5M-7Ni-u	99.53 ± 0.44	0.04 ± 0.01
WC-5Mo ₂ C-6.25TiC-7Ni	5M-7Ni-u	99.45± 0.32	0.05 ± 0.01

Table 4.27. Density and open porosity of the liquid phase sintered samples.

Sample (wt%)	Sample abbreviation	Densification (%)	Open porosity volume (%)
WC-0.5Cr ₃ C ₂ -10Co	10Co-LPS-Cr	99.93 ± 0.94	0.00 ± 0.00
WC-9.3Ni-n	9.3Ni-LPS-1430	99.94 ± 0.23	0.00 ± 0.00
WC-9.3Ni-n	9.3Ni-LPS-1510	99.97 ± 0.11	0.00 ± 0.00

Table 4.28. Density and open porosity of WC-9.3Ni (wt%) with 6.25 TiC (wt%) and 0-5 Mo₂C (wt%) additions, using nano (n) WC starting powders.

Sample (wt%)	Sample abbreviation	Densification (%)	Open porosity volume (%)
WC-10Ni	10Ni-n	99.62 ± 0.15	0.03 ± 0.01
WC-9.3Ni	9.3Ni-n	99.57 ± 0.44	0.07 ± 0.03
WC-8Ni	8Ni-n	99.44 ± 0.19	0.05 ± 0.02
WC-7Ni	7Ni-n	99.37 ± 0.11	0.08 ± 0.02
WC-6Ni	6Ni-n	99.54 ± 0.12	0.06 ± 0.02
WC-6.25TiC-9.3Ni	0M-n	99.14 ± 0.57	0.05 ± 0.02
WC-0.5Mo ₂ C -6.25TiC-9.3Ni	0.5M-n	99.20 ± 0.10	0.04 ± 0.01
WC-1Mo ₂ C- 6.25TiC-9.3Ni	1M-n	99.36 ± 0.35	0.06 ± 0.02
WC-2Mo ₂ C -6.25TiC-9.3Ni	2M-n	99.39 ± 0.76	0.08 ± 0.02
WC-3.5Mo ₂ C -6.25TiC-9.3Ni	3.5M-n	99.21 ± 0.10	0.02 ± 0.01
WC-5Mo ₂ C -6.25TiC-9.3Ni	5M-n	99.42 ± 0.23	0.08 ± 0.03
WC-3.5Mo ₂ C-6.25TiC-7Ni	3.5M-7Ni-n	99.53 ± 0.44	0.04 ± 0.01
WC-5Mo ₂ C-6.25TiC-7Ni	5M-7Ni-n	99.45± 0.32	0.05 ± 0.01

Chapter 5: Microstructure, constituent phases and mechanical properties

In this chapter, the effect of NbC additions to WC-10Co (wt%) , as well as TiC and Mo₂C to WC-9.3Ni (wt%) on the microstructure, phases and mechanical properties were deduced. The effect of WC starting size (submicron-nano) and comparison between SPS and LPS were also studied.

5.1 Microstructure

5.1.1 Microstructures of WC-NbC-Co cemented carbides

5.1.1.1 Microstructures of NbC addition to WC-0.5Cr₃C₂-10Co (wt%)

The SEM micrographs of WC-0.5Cr₃C₂-10Co (wt%), produced by LPS and SPS, are shown in Figure 5.1. The liquid phase sintered sample had larger WC grains (Figure 5.1 and Table 5.1), with more homogeneously distributed Co pools than the spark plasma sintered sample, although slight WC grain growth was observed in the latter (Table 5.1). Chromium carbide was not detected by EDX (Table 5.2).

Micrographs of the samples with up to 5 wt% NbC (minor additions, not meant to substitute for WC) are shown in Figure 5.2. A slight reduction in WC grain size (Table 5.1), and large and poorly distributed Co pools were observed. Niobium carbide and cobalt had similar contrast, making it difficult to differentiate between the two, especially at low NbC additions. The microstructures of 10-80 wt% NbC (WC substitution) samples are shown in Figure 5.3. The formation of a NbC skeleton (Figure 5.3), reduction in WC grain size (Table 5.1) and rounding of WC grains at the WC/NbC interfaces were observed for ≥ 20 wt% NbC additions (Figure 5.4). The difference in contrast between NbC and Co was more clear at higher magnification, as shown by the arrows in Figure 5.4 (b) and (d). Cobalt was mainly present between the WC grains, and rarely between the NbC grains (Table 5.2), which was found by HAADF STEM mapping (Figures 5.5 and 5.6). Chromium carbide was also found by HAADF STEM mapping (Figures 5.5 and 5.6).

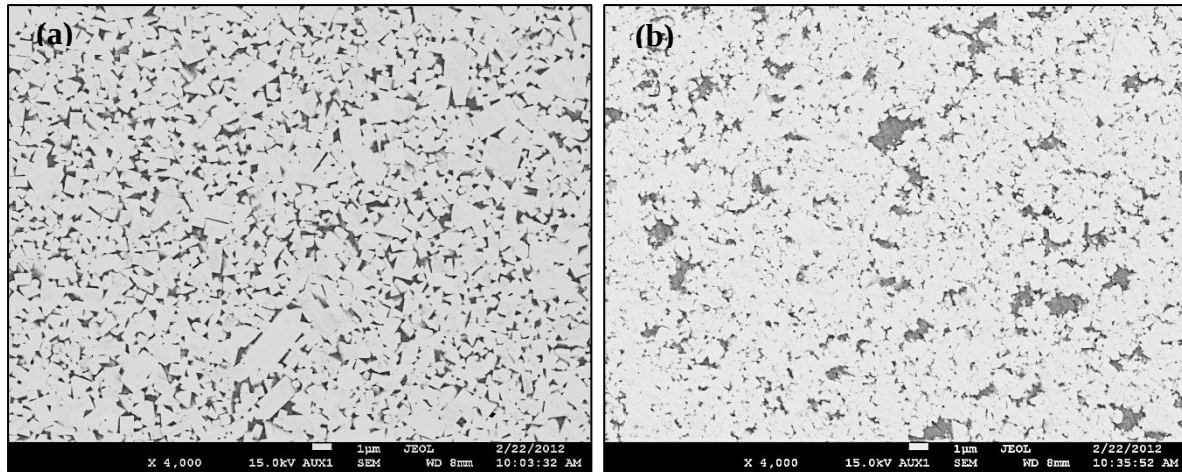


Figure 5.1. SEM-BSE images of WC-0.5Cr₃C₂-10Co (wt%) sintered by: (a) LPS and (b) SPS, showing WC (light), and Co (dark).

Table 5.1. Sintered WC grain sizes in WC-NbC-Co samples.

Sample abbreviation	WC sintered grain size (μm)		
	WC-Cr (s)	WC (u)	WC (n)
10Co (1430)	2.15 ± 0.11	-	-
10Co	0.85 ± 0.04	0.89 ± 0.12	0.87 ± 0.08
1N	0.83 ± 0.03	0.88 ± 0.06	0.87 ± 0.05
5N	0.82 ± 0.05	0.86 ± 0.05	0.85 ± 0.07
20N	0.78 ± 0.02	0.65 ± 0.03	0.68 ± 0.05
50N	0.76 ± 0.04	-	-

(s) 0.8 μm starting size, (u) 0.4 μm starting size, (n) 0.1 μm starting size.

Table 5.2. EDX analyses of WC-0.5Cr₃C₂-10Co (wt%) with 5 and 20 NbC (wt%) additions.

Sample abbreviation	Contrast	Composition (wt%)			
		W	C	Co	NbC
10Co-Cr	Light	81.1 ± 1.6	9.1 ± 1.8	9.8 ± 1.5	-
	Dark	21.2 ± 2.5	7.1 ± 2.8	71.7 ± 2.0	-
5 N-Cr	Light	79.8 ± 2.4	8.7 ± 0.4	11.6 ± 2.3	-
	Medium	11.5 ± 2.8	26.2 ± 2.1	1.3 ± 0.3	61.7 ± 0.6
20N-Cr	Dark	25.9 ± 1.6	10.1 ± 1.1	63.9 ± 1.7	-
	Light	61.9 ± 4.2	9.7 ± 1.5	7.24 ± 1.4	20.4 ± 2.7
	Medium	13.4 ± 1.2	22.4 ± 3.6	3.7 ± 1.2	60.6 ± 4.5
	Dark	26.7 ± 3.2	11.4 ± 1.8	56.4 ± 2.5	4.4 ± 0.8

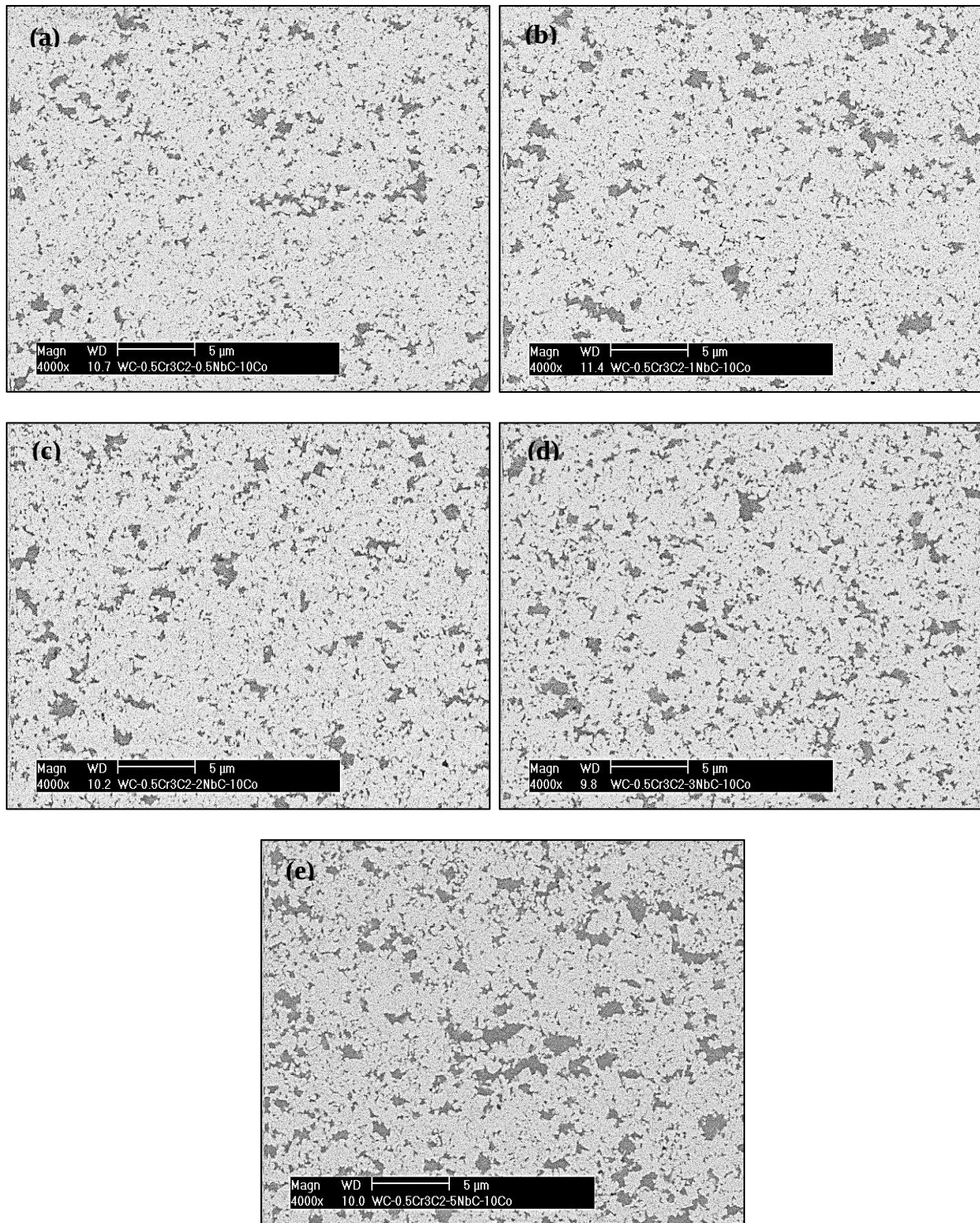


Figure 5.2. SEM-BSE images of WC-0.5Cr₃C₂-10Co (wt%) with: (a) 0.5, (b) 1, (c) 2, (d) 3, and (e) 5 NbC (wt%) additions: WC (light), NbC (medium) and Co (dark).

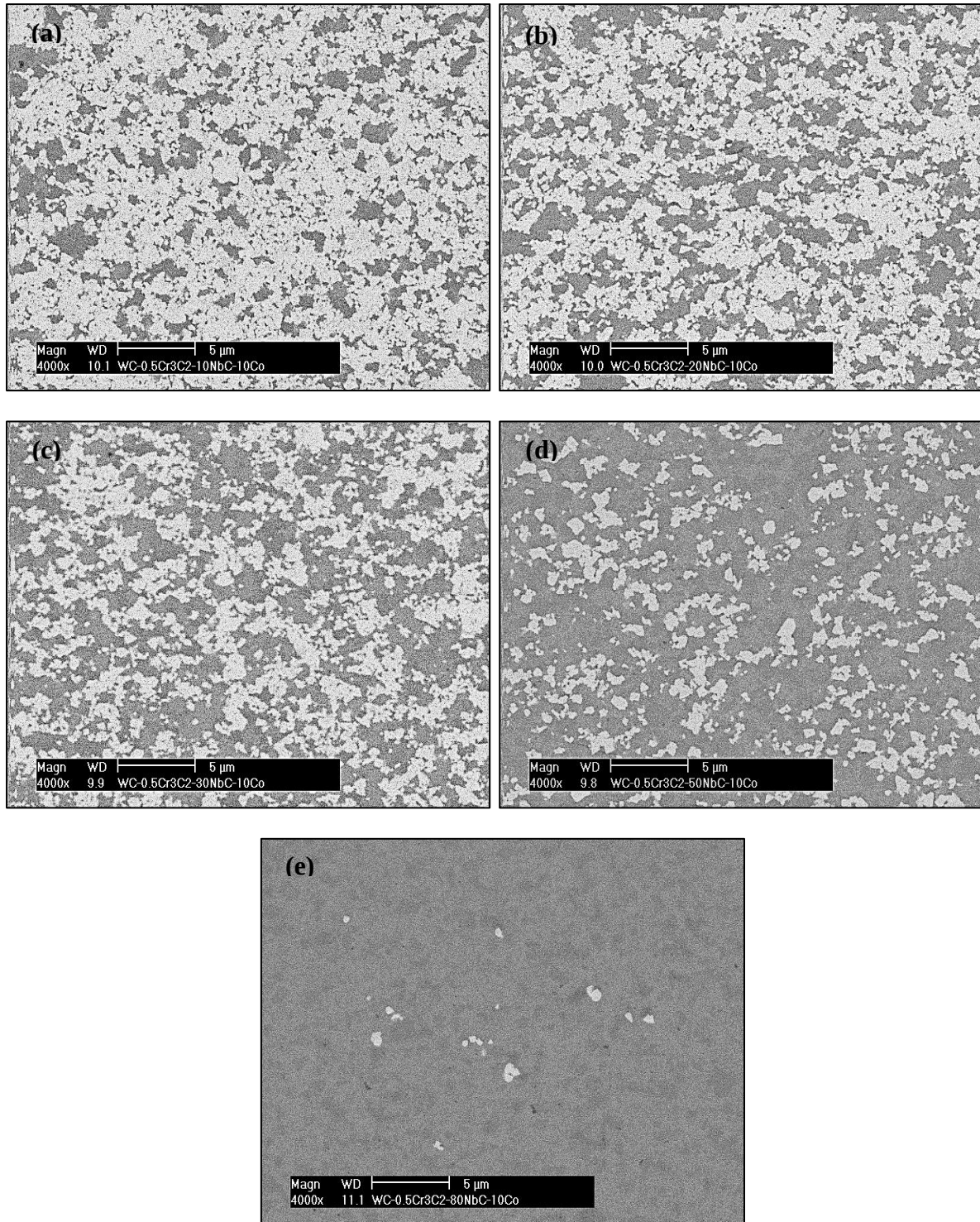


Figure 5.3. SEM-BSE images of WC-0.5Cr₃C₂-10Co (wt%) with: (a) 10, (b) 20, (c) 30, (d) 50, and (e) 80 NbC (wt%) additions: WC (light), NbC (medium) and Co (dark).

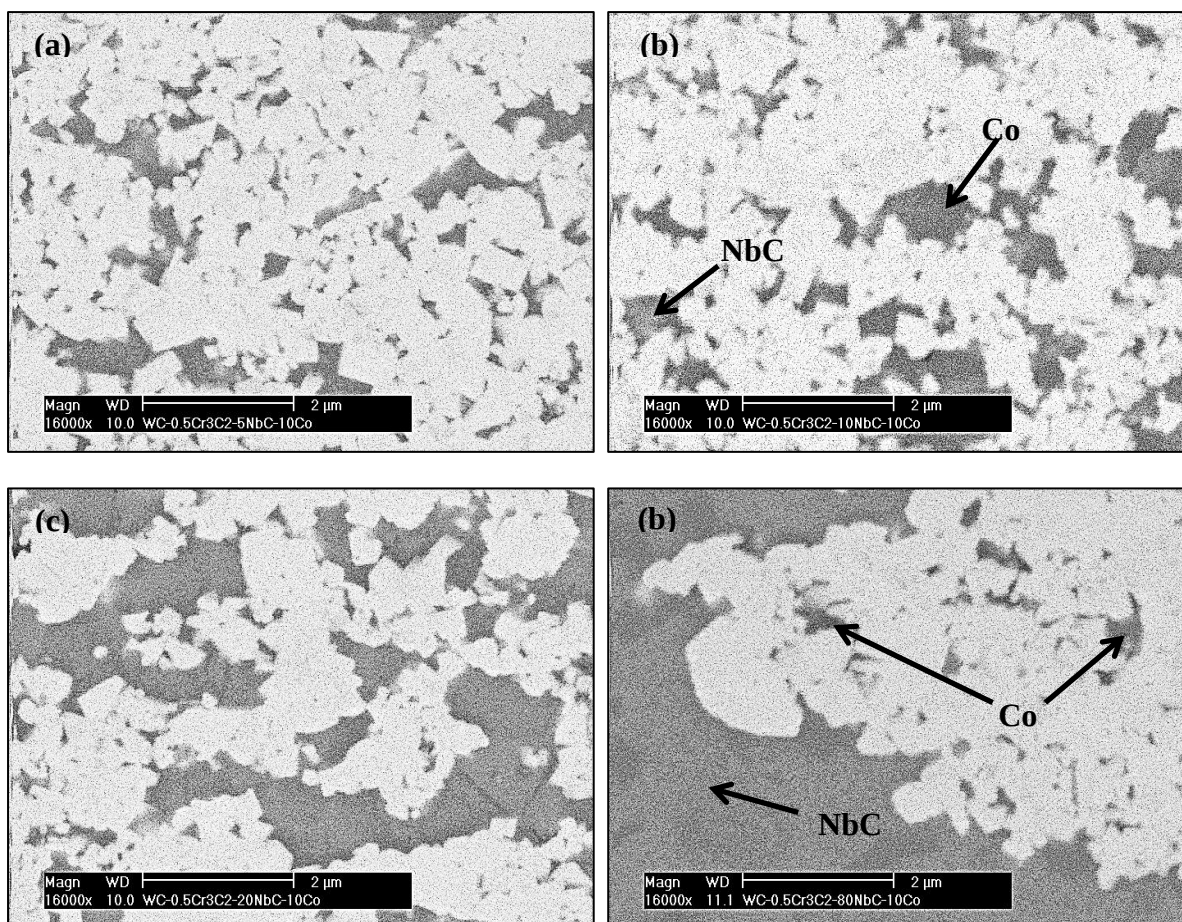


Figure 5.4. SEM-BSE images of WC-0.5Cr₃C₂-10Co (wt%) with: (a) 5, (b) 10, (c) 20, and (d) 80 NbC (wt%) additions, showing rounding of WC grains and difference in contrast between NbC and Co: WC (light), NbC (medium) and Co (dark).

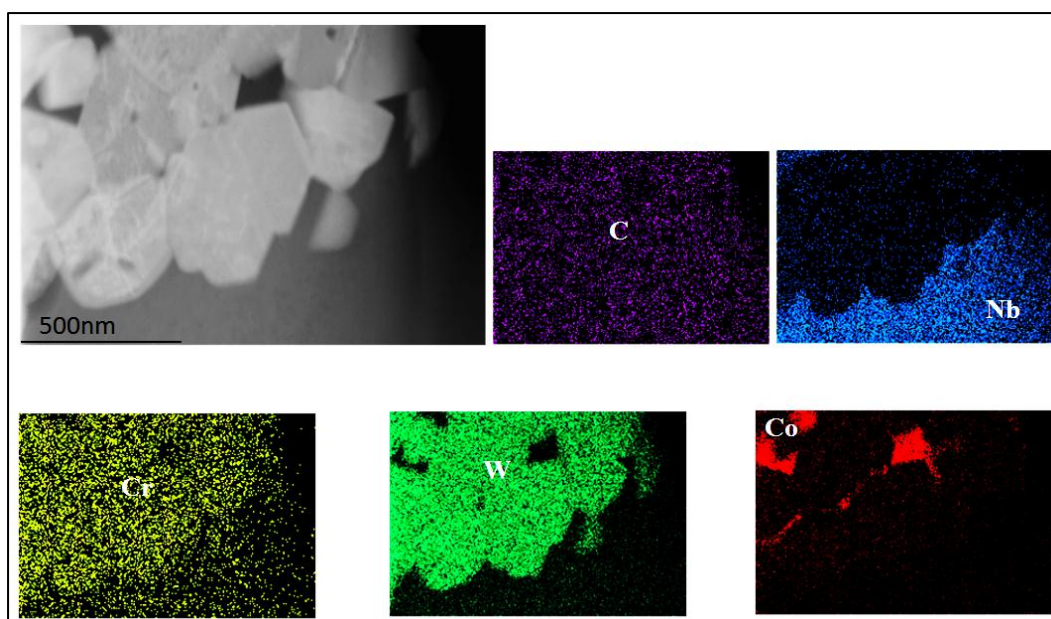


Figure 5.5. HAADF-STEM mapping images of WC-0.5Cr₃C₂-20NbC-10Co (wt%), showing C (purple), Nb (blue), Cr (yellow), W (green) and Co (red).

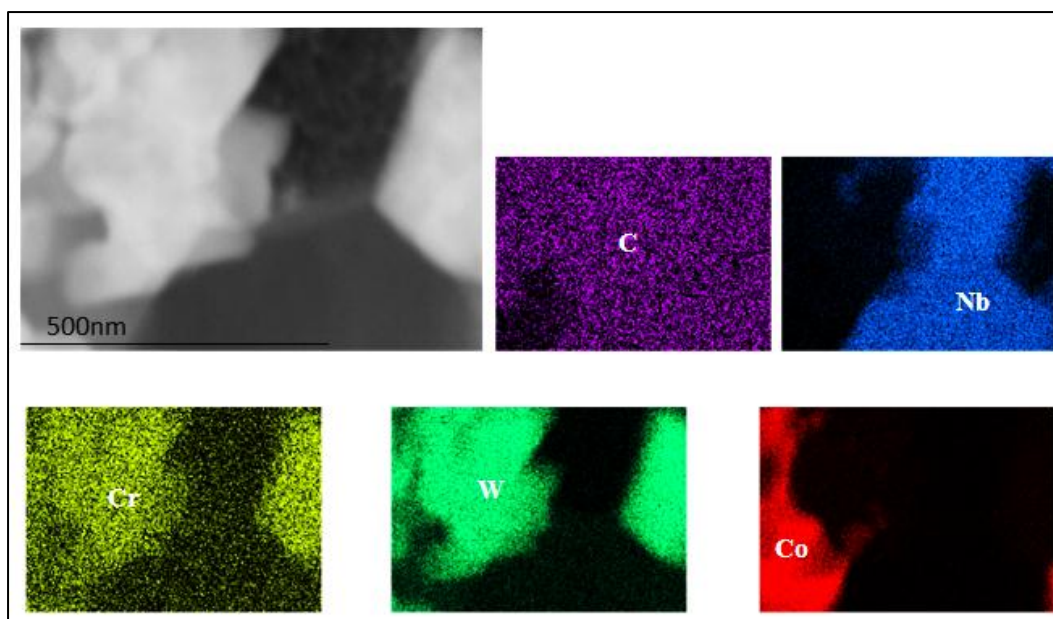


Figure 5.6. HAADF-STEM EDX mapping images of WC-0.5Cr₃C₂-20NbC-10Co (wt%), showing C (purple), Nb (blue), Cr (yellow), W (green) and Co (red).

5.1.1.2 Microstructures of WC-10Co (wt%) with NbC additions, produced from nano WC starting powders

Figure 5.7 shows the microstructures of WC-10Co (wt%) with additions of up to 20 wt% NbC, produced from nano WC starting powders. The WC-10Co (wt%) sample (Figure 5.7 (a)) had large and poorly distributed Co pools, similar to Figure 5.1 (b), and WC grain growth took place, giving a mean grain size of $0.87 \pm 0.08 \mu\text{m}$. Niobium carbide additions reduced the grain growth, with 20 wt% addition giving a mean grain size of $0.68 \pm 0.02 \mu\text{m}$. Similar to the WC-0.5Cr₃C₂ samples, Co was also mainly found between the WC grains and rarely between the NbC grains (Table 5.3). The change in shape of WC grains, from angular with faceted edges to more rounded, was also observed in the 20 wt% NbC addition sample (Figure 5.7 (e) and (f)).

Table 5.3. EDX analyses of WC-0.5Cr₃C₂-10Co (wt%) with 5 and 20 wt% NbC additions.

Sample abbreviation	Contrast	Composition (wt%)			
		W	C	Co	NbC
10Co-n	Light	86.5 ± 2.4	7.3 ± 0.7	6.9 ± 2.1	-
	Dark	27.8 ± 1.9	10.3 ± 2.2	62.7 ± 0.8	-
5 N-n	Light	84.0 ± 3.1	7.6 ± 1.8	9.1 ± 1.5	-
	Medium	10.1 ± 0.9	30.5 ± 3.2	1.2 ± 0.7	58.1 ± 2.2
	Dark	27.4 ± 4.7	16.4 ± 0.6	56.2 ± 2.1	-
20N-n	Light	64.2 ± 1.8	8.8 ± 0.4	9.9 ± 1.0	17.7 ± 1.2
	Medium	14.2 ± 0.9	27.5 ± 2.3	2.8 ± 2.2	55.5 ± 2.4
	Dark	23.1 ± 1.5	18.7 ± 1.7	55.4 ± 1.8	2.48 ± 1.3

5.1.1.3 Microstructures of WC-10Co (wt%) with NbC additions, produced from ultrafine WC starting powders

The microstructures of WC-10Co (wt%), with 0-20 NbC (wt%) additions, produced from ultrafine WC starting powders are shown in Figure 5.8. The WC-10Co (wt%) sample had large and poorly distributed Co pools and WC grains with a mean size of $0.89 \pm 0.12\mu\text{m}$ (Figure 5.8 and Table 5.1). This was similar to the WC-0.5Cr₃C₂-10Co (wt%) and WC-10Co (wt%) sample produced from nano starting powders. Additions of NbC reduced the WC grain size, with 20wt% NbC having the finest grain size (Table 5.1). Cobalt was mainly located between the WC grains and the WC grains changed in shape from angular with faceted edges to more a rounded shape for 20 wt% NbC.

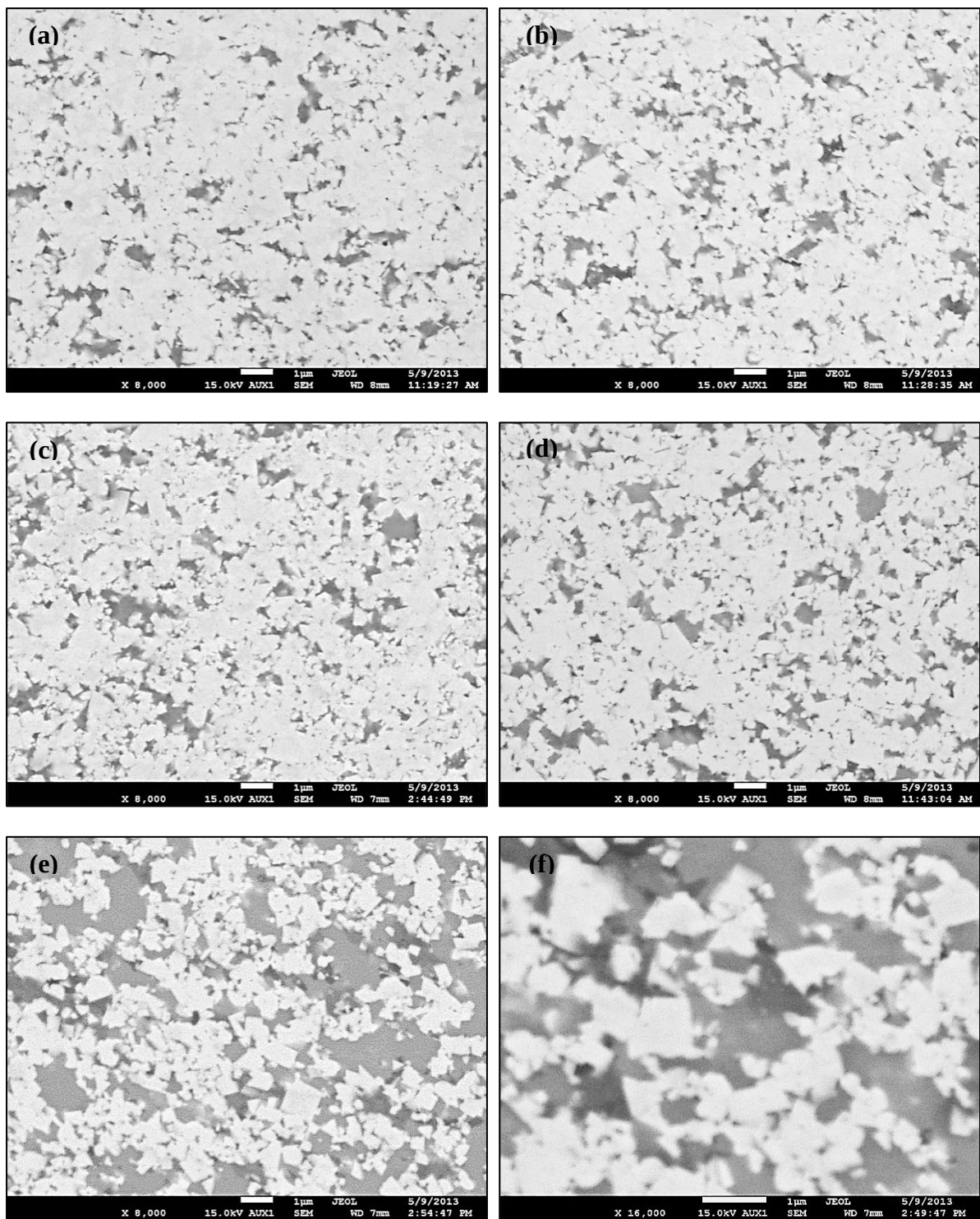


Figure 5.7. SEM-BSE images of WC-10Co (wt%) with: (a) 0, (b) 1, (c) 3, (d) 5, and (e and f) 20 wt% NbC additions: WC (light), NbC (medium) and Co (dark).

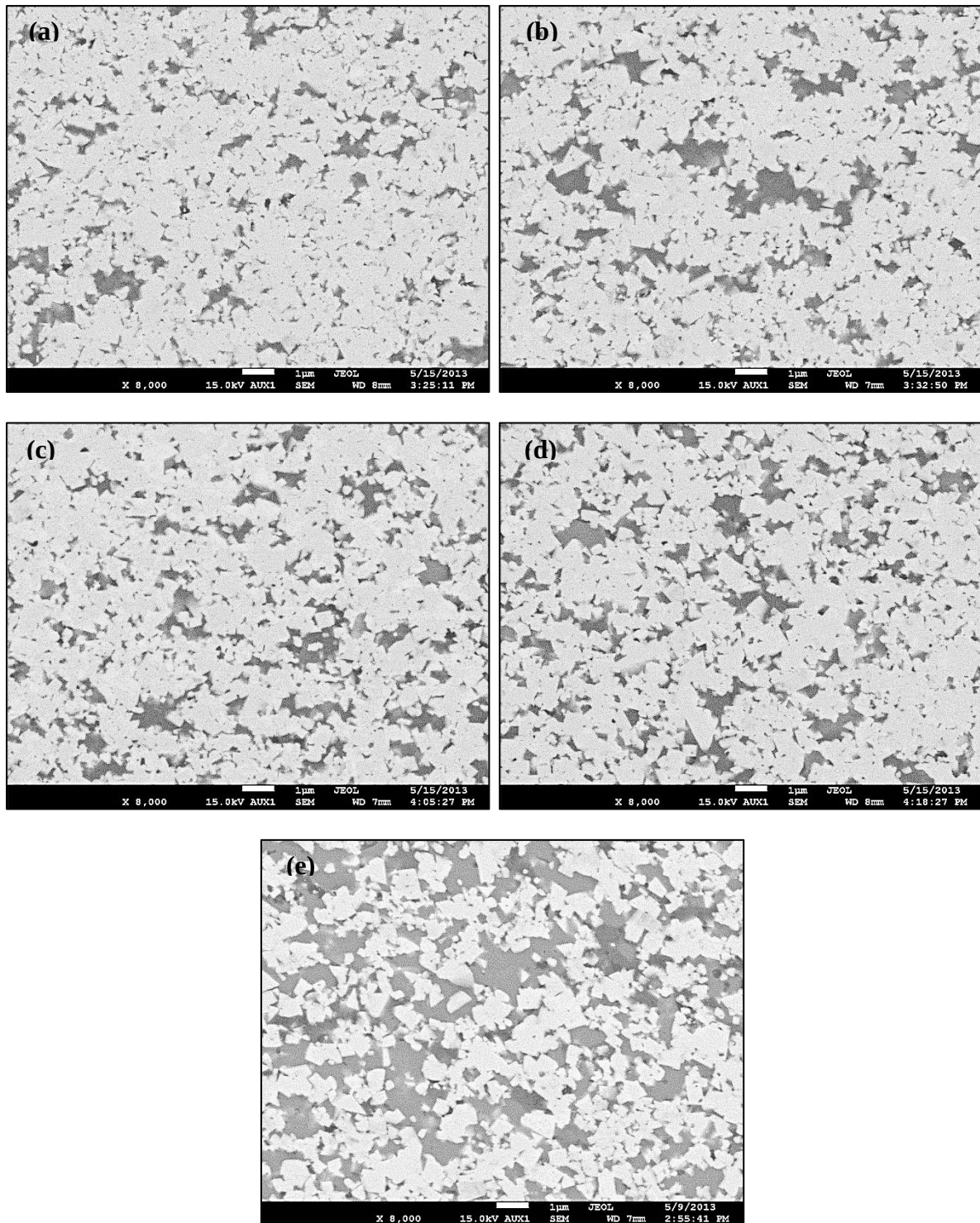


Figure 5.8. SEM-BSE images of WC-10Co (wt%) with: (a) 0, (b) 1, (c) 3, (d) 5, and (e) 20 NbC (wt%) additions: WC (light), NbC (medium) and Co (dark).

5.1.2 Microstructures of WC-Mo₂C-TiC-Ni cemented carbides

5.1.2.1 Microstructures of WC-0.5Cr₃C₂-9.3Ni (wt%) with TiC and Mo₂C additions

The microstructure of WC-0.5Cr₃C₂-9.3Ni (wt%) (Figure 5.9 (a)) had larger, poorer distributed Ni binder pools than WC-0.5Cr₃C₂-10Co (wt%) (Figure 5.9 (b)) and higher WC contiguity (Table 5.4 and Figure 5.9). Both samples were produced by SPS.

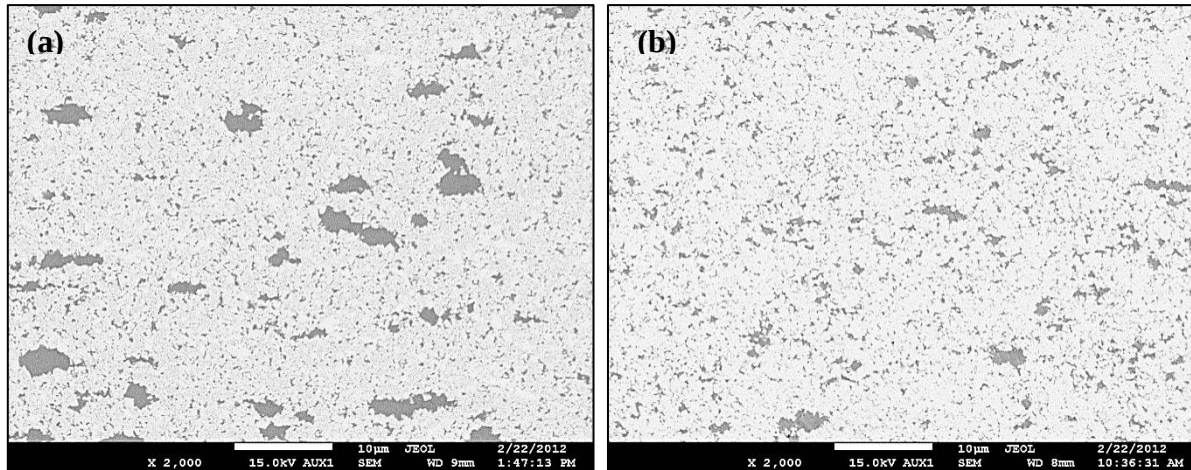


Figure 5.9. SEM-BSE images of (a) WC-0.5Cr₃C₂-9.3Ni (wt%) with WC (light), and Ni (dark), and (b) WC-0.5Cr₃C₂-10Co (wt%): WC (light) and Co (dark).

Table 5.4. Image analysis results of WC-0.5Cr₃C₂-9.3Ni (wt%) with TiC and Mo₂C additions (Figures 5.9, 5.10 and 5.11).

Sample abbreviation	Mean binder pool size (μm)	Contiguity (%)
10Co (LPS)	0.32 ± 0.06	56.49 ± 0.66
10Co	0.55 ± 0.14	61.69 ± 0.79
9.3Ni	1.72 ± 0.38	68.87 ± 1.14
1Mo ₂ C	0.36 ± 0.07	58.18 ± 1.85
3.5Mo ₂ C (1280)	0.43 ± 0.07	60.16 ± 2.26
3.5Mo ₂ C	0.21 ± 0.04	58.27 ± 2.13
5Mo ₂ C	0.17 ± 0.02	58.01 ± 1.92

Microstructures of WC-0.5Cr₃C₂-9.3Ni (wt%) with 6.25wt% TiC and varying Mo₂C additions, produced by SPS (Figure 5.10) had WC, Ni and TiC phases. EDX analyses showed up to 3.2 ± 0.3 wt% Mo and 12.7 ± 3.9 wt% C in the Ni binder of the 3.5 wt% Mo₂C sample (Table 5.5). Titanium carbide was observed within the WC continuous skeleton and at the WC/Ni binder interfaces. Increased Mo₂C resulted in the formation of smaller and more evenly distributed Ni binder pools, with 3.5 and 5 wt% Mo₂C additions having the best Ni

distribution, and lower WC contiguity (Table 5.4). The microstructures of WC-0.5Cr₃C₂-3.5Mo₂C-6.25TiC-9.3Ni (wt%) sintered at 1280°C and 1310°C are shown in Figures 5.11, the former had larger and poorly distributed Ni pools (Table 5.4).

Table 5.5. EDX analyses of WC-0.5Cr₃C₂-9.3Ni (wt%) with TiC and Mo₂C additions.

Sample abbreviation	Contrast	Composition (wt%)				
		W	C	Ni	Ti	Mo
9.3Ni	Light	84.3 ± 1.8	7.9 ± 1.8	7.3 ± 2.0	-	-
	Dark	20.8 ± 2.3	4.3 ± 3.1	75.0 ± 5.1	-	-
0 Mo ₂ C	Light	81.5 ± 7.8	11.1 ± 5.4	7.4 ± 2.5	-	-
	Medium	17.1 ± 6.7	9.0 ± 7.7	74.0 ± 7.5	-	-
	Dark	3.7 ± 4.7	31.9 ± 2.4	-	64.4 ± 5.8	-
1Mo ₂ C	Light	82.0 ± 1.1	9.6 ± 0.4	8.4 ± 0.7	-	-
	Medium	17.2 ± 2.0	15.6 ± 2.4	66.7 ± 2.1	-	0.4 ± 1.3
	Dark	4.6 ± 1.4	31.1 ± 1.3	-	64.5 ± 0.3	-
3.5Mo ₂ C	Light	84.0 ± 1.5	7.7 ± 1.9	6.6 ± 2.8	-	1.6 ± 1.8
	Medium	16.8 ± 1.6	12.6 ± 3.9	67.3 ± 4.8	-	3.2 ± 0.3
	Dark	3.9 ± 2.1	33.1 ± 1.3	-	63.1 ± 0.8	-

5.1.2.2 Microstructures of WC-9.3Ni (wt%) with TiC and Mo₂C additions, produced from nano starting powders

The micrographs of nano WC-9.3Ni (wt%), sintered by LPS (at 1430°C and 1510°C) and by SPS (1280°C) are shown in Figure 5.12. The liquid phase sintered samples had larger WC grains with mean WC grain sizes of $3.85 \pm 0.56 \mu\text{m}$ and $4.72 \pm 0.53 \mu\text{m}$ for the 1430°C and 1510°C samples (Table 5.6). The SPS sample had smaller WC grains; a mean grain size of $1.46 \pm 0.16 \mu\text{m}$ was attained. The LPS samples had thicker Ni binder pools which were more homogenously distributed compared to the SPS sample, and the 1510°C sample had the thickest binder pools.

Micrographs of WC-9.3Ni, with 6.25 wt% TiC and 0-5 wt% Mo₂C additions are shown in Figure 5.13, and comprised WC, TiC and Ni. Elemental Mo could only be detected by SEM-EDX area analysis (Table 5.7), but its exact location could not be confirmed. Titanium carbide was as mostly found at the WC/Ni boundaries and its addition had only a slight effect on the grain size reduction. However, addition of Mo₂C to WC-6.25TiC-9.3Ni (wt%) significantly improved the grain growth inhibition, with 1 wt% resulting in a mean grain size of $0.92 \pm 0.06 \mu\text{m}$ (Table 5.6) and 5 wt% having a WC grain size of $0.62 \pm 0.06 \mu\text{m}$ (Table 5.6, Figures 5.13 (f) and 5.14).

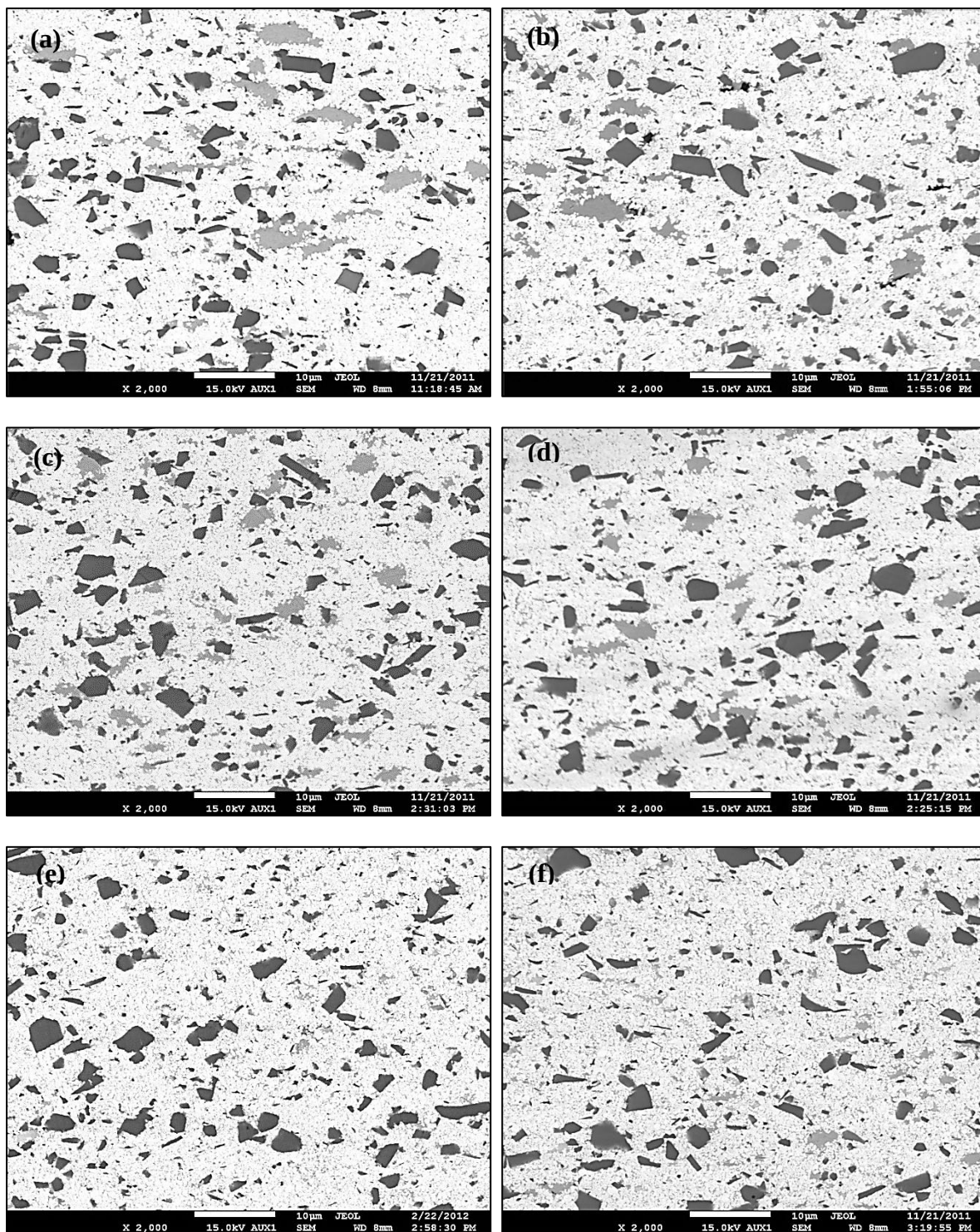


Figure 5.10. SEM-BSE images of WC-0.5Cr₃C₂-6.25TiC-9.3Ni (wt%) with: (a) 0, (b) 0.5, (c) 1, (d) 2, (e) 3.5, and (f) 5 Mo₂C (wt%), showing decreased Ni pool size: WC (light), Ni (medium) and TiC (dark).

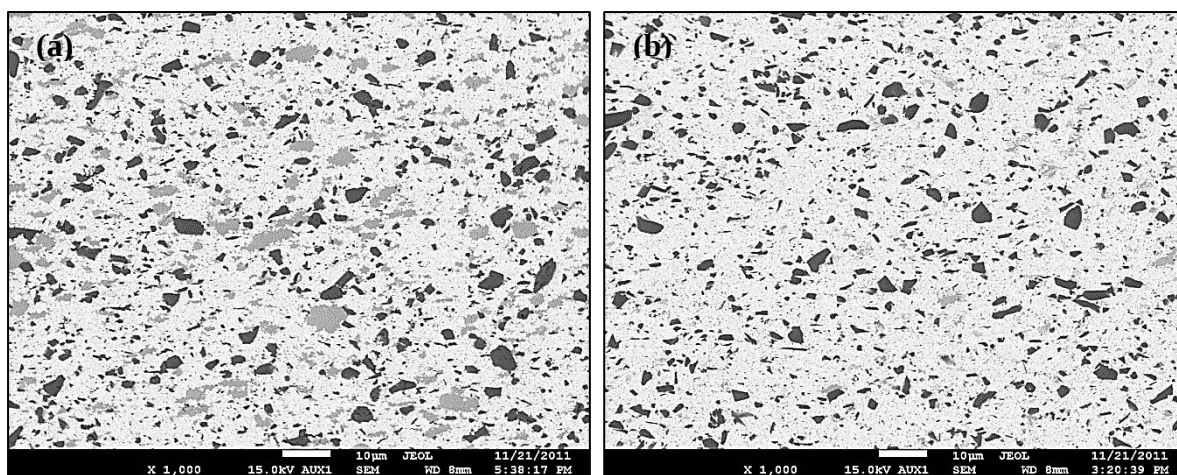


Figure 5.11. SEM-BSE images of WC-0.5Cr₃C₂-3.5Mo₂C-6.25TiC-9.3Ni (wt%) sintered at: (a) 1280°C, and (b) 1310°C: showing different Ni pool sizes: WC (light), Ni (medium) and TiC (dark).

Molybdenum was found between the WC grains by HAADF-STEM mapping (Figures 5.14 and 5.15) where some areas of overlap between W and Mo existed. These were identified to be WC grains under Mo₂C grains by bright field (BF) STEM (Figure 5.16). High-resolution (HR) STEM-EELS was conducted at the WC/Ni interface (Figure 5.17), and the individual line scans of the STEM-EELS mapping revealed a TiC layer at the WC/Ni interface.

The effect of reduction in Ni binder amount from 10 wt% to 6wt% is shown in Figure 5.18. Larger and poorly distributed Ni binder pools were observed in the 10 wt% and 9.3 wt% Ni samples, but further reduction in binder amount resulted in formation of smaller and sparsely distributed Ni pools, with 7 wt% and 6 wt% Ni having the smallest pools (Figures. 5.16 (d) and (e)).

Table 5.6. Effect of WC starting size, TiC and Mo₂C on WC sintered grain size.

Sample abbreviation	WC sintered grain size (µm)		
	WC (s)	WC (u)	WC (n)
9.3Ni (1510)	-	-	4.72 ± 0.53
9.3Ni (1430)	-	-	3.85 ± 0.36
9.3Ni	0.95 ± 0.11	1.12 ± 0.23	1.56 ± 0.09
1M	0.90 ± 0.08	0.94 ± 0.09	0.92 ± 0.06
5M	0.82 ± 0.08	0.54 ± 0.03	0.62 ± 0.06

(s) 0.8 µm starting size, (u) 0.4 µm starting size, (n) 0.1 µm starting size.

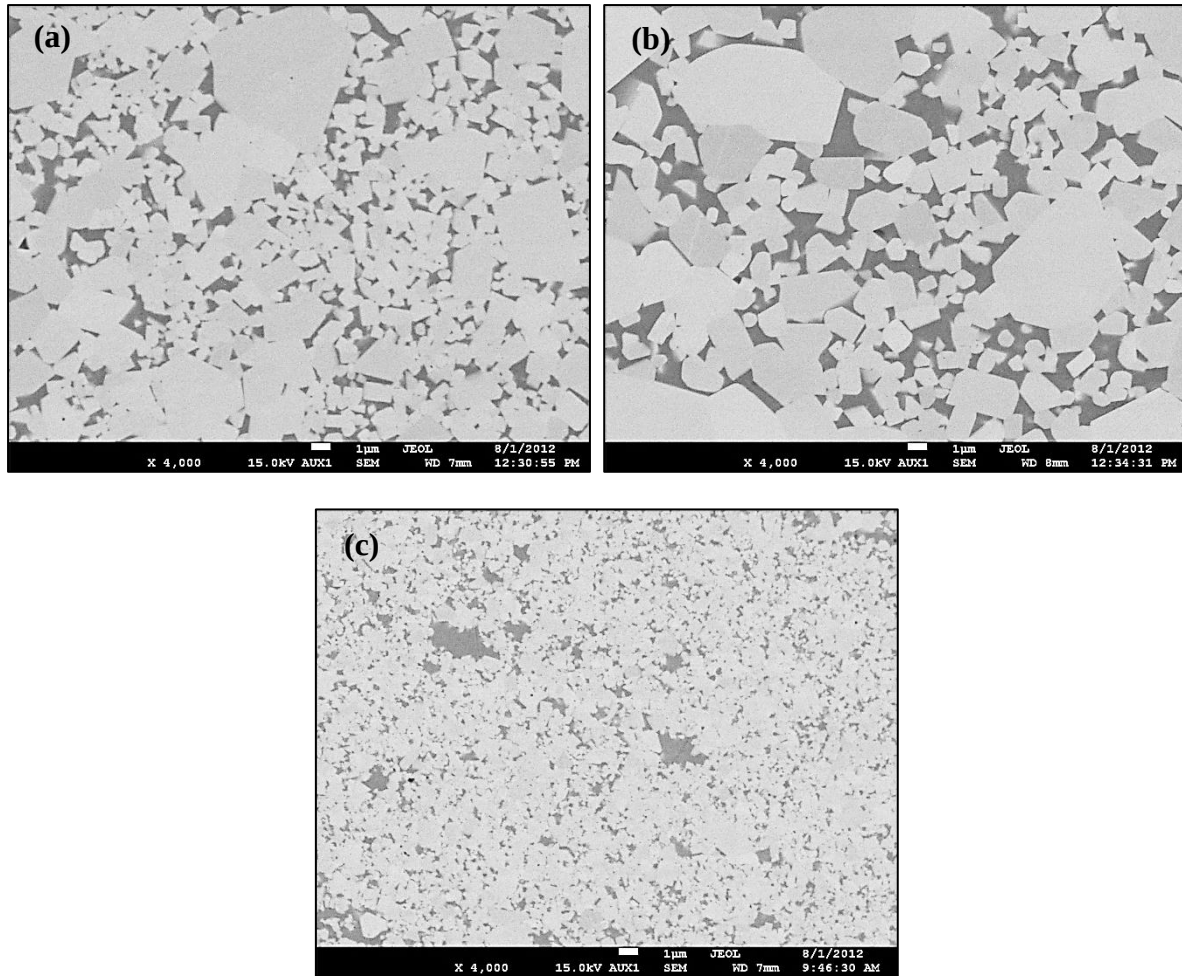


Figure 5.12. SEM-BSE images of WC-9.3Ni (wt%) sintered by: (a)LPS at 1430°C, (b) 1510°C, and (c) SPS at 1240°C, produced from nano WC powder: WC (light) and Ni (dark).

Table 5.7. EDX analyses of WC-9.3Ni (wt%) with TiC and Mo₂C additions with TiC and Mo₂C additions.

Sample abbreviation	Contrast	Composition (wt%)				
		W	C	Ni	Ti	Mo
9.3Ni-n	Light	83.0 ± 2.7	7.9 ± 1.3	9.1 ± 0.4	-	-
	Dark	20.9 ± 1.0	13.0 ± 0.8	66.1 ± 1.7	-	-
0 Mo ₂ C-n	Light	82.1 ± 4.2	9.6 ± 1.4	8.3 ± 1.2	-	-
	Medium	25.1 ± 2.1	13.6 ± 7.7	61.3 ± 4.5	-	-
	Dark	-	29.4 ± 1.1	-	71.6 ± 3.2	-
3.5Mo ₂ C-n	Light	80.8 ± 1.7	9.3 ± 0.4	7.0 ± 1.3	-	2.9 ± 0.6
	Medium	20.3 ± 2.9	17.8 ± 2.2	60.3 ± 3.5	-	1.6 ± 0.9
	Dark	-	27.8 ± 1.8	-	72.2 ± 2.3	-

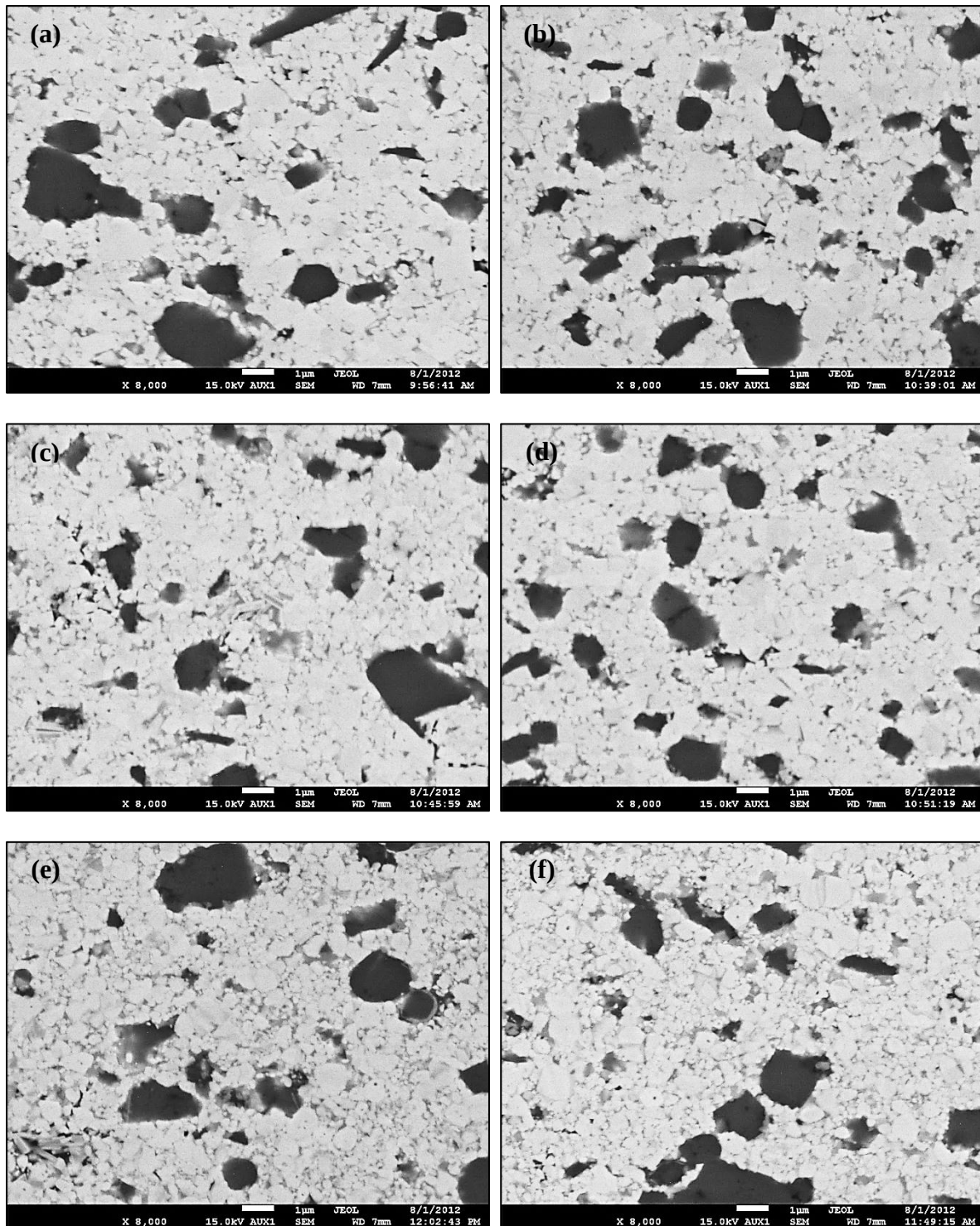


Figure 5.13. SEM-BSE images of: (a) WC-6.25TiC-9.3Ni (wt%), with (b) 0.5, (c) 1, (d) 2, (e) 3.5, and (f) 5 Mo_2C (wt%), produced from nano WC powder, showing reduction in WC grain size with additions of Mo_2C : WC (light), Ni (medium) and TiC (dark).

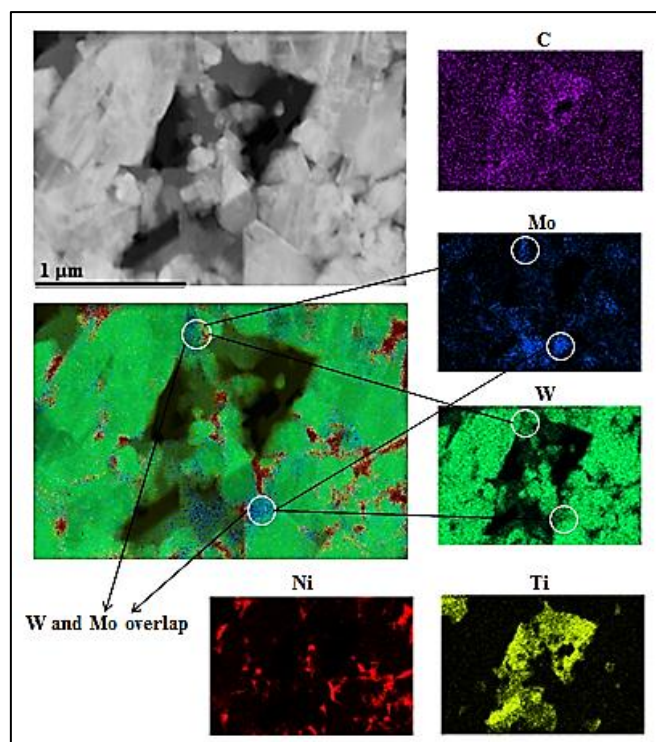


Figure 5.14. HAADF-STEM EDX mapping images of WC-6.25TiC-5Mo₂C-9.3Ni (wt%), showing C (purple), Mo (blue), W (green), Ni (red) and Ti (yellow).

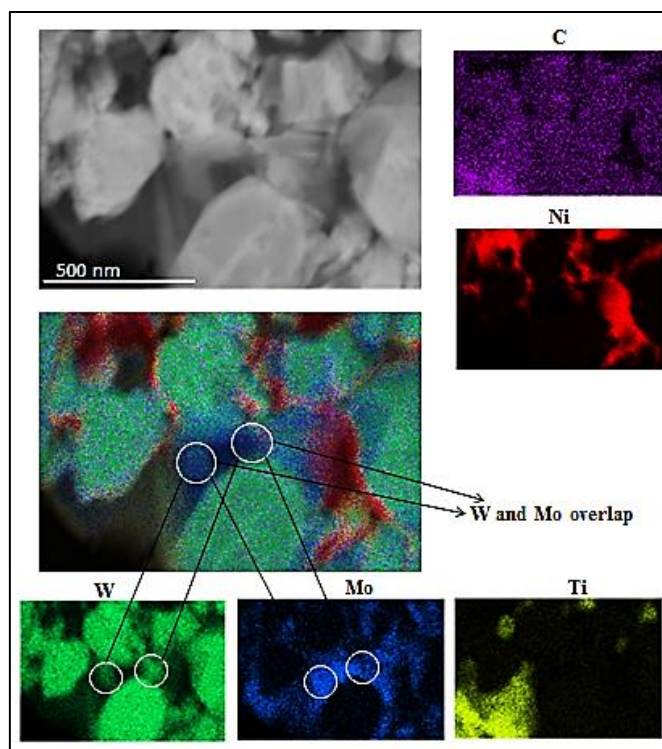


Figure 5.15. HAADF-STEM EDX mapping images of WC-5Mo₂C-6.25TiC-9.3Ni (wt%), showing C (purple), Mo (blue), W (green), Ni (red) and Ti (yellow).

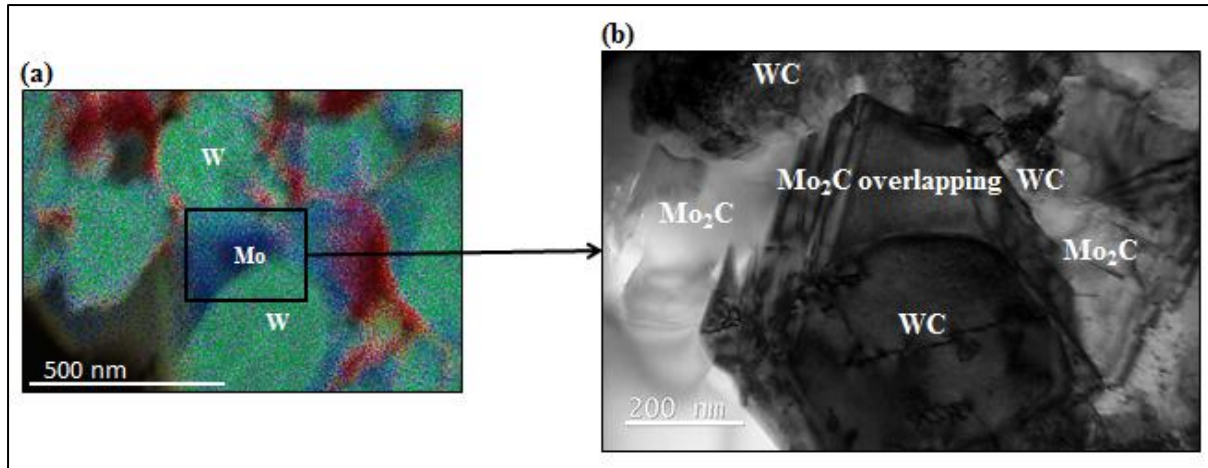


Figure 5.16. (a) HAADF-STEM EDX mapping image of WC-5Mo₂C-6.25TiC-9.3Ni (wt%), showing overlap between W and Mo, and (b) BF-STEM image, showing a WC grain (dark) under Mo₂C (light).

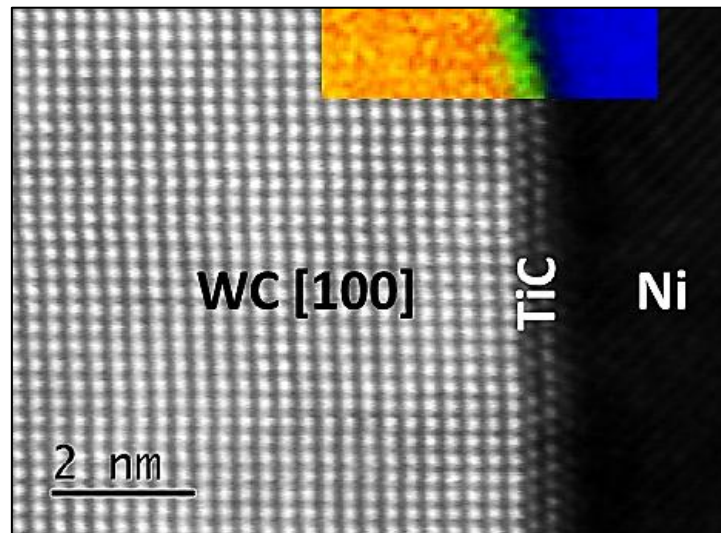


Figure 5.17. HR-STEM image of the WC-Ni interface of WC-5Mo₂C-6.25TiC-9.3Ni (wt%); the inset shows a STEM-EELS elemental map of (left to right) W (orange), C (red), Ti (green) and Ni (blue).

5.1.2.3 Microstructure of WC-9.3Ni (wt%) with TiC and Mo₂C additions, produced from ultrafine starting powders

Microstructures of WC-9.3Ni (wt%) produced from ultrafine WC starting powders with TiC and Mo₂C additions are shown in Figure 5.19. Large and poorly distributed Ni binder pools were observed in the WC-9.3Ni sample. Tungsten carbide grain growth took place during sintering, giving a mean grain size of $1.12 \pm 0.23 \mu\text{m}$ (Table 5.6). Titanium carbide was mostly found at the WC/Ni interfaces.

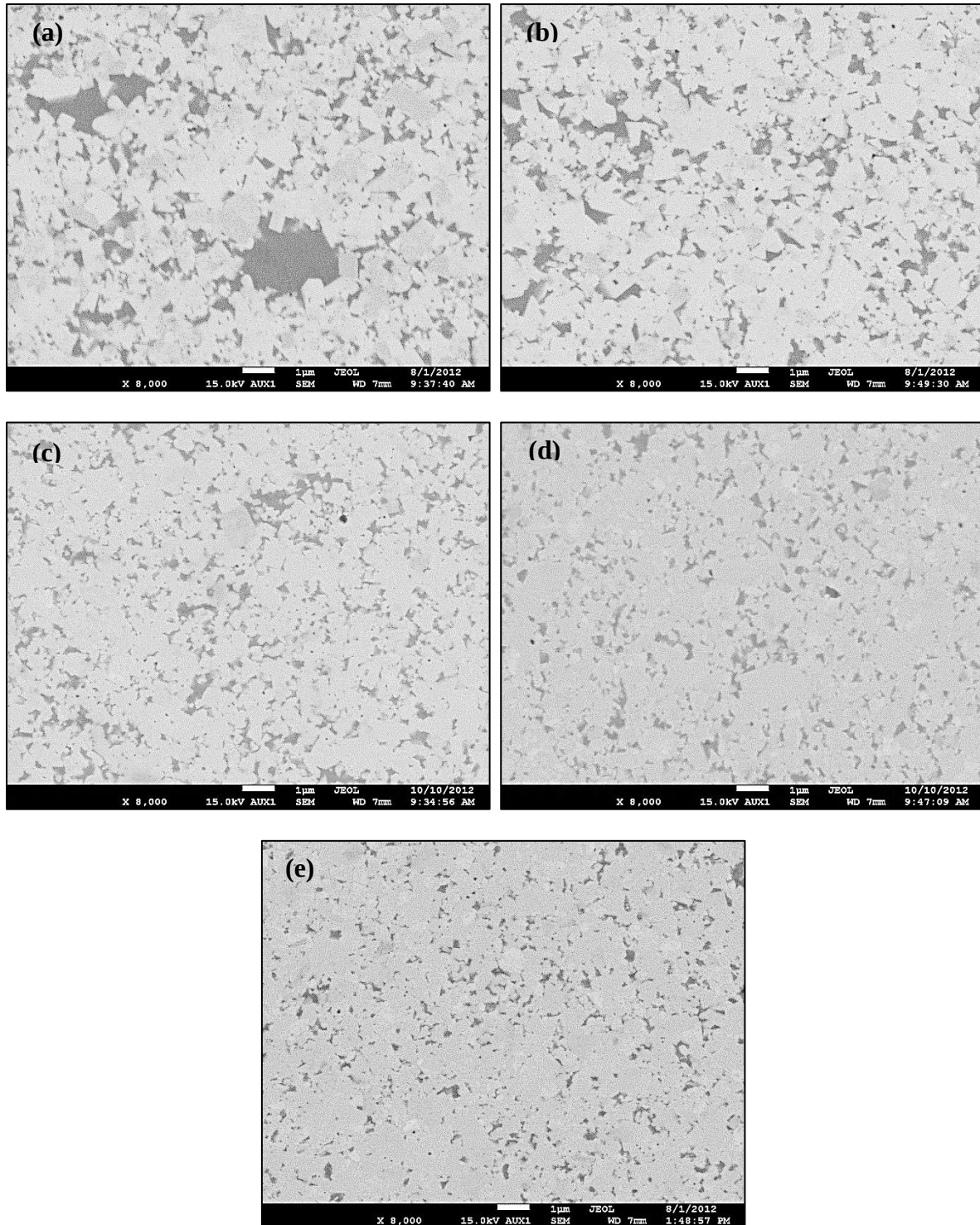


Figure 5.18. SEM-BSE images of WC-Ni (wt%) produced from nano WC powder: (a) 10wt%, (b) 9.3wt%, (c) 8wt%, (d) 7wt%, and (e) 6 wt%Ni: WC (light), Ni (dark).

Addition of Mo_2C to the WC-6.25TiC-9.3Ni (wt%) improved the grain growth inhibition, with 5 wt% addition producing a mean grain size of $0.54 \pm 0.03 \mu\text{m}$ (Table 5.6 and Figure 5.13), which was slightly finer than nano grade with wt% 5 Mo_2C . Addition of Mo_2C also resulted in reduction in the Ni binder pool size and improved the distribution. Molybdenum

carbide was found between WC grains and at the WC/Ni interface by HAADF-STEM EDX mapping (Figure 5.20).

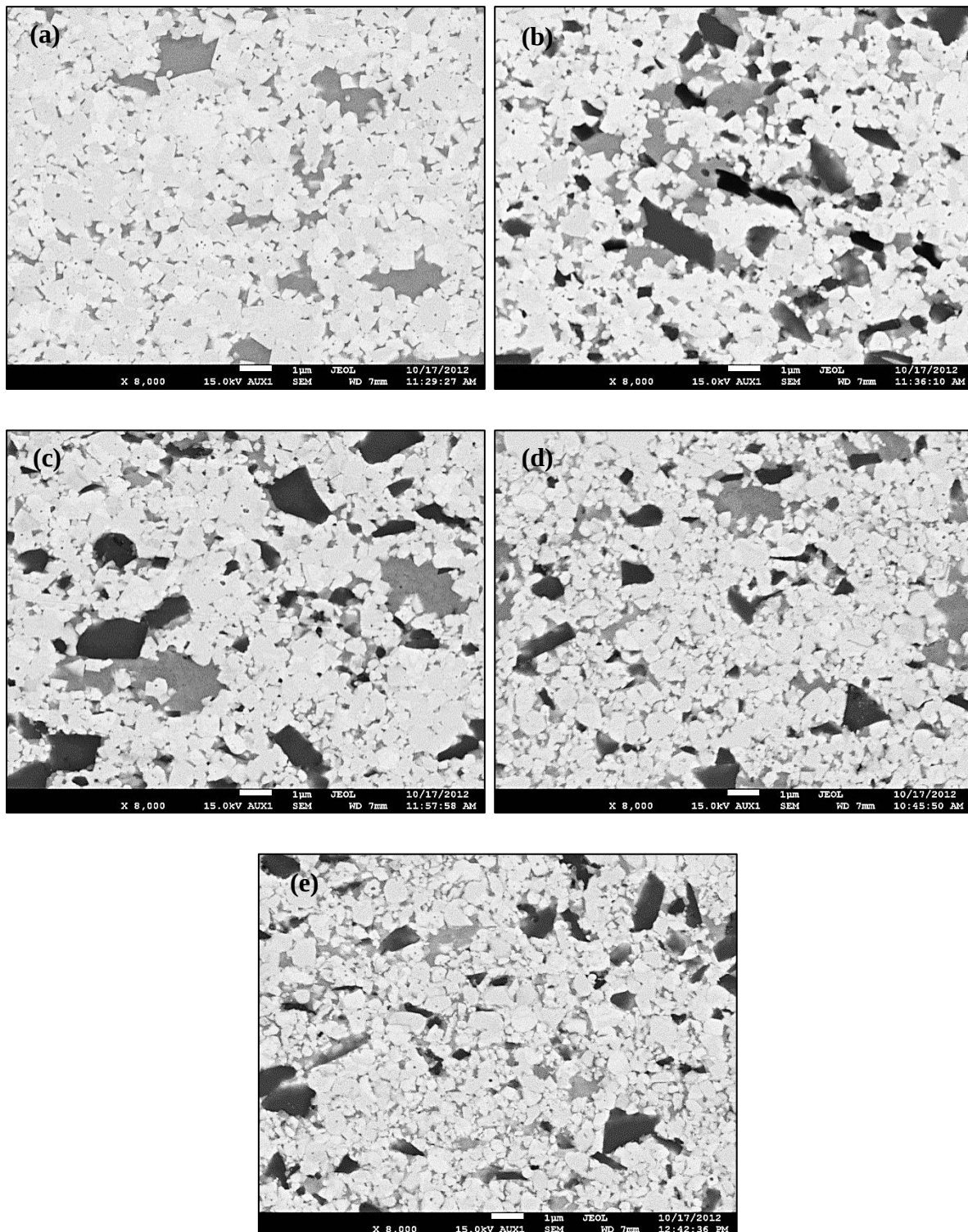


Figure 5.19. SEM-BSE images of: (a) WC-9.3Ni (wt%), (b) WC-6.25TiC-9.3Ni (wt%), with (c) 1 wt%, (d) 3.5 wt%, and (e) 5 wt% Mo_2C , produced from ultrafine WC powder: WC (light), Ni (medium) and TiC (dark).

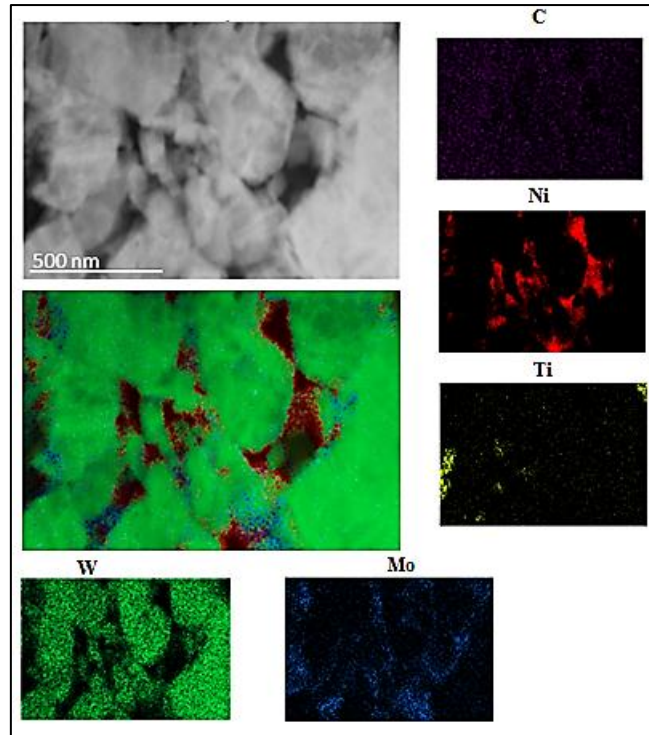


Figure 5.20. HAADF-STEM EDX mapping images of WC-5Mo₂C-6.25TiC-9.3Ni (wt%), showing C (purple), Ni (red), W (green), Mo (blue) and Ti (yellow).

5.1.2.4 Microstructures of WC-9.3Ni (wt%) with TiC and Mo₂C additions, produced from submicron starting powders.

The microstructure of WC-9.3Ni (wt%), with 6.25 wt% TiC and up to 5 wt% Mo₂C additions are shown in Figure 5.21. The WC-9.3Ni (wt%) composition had the largest and most poorly distributed binder pools (Figure 5.21 (a)), and a $0.95 \pm 0.11 \mu\text{m}$ WC mean grain size (Table 5.6), indicating slight grain growth from starting powders ($0.824 \mu\text{m}$ mean particle size) (Table 4.3). Titanium carbide was found mainly at the WC/Ni interfaces and addition of Mo₂C slightly reduced the WC grain size (Table 5.6), as well as resulting in the formation of smaller and better distributed Ni binder pools (Figures 5.21 (c) and (d)).

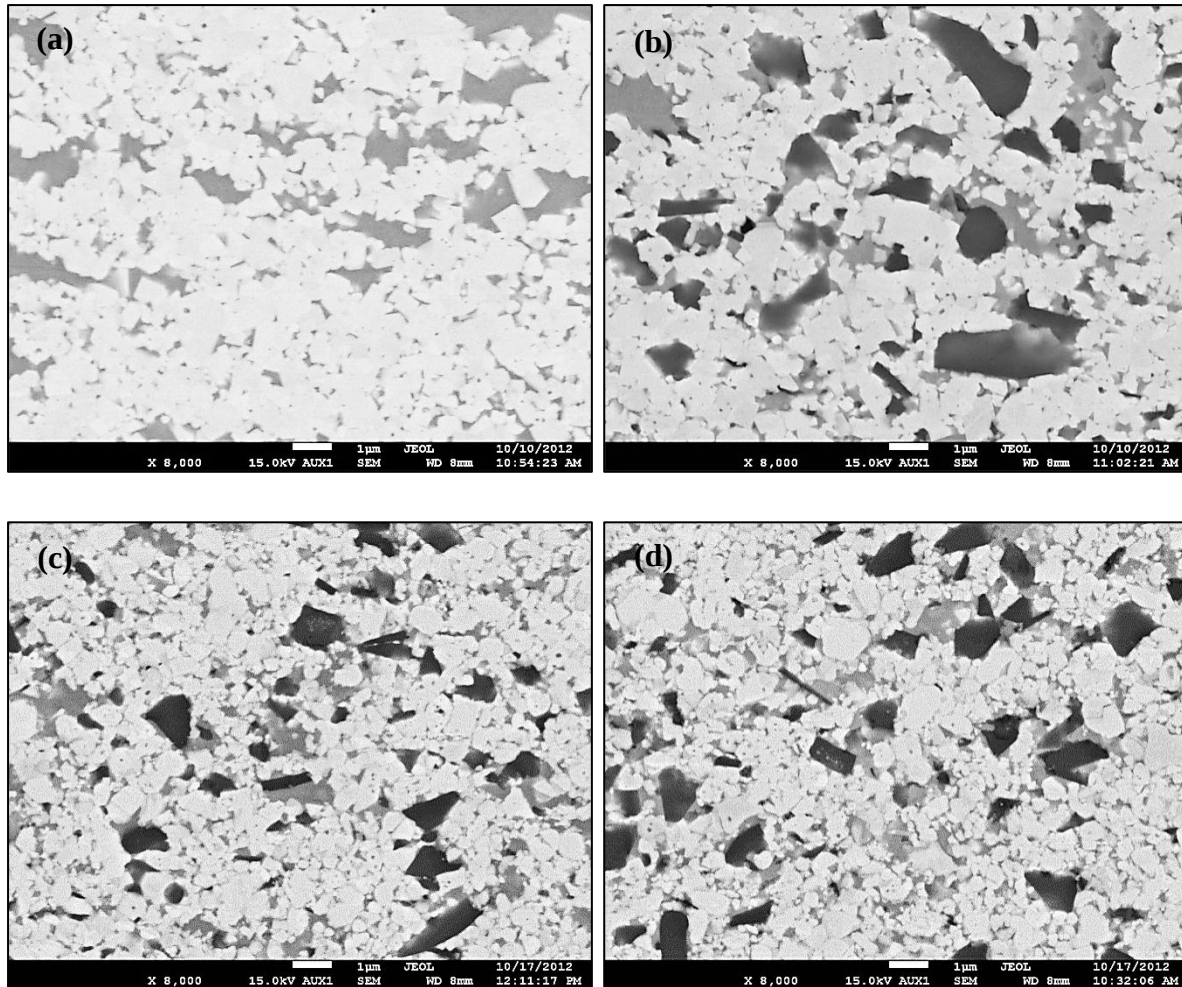


Figure 5.21. SEM-BSE images of WC-6.25TiC-9.3Ni (wt%) produced from submicron WC powder with: (a) WC-9.3Ni (wt%), (b) 0wt%, (c) 3.5wt%, and (d) 5 wt%Mo₂C: WC (light), Ni (medium) and TiC (dark).

5.2 Constituent phases

5.2.1 Phases present in the WC-NbC-Co compositions.

The XRD patterns of liquid phase sintered and spark plasma sintered WC-0.5Cr₃C₂-10Co (wt%) are shown in Figure 5.22. Both compositions had similar patterns, consisting of hexagonal WC and fcc Co, although Cr₃C₂ was not detected. X-ray diffraction patterns of NbC additions to WC-0.5Cr₃C₂-10Co (wt%) (Figure 5.23) showed the presence of hexagonal WC, fcc Co and cubic NbC phases. Increased NbC gave larger NbC peaks and reduced WC peak intensities. Tungsten carbide was not detected in the 80 wt% NbC addition pattern, while Cr₃C₂ was not detected in any of the NbC additions XRD patterns.

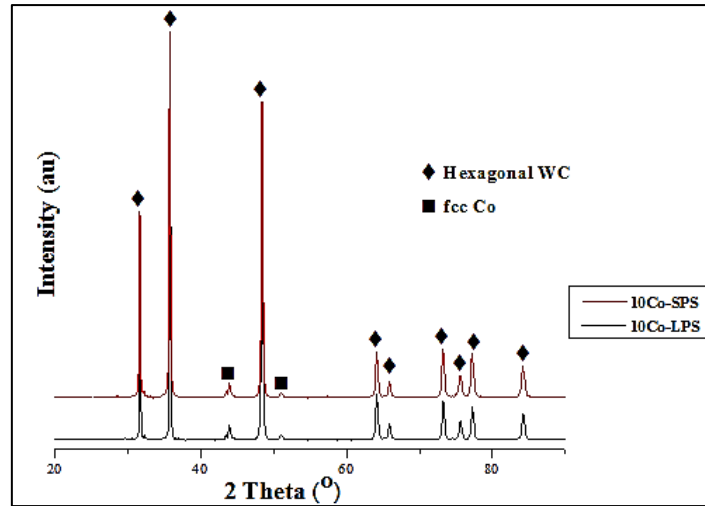


Figure 5.22. X-ray diffraction patterns for the WC-0.5Cr₃C₂-10Co (wt%), produced by LPS and SPS.

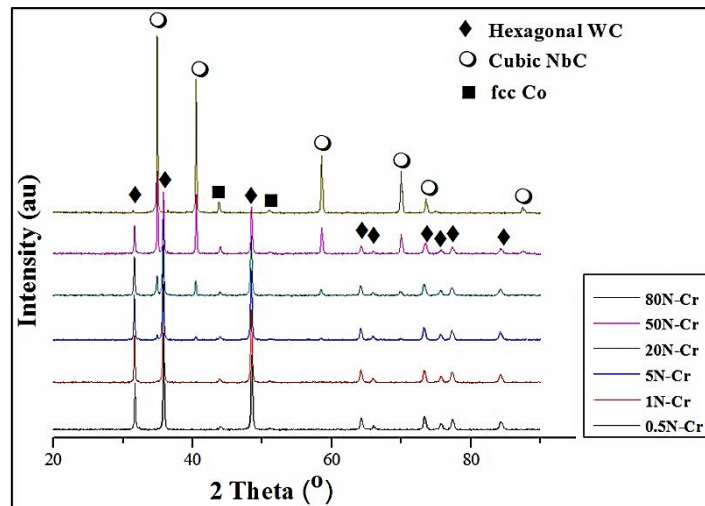


Figure 5.23. X-ray diffraction patterns for the WC-0.5Cr₃C₂-10Co (wt%), with 1-80 wt% NbC additions.

The XRD patterns for WC-10Co (wt%) produced from nano WC starting powders, with 1-20 wt% NbC additions are shown in Figure 5.24. Hexagonal WC, cubic NbC and fcc Co were detected, although the peaks were at different 2 theta angles than in Figure 5.23. The intensity of the NbC peaks increased with increased NbC content, while the WC peaks reduced in intensity. The XRD patterns for the ultrafine grades were similar to those of the nano grades.

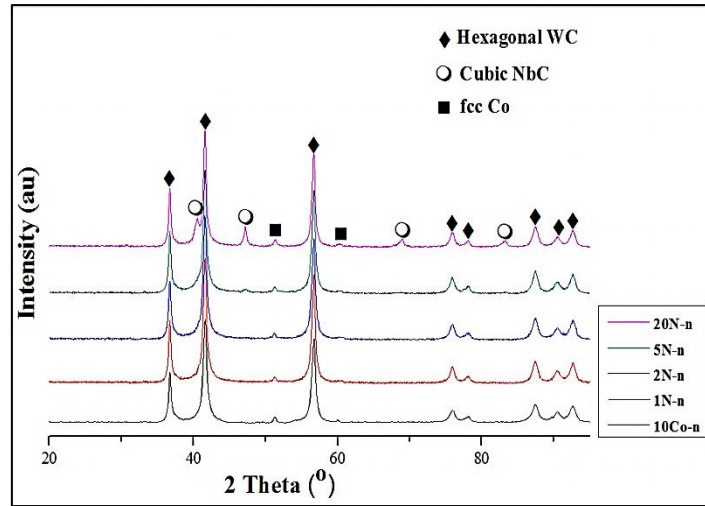


Figure 5.24. X-ray diffraction patterns for the WC-10Co (wt%) produced from nano WC, with 1-20 wt% NbC additions.

5.2.2 Phases present in the WC-Mo₂C-TiC-Ni compositions

Figure 5.25 shows the XRD patterns for addition of 6.25 wt% TiC and 1-5 wt% Mo₂C to WC-0.5Cr₃C₂-10Co (wt%). Hexagonal WC, cubic TiC and fcc Ni were present, but Mo₂C and Cr₃C₂ were not detected. The XRD patterns of similar compositions produced from nano WC starting powders (Figure 5.26) also showed hexagonal WC, cubic TiC and fcc Ni, although Mo₂C was not detected. The XRD patterns for the ultrafine and submicron grades were similar to those of the nano grades.

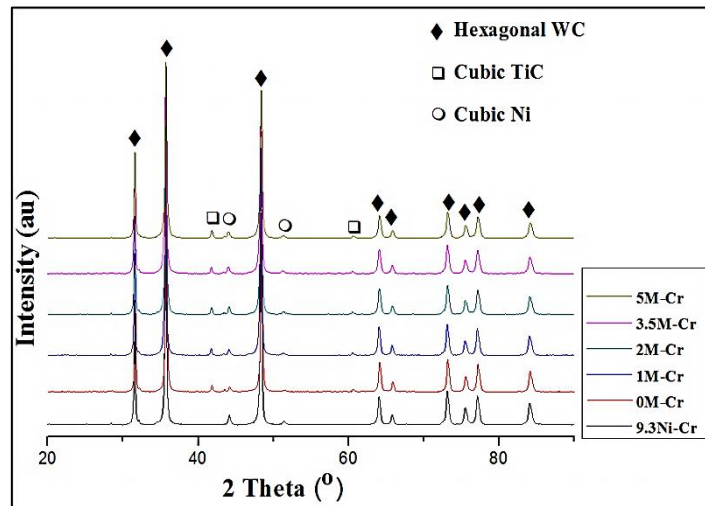


Figure 5.25. X-ray diffraction patterns of the WC-0.5Cr₃C₂-9.3Ni (wt%), with 6.25 wt% TiC and 1-5 wt% Mo₂C additions.

5.3 Mechanical Properties:

5.3.1 Hardness

5.3.1.1 Hardness of WC-NbC-Co compositions

Spark plasma sintering of WC-0.5Cr₃C₂-10Co (wt%) resulted in >3 GPa higher Vickers hardness and >2.5 HRA higher Rockwell-A hardness than liquid phase sintered WC-0.5Cr₃C₂-10Co (wt%) (Tables 5.8-5.10). Small NbC additions (up to 5 wt%) slightly reduced the hardness in all grades, but additions above 20 wt% significantly reduced the hardness with 80 wt% resulting in the lowest hardness. Although the HV₁₀ values were slightly higher than HV₃₀, both tests showed decreased hardness with increased NbC additions, and this was confirmed by the Rockwell-A hardness test. Nano grade WC-10Co (wt%) had a slightly higher hardness than both WC-0.5Cr₃C₂-10Co (wt%) and ultrafine WC-10Co (wt%) grades.

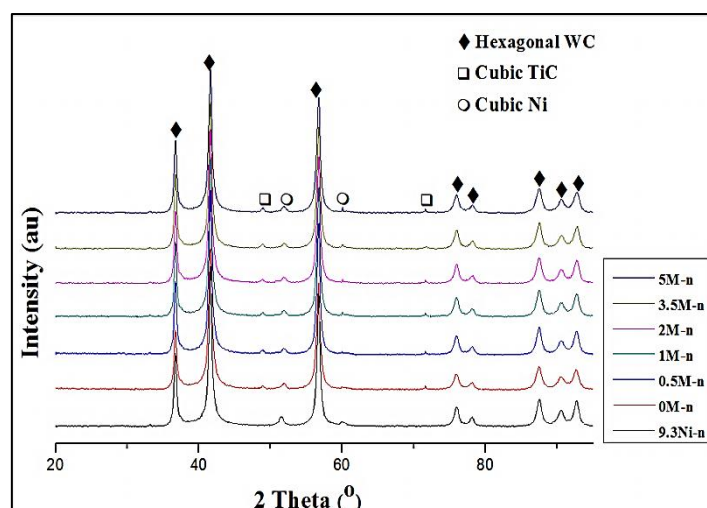


Figure 5.26. X-ray diffraction patterns of the WC-9.3Ni (wt%) produced from nano WC starting powders, with 6.25 wt% TiC and 1-5 wt% Mo₂C additions.

5.3.1.2 Hardness of WC-Mo₂C-TiC-Ni compositions

Use of SPS significantly improved the hardness of WC-0.5Cr₃C₂-9.3Ni compared to LPS, resulting in increased Vickers hardness by >5GPa and Rockwell-A hardness by >3 HRA (Tables 5.11-5.13). The spark plasma sintered WC-0.5Cr₃C₂-9.3Ni (wt%) had a lower hardness than WC-0.5Cr₃C₂-10Co (wt%) produced by SPS (Tables 5.8-5.13). In all grades, addition of 6.25 wt% TiC to WC-9.3Ni (wt%) (0M) (Tables 5.11-5.13) slightly improved the hardness, but additions of Mo₂C significantly increased the hardness, with 5 wt% resulting in the highest hardness. This was observed in both Vickers hardness tests, and confirmed by Rockwell-A hardness test. Additionally, reduction in Ni binder from 9.3 wt% to 7 wt% in the

nano and ultrafine 5M-7Ni grades led to Vickers hardness of >20 GPa and Rockwell-A hardness number of >94 HRA. The WC-0.5Cr₃C₂-3.5Mo₂C-6.25TiC-9.3Ni (wt%) sample sintered at 1280°C (3.5M (1280)) (Tables 5.11-5.13) had a lower hardness than the similar composition sintered at 1310°C.

Table 5.8. Effect of WC starting grain size on the Vickers hardness (HV₃₀) of WC-NbC-10Co (wt%).

Sample abbreviation	Vickers hardness, HV ₃₀ (GPa)		
	WC-0.5Cr ₃ C ₂ (s)	WC (u)	WC (n)
10Co (1430)	14.07 ± 0.39	-	-
10Co	17.80 ± 0.21	17.71 ± 0.14	18.03 ± 0.27
0.5N	17.97 ± 0.15	-	-
1N	17.75 ± 0.26	17.68 ± 0.25	17.92 ± 0.33
2N	17.67 ± 0.32	17.45 ± 0.12	17.53 ± 0.14
3N	17.50 ± 0.21	-	-
5N	17.47 ± 0.47	17.23 ± 0.36	17.30 ± 0.10
10N	16.67 ± 0.39	-	-
20N	16.31 ± 0.13	16.21 ± 0.17	16.06 ± 0.24
30N	15.36 ± 0.40	-	-
50N	14.73 ± 0.38	-	-
80N	13.99 ± 0.41	-	-

(s) 0.8 µm starting size, (u) 0.4 µm starting size, (n) 0.1 µm starting size.

Table 5.9. Effect of WC starting grain size on the Vickers hardness (HV₁₀) of WC-NbC-10Co (wt%).

Sample abbreviation	Vickers hardness, HV ₁₀ (GPa)		
	WC-0.5Cr ₃ C ₂ (s)	WC (u)	WC (n)
10Co (1430)	15.12 ± 0.18	-	-
10Co	18.04 ± 0.15	17.91 ± 0.18	18.31 ± 0.21
0.5N	18.23 ± 0.10	-	-
1N	18.08 ± 0.22	17.86 ± 0.19	18.02 ± 0.24
2N	17.87 ± 0.12	17.68 ± 0.22	17.79 ± 0.41
3N	17.74 ± 0.24	-	-
5N	17.56 ± 0.31	17.42 ± 0.15	17.39 ± 0.25
10N	17.15 ± 0.17	-	-
20N	16.42 ± 0.11	16.24 ± 0.43	16.08 ± 0.33
30N	16.03 ± 0.29	-	-
50N	15.36 ± 0.32	-	-
80N	14.21 ± 0.19	-	-

(s) 0.8 µm starting size, (u) 0.4 µm starting size, (n) 0.1 µm starting size.

Table 5.10. Effect of WC starting grain size on the Rockwell-A hardness of WC-NbC-10Co (wt%).

Sample abbreviation	Rockwell-A hardness, (60Kgf) (HRA)		
	WC-0.5Cr ₃ C ₂ (s)	WC (u)	WC (n)
10Co (1430)	89.97 ± 0.09	-	-
10Co	92.73 ± 0.04	92.84 ± 0.03	92.82 ± 0.11
0.5N	92.90 ± 0.07	-	-
1N	92.87 ± 0.06	92.88 ± 0.07	92.79 ± 0.08
2N	92.83 ± 0.04	92.74 ± 0.19	92.67 ± 0.05
3N	92.83 ± 0.06	-	-
5N	92.77 ± 0.02	92.66 ± 0.04	92.63 ± 0.10
10N	92.73 ± 0.05	-	-
20N	92.50 ± 0.08	92.47 ± 0.07	92.52 ± 0.06
30N	92.33 ± 0.10	-	-
50N	91.83 ± 0.05	-	-
80N	89.07 ± 0.12	-	-

(s) 0.8 µm starting size, (u) 0.4 µm starting size, (n) 0.1 µm starting size.

Table 5.11. Effect of WC starting grain size on the Vickers hardness (HV₃₀) of WC-Mo₂C-6.25TiC-9.3Ni (wt%).

Sample abbreviation	Vickers hardness, HV ₃₀ (GPa)			
	WC-0.5Cr ₃ C ₂ (s)	WC (s)	WC (u)	WC (n)
9.3Ni (1510)	-	-	-	10.55 ± 0.19
9.3Ni (1430)	-	-	-	12.18 ± 0.24
9.3Ni	16.39 ± 0.09	15.98 ± 0.23	15.89 ± 0.17	15.71 ± 0.36
0M	17.67 ± 0.18	16.15 ± 0.18	16.21 ± 0.39	16.17 ± 0.45
0.5M	18.15 ± 0.21	-	-	16.94 ± 0.17
1M	18.27 ± 0.19	16.57 ± 0.25	17.03 ± 0.41	17.40 ± 0.24
2M	18.51 ± 0.34	17.58 ± 0.23	17.99 ± 0.17	18.09 ± 0.30
3.5M (1280)	10.54 ± 0.27	-	-	-
3.5M	19.18 ± 0.16	17.79 ± 0.58	19.18 ± 0.46	19.17 ± 0.32
5M	19.43 ± 0.12	18.88 ± 0.49	20.10 ± 0.13	19.77 ± 0.15
5M-7Ni	-	-	20.43 ± 0.19	20.06 ± 0.23
10Ni	-	-	-	15.52 ± 0.20
8Ni	-	-	-	17.32 ± 0.18
7Ni	-	-	-	18.45 ± 0.24
6Ni	-	-	-	19.03 ± 0.31

(s) 0.8 µm starting size, (u) 0.4 µm starting size, (n) 0.1 µm starting size.

Table 5.12. Effect of WC starting grain size on the Vickers hardness (HV₁₀) of WC-Mo₂C-6.25TiC-9.3Ni (wt%).

Sample abbreviation	Vickers hardness, HV ₁₀ (GPa)			
	WC-0.5Cr ₃ C ₂ (s)	WC (s)	WC (u)	WC (n)
9.3Ni (1510)	-		-	10.73 ± 0.28
9.3Ni (1430)	-	-	-	12.33 ± 0.18
9.3Ni	16.30 ± 0.16	15.91 ± 0.52	15.72 ± 0.81	15.97 ± 0.60
0M	17.90 ± 0.06	16.28 ± 0.40	16.19 ± 0.95	16.29 ± 0.36
0.5M	18.09 ± 0.06	-	-	17.15 ± 0.27
1M	18.36 ± 0.08	17.49 ± 0.64	17.36 ± 0.61	17.84 ± 0.30
2M	18.41 ± 0.07	17.79 ± 0.34	18.89 ± 0.17	18.62 ± 0.72
3.5M (1280)	10.93 ± 0.31	-	-	-
3.5M	19.39 ± 0.16	18.17 ± 0.32	19.65 ± 0.40	19.54 ± 0.47
5M	19.57 ± 0.12	19.01 ± 0.53	20.99 ± 0.23	19.87 ± 0.30
5M-7Ni	-		21.58 ± 0.34	20.85 ± 0.52

(s) 0.8 µm starting size, (u) 0.4 µm starting size, (n) 0.1 µm starting size.

Table 5.13. Effect of WC starting grain size on the Rockwell-A hardness of WC-Mo₂C-6.25TiC-9.3Ni (wt%).

Sample abbreviation	Rockwell-A hardness, (60Kgf) (HRA)			
	WC-0.5Cr ₃ C ₂ (s)	WC (s)	WC (u)	WC (n)
9.3Ni (1430)	-	-	-	88.42 ± 0.10
9.3Ni	91.82 ± 0.13	91.34 ± 0.07	91.51 ± 0.18	91.63 ± 0.12
0M	92.76 ± 0.11	92.56 ± 0.07	92.46 ± 0.06	92.77 ± 0.13
0.5M	93.38 ± 0.02	-	-	92.80 ± 0.17
1M	93.30 ± 0.12	92.92 ± 0.34	92.80 ± 0.61	92.92 ± 0.14
2M	93.88 ± 0.07	93.34 ± 0.14	93.52 ± 0.09	93.44 ± 0.72
3.5M (1280)	87.86 ± 0.38	-	-	-
3.5M	93.73 ± 0.02	93.62 ± 0.32	93.74 ± 0.11	93.61 ± 0.11
5M	94.02 ± 0.08	93.62 ± 0.06	94.09 ± 0.10	93.99 ± 0.09
5M-7Ni	-	-	94.20 ± 0.10	94.12 ± 0.15

(s) 0.8 µm starting size, (u) 0.4 µm starting size, (n) 0.1 µm starting size.

5.3.2 Fracture toughness (K_{1C})

5.3.2.1 Fracture toughness of WC-NbC-Co compositions

The liquid phase sintered WC-0.5Cr₃C₂-10Co (wt%) had higher fracture toughness than the samples of similar composition produced by SPS (Tables 5.14 and 5.15). Small additions of NbC of 0-5 wt% slightly reduced the K_{1C}, while additions above 10 wt% significantly reduced the K_{1C}. This trend was observed in both the HV₃₀ and HV₁₀ K_{1C} measurements, irrespective of starting WC particle size.

5.3.2.2 Fracture toughness of WC-Mo₂C-TiC-Ni compositions

Spark plasma sintered WC-0.5Cr₃C₂-9.3Ni (wt%) had a lower K_{1C} than WC-0.5Cr₃C₂-10Co (wt%) produced by SPS (Tables 5.14 and 5.15). Addition of TiC and Mo₂C had negligible effects on the K_{1C}. The WC-0.5Cr₃C₂-3.5Mo₂C-6.25TiC-9.3Ni (wt%) sample sintered at 1280°C (3.5M (1280)), had a much lower K_{1C} than the similar sample sintered at 1310°C. Nano grade WC-9.3Ni (wt%) samples produced by LPS had much higher K_{1C} than the similar spark plasma sintered composition samples (Tables 5.16 and 5.17), with 9.3Ni (1510) having the highest K_{1C}. The nano grades had lower K_{1C} than similar compositions in the all the other grades for both HV₃₀ and HV₁₀ K_{1C} measurements (Tables 5.16 and 5.17). The K_{1C} reduced with decreased Ni binder amount from 9.3 to 7wt %.

Table 5.14. Effect of WC starting grain size on the fracture toughness with HV₃₀ indentation load on WC-NbC-10Co (wt%).

Sample abbreviation	HV ₃₀ Fracture toughness (MPa.m ^{1/2})		
	WC-0.5Cr ₃ C ₂ (s)	WC (u)	WC (n)
10Co (1430)	13.61 ± 0.52	-	-
10Co	12.88 ± 0.45	12.84 ± 0.46	12.71 ± 0.52
0.5N	12.82 ± 0.26	-	-
1N	12.76 ± 0.41	12.73 ± 0.53	12.68 ± 0.76
2N	12.79 ± 0.29	12.62 ± 0.45	12.52 ± 0.42
3N	12.64 ± 0.31	-	-
5N	12.51 ± 0.22	12.49 ± 0.28	12.38 ± 0.69
10N	11.64 ± 0.16	-	-
20N	10.94 ± 0.55	10.58 ± 0.31	10.72 ± 0.49
30N	10.56 ± 0.14	-	-
50N	9.76 ± 0.52	-	-
80N	8.44 ± 0.17	-	-

(s) 0.8 µm starting size, (u) 0.4 µm starting size, (n) 0.1 µm starting size.

Table 5.15. Effect of WC starting grain size on the fracture toughness with HV₁₀ indentation load on WC-NbC-10Co (wt%).

Sample abbreviation	HV ₁₀ Fracture toughness (MPa.m ^{1/2})		
	WC-0.5Cr ₃ C ₂ (s)	WC (u)	WC (n)
10Co (1430)	14.06 ± 0.51	-	-
10Co	12.89 ± 0.27	12.75 ± 0.43	12.88 ± 0.21
0.5N	12.83 ± 0.41	-	-
1N	12.82 ± 0.55	12.67 ± 0.50	12.75 ± 0.46
2N	12.61 ± 0.32	12.62 ± 0.65	12.56 ± 0.32
3N	12.56 ± 0.28	-	-
5N	12.53 ± 0.27	12.41 ± 0.37	12.50 ± 0.29
10N	11.22 ± 0.33	-	-
20N	10.73 ± 0.55	10.34 ± 0.52	10.52 ± 0.49
30N	10.42 ± 0.19	-	-
50N	9.52 ± 0.29	-	-
80N	8.73 ± 0.47	-	-

(s) 0.8 µm starting size, (u) 0.4 µm starting size, (n) 0.1 µm starting size.

Table 5.16. Effect of WC starting grain size on the fracture toughness with HV₃₀ indentation load on WC-Mo₂C-6.25TiC-9.3Ni (wt%).

Sample abbreviation	HV ₃₀ Fracture toughness (MPa.m ^{1/2})			
	WC-0.5Cr ₃ C ₂ (s)	WC (s)	WC (u)	WC (n)
9.3Ni (1510)	-	-	-	15.15 ± 0.24
9.3Ni (1430)	-	-	-	14.74 ± 0.42
9.3Ni	11.45 ± 0.57	11.51 ± 0.64	11.87 ± 0.67	10.86 ± 0.35
0M	11.41 ± 0.26	11.23 ± 0.50	11.18 ± 0.56	10.52 ± 0.51
0.5M	11.48 ± 0.20	-	-	10.37 ± 0.46
1M	11.55 ± 0.28	11.49 ± 0.41	11.12 ± 0.32	10.60 ± 0.23
2M	11.23 ± 0.33	11.35 ± 0.27	11.24 ± 0.17	10.51 ± 0.65
3.5M (1280)	8.66 ± 0.43	-	-	-
3.5M	11.14 ± 0.21	11.31 ± 0.48	11.32 ± 0.48	10.67 ± 0.70
5M	11.33 ± 0.30	11.24 ± 0.60	11.34 ± 0.23	10.51 ± 0.25
5M-7Ni	-	-	10.46 ± 0.38	10.11 ± 0.31
10Ni	-	-	-	11.92 ± 0.61
8Ni	-	-	-	10.42 ± 0.18
7Ni	-	-	-	10.14 ± 0.38
6Ni	-	-	-	9.75 ± 0.23

(s) 0.8 µm starting size, (u) 0.4 µm starting size, (n) 0.1 µm starting size.

Table 5.17. Effect of WC starting grain size on the fracture toughness with HV₁₀ indentation load on WC-Mo₂C-6.25TiC-9.3Ni (wt%).

Sample abbreviation	HV ₁₀ Fracture toughness (MPa.m ^{1/2})			
	WC-0.5Cr ₃ C ₂ (s)	WC (s)	WC (u)	WC (n)
9.3Ni (1510)	-	-	-	15.34 ± 0.74
9.3Ni (1430)	-	-	-	14.88 ± 0.62
9.3Ni	11.74 ± 0.34	11.63 ± 0.61	11.80 ± 0.30	10.71 ± 0.22
0M	11.81 ± 0.60	11.47 ± 0.36	11.48 ± 0.55	10.86 ± 0.35
0.5M	11.32 ± 0.31	-	-	10.54 ± 0.61
1M	11.64 ± 0.24	11.04 ± 0.21	11.27 ± 0.34	10.91 ± 0.77
2M	11.45 ± 0.21	11.41 ± 0.52	11.34 ± 0.46	10.82 ± 0.91
3.5M (1280)	8.81 ± 0.52	-	-	-
3.5M	11.62 ± 0.42	11.43 ± 0.17	11.16 ± 0.23	10.55 ± 0.43
5M	11.51 ± 0.30	11.59 ± 0.53	11.37 ± 0.72	10.80 ± 0.92
5M-7Ni	-	-	10.27 ± 0.82	10.35 ± 0.24

(s) 0.8 µm starting size, (u) 0.4 µm starting size, (n) 0.1 µm starting size.

5.3.3 Elastic modulus

5.3.3.1 Elastic modulus of WC-NbC-Co compositions

From Table 5.18, liquid phase sintered WC-0.5Cr₃C₂-10Co (wt%) had a slightly higher modulus of elasticity than the spark plasma sintered WC-0.5Cr₃C₂-10Co (wt%). Addition of up to 5 wt% NbC slightly reduced the modulus of elasticity, but higher additions of ≥20 wt% led to significant reduction, in all the grades.

Table 5.18. Elastic modulus of WC-NbC-10Co (wt%) cemented carbides.

Sample abbreviation	Elastic modulus (GPa)		
	WC-0.5Cr ₃ C ₂ (s)	WC (u)	WC (n)
10Co (1430)	596 ± 1	-	-
10Co	584 ± 3	579 ± 1	586 ± 3
1N	578 ± 1	577 ± 1	579 ± 1
2N	581 ± 2	577 ± 3	575 ± 0
5N	571 ± 4	574 ± 1	570 ± 2
20N	539 ± 2	544 ± 2	551 ± 1
80N	442 ± 4	-	-

(s) 0.8 µm starting size, (u) 0.4 µm starting size, (n) 0.1 µm starting size.

5.3.3.2 Elastic modulus of WC-Mo₂C-TiC-Ni compositions

The WC-0.5Cr₃C₂-9.3Ni (wt%) sample produced by LPS had a higher modulus of elasticity than that produced by SPS (Table 5.19). Spark plasma sintered WC-0.5Cr₃C₂-10Co (wt%) had slightly higher modulus of elasticity than WC-0.5Cr₃C₂-9.3Ni (wt%). Additions of TiC

and Mo₂C had little effect on the modulus of elasticity, although reduction in binder amount in the nano and ultrafine 5M grades from 9.3 wt% to 7 wt% slightly increased the modulus of elasticity. Sample 3.5M sintered at 1280°C had a much lower modulus of elasticity than 3.5M sintered at 1310°C.

Table 5.19. Elastic modulus of WC-9.3Ni (wt%), with 6.25 wt% TiC and 1-5 wt% Mo₂C.

Sample abbreviation	Elastic modulus(GPa)			
	WC-0.5Cr ₃ C ₂ (s)	WC (s)	WC (u)	WC (n)
9.3Ni (1430)	-	-	-	589 ± 1
9.3Ni	578 ± 2	577 ± 1	574 ± 0	570 ± 3
0M	568 ± 1	572 ± 2	565 ± 3	569 ± 2
1M	574 ± 2	559 ± 6	571 ± 5	559 ± 1
2M	568 ± 4	567 ± 3	575 ± 3	561 ± 2
3.5M (1280)	434 ± 6	-	-	-
3.5M	563 ± 2	571 ± 3	577 ± 1	564 ± 2
5M	571 ± 3	575 ± 1	576 ± 3	574 ± 1
5M-7Ni	-	-	585 ± 3	581 ± 1

(s) 0.8 µm starting size, (u) 0.4 µm starting size, (n) 0.1 µm starting size.

5.3.4 Magnetic saturation

Both spark plasma sintered and liquid phase sintered WC-0.5Cr₃C₂-10Co (wt%) had the lowest magnetic saturation, with the latter having the lowest value (Table 5.20). The magnetic saturation increased with increased NbC additions.

Table 5.20. Magnetic saturation of WC-0.5Cr₃C₂-10Co (wt%), with 0.5-80 NbC (wt%) additions.

Sample abbreviation	Magnetic saturation	
	wt% Co	µTm ³ kg ⁻¹
10Co (1430)	8.65 ± 0.32	17.43 ± 0.53
10Co	8.78 ± 0.24	17.71 ± 0.48
0.5N	8.78 ± 0.17	17.72 ± 0.31
1N	8.82 ± 0.22	17.72 ± 0.63
2N	8.81 ± 0.34	17.75 ± 0.41
3N	8.83 ± 0.25	17.77 ± 0.44
5N	8.92 ± 0.39	17.85 ± 0.27
10N	9.05 ± 0.16	18.08 ± 0.34
20N	9.12 ± 0.14	18.25 ± 0.47
30N	9.23 ± 0.22	18.50 ± 0.31
50N	9.35 ± 0.17	18.75 ± 0.35
80N	9.47 ± 0.24	19.05 ± 0.21

5.3.5 Transverse rupture strength (TRS)

Effects of starting grain size, different binders, additions of NbC to WC-Co, as well as additions of TiC and Mo₂C to WC-Ni on the TRS of the sintered compositions are shown in Table 5.21. Liquid phase sintered WC-0.5Cr₃C₂-10Co (wt%) had the highest TRS, followed by liquid phase sintered WC-9.3Ni (wt%) produced from nano WC. Spark plasma sintered WC-0.5Cr₃C₂-10Co (wt%) had highest TRS of all the WC-9.3Ni (wt%) grades. Addition of 5 wt% NbC to WC-0.5Cr₃C₂-10Co (wt%) slightly reduced the TRS, while additions of TiC and Mo₂C to WC-9.3Ni (wt%) reduced the TRS. Reduction of Ni from 9.3 wt% to 7 wt% in the 5M samples decreased TRS.

Table 5.21. Transverse rupture strength of WC-Co and WC-Ni cemented carbides.

Sample abbreviation	Transverse rupture strength (MPa)			
	WC-0.5Cr ₃ C ₂ (s)	WC (s)	WC (u)	WC (n)
10Co (1430)	2286 ± 62	-	-	-
9.3Ni (1430)	-	-	-	2175 ± 71
10Co	2033 ± 55	-	-	-
9.3Ni	1875 ± 84	1830 ± 97	1817 ± 82	1785 ± 82
0M	1781 ± 60	1718 ± 43	1741 ± 79	1718 ± 43
5N	1954 ± 72	-	-	-
5M	1692 ± 89	1658 ± 85	1598 ± 85	1614 ± 78
5M-7Ni	-	-	1467 ± 71	1496 ± 52

(s) 0.8 µm starting size, (u) 0.4 µm starting size, (n) 0.1 µm starting size.

Chapter 6: Sliding wear, thermal shock and impact resistance results

The response of the sintered compositions to induced stresses due to sliding wear, rapid changes in temperature and impact loading are described in this chapter.

6.1 Sliding wear

6.1.1 Sliding wear due to 100 Cr6 steel ball

6.1.1.1 Optical images of wear tracks

The wear tracks for liquid phase sintered (LPS) WC-0.5Cr₃C₂-10Co (wt%) (10Co (1430)), and spark plasma sintered (SPS) WC-0.5Cr₃C₂-5NbC-10Co (wt%) (5N-Cr) and WC-5Mo₂C-6.25TiC-7Ni (5M-7Ni-u) from the 100 Cr6 steel ball are shown in Figure 6.1.

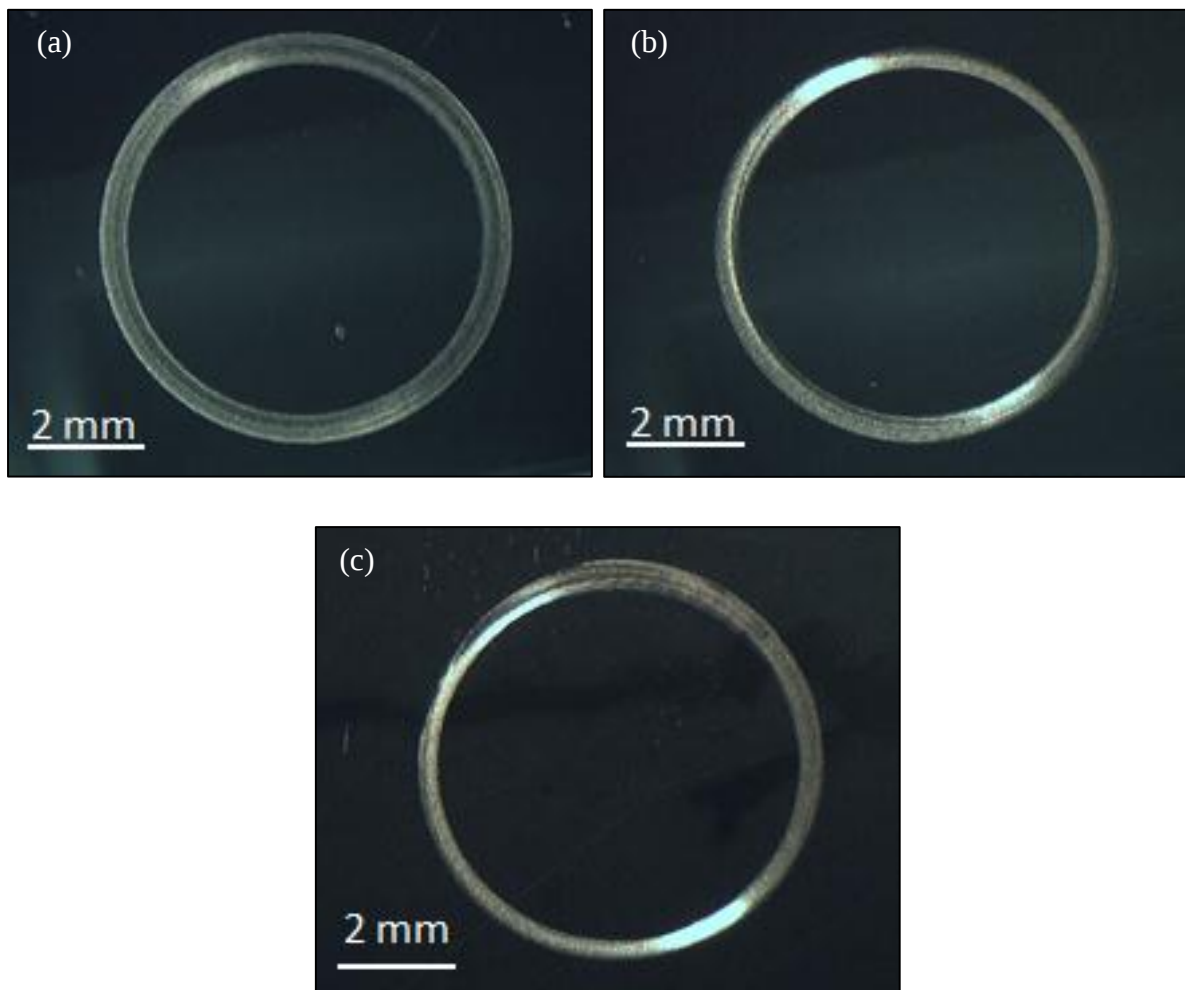


Figure 6.1. Optical images of wear tracks of: (a) 10Co (1430) produced by LPS, (b) 5N-Cr, and (c) 5M-7Ni-u produced by SPS.

The 10Co (1430) sample had a wider track than both SPS samples. Although the width of the wear track for the 5M-7Ni-u sample was slightly less than for the 5N-Cr sample for most of the track, certain regions were thicker.

6.1.1.2 Laser confocal analysis

The 3D topographic maps and wear track profiles for 10Co (1430) and liquid phase sintered WC-9.3Ni (wt%) (9.3Ni (1430)) samples are shown in Figure 6.2. A wider wear track and greater volume loss was observed for the 10Co (1430) sample than the 9.3Ni (1430) sample. Most of the volume loss in the 10Co (1430) sample was on the both edges of the track, while for the 9.3Ni (1430) sample, it was mostly in between the track, as shown by the wear track profiles. Spark plasma sintering improved the resistance to wear, with all grades of WC-9.3Ni (wt%) (9.3Ni) having a lower volume loss than the 9.3Ni (1430) sample (Figures 6.3-6.5 and Table 6.1). The 5N-Cr sample had a lower volume loss and better sample wear rate than 10Co (1430) and all grades of 9.3Ni and WC-6.25TiC-9.3Ni (wt%) (0M) (Figures 6.1-6.4 and Table 6.1).

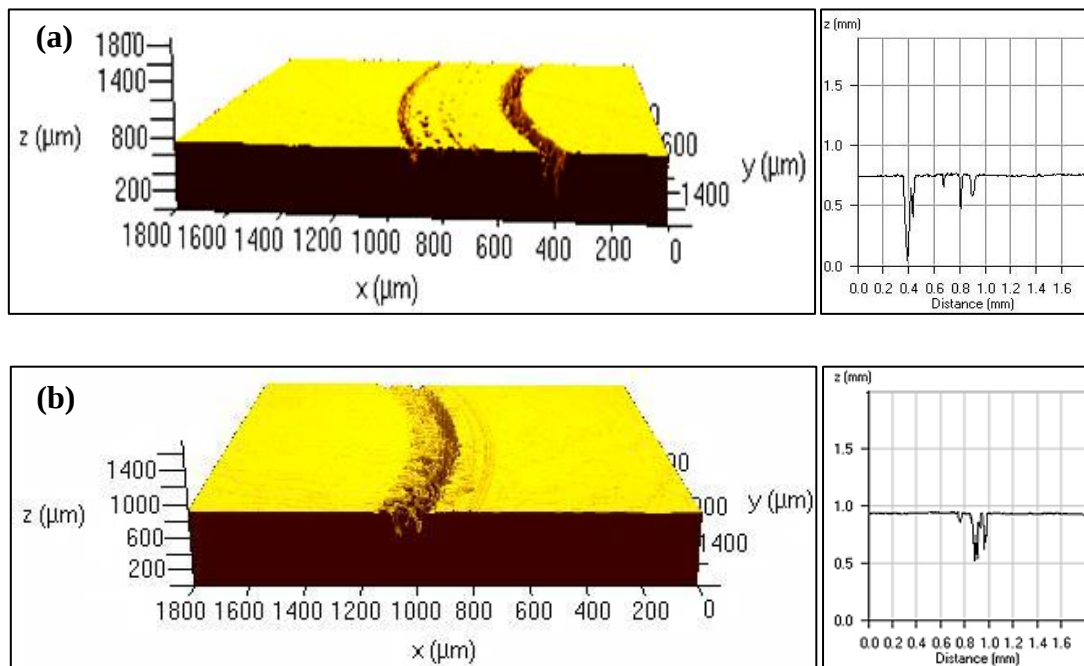


Figure 6.2. Laser confocal 3D topographic maps and wear track profiles of the wear tracks for: (a) 10Co (1430), and (b) 9.3Ni (1430) samples produced by LPS.

Additions of up to 5 Mo₂C (wt%) and reduced Ni binder amount, from 9.3 wt% to 7 wt%, significantly improved the resistance to wear, so that the 5M-s, 5M-7Ni-u and 5M-7Ni-n samples having the lowest sample wear rates (Figures 6.3-6.5 and Table 6.1). The 3D

topographic maps for the 0M-n (Figure 6.3 (b)), 9.3Ni-u, 0M-u (Figures 6.4 (a) and (b)) and 0M-s (Figure 6.5 (b)) showed greater wear on the edges of the wear track than at the centre.

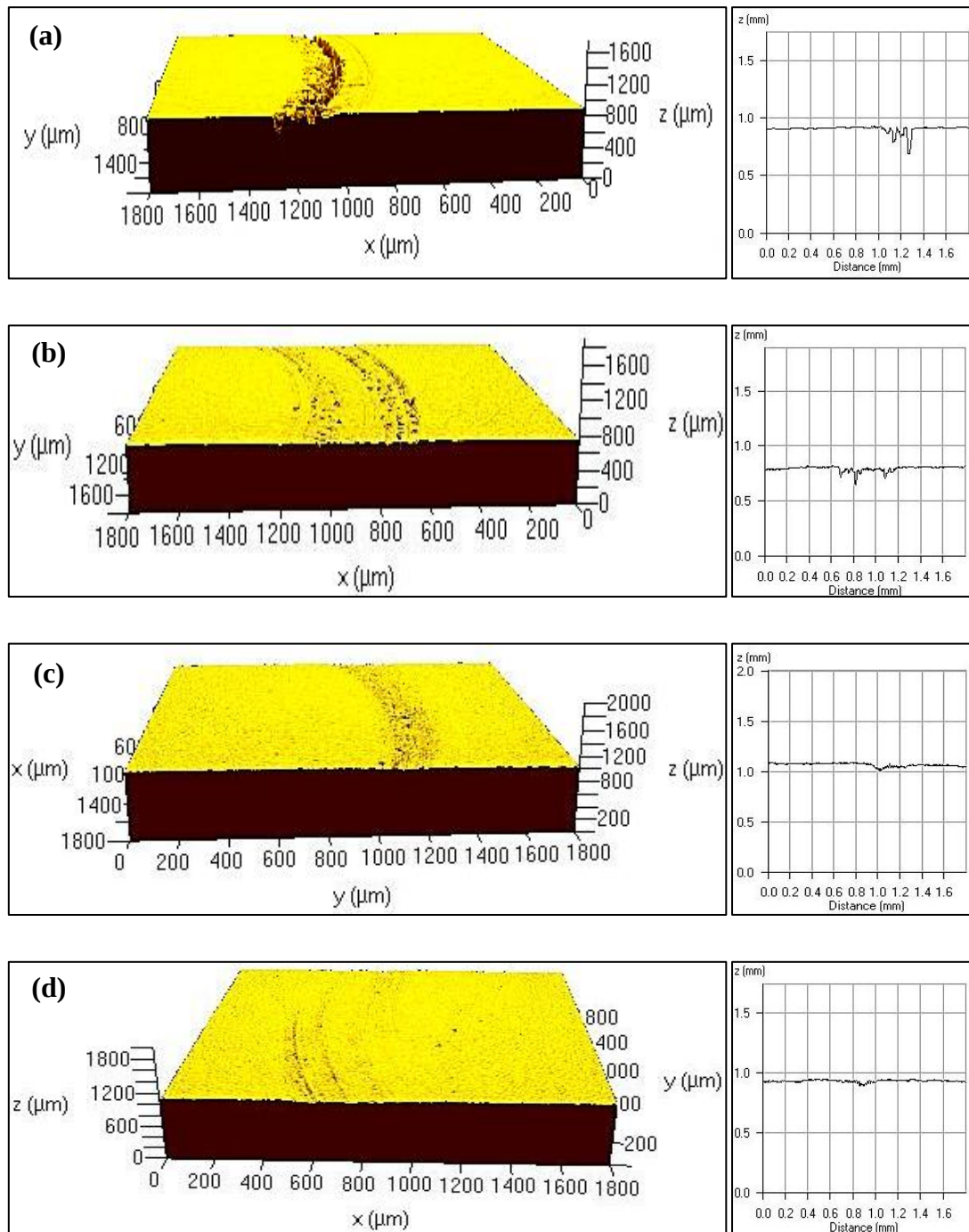


Figure 6.3. Laser confocal 3D topographic maps and wear track profiles of the wear tracks for: (a) 9.3Ni-n, (b) 0M-n, (c) 5N-Cr, and (d) 5M-7Ni-n samples.

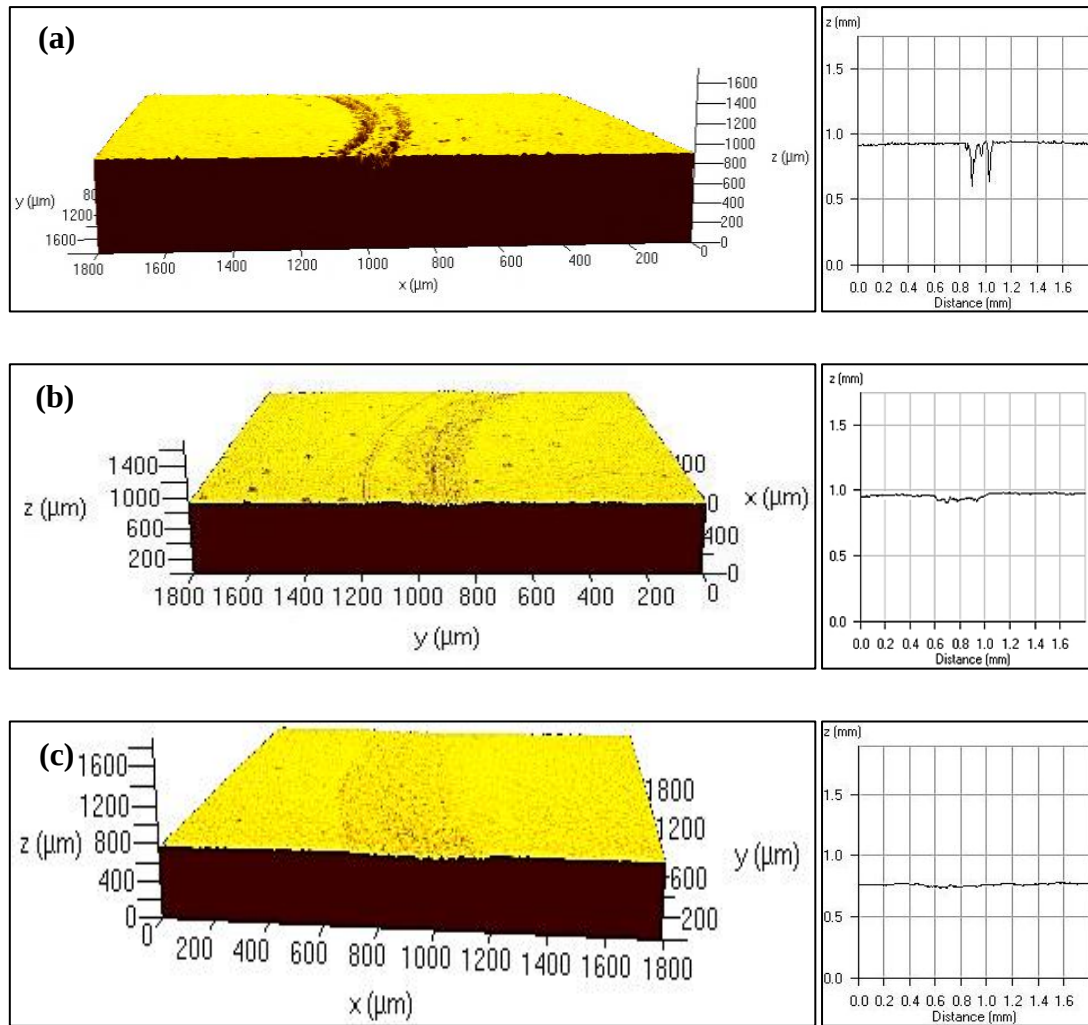


Figure 6.4. Laser confocal 3D topographic maps and wear track profiles of the wear tracks for: (a) 9.3Ni-u, (b) 0M-u, and (c) 5M-7Ni-u samples.

6.1.1.3 Optical images of the 100 Cr6 steel balls wear scars

Optical images of the wear scars on the 100 Cr6 steel balls by 10Co (1430), 5N-Cr and 5M-7Ni-u samples are shown in Figure 6.6. The 10Co (1430) sample had a wear scar with the smallest diameter, while the 5M-7Ni-u sample gave ball wear scars with the largest diameters (Figure 6.6). The ball wear scars from 5N-Cr and 5M-7Ni-u samples had larger scratches and pull-out compared to the 10Co (1430) sample, which only had scratches. The ball wear scar from the 5M-7Ni-u sample had wider scratches and more pull-out than the ball wear scar from the 5N-Cr sample.

Table 6.1. Sliding wear results from 100 Cr6 steel balls.

Sample abbreviation	Sample worn volume ($\times 10^{-1} \text{ mm}^3$)	Sample wear rate ($\times 10^{-5} \text{ mm}^3/\text{N.m}$)
10Co (1430)	9.05 ± 0.13	30.210 ± 0.010
9.3Ni (1430)	8.04 ± 0.32	26.827 ± 0.009
9.3Ni-n	5.18 ± 0.31	18.155 ± 0.006
9.3Ni-u	5.44 ± 0.42	17.343 ± 0.004
9.3Ni-s	4.88 ± 0.31	16.317 ± 0.005
0M-n	3.66 ± 0.24	12.253 ± 0.006
0M-u	3.61 ± 0.21	12.071 ± 0.004
0M-s	3.68 ± 0.30	12.565 ± 0.004
5N-Cr	3.49 ± 0.28	11.126 ± 0.005
5M-s	2.95 ± 0.19	9.823 ± 0.007
5M-7Ni-n	0.88 ± 0.16	2.918 ± 0.005
5M-7Ni-u	0.85 ± 0.12	2.830 ± 0.007

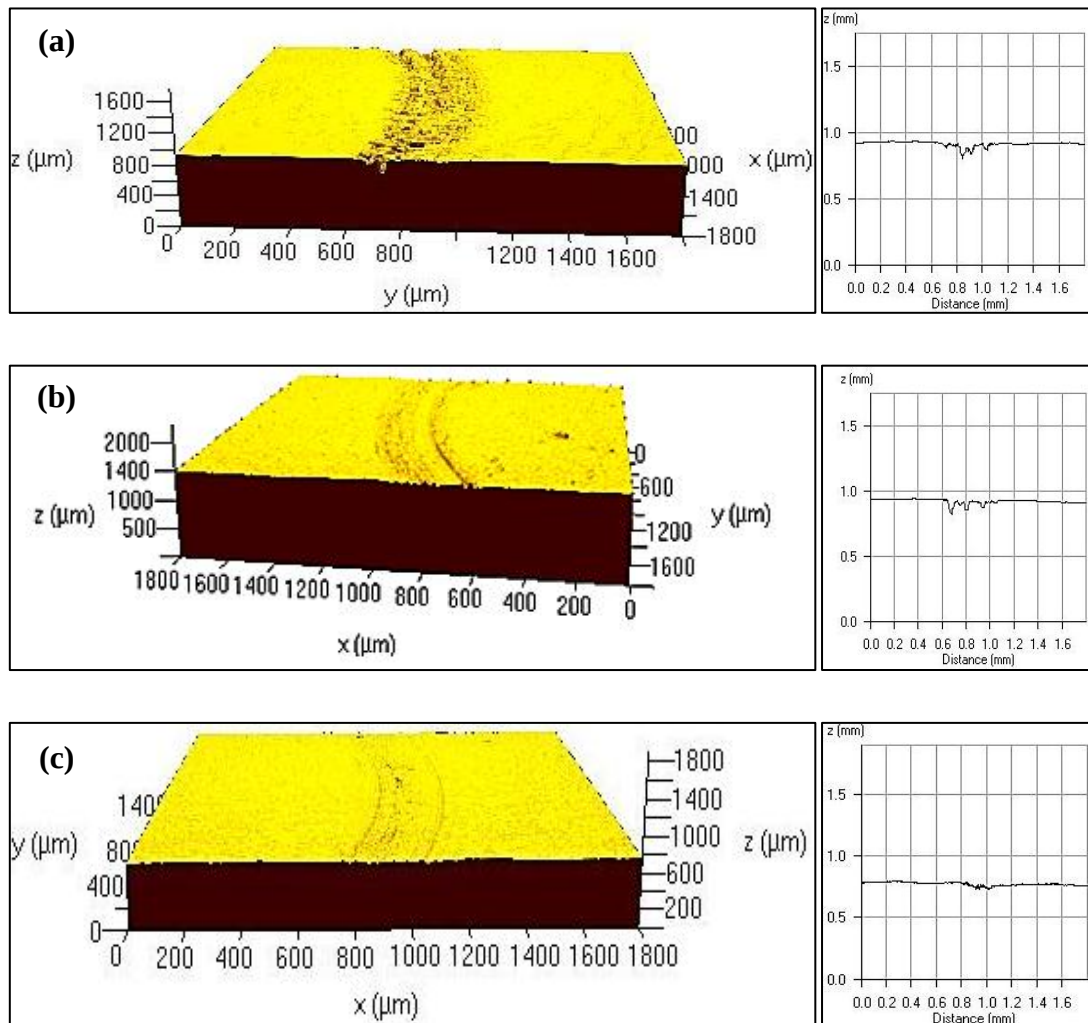


Figure 6.5. Laser confocal 3D topographic maps and wear track profiles of the wear tracks for: (a) 9.3Ni-s, (b) 0M-s, and (c) 5M-s samples.

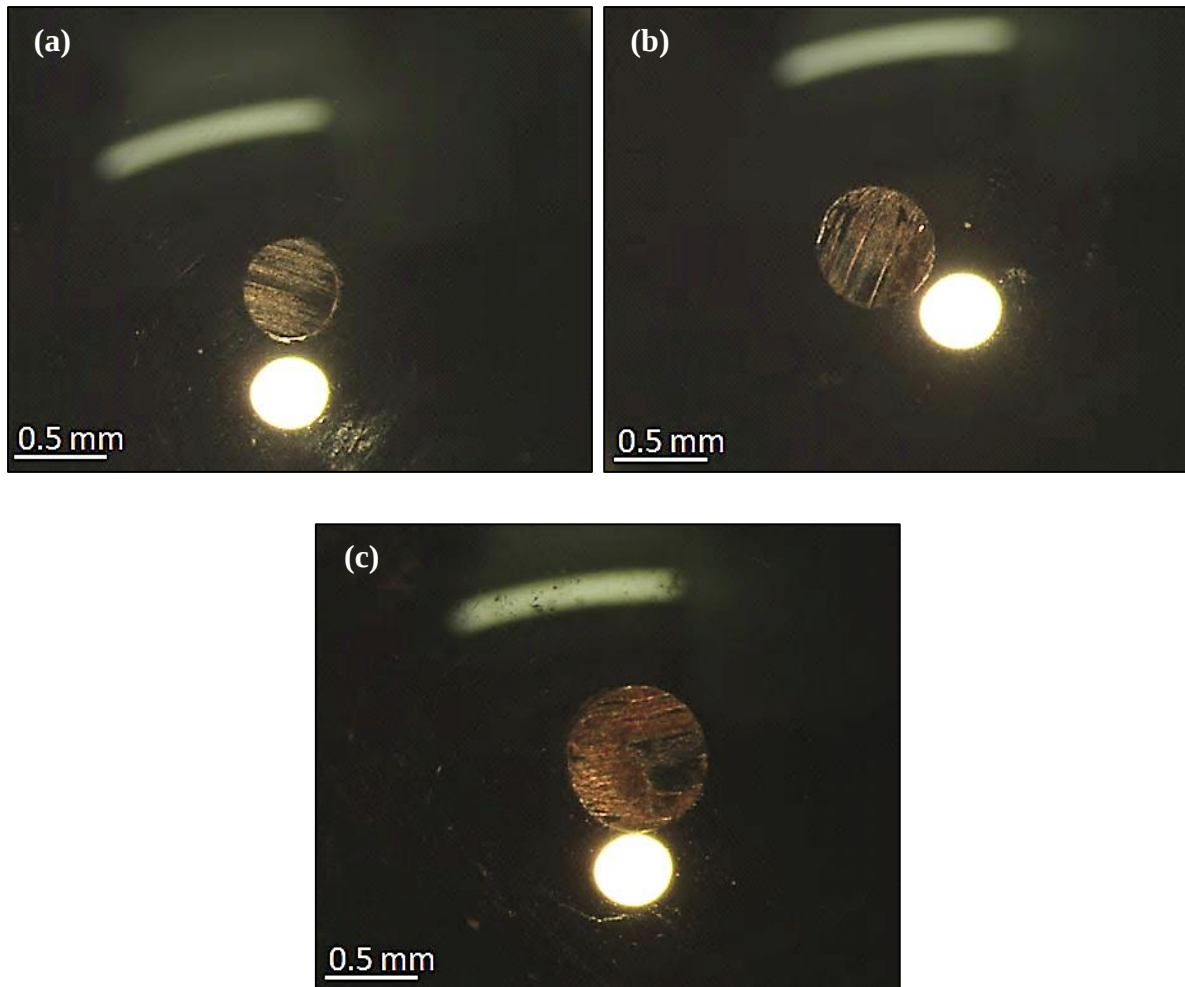


Figure 6.6. Optical images of the 100 Cr6 steel balls wear scars from the: (a) 10Co (1430), (b) 5N-Cr, and (c) 5M-7Ni-u samples.

6.1.1.4 Microstructures of wear tracks

The microstructures of the 10 Co (1430), 5N-Cr and 5M-7Ni-u samples wear track surfaces from the 100 Cr6 steel balls are shown in Figure 6.7. Debris was observed on the surfaces of the 5N-Cr (dark phase) and 5M-7Ni-u (medium dark phase) samples, but were not present on the wear track surface of the 10 Co (1430) sample. The 5M-7Ni-u sample had more debris than the 5N-Cr sample. The debris was identified to be iron oxide by SEM-EDX mapping (Figure 6.8).

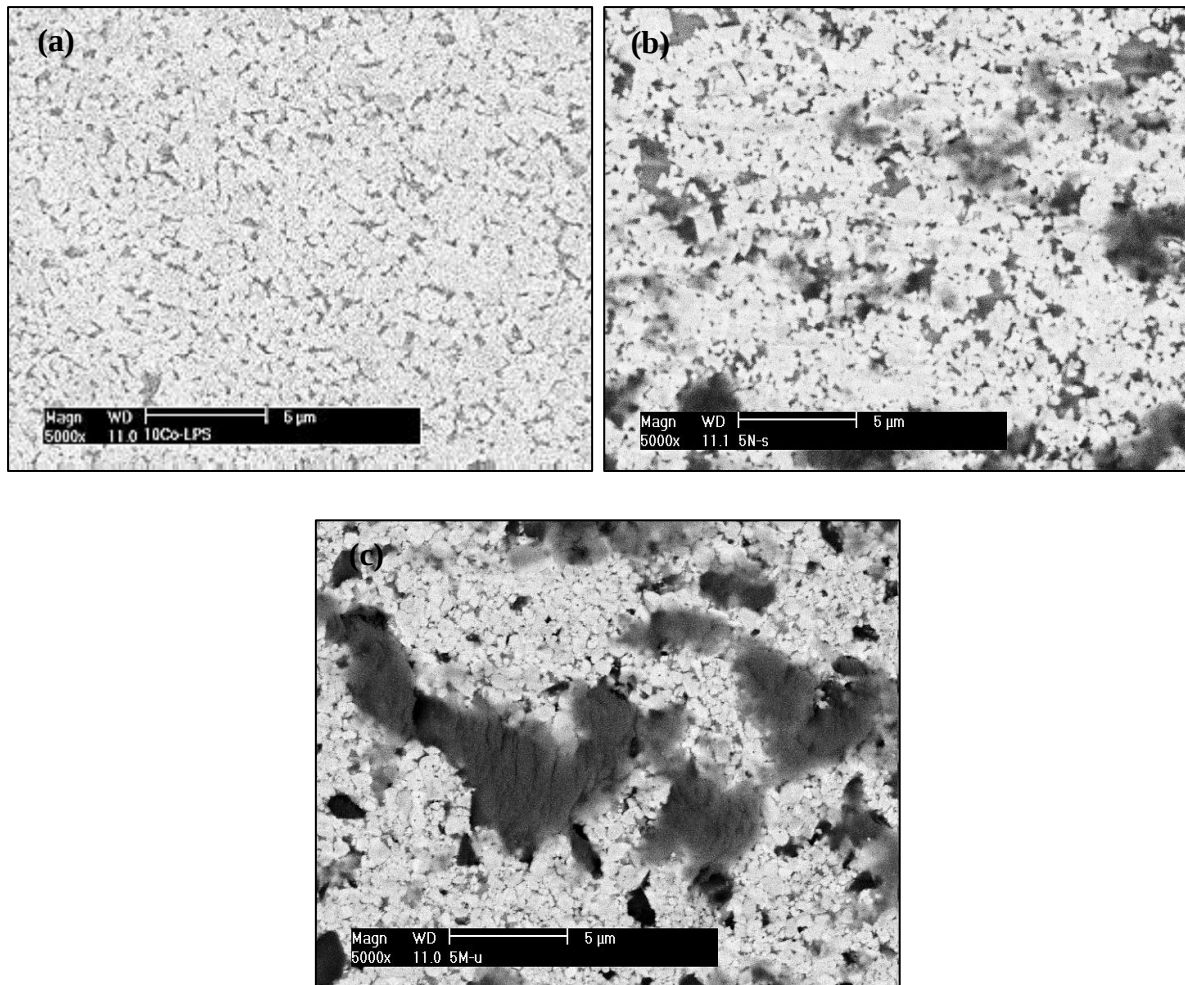


Figure 6.7. SEM-BSE images of the wear tracks of: (a) 10Co (1430), showing WC (light), and Co (dark), (b) 5N-Cr, showing WC (light), NbC (medium light), Co (medium dark) and debris (dark), and (c) 5M-7Ni-u, showing WC (light), Ni (medium light), debris (medium dark) and TiC (dark).

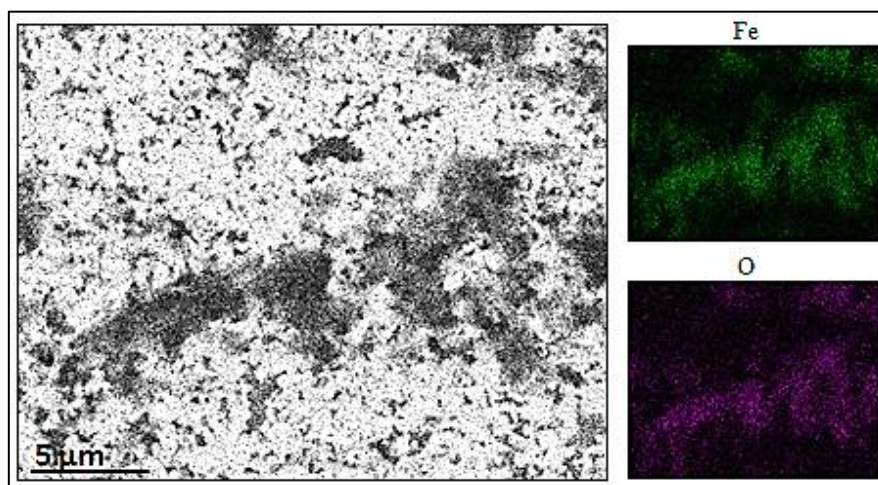


Figure 6.8. SEM-BSE image and X-ray maps of the 5N-Cr sample wear track, showing WC (light), NbC (medium light), Co (medium dark) and iron oxide (dark) on the sample surface.

The SEM-BSE image of a polycrystalline diamond (PCD) sample that was exposed to the same sliding wear test (using a 100 Cr6 steel ball) is shown in Figure 6.9. Light grey debris was found on the surface of the wear track, and this was identified to be iron oxide by SEM-EDX mapping (Figure 6.10).

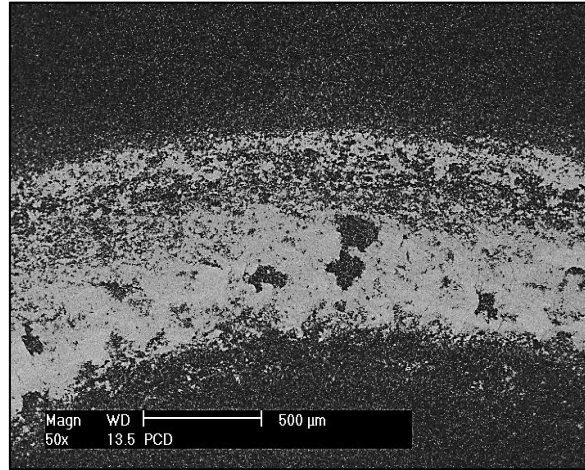


Figure 6.9. SEM-BSE image of the PCD sample wear track, C (dark) and debris (light grey).

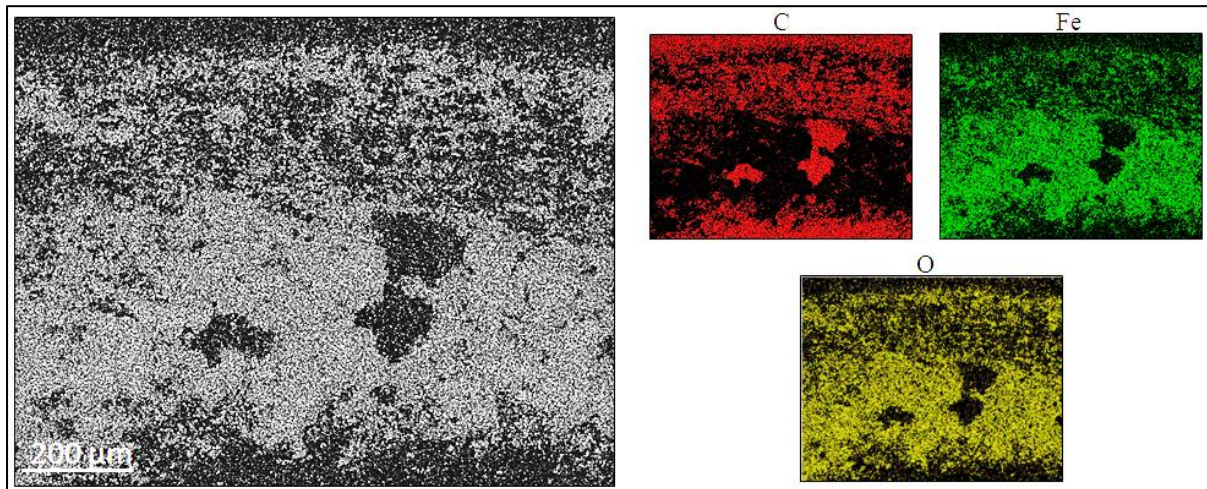


Figure 6.10. SEM-BSE image and X-ray maps of the PCD sample wear track, showing C (red), Fe (green) and O₂ (yellow).

6.1.1.5 100 Cr6 steel ball wear results

The liquid phase sintered samples (10Co (1430) and 9.3Ni (1430)) had lower ball worn volumes than all the spark plasma sintered samples, and thus lower ball wear rates (Table 6.2). However, the 9.3Ni (1430) sample had a higher ball wear rate than the 10Co (1430) sample. Spark plasma sintering and addition of 5 wt% NbC to WC-0.5Cr₃C₂-10Co (wt%) resulted in a much higher ball wear rate than the 10Co (1430) sample. Addition of 6.25 wt%

TiC to WC-9.3Ni (wt%) increased the ball wear rate in all grades (0M-n, 0M-u and 0M-Cr) (Table 6.2). Further additions up to 5 wt% Mo₂C and reduction in the Ni binder amount, from 9.3 wt% to 7 wt%, significantly increased the ball wear rate (Table 6.2).

The 10Co (1430) and 9.3Ni 1430 samples had higher coefficients of friction (μ) than all the spark plasma sintered samples (Table 6.2). The μ reduced with additions of 5 wt% NbC to WC-0.5Cr₃C₂-10Co (wt%), as well as 6.25 wt% TiC and 5 wt% Mo₂C to WC-9.3Ni (wt%) (Table 6.2 and Figure 6.11). The Hertzian pressure, the maximum contact pressure at the ball/sample surface interface [1985Las], for the WC-cemented carbides ranged between 1.764 and 1.765 GPa, while the PCD sample experienced a much higher pressure, 1.894 GPa.

Table 6.2. 100 Cr6 steel ball sliding wear analysis.

Sample abbreviation	Ball worn volume ($\times 10^{-3} \text{ mm}^3$)	Ball wear rate ($\times 10^{-7} \text{ mm}^3/\text{N.m}$)	Av. coefficient of friction, μ	Hertzian pressure (GPa)
10Co (1430)	2.19 $\pm$ 0.03	7.32 $\pm$ 0.22	0.88 $\pm$ 0.02	1.765
9.3Ni (1430)	3.41 $\pm$ 0.08	11.32 $\pm$ 0.36	0.85 $\pm$ 0.01	1.765
9.3Ni-n	4.84 $\pm$ 0.03	16.12 $\pm$ 0.18	0.83 $\pm$ 0.02	1.764
9.3Ni-u	4.74 $\pm$ 0.07	15.80 $\pm$ 0.43	0.82 $\pm$ 0.03	1.764
9.3Ni-s	4.95 $\pm$ 0.06	16.58 $\pm$ 0.36	0.84 $\pm$ 0.02	1.764
0M-n	5.09 $\pm$ 0.04	16.97 $\pm$ 0.08	0.80 $\pm$ 0.03	1.764
0M-u	5.32 $\pm$ 0.01	17.22 $\pm$ 0.19	0.82 $\pm$ 0.02	1.764
0M-s	5.22 $\pm$ 0.03	17.56 $\pm$ 0.18	0.80 $\pm$ 0.01	1.764
5N-Cr	5.72 $\pm$ 0.06	19.08 $\pm$ 0.32	0.81 $\pm$ 0.03	1.764
5M-s	6.04 $\pm$ 0.02	20.12 $\pm$ 0.22	0.77 $\pm$ 0.02	1.764
5M-7Ni-n	6.81 $\pm$ 0.09	22.70 $\pm$ 0.09	0.75 $\pm$ 0.03	1.765
5M-7Ni-u	7.03 $\pm$ 0.07	23.44 $\pm$ 0.27	0.76 $\pm$ 0.02	1.764
PCD	75.42 $\pm$ 0.21	251.41 $\pm$ 0.69	0.73 $\pm$ 0.02	1.894

The coefficient of friction (μ) graphs (Figure 6.11) had similar profiles for approximately the first 10 m (first stage), showing rapid increases in μ . In second stage, the 10Co (1430) sample had a steeper increase than the other samples. This was followed by a plateau stage (steady-state) for the all samples, apart from 5N-Cr which had a slight increase before the steady-state. Instabilities were observed during the steady state stage, particularly for the 10Co (1430) and 5M-7Ni-u samples.

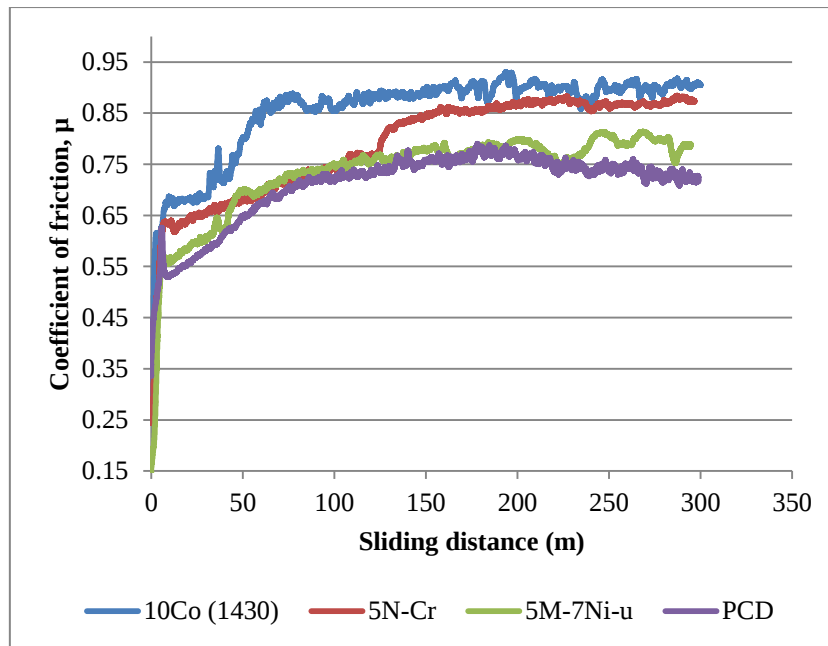


Figure 6.11. Coefficient of friction curves for the 10Co (1430), 5N-Cr, 5M-7Ni-u and PCD samples.

6.1.2 Sliding wear from silicon nitride (Si_3N_4) balls

6.1.2.1 Optical images of wear tracks

The wear tracks for the 10Co (1430), 5N-Cr and 5M-7Ni-u samples from the Si_3N_4 balls are shown in Figure 6.12. The 10Co (1430) sample had a slightly wider track than both SPS samples. Some regions on the wear track of the 5M-7Ni-u sample were thinner than the wear track for the 5N-Cr sample, but generally the difference in width between the two samples' wear tracks was not discernable from the optical images.

6.1.2.2 Laser confocal analysis

The 3D topographic maps and wear track profiles of the wear tracks for 10Co (1430) and 9.3Ni (1430) samples are shown in Figure 6.13. The 10Co (1430) sample had a wider wear track and greater volume loss than 9.3Ni (1430) (Table 6.3). The wear for the 10Co (1430) samples was both within and on the edges of the wear track, while most of wear for the 9.3Ni (1430) sample was at the inner edge of the track. Spark plasma sintering of the WC-9.3Ni (wt%) compositions slightly improved the resistance to wear volume loss (Table 6.3). The 5N-Cr sample had lower volume loss and wear rate than 10Co (1430) sample (Figure 6.14 and Table 6.3). The wear loss for the 5N-Cr sample was mainly on the edges of the wear track (Figure 6.14 (b)). Additions of up to 5wt% Mo_2C and reduced Ni binder from 9.3 wt%

to 7 wt%, reduced the wear volume loss, resulting in the 5M-s, 5M-7Ni-u and 5M-7Ni-n samples having the lowest wear rates (Figure 6.14 and Table 6.3).

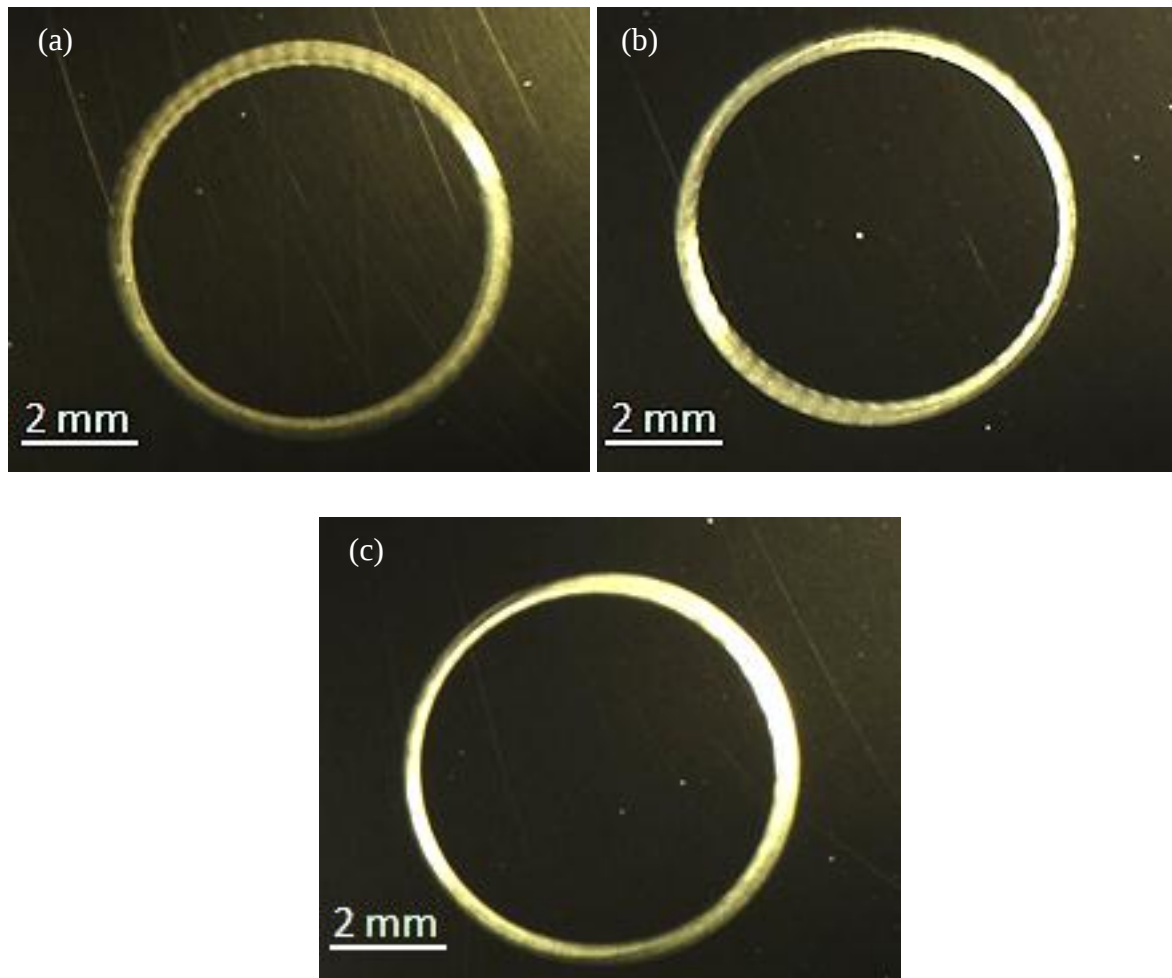


Figure 6.12. Optical images of wear tracks of: (a) 10Co (1430), (b) 5N-Cr, and (c) 5M-7Ni-u from the Si_3N_4 ball.

Table 6.3. Sample sliding wear properties from the of Si_3N_4 ball.

Sample abbreviation	Sample Worn volume ($\times 10^{-1} \text{ mm}^3$)	Sample wear rate ($\times 10^{-5} \text{ mm}^3/\text{N.m}$)
10Co (1430)	10.14 ± 0.05	33.812 ± 0.011
9.3Ni (1430)	9.13 ± 0.01	30.417 ± 0.010
9.3Ni-n	7.45 ± 0.02	25.165 ± 0.008
5N-Cr	5.21 ± 0.03	17.332 ± 0.006
5M-7Ni-n	1.69 ± 0.02	5.441 ± 0.005
5M-7Ni-u	1.59 ± 0.03	5.314 ± 0.003

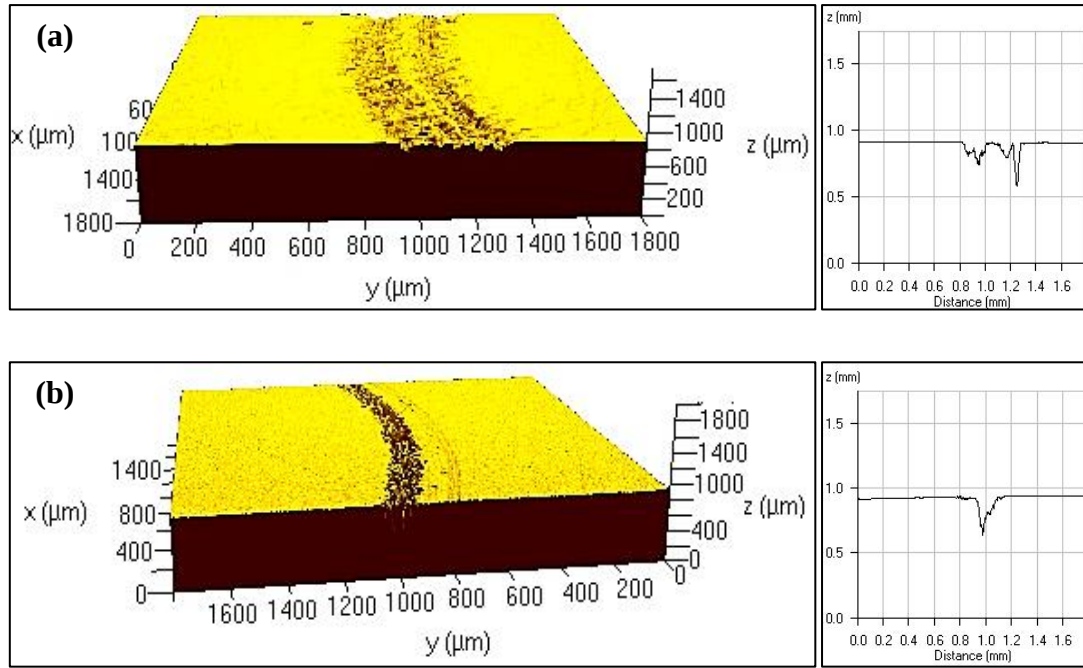


Figure 6.13. Laser confocal 3D maps and wear track profiles of wear tracks for: (a) 10Co (1430), and (b) 9.3Ni (1430).

6.1.2.3 Optical images of the Si_3N_4 ball wear scars

The optical images of the wear scars on the Si_3N_4 balls from the 10Co (1430), 5N-Cr and 5M-7Ni-u samples are shown in Figure 6.15. The 5N-Cr and 5M-7Ni-u samples had larger wear scars than 10Co (1430), with the 5M-7Ni-u sample having the largest diameter (Figure 6.15), giving the highest ball worn volume (Table 6.4).

6.1.2.4 Microstructure of wear tracks due to the Si_3N_4 ball

The SEM micrographs of the wear tracks for the 10Co (1430) sample in BSE and SE modes (Figure 6.16), show depressions and fragmentation WC grains. The wear track for the 5N-Cr sample had mainly scratches (Figure 6.17) and some fragmentation of WC grains around large (Co) binder pools and between the WC continuous skeleton (Figures 6.17 (b) and (d) shown by arrows). The wear track for the 5M-7Ni-u sample had fewer scratches that were wider than those in the 5N-Cr sample. There was no pull-out of WC and TiC grains (Figure 6.18), and transgranular crack propagation between WC grains was observed (Figure 6.18 (b), between the arrows).

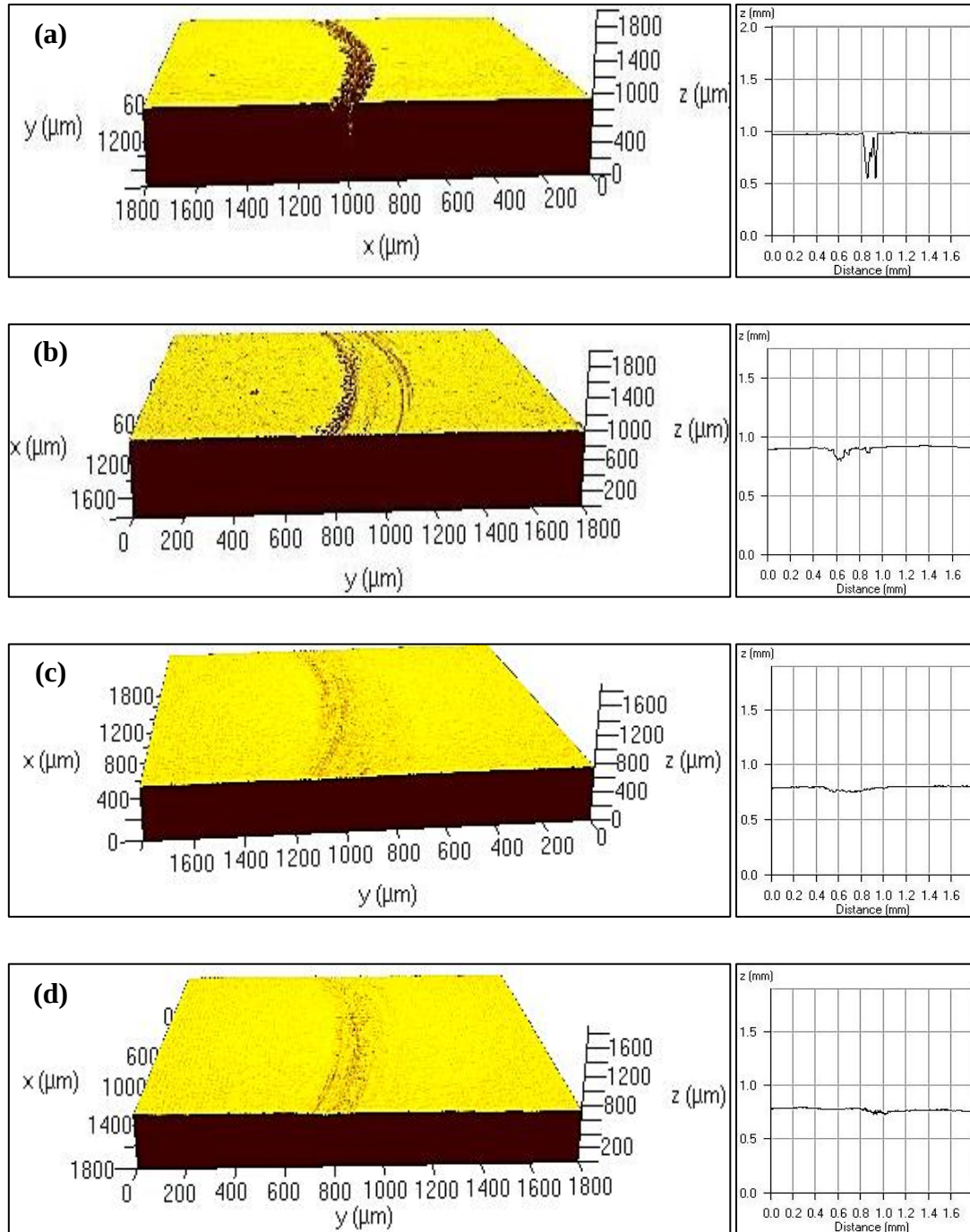


Figure 6.14. Laser confocal 3D maps and wear track profiles of wear tracks for: (a) 9.3Ni-n, (b) 5N-Cr, (c) 5M-7Ni-n, and (d) 5M-7Ni-u samples.

6.1.2.5 Si_3N_4 ball wear

The 9.3Ni (1430) sample had a slightly higher ball wear rate than the 10Co (1430) sample. The 10Co (1430) and 9.3Ni (1430) samples had the lowest ball worn volumes compared to all spark plasma sintered samples (Table 6.4), although the difference in ball wear rate of the

9.3Ni-n and the 9.3Ni (1430) samples was much smaller than the differences in the 100 Cr6 steel ball test.

Table 6.4. Silicon nitride ball sliding wear results.

Sample abbreviation	Ball worn volume ($\times 10^{-3} \text{ mm}^3$)	Ball wear rate ($\times 10^{-7} \text{ mm}^3/\text{N.m}$)	Av. coefficient of friction, μ ($\times 10^{-1}$)	Hertzian pressure (GPa)
10Co (1430)	2.01 ± 0.01	7.00 ± 0.12	0.62 ± 0.02	2.17
9.3Ni (1430)	2.46 ± 0.05	8.21 ± 0.31	0.63 ± 0.01	2.17
9.3Ni-n	3.53 ± 0.03	11.75 ± 0.21	0.66 ± 0.03	2.17
5N-Cr	3.77 ± 0.01	12.56 ± 0.11	0.66 ± 0.01	2.17
5M-7Ni-n	3.92 ± 0.04	13.08 ± 0.22	0.69 ± 0.02	2.17
5M-7Ni-u	4.09 ± 0.03	13.63 ± 0.34	0.71 ± 0.01	2.17

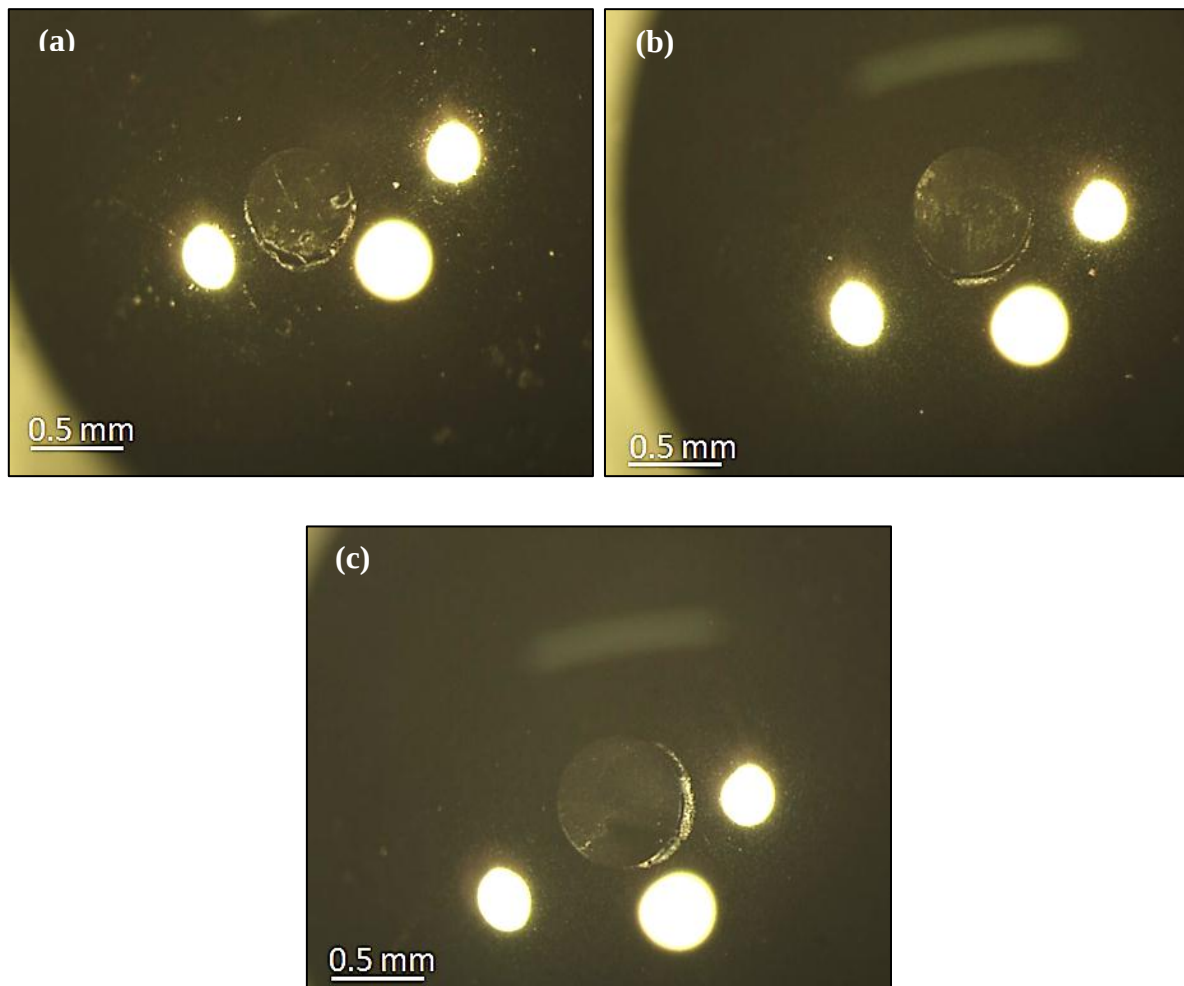


Figure 6.15. Optical images of the Si₃N₄ ball wear scars from: (a) 10Co (1430), (b) 5N-Cr, and (c) 5M-7Ni-u samples.

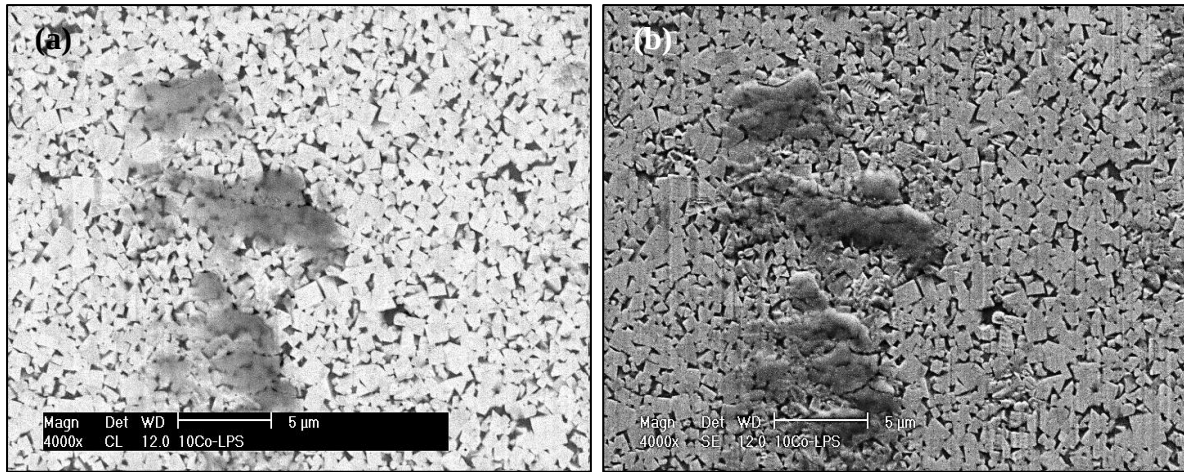


Figure 6.16. SEM images of 10Co-(1430) of the wear track in (a) BSE mode, and (b) SE mode, showing depressions and fragmentation of WC grains: WC (light), and Co (dark).

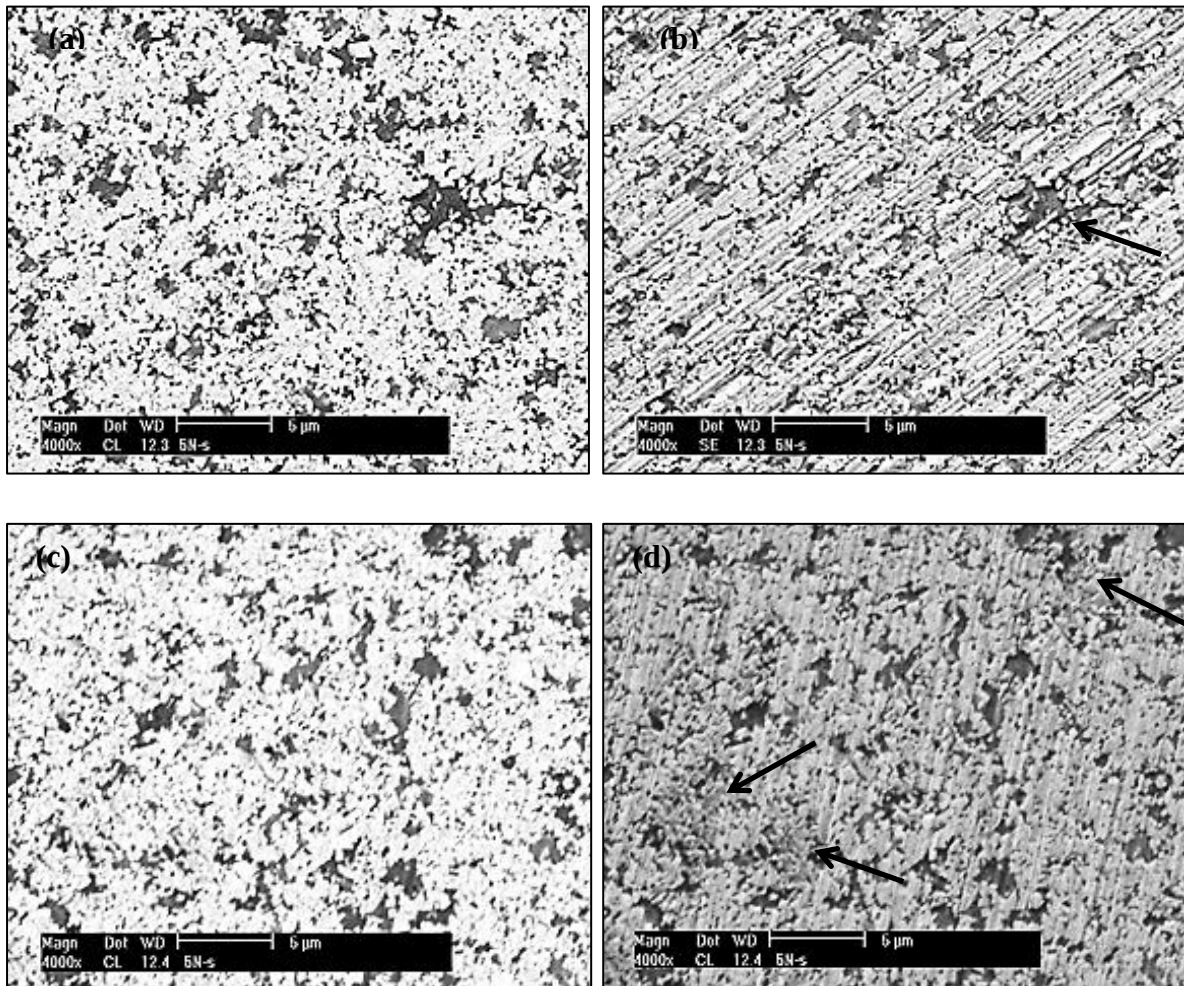


Figure 6.17. SEM images of 5N-Cr of the wear track in BSE ((a) and (c)) mode and SE ((b) and (d)), showing scratches and fragmentation of WC grains (arrows): WC (light), NbC (medium) and Co (dark).

The 5N-Cr sample had a higher ball wear rate than 10Co (1430) and additions of 6.25wt% TiC and 5 wt% Mo₂C to WC-7Ni (wt%) increased the ball wear rate (Table 6.4). The 10Co (1430) and 9.3Ni (1430) samples had lower coefficients of friction (μ) than all the spark plasma sintered samples (Table 6.4). The 5M-7Ni-u and 5M-7Ni-n had the highest μ , followed by the 5N-Cr sample (Table 6.4 and Figure 6.19).

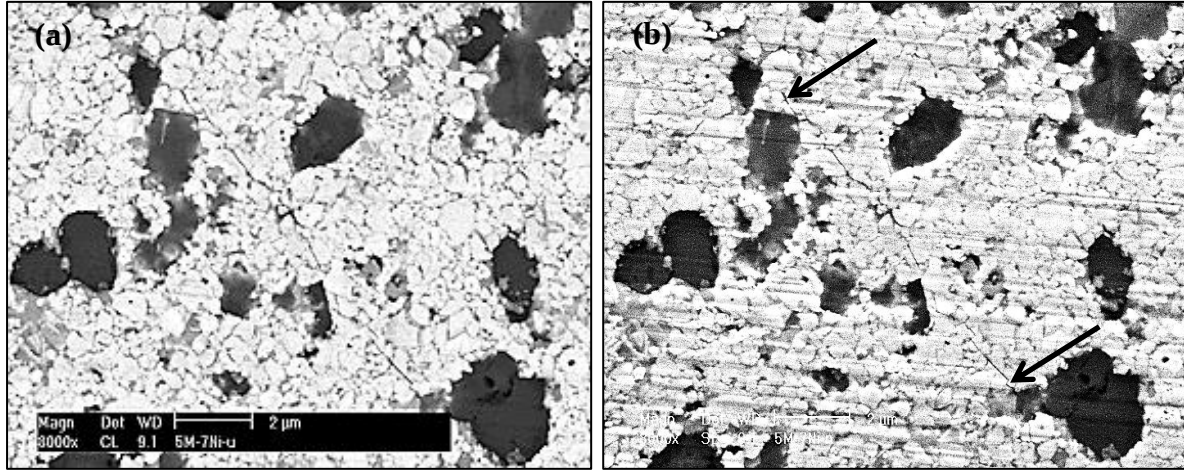


Figure 6.18. SEM images of 5M-7Ni-u of the wear track in BSE ((a) and (c)) and SE ((b) and (d)) modes, showing scratches and transgranular crack propagation (arrows): WC (light), Ni (medium) and TiC (dark).

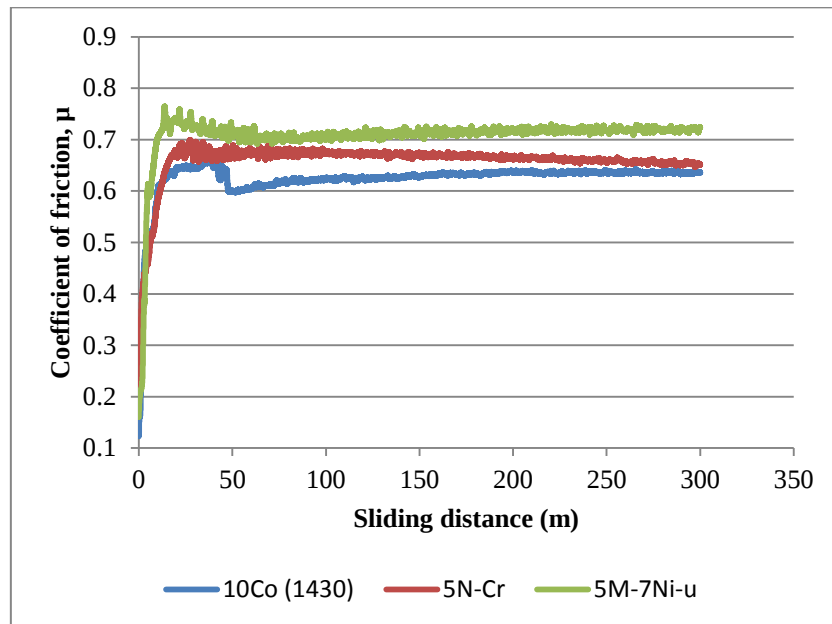


Figure 6.19. Coefficient of friction curves for 10Co (1430), 5N-Cr and 5M-7Ni-u samples.

The coefficient of friction graphs for the 10Co (1430), 5N-Cr and 5M-7Ni-u samples had similar profiles, rapid increase in μ for approximately the first 10 m to 15 m, followed by a slight drop and then a plateau stage (Figure 6.19).

6.2 Thermal shock and impact resistance

6.2.1 Optical images of insert cutting edges

Optical images of the 10Co (1430) and 5N-Cr insert cutting edges after milling at a cutting speed (v_c) of 40 m/minute and 1mm depth of cut (a_p) had negligible flank wear (VB), but the 5M-7Ni-u insert had a VB of 287.7 μm (Figure 6.20). Increased v_c to 60 m/minute, while maintaining the same a_p , increased the VB in all three inserts, and the 10Co (1430) insert had the lowest VB of 66.2 μm , while the 5M-7Ni-u insert had the highest of 314.9 μm (Figure 6.21). The same trend was observed when both the v_c was increased to 75 m/minute, and the a_p to 2 mm (Figure 6.22). The 5M-7Ni-u insert's cutting edge was completely damaged (catastrophic failure), giving in the highest VB of 707.5 μm (Figure 6.22) and the 9.3Ni (1430) insert had a slightly lower VB than the 10Co (1430) insert (Figure 6.23).

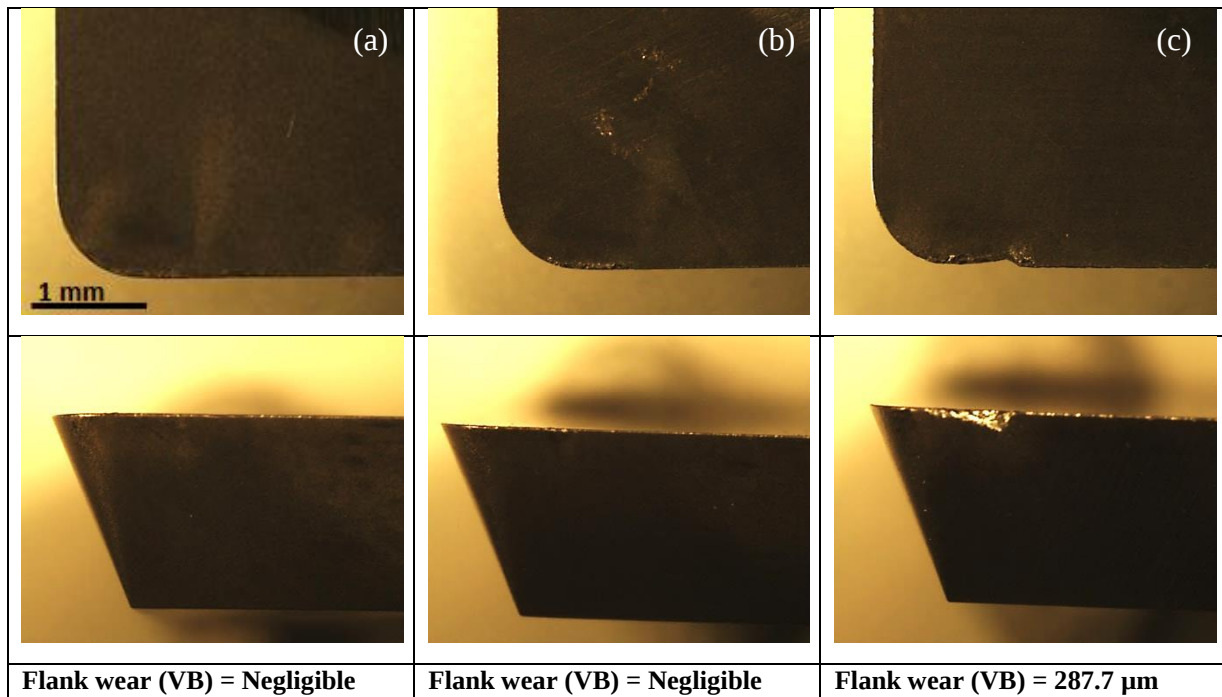


Figure 6.20. Flank wear on: (a) 10Co (1430), (b) 5N-Cr, and (c) 5M-7Ni-u cutting tool inserts after a 40 m/minute v_c and 1 mm a_p .

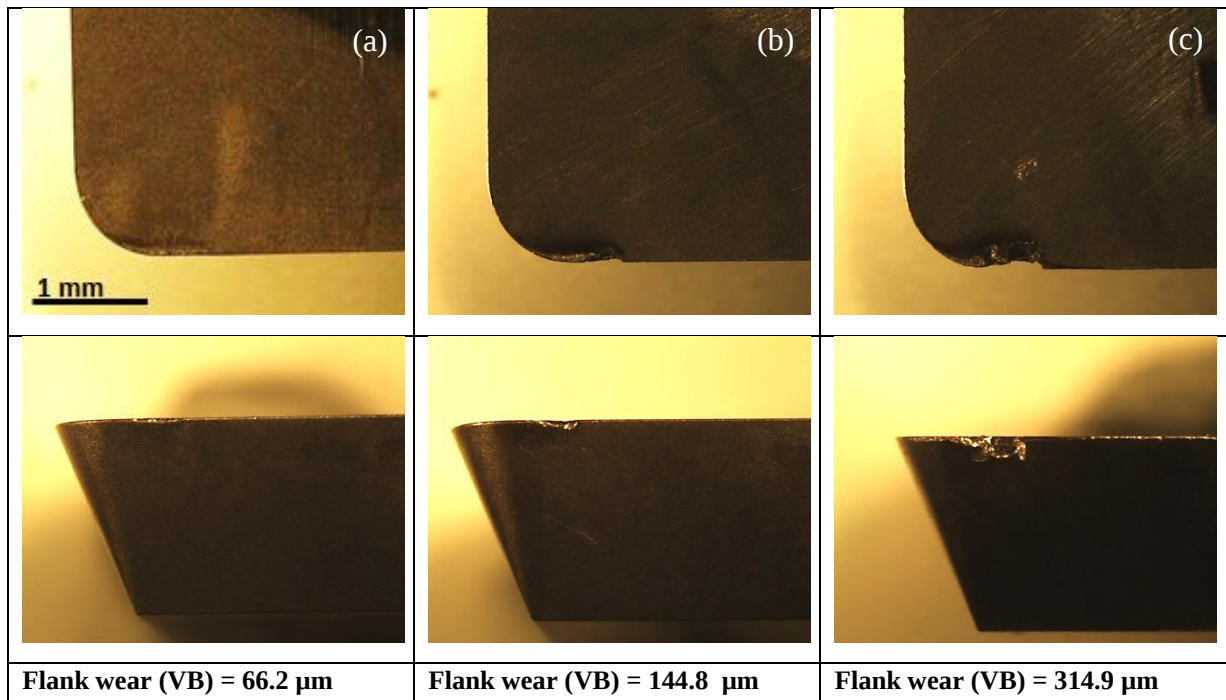


Figure 6.21. Flank wear on: (a) 10Co (1430), (b) 5N-Cr, and (c) 5M-7Ni-u cutting tool insets after a 60 m/minute v_c and 1 mm a_p .

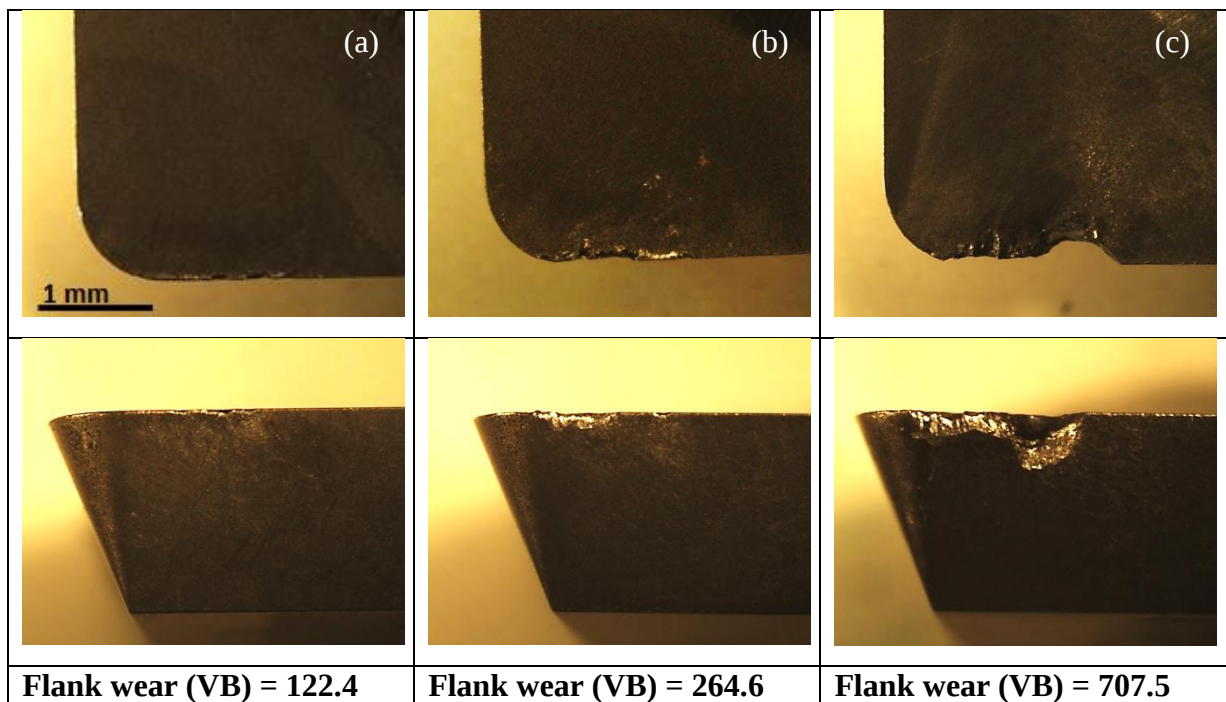


Figure 6.22. Flank wear on: (a) 10Co (1430), (b) 5N-Cr, and (c) 5M-7Ni-u cutting tool insets after a 75 m/minute v_c and 2 mm a_p .

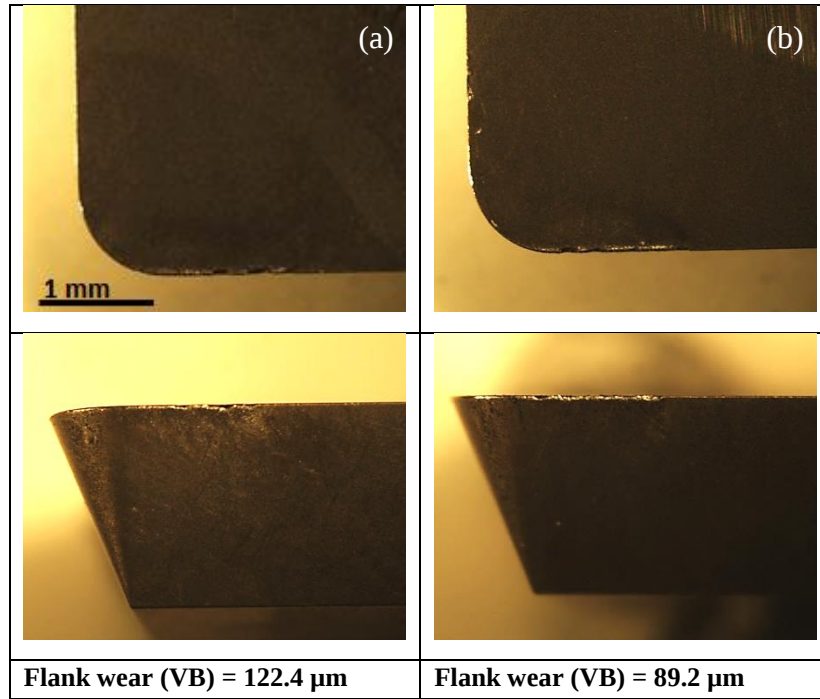


Figure 6.23. Flank wear on: (a) 10Co (1430), (b) 9.3Ni (1430) cutting tool inserts after a 75 m/minute v_c and 2 mm a_p .

The shape and thickness of the cutting edge of the untested PCD insert, as well as the tested PCD inserts tested at a v_c of 60 and 150 m/minute using a a_p 0.5 mm are shown in Figure 6.24. The VB increased with increased v_c .

6.2.2 Microstructure of fractured cutting edges

The SEM BSE and SE images in Figure 6.25 showed that the 5M-7Ni-u insert fractured at the cutting edge with a v_c of 40 m/minute and a_p of 1 mm. The presence of Ti-6Al-4V (dark grey contrast in Figure 6.25 (a) and (b)) and carbon debris (dark phase in Figure 6.25 (c) and (d)) were observed on the surface on the cutting edge. The highest amount of fracture was occurred at the furthest point from the curved end of the cutting edge (nose) (shown by arrow on Figure 6.25 (b)). There were no cracks parallel to the fractured edge (Figures 6.25 (c) and (d)). Higher magnification of the fractured surface showed fragmentation and pull-out of WC grains with interconnected microvoids ($\sim 1\mu\text{m}$ diameter) between them (indicated by arrows in Figure 6.25 (f)). The BSE and SE images of the 5N-Cr fractured surface due to a v_c of 60 m/minute and a a_p of 1 mm are shown in Figure 6.26.

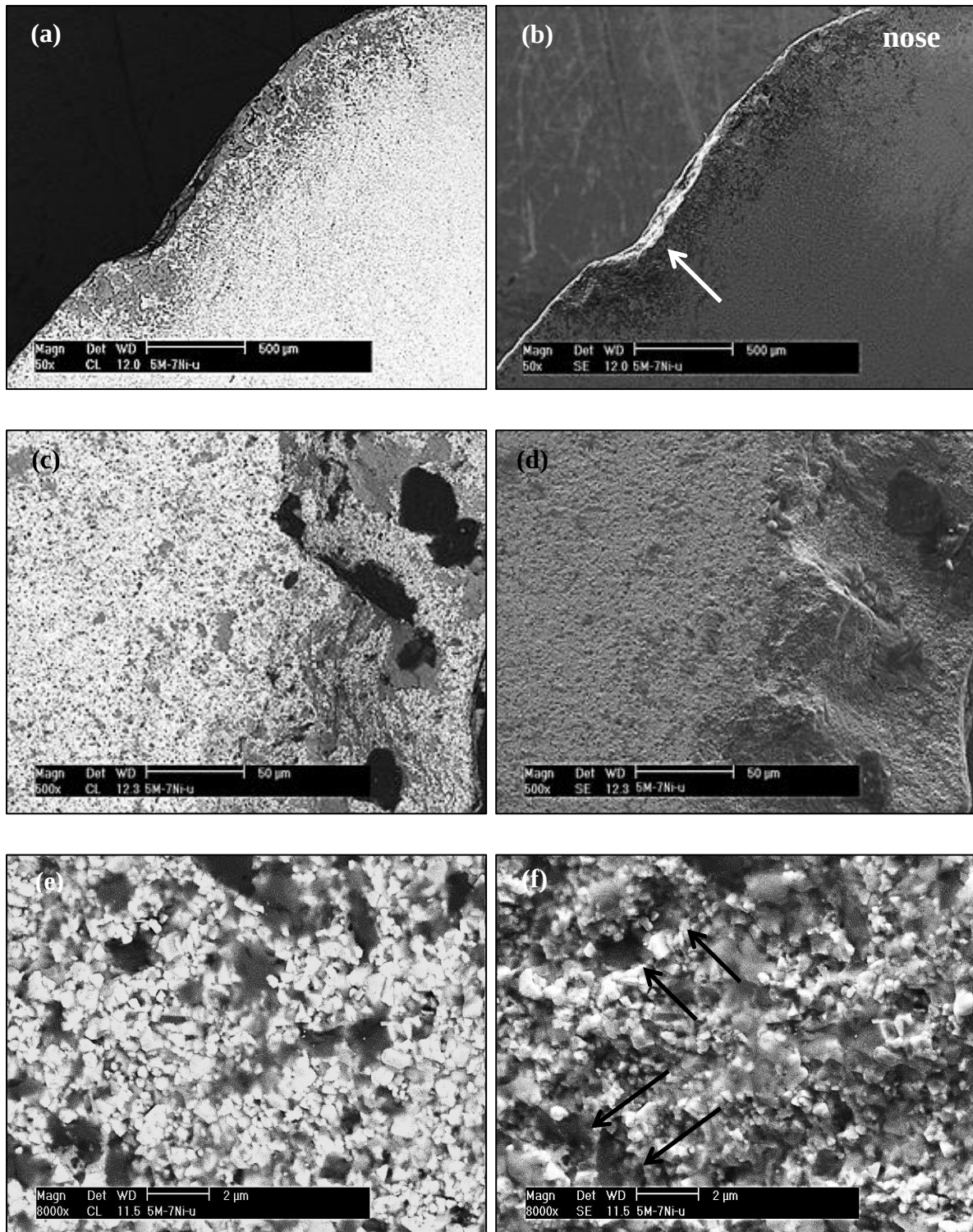


Figure 6.25. SEM BSE and SE images of the fractured cutting edge of the 5M-7Ni-u cutting tool insert after 40 m/minute v_c and 1 mm a_p , showing: (a) and (b) Ti-6Al-4V debris (dark grey), (c) and (d) Ti-6Al-4V debris (medium) and carbon debris (dark), and (f) interconnected microvoids (arrows): WC (light), Ni (medium), TiC (dark).

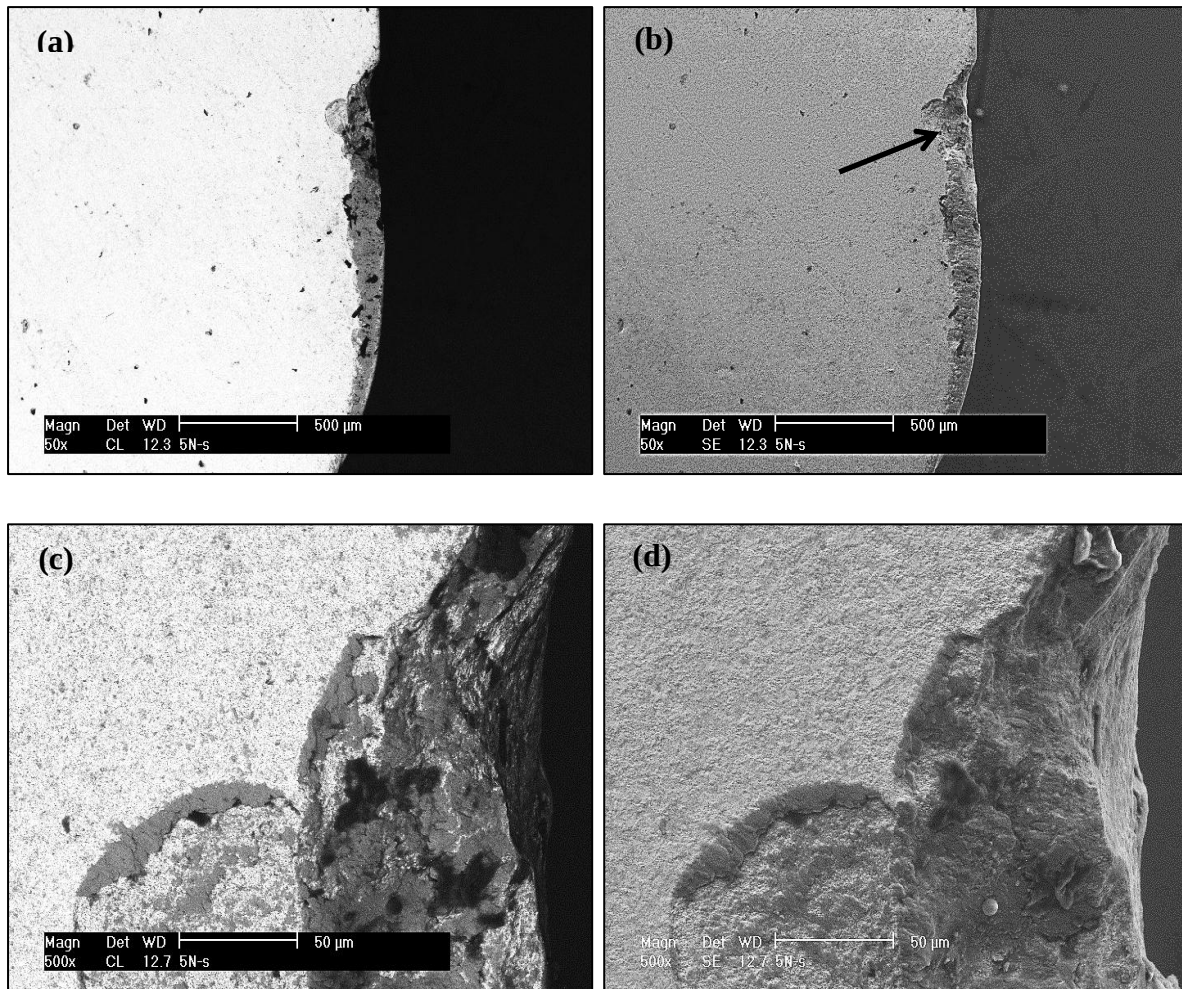


Figure 6.26. SEM images of the fractured cutting edge of the 5N-Cr cutting tool insert after a 60 m/minute v_c and 1 mm a_p .

6.2.3 Flank wear rate, thermal shock and impact force measurements

Plots of change in resultant force with time after a 40 m/minute v_c and 1mm a_p on the 10Co (1430), 5N-Cr and 5M-7Ni-u inserts are shown in Figures 6.28-6.31. After ~100 seconds, significant increase in resultant force rapidly occurred (inflection) in the 5M-7Ni-u insert (Figure 6.32), which was not observed in the other two inserts (Figures 6.28 and 6.31). The 10Co (1430) insert experienced higher resultant cutting forces than the 5N-Cr and 5M-7Ni-u (before the inflection point) (Table 6.5 and Figure 6.31). The graphs for the 5M-7Ni-u (Figure 6.28) and 5N-Cr (Figure 6.29) inserts had points of rapid increase and decrease of resultant force (spikes) every ~30 seconds, but the graph for the 10Co (1430) insert did not have these spikes (Figures 6.30 and 6.31). The 5M-7Ni-u insert experienced the highest thermal variation per second, and the 5N-Cr insert had the lowest (Table 6.5). Both the 10Co

(1430) and 5N-Cr inserts had negligible flank wear rates, but the 5M-7Ni-u insert had a flank wear rate (FWR) of 143.6 $\mu\text{m}/\text{minute}$.

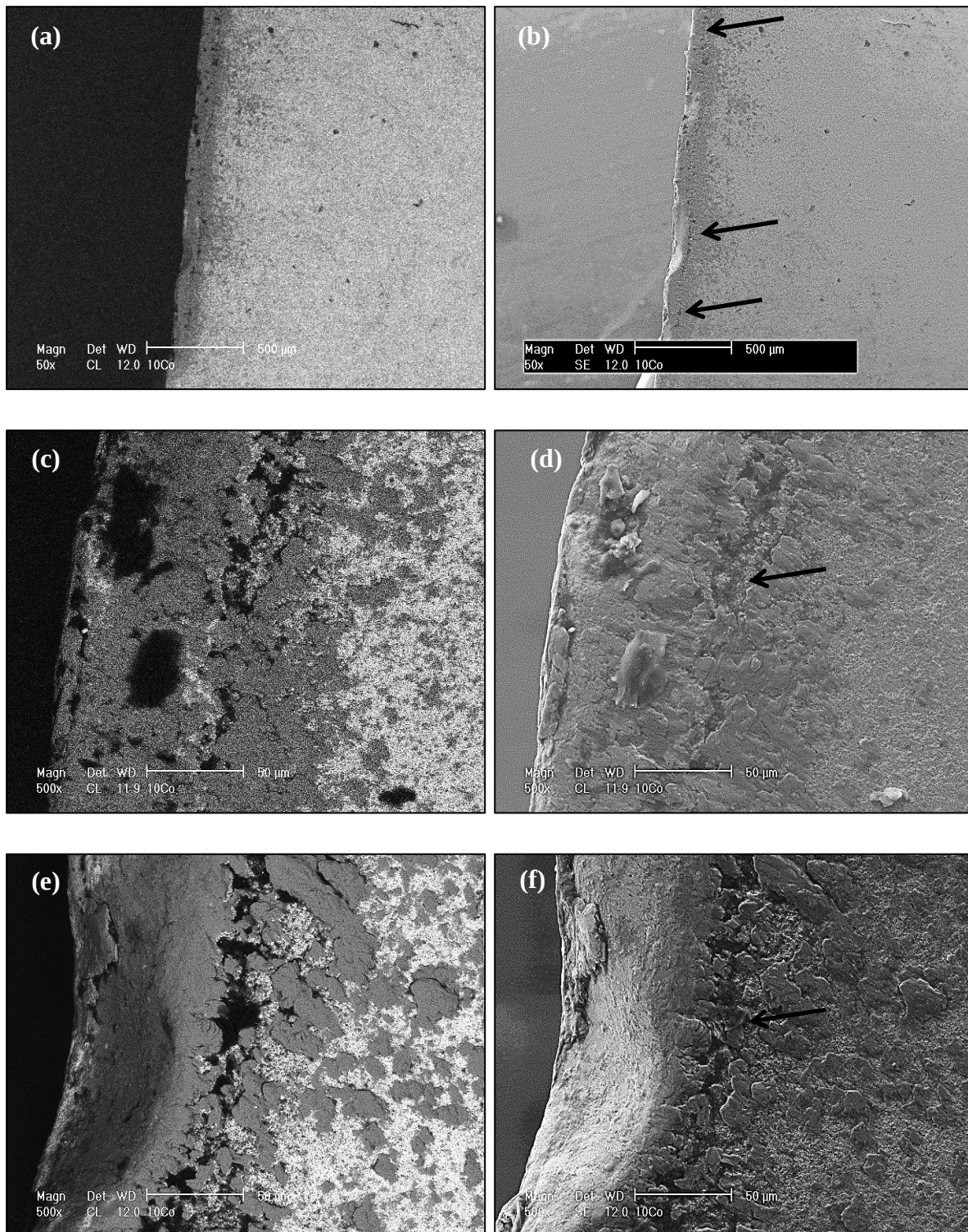


Figure 6.27. SEM images of the fractured cutting edge of the 10Co (1430) cutting tool insert after a 75 m/minute v_c and 1 mm a_p , showing cracks parallel to the cutting edge (arrows).

Increased cutting speed from 40 to 60 m/minute led to higher resultant forces, thermal variations per second and FWR in all inserts (Table 6.5 and Figure 6.32). The 5M-7Ni-u experienced the highest resultant force, even before the inflection point on the graph (Figure 6.33 and Table 6.5), as well as slightly higher thermal variation per second and had a significantly higher FWR than all the other inserts. Spikes were observed after every ~25 seconds in the graphs for all inserts (Figures 6.33-6.35). Although the 5N-Cr insert experienced similar resultant force and thermal variations per second to 10Co (1430) and 9.3Ni (1430) inserts (Figure 6.32), it had a higher FWR. Both the 10Co (1430) and 9.3Ni (1430) inserts had the lowest FWR. Applying 75 m/minute v_c and 2 mm a_p gave the highest resultant forces, thermal variations per second and flank wear rates (Table 6.5 and Figure 6.32). Although all the inserts experienced similar thermal variations per second, the 5M-7Ni-u insert had the highest average resultant force and FWR, followed by the 5N-Cr insert (Table 6.5). The 10Co (1430) insert experienced slightly higher resultant forces and had a slightly higher FWR than the 9.3Ni (1430) insert (Table 6.5, Figures 6.36 and 6.37).

Table 6.5. Comparison of insert properties due to variation of milling conditions.

Milling conditions	Properties*	Cutting tool inserts			
		10Co (1430)	9.3Ni (1430)	5N-Cr	5M-7Ni-u
$v_c = 40$ m/minute, $a_p = 1$ mm	Av. F_R (N)	354.4 ± 27.7	-	279.6 ± 13.1	301.2 ± 19.1
	$\Delta T/s$ ($^{\circ}C/sec$)	396.2 ± 46.4	-	358.1 ± 26.0	411.4 ± 24.2
	FWR ($\mu m/min$)	Negligible	-	Negligible	143.6
$v_c = 60$ m/minute, $a_p = 1$ mm	Av. F_R (N)	341.4 ± 20.8	363.9 ± 24.3	358.1 ± 32.5	435.2 ± 30.4
	$\Delta T/s$ ($^{\circ}C/sec$)	489.2 ± 34.4	504.6 ± 37.2	494.3 ± 29.9	518.5 ± 18.7
	FWR ($\mu m/min$)	58.4	54.9	126.7	277.7
$v_c = 75$ m/minute, $a_p = 2$ mm	Av. F_R (N)	752.1 ± 44.2	720.3 ± 18.2	749.6 ± 24.7	776.8 ± 21.3
	$\Delta T/s$ ($^{\circ}C/sec$)	603.4 ± 26.8	596.5 ± 31.7	610.0 ± 19.2	617.6 ± 22.5
	FWR ($\mu m/min$)	147.3	119.8	293.5	849.4

*Av. FR is the average resultant force, $\Delta T/s$ is the average thermal variation per second and FWR is the flank wear rate.

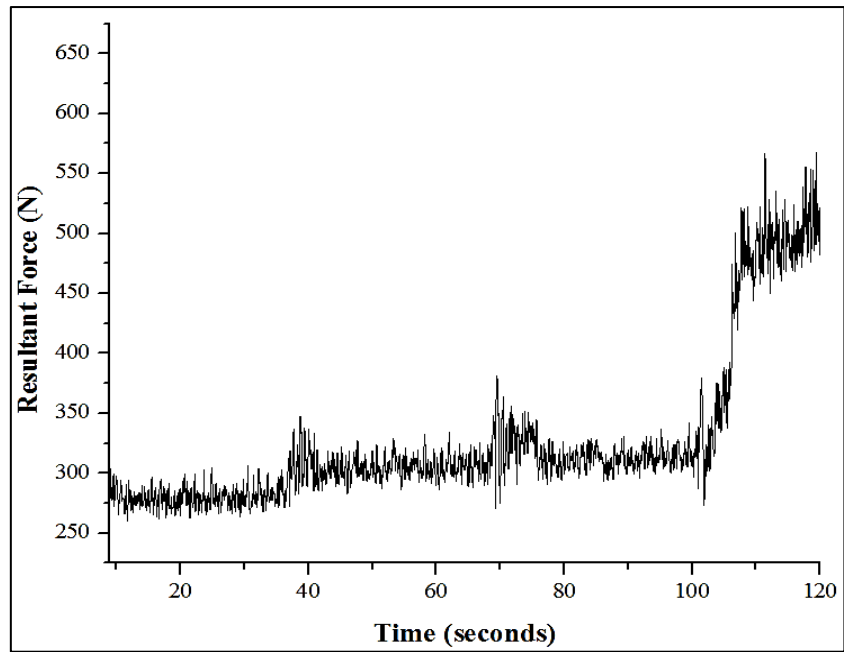


Figure 6.28. Variation of resultant force with time of the 5M-7Ni-u insert with a 40 m/minute v_c and 1 mm a_p .

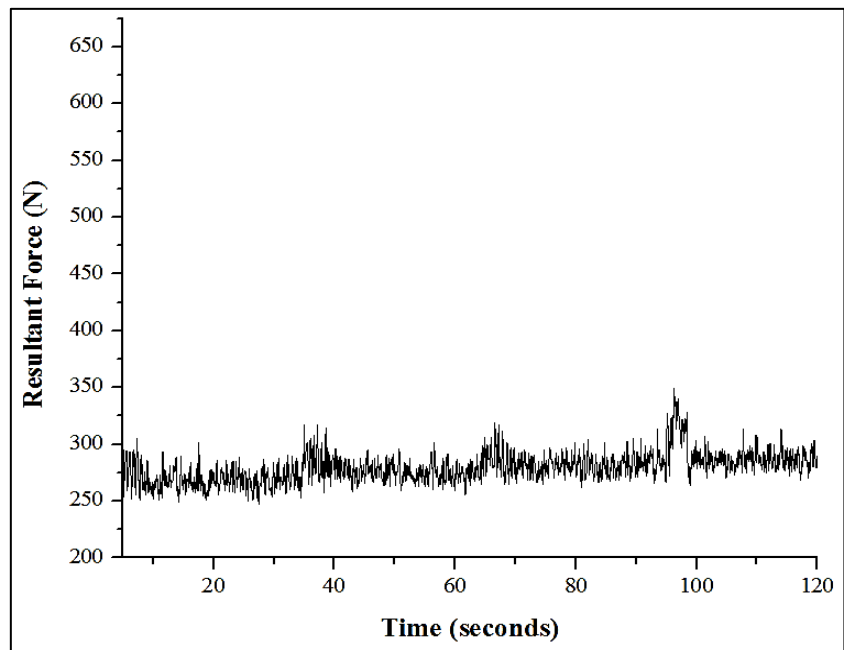


Figure 6.29. Variation of resultant force with time of the 5N-Cr insert with a 40 m/minute v_c and 1 mm a_p .

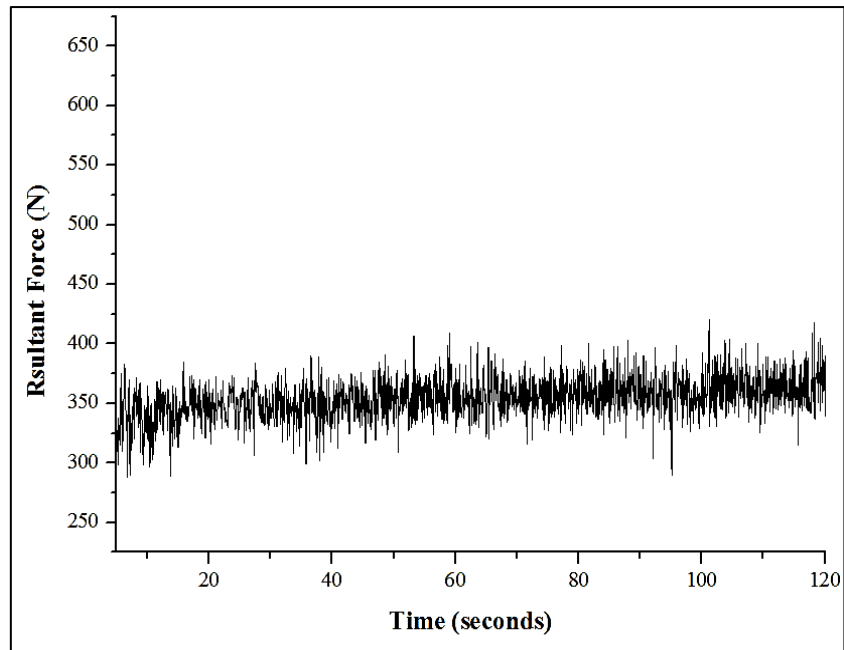


Figure 6.30. Variation of resultant force with time of the 10Co (1430) insert with a 40 m/minute v_c and 1 mm a_p .

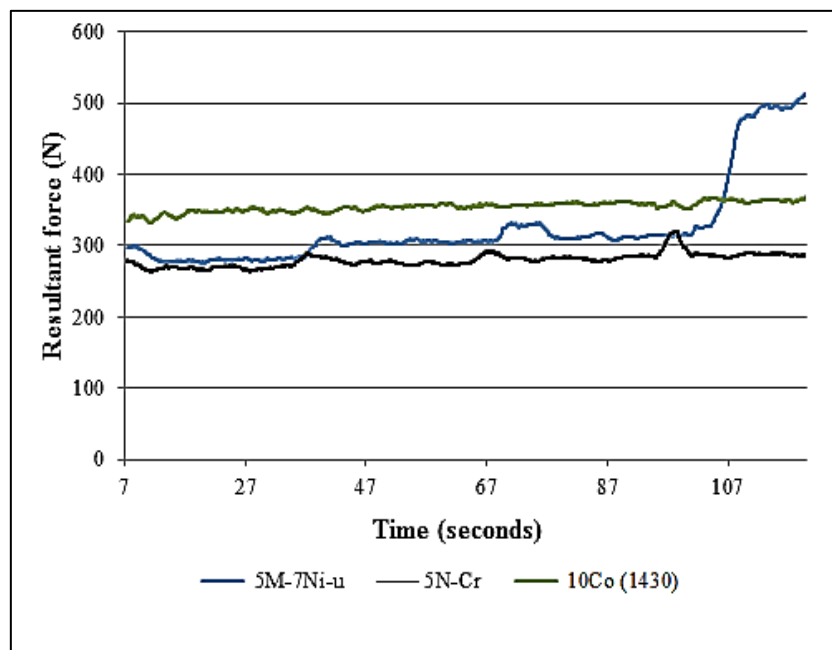


Figure 6.31. Comparison of the variation resultant force with time for the 10 Co (1430), 5N-Cr and 5M-7Ni-u cutting tool inserts with a 40 m/minute v_c and 1 mm a_p .

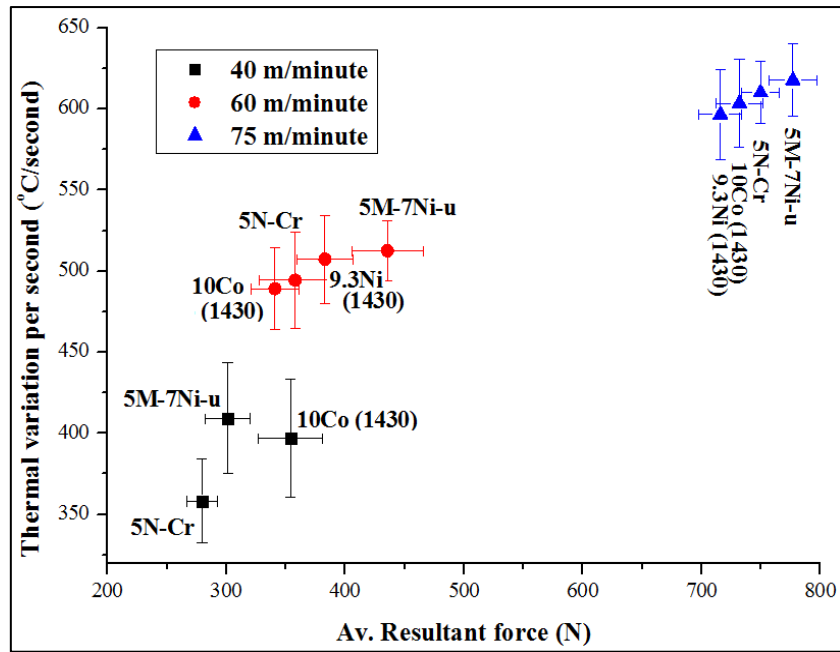


Figure 6.32. Comparison between sample thermal variations per second and average resultant cutting forces.

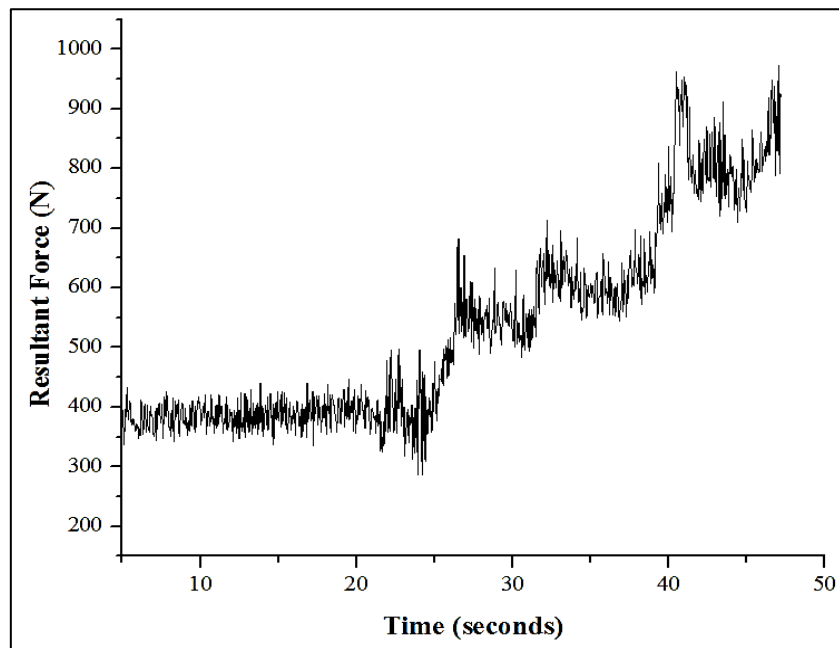


Figure 6.33. Variation of resultant force with time of the 5M-7Ni-u insert with a 60 m/minute v_c and 1 mm a_p .

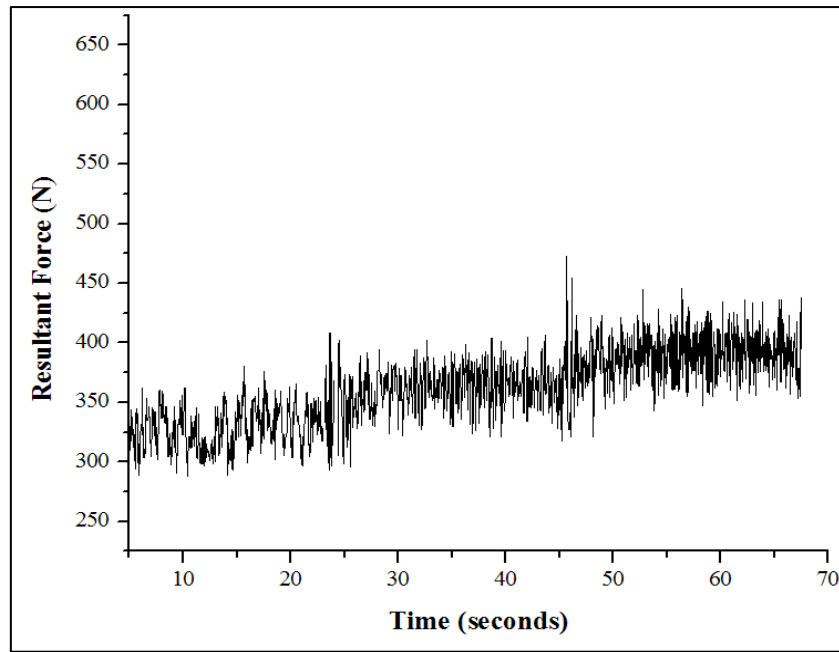


Figure 6.34. Variation of resultant force with time of the 5N-Cr insert with a 60 m/minute v_c and 1 mm a_p .

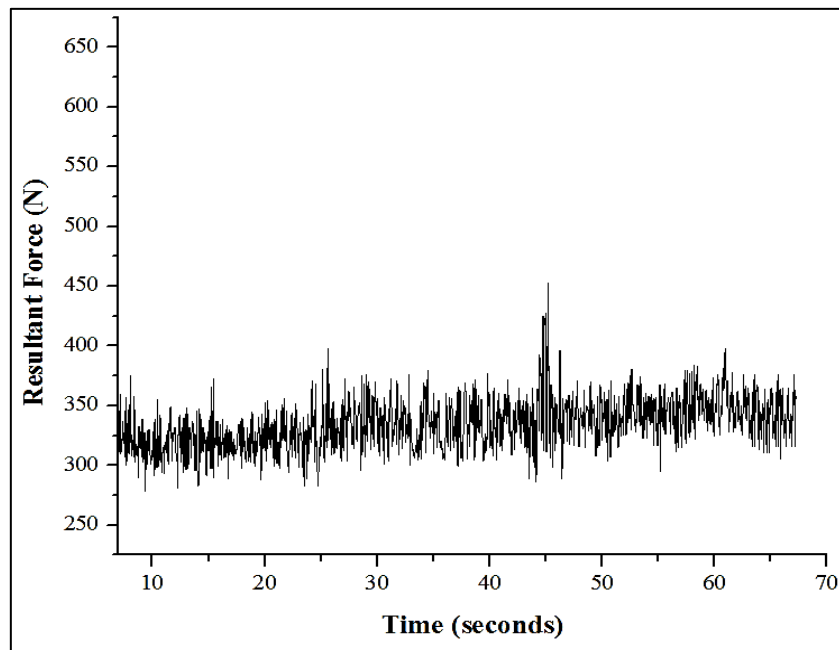


Figure 6.35. Variation of resultant force with time of the 10Co (1430) insert with a 60 m/minute v_c and 1 mm a_p .

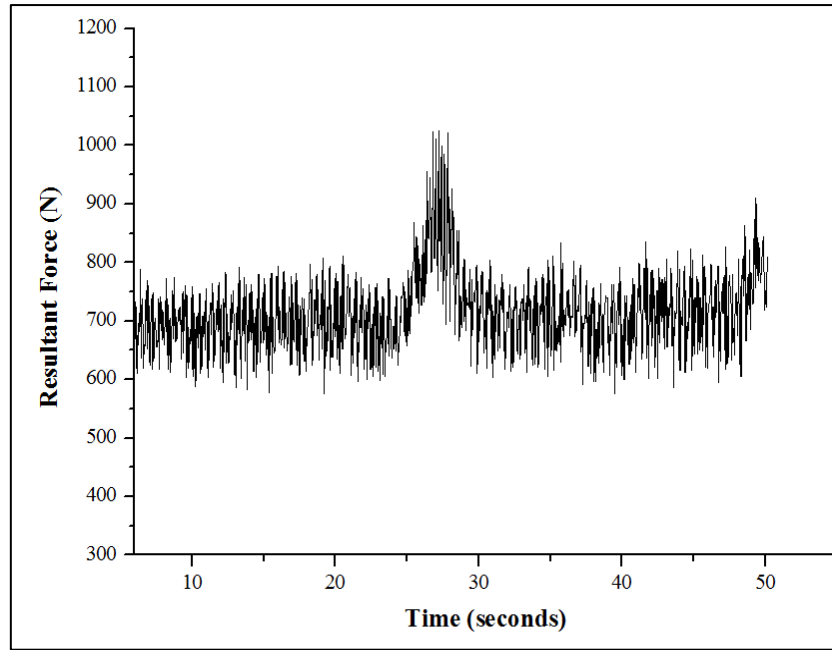


Figure 6.36. Variation of resultant force with time of the 10Co (1430) insert with a 75 m/minute v_c and 2 mm a_p .

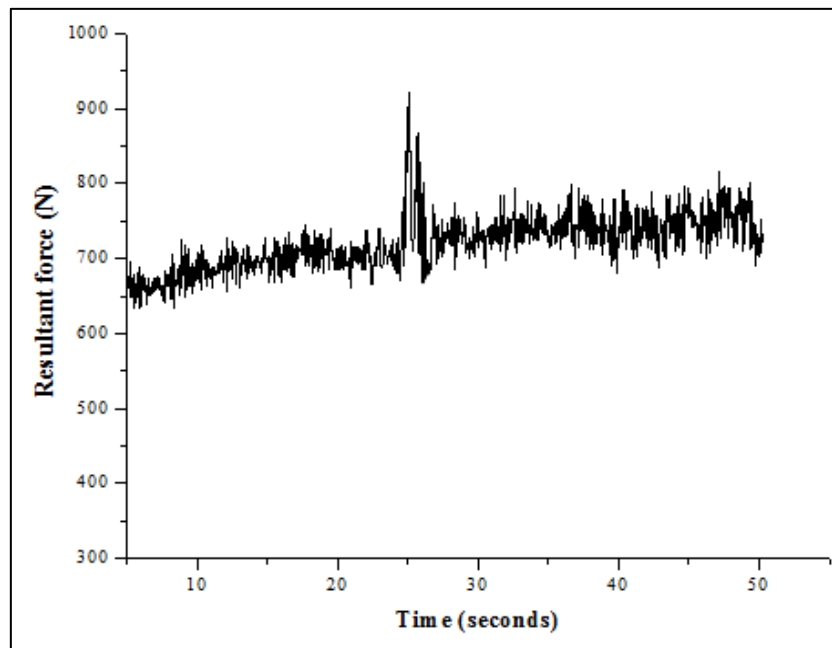


Figure 6.37. Variation of resultant force with time of the 9.3Ni (1430) insert with a 75 m/minute v_c and 2 mm a_p .

The PCD insert used at a 60 m/minute v_c had a higher FWR than the 10Co (1430) and 9.3Ni (1430) inserts, even though a shorter a_p of 0.5 mm was used (Table 6.6). Increased v_c from 60 to 150 m/minute, resulted in higher resultant forces (Figures 6.38 and 6.39), thermal variations per second and FWR (Table 6.6).

Table 6.6. Comparison of PCD insert properties due to variation of milling conditions.

Milling conditions	Properties *	PCD insert
$v_c = 60$ m/minute, $a_p = 0.5$ mm	Av. F_R (N)	170.1 ± 16.1
	$\Delta T/s$ ($^{\circ}C/sec$)	357.6 ± 36.2
	FWR ($\mu m/min$)	107.2
$v_c = 150$ m/minute, $a_p = 0.5$ mm	Av. F_R (N)	252.7 ± 56.3
	$\Delta T/s$ ($^{\circ}C/sec$)	486.9 ± 54.5
	FWR ($\mu m/min$)	473.7

* Av. F_R is the average resultant force, $\Delta T/s$ is the average thermal variation per second and FWR is the flank wear rate.

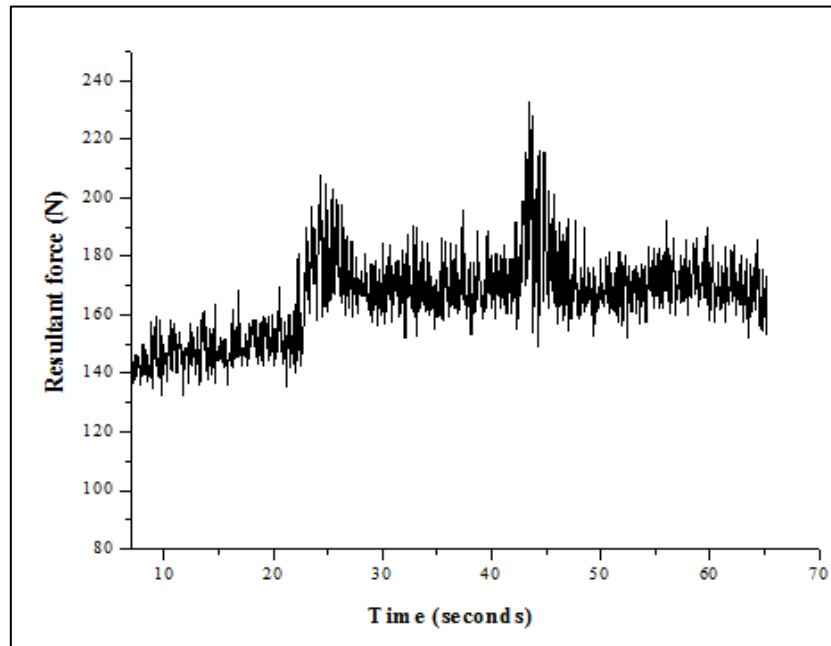


Figure 6.38. Variation of resultant force with time of the PCD insert with a 60 m/minute v_c and 0.5 mm a_p .

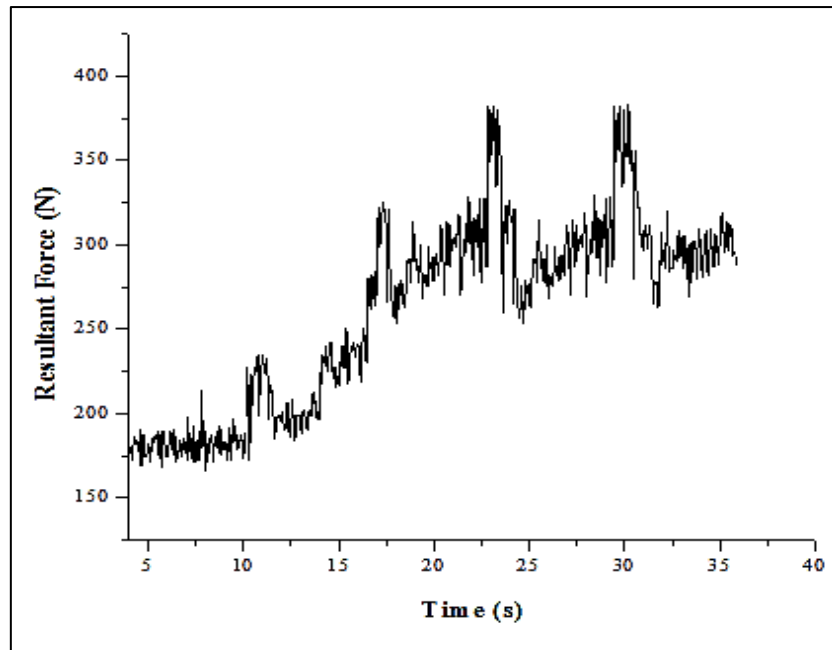


Figure 6.39. Variation of resultant force with time of the PCD insert with a 150 m/minute v_c and 0.5 mm a_p .

Chapter 7: Discussion

7.1 Characterisation of starting powders

The starting powders consisted of particles of varying sizes (Figures 4.10-4.18), shown by the D_{10} , D_{50} and D_{90} particle sizes (Table 4.1 and Figures 4.1-4.9). The mean and D_{50} (median value) particle sizes were similar to the particles sizes stated by the powder suppliers, apart from the very fine powders ($0.1\mu\text{m}$ WC and $0.2\mu\text{m}$ Ni) that were slightly larger, due to formation of agglomerates that were difficult to break up, because of the high surface areas and energies [2005Man]. The high surface areas and energies increase the driving force for the fine particle to come together (agglomerate) so as to reduce the total free surface energy of the particles [2005Kan, 2005Man]. The D_{50} and mean particle sizes were used as indications of the overall powder particle [1999ISO].

Although the submicron WC- $0.5\text{Cr}_3\text{C}_2$ powders had a smaller D_{50} and mean particle size than the $1\mu\text{m}$ WC powder (WC-m), it had a wider particle size distribution curve (PSDC) (Figures 4.1 and 4.2 and Table 4.1). The PSDC for the WC-m powder was wider before the D_{50} peak, indicating more finer particles below the D_{50} size than coarser particles above [1999ISO]. The WC- $0.5\text{Cr}_3\text{C}_2$ PSDC was steeper before the D_{50} peak and had wider distribution towards the larger particle sizes, indicating more particles larger than the D_{50} particle size with a wider size distribution than those finer than the D_{50} size. The nano WC powders PSDC (Figure 4.3) had a very high D_{50} peak, followed by a long distribution at the larger particle sizes. This was because most of the particles were approximately the D_{50} size, and the wide distribution after the D_{50} was due to large agglomerates, that were confirmed by SEM (Figure 4.12). The Co powder PSDC had a near uniform distribution and this was confirmed by the SEM image of the powder (Figure 4.13). The $3\mu\text{m}$ Ni powder PSDC (Figure 4.5) was slightly wider before the D_{50} peak and much steeper towards the larger particle sizes, showing particles finer than the D_{50} size had a larger size distribution and were more plentiful than those larger than the D_{50} size. The ultrafine Ni powder PSDC (Figure 4.6) was steeper before and just after the D_{50} peak, followed by significantly smaller but wide distribution towards the larger particle sizes. This indicated that most particles were close to the D_{50} size, and large agglomerates were present (Figure 4.15). The NbC and TiC powders had similar PSDCs to the WC-m powders, but they had a wider taper at larger particle sizes (Figures 4.7 and 4.8), indicating the presence of more large particles which was confirmed by the SEM images (Figures 4.16 and 4.17). Molybdenum carbides PSDC had two peaks of two

particle size ranges (bimodal) [1999ISO]; this was confirmed by SEM images (Figure 4.18). The Mo₂C PSDC was wider before the D₅₀ size than after; it had more particles finer than the D₅₀ size than larger.

X-ray diffraction was done on the powders (Figures 4.19-4.24) to identify their crystal structures, and the presence of hexagonal WC, cubic Ni, hexagonal Co, cubic NbC, cubic TiC and hexagonal Mo₂C were confirmed. Chromium carbide was not detected by EDX analysis and XRD of the WC-0.5Cr₃C₂ powders due to the low amount [1992War, 1997Bar]. However, 0.71Cr₃C₂ (wt%) and 99.29 W (wt%) were detected by XRF analysis; C was not detected because the XRF technique cannot accurately analyse elements lighter than sodium due to low X-ray yields [1983Ani, 2007Ver]. The values of W and Cr were higher than expected, as a result of the absence of C.

7.2 Optimisation of milling

Use of WC-10Co (wt%) balls during milling of WC-0.5Cr₃C₂-10Co (wt%) resulted in a D₅₀ particle size of 0.816µm after 9 h, beyond which no further significant reduction in particle size took place (Figure 4.25). However, after 20 h milling with steel balls, a D₅₀ of about 0.95 µm was attained (Figure 4.25), indicating WC-10Co (wt%) balls were more effective in agglomerate breakdown. Since the starting particle sizes of WC-0.5Cr₃C₂ was 0.8 µm and Co was 0.9 µm (Table 4.1), a D₅₀ of ~0.8 µm was used as the indication of good agglomerate breakdown. The better performance of the WC-10Co (wt%) balls was attributed to their higher density, i.e. each WC-10Co (wt%) ball weighed about 2.86 g, while the steel balls weighed only 0.26 g. To attain 300 g of milling media, 105 balls of WC-10Co (wt%) compared to 1154 balls of steel were required. The large number of steel balls resulted in dense packing, reducing the mean free path for ball-to-powder collision [1996Koc]. Higher milling energies were required to break down agglomerates of the fine powders (0.1 µm WC and 0.2 µm Ni) due to high surface energy of the fine powders [2005Man]. This was achieved by increasing the WC-10Co (wt%) ball to powder ratio from 3:1 to 6:1 (Figure 4.27). After about 12 h of milling using the 6:1 ratio, a D₅₀ particle size of less than 0.2 µm was attained, beyond which no further significant reduction was observed, while milling for 20 h using the 3:1 ratio resulted in a particle size >0.3 µm. The 6:1 ratio was more effective because of higher milling energy resulting from increased ball to powder collision [1996Koc].

For reduction in WC particle size from 1 μm to 0.8 μm and 0.4 μm sizes, even much higher milling energy was required, and this was achieved by using a larger capacity mill (1 kg mill instead of the 100 g mill). This enabled much higher ball-to-powder ratios, significantly increasing the milling energy [1996Koc, 1998Upa]. A ball-to-powder milling ratio of 10:1 and a milling time of 19 h was used to attain a particle size of 0.8 μm , and the 0.4 μm particle size was achieved by using a ball-to-powder milling 15:1 for 30 h. X-ray diffraction was done to check for Co and Fe impurities from the WC-10Co (wt%) balls and the steel milling pots, the patterns revealed no impurities were present (Figure 4.32). Trace amounts Ga and Nb were detected by XRF analysis, but these impurities were present in the 1 μm WC starting powders (Table 4.3). Oxygen analysis of the powders showed no significant increase in oxygen content during high energy milling (Table 4.4).

7.3 Optimisation of Sintering

The effects of SPS temperature, pressure and time on the densification of the WC cemented carbides were investigated, with aim of achieving good densification (>99%) [1985Ger]. Sintering temperature was varied from 1050-1240°C during SPS of WC-0.5Cr₃C₂-10Co (wt%) (Table 4.5), and the densification increased with increased temperature (Table 4.6). The samples sintered at low temperatures (1050-1190°C) had poor densification with high amounts of open porosity, and this was confirmed by their microstructures that had many pores (Figure 4.34). The poor densification was due to incomplete sintering at low sintering temperatures [1975Bro, 1997Luy], since the best densification was achieved at 1220°C. The density of Sample 1.5 (sintered at 1240°C) was higher than the theoretical density (>100 %) due to loss of (Co) (lower density phase) that was squeezed out of the sample and onto the rams (as a silver shiny coating) (Figure 4.33 (b)), because of the retained liquid phase at high temperatures. During SPS, the liquid metal binder phase is only momentarily formed, followed by rapid solidification [1999Tok, 2006Son], although sintering at a temperature above the densification temperature, resulted in prolonged retention of the liquid binder phase that was squeezed out of the sample by the applied pressure [2013Gen1]. Loss of the lower density cobalt resulted in increased volume fraction of the higher density WC phase, leading to higher density than the theoretical value, thus >100% densification. The loss of the Co was confirmed by the smaller and sparsely distributed (Co) binder pools in the microstructure of Sample 1.5, compared to all the other microstructures (Figure 4.34). The magnetic saturation decreased with increased sintering temperature (Table 4.7), due to increased W solubility in

Co [1954Gur]. The coersivity increased with increased sintering temperature (Table 4.7), indicating reduction in the size of Co binder pools [1944Ker] because of improved solubility between WC and Co [1966Suz]. However, the much lower magnetic saturation and significantly higher coersivity of Sample 1.5, was due to the loss of the Co binder [1975Bro, 1998Luy, 1998Upa].

Three different pressure application criteria were investigated as shown in Table 4.8. Sample 2.3 had the highest densification (99.22 ± 0.42 %) with negligible open porosity (Table 4.9), because of systematic increase in pressure at different stages, facilitating better compaction [1998Upa]. During pressing at the start of sintering, particles of powders are poorly arranged, with pores between them, and due to the rapid sintering process, these pores may not be fully eliminated (Sample 2.1), but an additional pressing stage at higher temperatures and pressure improved the compaction, as well as the distribution of the binder phase, eliminating the pores (Sample 2.3) [1998Upa]. Sample 2.2 had the lowest densification and highest open porosity as a result of poor pressure application during sintering, and this was confirmed by its highest amount of porosity in its microstructure (Figure 4.35 (b)). The microstructure for Sample 2.3 had smaller Co pools compared to Sample 2.1, and this was because of good Co binder distribution due to better pressure application (Figure 4.35).

The sintering dwell time was varied from 1-5 minutes, while using the sintering temperature of 1220°C and the pressure application criterion for Sample 2.3. The dwell time of 1 minute (Sample 3.1) gave the lowest densification, while 2-5 minutes (Samples 3.2–3.5) led to >99% densification. The short dwell time of 1 minute did not allow for complete elimination of porosity, although a slightly longer sintering dwell time of 2 minutes enabled pore elimination, increasing the densification [1969Bro] (Table 4.9). Beyond 2 minutes, no significant increase in densification occurred. Thus, a sintering time of 2 minutes was used WC-0.5Cr₃C₂-10Co (wt%).

7.3.1 Addition of NbC to WC-0.5Cr₃C₂-10Co (wt%)

The addition of ≥ 1 NbC (wt%) to WC-0.5Cr₃C₂-10Co (wt%) inhibited densification (Table 4.11) [2008Hua1] and this was confirmed by lower relative piston travel (shrinkage) for the WC-0.5Cr₃C₂-1NbC-10Co (wt%) and WC-0.5Cr₃C₂-10NbC-10Co (wt%) samples than for WC-0.5Cr₃C₂-10Co (wt%) sample (Figure 4.36). Although the 1 and 10 NbC (wt%) samples achieved lower shrinkage, their densification curves were still increasing throughout the sintering dwell time, indicating incomplete sintering at 1220°C for 2 minutes. Thus, to

improve the densification, higher sintering temperature, pressure and time were used [1975Bro]. From Figure 4.37 and Table 4.12, increased sintering temperature from 1220-1260°C, pressure from 50 to 60 MPa and time from 2 to 5 minutes of sintering, facilitated elimination of porosity and increased shrinkage [1969Bro], leading to good densification (>99 %) in the 1 NbC (wt%) and 10 NbC (wt%) samples (Figures 4.37 and 4.38). Elimination of porosity in the 1 and 10 wt% NbC addition samples was confirmed by SEM images (Figures 4.39 and 4.40). This sintering profile was used for addition of 1-80 NbC (wt%) to WC-0.5Cr₃C₂-10Co (wt%). Similar compositions to those in Table 4.16 were produced from nano and ultrafine WC powders that were not doped with Cr₃C₂. Slightly higher sintering temperatures were used for nano and ultrafine WC compositions (Table 4.18) than for similar WC-0.5Cr₃C₂ compositions to achieve full densification, due to the fact that Cr₃C₂ lowers the sintering temperatures of WC-cemented carbides [1999Car].

7.3.2 Sintering WC-Ni

Sintering temperature was varied from 1140-1300°C and pressure from 50 to 60 MPa during SPS of WC-0.5Cr₃C₂-9.3Ni (wt%) for a dwell time of 5 minutes (Table 4.13). Increased sintering temperature and pressure improved the densification (Table 4.13), with 1280°C (Sample 5.4) having the best densification, above which (1300°C) the longer retained liquid phase formed during sintering was squeezed onto the rams, resulting in loss of (Ni) binder in the sample, explaining the 101.42 ± 0.35 % densification in Sample 5.5 (Table 4.13). Higher sintering temperature (1280°C), pressure (60MPa) and slightly longer dwell time (5 minutes) were used to achieve good densification of WC-0.5Cr₃C₂-9.3Ni (wt%) sample, than the WC-0.5Cr₃C₂-Co (wt%) sample, i.e. the previous sintered at 1220°C had a densification of 95.83 ± 0.24 % compared to the latter of 99.17 ± 0.51 % (Tables 4.10 and 4.13). This was due to the lower solubility of WC in Ni (15 wt%) than Co (22 wt%) at eutectic temperature [1987Upa] and poorer wetting of WC by Ni than Co [1988Alm, 1998Upa].

7.3.3 Addition of TiC and Mo₂C to WC-0.5Cr₃C₂-Ni (wt%)

The additions TiC and Mo₂C to WC-0.5Cr₃C₂-9.3Ni (wt%) inhibited densification at 1280°C, 60MPa for 5 minutes (Figure 4.41 and Table 4.14), thus higher sintering pressures and temperatures were required [2013Gen1]. Increased pressure from 60 MPa to 70 MPa improved the shrinkage of the WC-0.5Cr₃C₂-6.25TiC-9.3Ni (wt%) (Figure 4.42), leading to good densification. For the addition of 3.5 Mo₂C to WC-0.5Cr₃C₂-6.25TiC-9.3Ni (wt%), higher sintering temperatures was required (Table 4.15 and Figure 4.43). The best

densification was achieved at 1310°C (Sample 6.2) (Table 4.13 and Figure 4.43), above which loss of the Ni binder occurred. Increased Mo₂C additions increased sintering temperature, since the solubility of Mo₂C in WC and Mo₂C in Ni increases with increased sintering temperature [1988Alm, 1991Kem, 1998Upa]. Compositions similar to those in Table 4.17 were produced using nano, ultrafine and submicron WC starting powders. Slightly higher sintering temperatures were used for the 1, 3.5 and 5 wt% Mo₂C (Table 4.19) compared to the compositions produced using WC-0.5Cr₃C₂ starting powders. The use of higher sintering temperatures to attain full densification was attributed the absence of Cr₃C₂, which lowers the sintering temperatures of WC-cemented carbides [1999Car].

7.4 Microstructure of WC cemented carbides

7.4.1 Microstructure of WC-NbC-Co cemented carbides

The liquid phase sintered WC-0.5Cr₃C₂-10Co (wt%) sample had larger WC grains (Table 5.1) with more homogeneously distributed (Co) pools than the spark plasma sintered WC-0.5Cr₃C₂-10Co (wt%) sample. The finer WC grains in the spark plasma sintered sample were due to the short sintering period and lower sintering temperature that prevented continuous Ostwald ripening [1999Tok, 2005Cha]. Grain growth due to Ostwald ripening increases with increased sintering time and temperature [1897Ost, 1959Kin], hence the higher sintering temperature (1430°C) and longer sintering time (75 minutes) during LPS, formed larger WC [2008Hua1, 2008Wan]. The better (Co) pool distribution in the liquid phase sintered sample was due to the formation of the (Co) liquid phase during sintering that enhanced WC solubility [1953Can, 1959Kin], as well as the capillarity action of the liquid phase in the pores during the secondary rearrangement stage of sintering [1959Kin]. However, during SPS, the liquid binder phase is only momentary formed, followed by rapid solidification [1999Tok, 2006Son], preventing the enhanced WC solubility and secondary rearrangement due to capillary action of the liquid phase, resulting in poorer binder distribution (i.e. larger binder pools than in LPS). Chromium carbide was not detected by EDX (Table 5.2) due to the small amount (0.5 wt%) [1997Bar], but was found within the WC grains by HAADF STEM mapping (Figures 5.5 and 5.6). Minor NbC additions of up to 5 wt% gave slightly reduced WC grain size due to its grain growth inhibition action [1999Zen, 2008Hua1]. Higher NbC additions led to the formation of a NbC skeleton (Fig. 5.3) because of the increased NbC volume fraction (≥ 20 wt%) [2008Hua1, 2008Hua2], and rounding of WC grains at the WC/NbC interfaces (Figure 5.4). The rounding of WC grains was attributed to

formation of the (Nb,W)C solid solution, from the dissolution of WC in (Co) and subsequent reprecipitation on NbC [2007Hua1]. This was confirmed by increased magnetic saturation with increased NbC (Table 13), because of the reduced W amount in the (Co) binder [1997Luy]. For WC-Co, the maximum magnetization induced in (Co) decreases linearly with increased W solubility, and is not affected by the amount of C in the solution [1997Luy]. Cobalt was mainly found between the WC grains and rarely at the NbC grains (Figures 5.2 and 5.3) by HAADF STEM mapping (Figures 5.5 and 5.6). This was because, compared to NbC, the solubility of WC in Co and wetting of WC by Co are much higher [2007Hua1]. It was not easy to differentiate the grey contrast between NbC and Co because of their similar atomic numbers (SEM-BSE mode is dependent on the atomic number [1980Pos]).

The microstructures of WC-10Co (wt%) with 0-20 wt% NbC additions produced from nano and ultrafine WC starting powders are shown in Figures 5.7 and 5.8. The WC-10Co (wt%) samples (Figures 5.7 (a) and 5.8 (a)) had large and poorly distributed Co pools, similar to Figure 5.1 (b), and WC grains with a mean grain size of $>0.8\ \mu\text{m}$. The poor Co binder distribution was attributed to the rapid solidification of the (Co) liquid phase, preventing enhanced WC solubility and secondary rearrangement during SPS. The increased WC grain size was attributed to rapid grain growth in the nano and ultrafine grades, due to coalescence grain growth mechanism [1993Fan, 2002Zhe]. Coalescence is thermally activated, and usually occurs in the early stages of sintering, during which grains adjust their relative orientation by rotating or shifting, and two or more grains can become one when their orientations match [1993Fan, 2002Zhe, 2008Wan]. This process is favored by finer initial grains with higher surface energies [2002Zhe]. Addition of NbC to WC-10Co (wt%) improved the grain growth inhibition, with higher additions (20 wt%) having a greater effect in both nano and ultrafine grades. Formation of a NbC skeleton and rounding of WC grains was also observed at high NbC additions. Cobalt was also mainly found between the WC grains and rarely at the NbC grains.

7.4.2 Microstructure of WC-Mo₂C-TiC-Ni cemented carbides

The microstructure of the SPS WC-0.5Cr₃C₂-9.3Ni (wt%) sample had larger, poorer distributed (Ni) binder pools with higher contiguity than SPS WC-0.5Cr₃C₂-10Co (wt%) (Figure 5.9 and Table 5.4). This was due to the poorer solubility of WC in Ni and wetting of WC by Ni [1955Daw, 1956Hum], preventing good distribution of the binder between the WC grains during the short sintering time [2013Gen1, 2013Gen2]. The microstructures of the WC-0.5Cr₃C₂-9.3Ni (wt%) sample, with 6.25TiC (wt%) and 0.5-5 Mo₂C (wt%) additions, are

shown in Figure 5.10. Titanium carbide was mostly detected within the WC continuous skeleton and rarely in the (Ni) binder, due to the poor solubility between TiC and Ni (Table 5.5 and Figure 5.10) [1956Par]. Molybdenum carbide was found to between the WC grains and in the Ni binder due to its good solubility with both WC and Ni [1986Roe]. The microstructures were strongly influenced by the Mo₂C content and the sintering temperature. Addition of Mo₂C to WC-0.5Cr₃C₂-6.25TiC-9.3Ni (wt%) inhibited SPS of WC-0.5Cr₃C₂-6.25TiC-9.3Ni (wt%), so higher sintering temperatures were required to achieve good densification (Figures 4.43 and Table 4.15). This was evident in Figure 5.11 (a) and (b), showing WC-0.5Cr₃C₂-3.5Mo₂C-6.25TiC-9.3Ni (wt%) sintered at 1280°C and 1310°C respectively, where the 1280°C sample had larger and poorly distributed (Ni) pools (Table 5.4). The large and poor (Ni) pool distribution of the 1280°C sample was attributed to the poor diffusion during sintering at relatively lower temperature, resulting in incomplete sintering and low densification (96.65%) [1985Sha, 1998Upa]. The increased Mo₂C in WC-0.5Cr₃C₂-6.25TiC-9.3Ni (wt%) led to the formation of smaller and more evenly distributed (Ni) pools (Table 5.4), because of improved wetting of WC by Ni [2008Guo2, 2013Gen1]. The improved (Ni) distribution was also aided by increased sintering temperature. The best (Ni) distribution was observed in the 3.5 and 5wt% Mo₂C samples sintered at 1310°C and 1320°C, which are close to the Ni-Mo eutectic of ~1317°C [2009Ger], resulting in increased diffusion, wetting of WC by the binder and WC solubility [1998Upa]. Additions of 3.5 and 5 Mo₂C (wt%) to WC-0.5Cr₃C₂-6.25TiC-9.3Ni (wt%) gave smaller (Ni) binder pools with a better distribution than the (Co) binder in the spark plasma sintered WC-0.5wt%Cr₃C₂-10wt%Co (Table 5.4).

Liquid phase sintered nano grade WC-9.3Ni (wt%), sintered at 1430°C and 1510°C had larger WC mean size grains than the similar composition produced by SPS (Figure 5.12 and Table 5.6). Although the SPS sample had finer WC grains, the mean grain size was >1.0 μm, indicating that rapid grain growth occurred due to coalescence [1993Fan, 2002Wan]. Rapid grain growth was also observed in the ultrafine grade 9.3Ni-u sample, but slight grain growth occurred in the submicron grade 9.3Ni-s sample (Table 5.6). The slight grain growth in the submicron grade was because the larger WC starting particles have a lower driving force to coalesce and grow than the nano and ultrafine particles, due to their lower surface areas and energies [2008Wan]. The grain growth of nano powders during LPS took place in two stages, an initial rapid grain growth stage during heating up (coalescence) and later, during the isothermal hold (Ostwald ripening), explaining the larger WC grains [1998Upa, 1999Yao,

2008Wan]. The LPS samples had thicker (Ni) binder pools that were more homogeneously distributed compared to the SPS sample, the 1510°C sample had the widest binder pools. The wider (Ni) pools were due to the larger WC grains, because binder thickness decreases with decreased WC grain size [1998Upa].

Micrographs of nano, ultrafine and submicron grade 9.3Ni samples, with 6.25 TiC (wt%) and 0-5 Mo₂C (wt%) additions are shown in Figures 5.13, 5.20 and 5.21. Titanium carbide was mainly found at the WC/(Ni) interfaces by high resolution (HR) STEM electron energy loss spectroscopy (EELS) mapping (Figure 5.18). This suggests that TiC may have interfered with the WC/(Ni) interfacial energies, inhibiting solution re-precipitation (Ostwald ripening) [2002Wit]. Molybdenum carbide was detected by SEM-EDX area analysis, but its exact location was difficult to discern in the fine microstructures. However, Mo was confirmed to be between the WC grains by HAADF STEM mapping (Figures 5.15, 5.16 and 5.21), with areas of overlap between W and Mo. These were confirmed to be WC grains under Mo₂C grains by bright field (BF) STEM (Figure 5.17), indicating the good distribution between the two phases. Addition of Mo₂C to WC-6.25TiC-9.3Ni (wt%) significantly improved the grain growth inhibition in the nano and ultrafine grades, with 5 (wt%) addition, giving the finest WC grain size (Table 5.6 and Figure 5.14). The good grain growth inhibition was due to Mo₂C delaying the aggregation of the fine WC grains, thus preventing coalescence [2008Wan]. The presence of Mo₂C between the WC grains in the WC-6.25TiC-5Mo₂C-9.3Ni (wt%) sample produced from ultrafine WC powder was also shown by HAADF STEM mapping (Figure 5.21). From Figure 5.14 and Table 5.6, the WC-5Mo₂C-6.25TiC-9.3Ni (wt%) sample produced from ultrafine WC powder had the finest average WC grain size of $0.54 \pm 0.03\mu\text{m}$ compared to the similar nano composition of $0.62 \pm 0.06\mu\text{m}$. The finer WC grain size in the ultrafine grade than in the nano grade could be due to a poorer distribution from the mixing of larger grained Mo₂C (1.7 μm) grain growth inhibitor with the nano powders during ball milling [2003Kim]. Kim *et al.* [2003Kim] found limitations in achieving uniform mixing of nano and micron powers during ball milling from the difference in the powder sizes, and as a result, new mixing techniques, such as chemical doping are currently being developed. The finer WC grain size in the 5 wt% Mo₂C ultrafine grade than in the nano grade could also be due to the higher surface areas and energies in the smaller nano starting powders, resulting in a higher driving force for WC grains to coalesce and grow [2008Wan], even though Mo₂C was added. Finer WC grains were observed with 5wt% Mo₂C than 6.25

wt% TiC (Fig. 3), due to the stronger grain growth inhibition effect of Mo₂C than TiC [1999Yao].

The effect of reduction in Ni binder amount from 10 wt% to 6 wt% on the microstructure is shown in Figure 5.19. Larger and poorly distributed (Ni) binder pools were observed in the 10 wt% and 9.3 wt% Ni samples, but further reduction in binder amount resulted in formation of smaller and sparsely distributed (Ni) pools, with 7 wt% and 6 wt% Ni having the smallest pool sizes (Figures. 5.17 (d) and (e)). The reduction in (Ni) binder pool size was attributed to reduction in volume fraction the Ni binder phase [1998Upa]. The ultrafine and submicron WC-9.3Ni (wt%) samples had larger (Ni) binder pools than the nano sample (Figures 5.13, 5.20 and 5.22), which was due to larger Ni starting powders (2.5 µm) in ultrafine and submicron samples than in the nano (0.2 µm) samples [2002Eng, 2013Gen2]. Increased Mo₂C addition to WC-0.5Cr₃C₂-6.25TiC-9.3Ni (wt%) also led to the formation of smaller and more evenly distributed (Ni) pools (Table 5.4 and Figure 5.10), because of improved wettability between WC and Ni [1988Reo]. and increased sintering temperature [2013Gen1].

7.5 Constituent phases

7.5.1 Phases present in the WC-NbC-Co compositions

The XRD patterns of liquid phase sintered and spark plasma sintered WC-0.5Cr₃C₂-10Co (wt%) are shown in Figure 5.23, and both compositions had similar patterns, consisting of hexagonal WC and fcc Co. This is consistent with previous work [1998Upa, 2008Hua1] that showed dissolution of W and/or C in the (Co) binder during sintering, leading to the stabilisation of the ductile fcc allotrope. Chromium carbide was not detected because the small amount was below the XRD detection limit [1992War], but was confirmed by HAADF-STEM. X-ray diffraction patterns of 0-80 wt% NbC additions to WC-0.5Cr₃C₂-10Co (wt%) (Figure 5.24), showed the presence of hexagonal WC, fcc Co and cubic NbC phases. Huang *et al.* [2007Hua1, 2008Hua1] showed that NbC can accommodate >10 WC (wt%) when liquid phase sintered for 1 hour at 1360°C [2007Hua1]. However, the positions of the NbC diffraction peaks did not vary, showing similar W solubility in NbC in all samples. Increased NbC content resulted in larger NbC peaks and the reduction in WC peak intensity, because of the reduced WC volume fraction [2008Hua1]. Tungsten carbide was not detected in the 80 wt% NbC pattern due to the low volume fraction of 5.3 vol. % that was close to the XRD detection limit.

The XRD patterns for WC-10Co (wt%) produced from nano WC starting powders with 1-20 NbC (wt%) (Figure 5.25) also showed the presence of hexagonal WC, cubic NbC and fcc Co, although the peaks were at different 2 theta angles than in Figure 5.24. The difference in 2 theta values was due to the change from a Co X-ray source to a Cu X-ray source resulting in a difference of approximately 10° [2008Pec]. No carbon was detected by XRD (Figures 5.23-5.25); this is beneficial for good mechanical properties [1975Bro].

7.5.2 Phases present in the WC-Mo₂C-TiC-Co compositions

The XRD patterns of WC-0.5Cr₃C₂-9.3Ni (wt%) with additions of 6.25 TiC (wt%) and up to 5 Mo₂C (wt%) (Figure 5.26) showed the presence of hexagonal WC, cubic TiC and fcc Ni. Molybdenum carbide was not detected in the XRD patterns because of the low amounts (≤ 5 wt%) [1992war], but was confirmed by EDX (Table 5.5). The XRD patterns of similar compositions produced from nano WC starting powders (Figure 5.27) also showed the presence of hexagonal WC, cubic TiC and fcc Ni, although Mo₂C was not detected because of the low amount. The presence of Mo₂C was confirmed by EDX analysis (Table 5.7) and HAADF STEM (Figures 5.15 and 5.16).

7.6 Mechanical Properties

7.6.1 Hardness

7.6.1.1 Hardness of WC-NbC-Co compositions

Spark plasma sintering of WC-0.5Cr₃C₂-10Co (wt%) resulted in >3 GPa higher Vickers hardness and >2.5 higher HRA Rockwell-A hardness than liquid phase sintered WC-0.5Cr₃C₂-10Co (wt%) (Tables 5.8-5.10), due to finer WC grains. Small NbC additions (up to 5 wt%) slightly reduced the hardness, in all grades, but additions above 20 wt% significantly reduced the hardness with 80 wt%, giving the lowest hardness. Although additions of NbC resulted in reduced WC grain size (Table 5.1, Figure 7.1), the hardness decreased. In WC-Co, generally the hardness and fracture toughness can be related to the WC grain size; reduced WC grain size results in increased hardness and reduced K_{1C} [1975Bro, 1997Luy]. However, due to the addition of NbC, these properties did not only depend on the WC grain size, but also on the WC volume fraction [2008Hua1, 2008Hua2]. The hardnesses of WC and NbC are 22.5 GPa and 19.4 GPa respectively [1999Yao, 2008Hua1], and hence the reduction in WC volume with increased NbC content reduced the hardness (Figure 7.2). Although the HV₁₀ values were slightly higher than HV₃₀, both tests showed a decrease in hardness with increased NbC additions, and this was confirmed by the Rockwell-A hardness test. The

slightly higher hardness values attained in the test were as a result of the lower indentation load, due to the indentation size effect [1951Bro, 1959Buc]. This effect occurs because of experimental errors from the limitation in resolution of objective lens [1951Bro, 1959Buc] and the sensitivity of the loading cell [1991Mas].

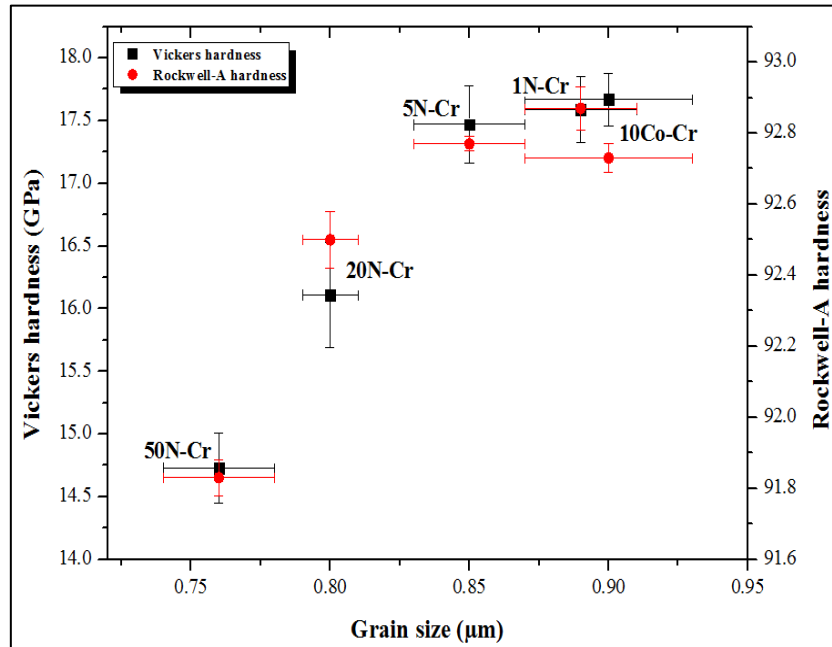


Figure 7.1. Effect of WC grain size on hardness for WC-0.5Cr₃C₂-NbC-10Co (wt%) samples.

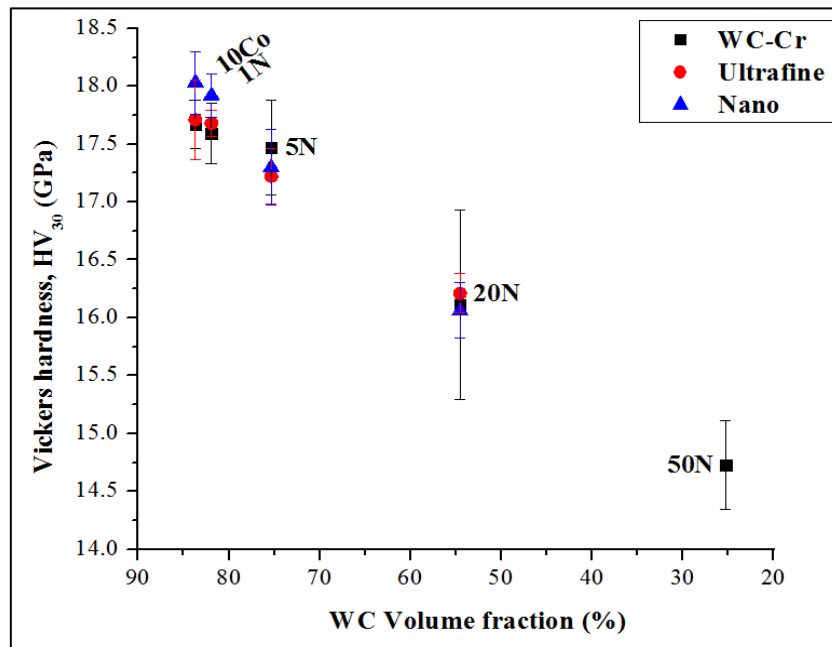


Figure 7.2. Effect of WC volume fraction on Vickers hardness for WC-0.5Cr₃C₂-NbC-10Co (wt%) samples.

Increased NbC content led to increased formation of the (Nb,W)C solid solution, due to more W reprecipitating on the NbC grains, instead of on the WC grains, reducing the fraction of WC in the cemented carbide [2008Hua1], and thus reduced the hardness [2008Hua1].

7.6.1.2 Hardness of WC-Mo₂C-TiC-Ni compositions

The WC-0.5Cr₃C₂-9.3Ni (wt%) sample had lower hardness than WC-0.5Cr₃C₂-10Co (wt%) sample (both produced by SPS) (Tables 5.8-5.13) because of the poorer wetting of WC by Ni, leading to poor Ni distribution (Figures 5.9 and 7.3), and higher plasticity in the Ni binder [1998Upa, 2008]. The addition of 6.25 wt% TiC and 0-5 wt% Mo₂C to WC-0.5Cr₃C₂-9.3Ni (wt%) increased the hardness with 0.5 wt% Mo₂C resulted in a higher hardness than SPS WC-0.5Cr₃C₂-10Co (wt%). Higher Mo₂C additions further increased the hardness, with 5 wt% producing the highest hardness (Tables 5.11-5.13). Addition of TiC to WC-0.5Cr₃C₂-9.3Ni (wt%) resulted in a slight increase in hardness because TiC has a higher hardness than WC, by about 5GPa [2007Kim]. Molybdenum carbide improved the Ni binder distribution, increasing the hardness [1986Roe, 2013Gen1]. Roebuck *et al.* [1986Roe] reported Mo partitioning at the WC/Ni interfaces promoted a stronger carbide/binder interface, improving the hardness and fracture toughness. The increased sintering temperature with increased Mo₂C content improved the diffusion between WC and Ni, leading to better (Ni) binder distribution and good density, hence increasing the hardness [1995Ben]. The effect of increased sintering temperature was seen in the mechanical properties of the 3.5 wt% Mo₂C addition samples sintered at 1280°C (3.5M (1280)) and 1310°C. The 3.5M (1280) sample had lower hardness (Tables 5.11-5.13) due to poor densification and the large (Ni) pools in the microstructure (Figure 5.11) [1995Ben, 2013Gen].

Use of SPS significantly improved the hardness of the nano grade WC-9.3Ni (wt%) compared to similar LPS sample, resulting in an increased Vickers hardness by >5GPa and Rockwell-A hardness by >3 HRA (Tables 5.11-5.13). The ultrafine and submicron WC-9.3Ni (wt%) grades also had higher hardness values than the WC-9.3Ni (wt%) produced by LPS (Tables 5.11-5.13). However, all grades of WC-9.3Ni (wt%) had lower hardnesses than WC-0.5Cr₃C₂-10Co (wt%) produced by SPS (Tables 5.8-5.13) and this was due to poor wetting of WC by Ni [1955Daw] and higher plasticity of the Ni binder [2008Hua1]. Additions of Mo₂C significantly increased the hardness in the nano, ultrafine and submicron grades, with 5 wt% resulting in the highest hardness. This was due to Mo₂C good grain growth inhibition (Table 5.6 and Figure 7.4) [1999Yao] and improved wettability of WC by Ni [1986Roe, 2008Guo1, 2008Guo2, 2013Gen1]. The ultrafine 5 wt% Mo₂C sample (5M-u) had a higher hardness than

the nano 5wt% Mo₂C (5M-n) sample (Tables 5.11-5.13), which was attributed the finer WC grain size (Figure 5.31). Reduction in Ni binder amount in the nano WC-Ni from 10 wt% to 6 wt% increased the hardness because of the increased WC proportion [1975Bro, 1997Luy].

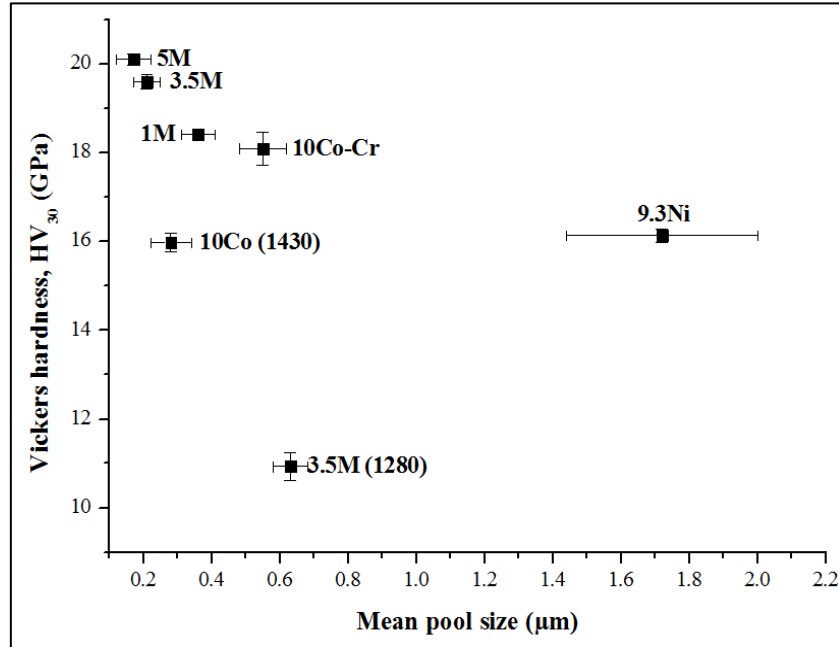


Figure 7.3. Effect of binder mean pool size on Vickers hardness.

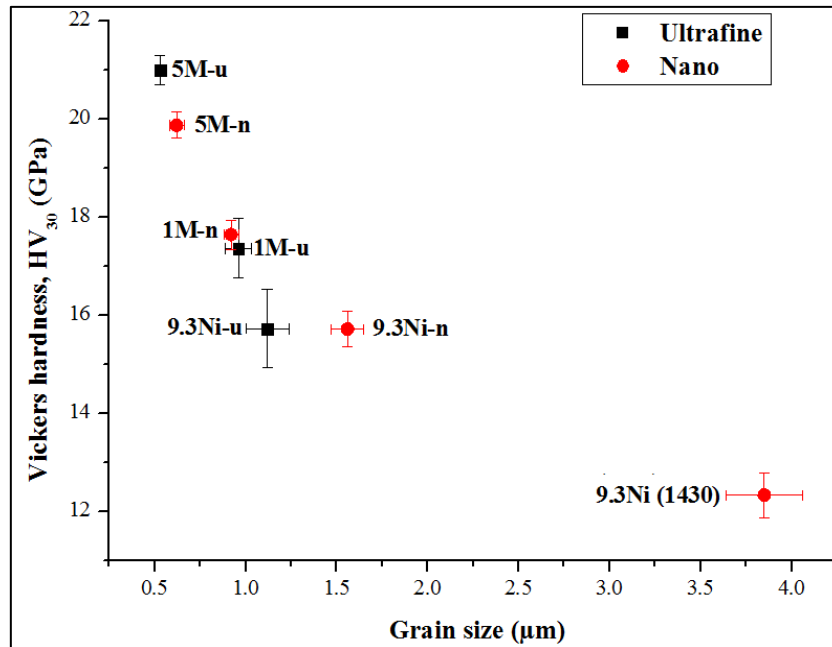


Figure 7.4. Effect of WC grain size on the Vickers hardness for nano and ultrafine WC-Mo₂C-TiC-Ni samples.

Additionally, reduction in Ni binder amount from 9.3 wt% to 7 wt% in the nano and ultrafine 5M-7Ni grades led to Vickers hardness of >20 GPa and Rockwell-A hardness of >94 HRA.

7.6.2 Fracture toughness (K_{1C})

7.6.2.1 Fracture toughness of WC-NbC-Co compositions

The liquid phase sintered WC-0.5Cr₃C₂-10Co had higher fracture toughness than the sample of similar composition produced by SPS (Tables 5.14 and 5.15). The high K_{1C} in the liquid phase sintered sample was due to the more homogeneously distributed (Co) binder pools (Figure 5.1), resulting in lower contiguity (Table 5.4), hence reducing the amount WC/WC interface fracture, which is the most critical fracture in WC-cemented carbides [1976Che]. Small additions of up to 5 wt% NbC slightly reduced the K_{1C} , while additions above 10 wt% NbC (Tables 5.14 and 5.15) significantly reduced the K_{1C} , irrespective of starting WC particle size. Reduction in K_{1C} was attributed to the decreased volume fraction of the tougher WC-Co and increased formation of the (Nb,W)C mixed carbide solid solution that is more brittle than WC [2008Hua1]. Huang *et al.* [2008Hua1] reported transgranular crack propagation of the interconnected brittle (Nb,W)C skeleton, limiting the contribution of crack deflection as a toughening mechanism. Reduction in K_{1C} was not inversely related to hardness (Figure 7.5) as is normally expected, since it was not dependent on the WC grain size, but instead on the WC volume fraction (Figure 7.6) and (Nb,W)C solid solution.

7.6.2.2 Fracture toughness of WC-Mo₂C-TiC-Ni compositions

Nano grade WC-9.3Ni (wt%) samples produced by LPS much higher K_{1C} than the sample of similar composition produced by SPS (Tables 5.16 and 5.17), with 9.3Ni (1510) having the highest K_{1C} . This was due to the thicker (Ni) binder pools, resulting in a thicker, tougher layer to inhibit the cracks propagating between WC grains [1976Che, 2011Bas2], and were also well distributed between the larger WC grains (Figure 5.12). The WC-0.5Cr₃C₂, ultrafine and submicron grades had generally higher fracture toughnesses than similar nano grades (Tables 5.16 and 5.17), because of the thicker Ni binder pools resulting from the larger Ni starting powders in the ultrafine and submicron grades (~2.5µm) than the similar nano grades (~0.2µm) [2002Eng, 2013Gen2]. The WC-0.5Cr₃C₂-3.5Mo₂C-6.25TiC-9.3Ni (wt%) sample sintered at 1280°C (3.5M (1280)), had a much lower K_{1C} than the similar sample sintered at 1310°C because of the poor (Ni) distribution (Figure 5.11), leading to higher WC contiguity (Table 5.4), allowing increased WC/WC interface fracture [1985Sha]. Another contributory factor was residual porosity from poor densification (96.65%), since pores act as crack initiation and/or crack propagation sites [1974Rom, 1976Che, 2003Sob]. The K_{1C} reduced with decreased Ni binder amount to 7 wt % (Figure 7.7), because of the reduction of the tougher Ni binder phase proportion [1975Bro, 1997Luy]. The K_{1C} was inversely related to

the hardness (Figures 7.7 and 7.8) due to reduction in WC grain size and poor binder distribution [1975Bro, 1997Luy, 1998Shc] in the SPS samples.

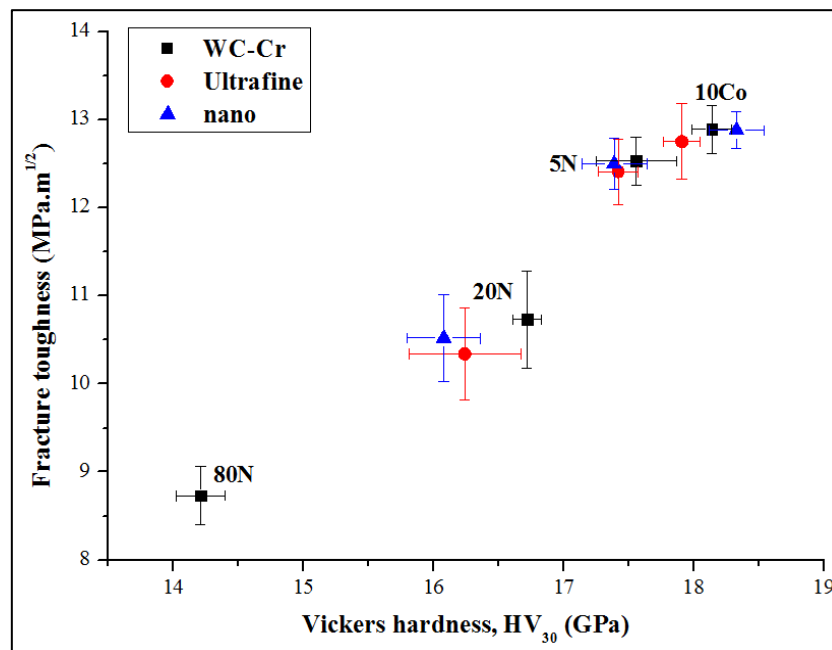


Figure 7.5. Relationship of Vickers hardness and fracture toughness in WC-NbC-Co samples.

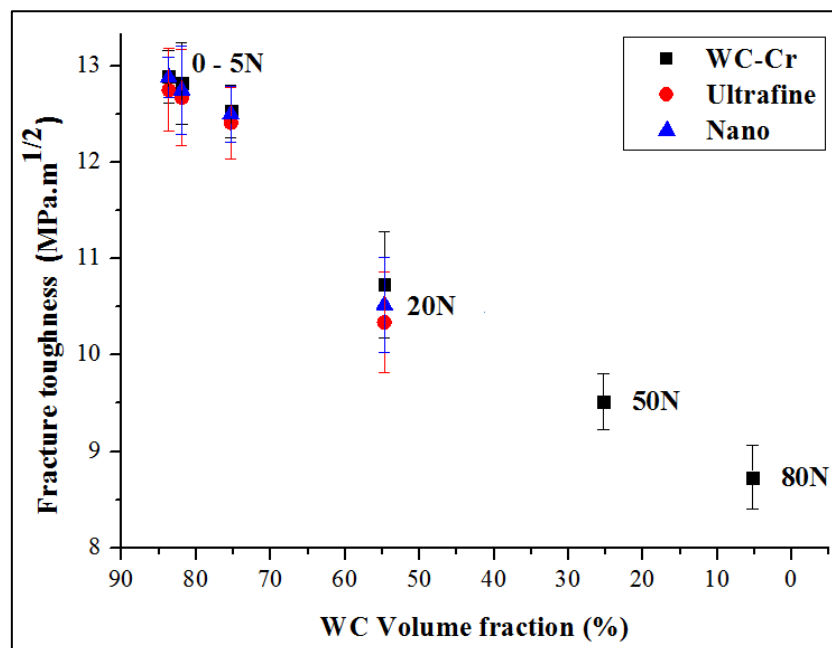


Figure 7.6. Effect of WC volume fraction on fracture toughness in WC-NbC-Co samples.

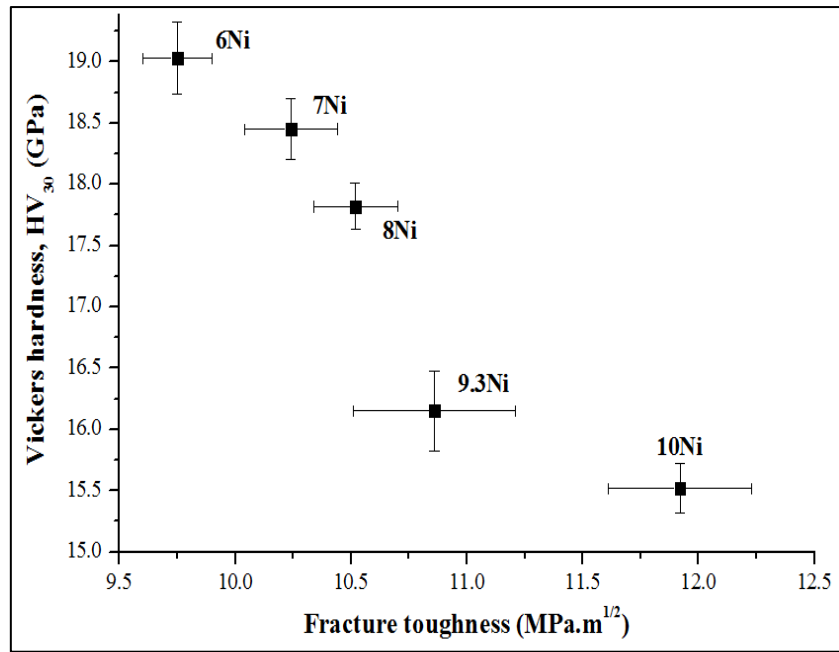


Figure 7.7. Relationship of fracture toughness and Vickers hardness with Ni binder amounts in nano grade WC-Ni samples.

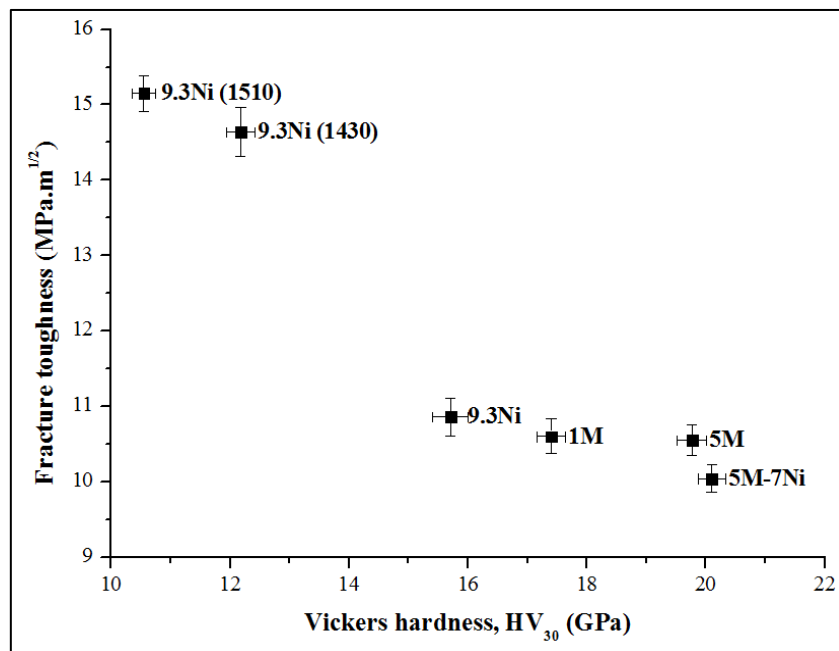


Figure 7.8. Relationship between Vickers hardness and fracture toughness in nano grade WC-Ni samples.

7.7 Elastic modulus

7.7.1 Elastic modulus of WC-NbC-Co compositions

Liquid phase sintered WC-0.5Cr₃C₂-10Co (wt%) had a slightly higher modulus of elasticity than the spark plasma sintered WC-0.5Cr₃C₂-10Co (wt%) (Table 5.18), due to the higher sintering temperatures that increased WC solubility in (Co) [1998Upa], resulting in better bonding. Generally, increase in modulus of elasticity is due to better bonding in the material [1977Pag]. Additions of NbC up to 5 wt%, slightly reduced the elastic modulus, but higher additions (20 wt%), led to significant reduction in all the grades, because of the reduction in the WC volume fraction (Figure 7.9). Tungsten carbide has a significantly higher elastic modulus, 696 GPa, compared to NbC, 338 GPa.[1992Scu], thus reduction of WC in the cemented carbide decreased the elastic modulus. Furthermore, the poor solubility of NbC in Co and wetting of NbC by Co also lowered the elastic modulus [2013Gen1].

7.7.2 Elastic modulus of WC-Mo₂C-TiC-Ni compositions

The WC-Ni cemented carbides had slightly lower moduli of elasticity than the WC-Co cemented carbides, even though Mo₂C was added (Table 6), and this was attributed to the poor wetting of the WC by the Ni and solubility of WC in Ni, affecting the material bonding during sintering [2013Gen1]. Liquid phase sintered WC-0.5Cr₃C₂-9.3Ni (wt%) had a slightly higher elastic modulus than that produced by SPS (Table 5.19). Addition of TiC and Mo₂C had little effect on the elastic moduli, although reduction in binder content in the 5M sample from 9.3 wt% to 7wt% slightly increased the elastic modulus in the nano and ultrafine grades. This was due to increased WC amount, since it has a much higher elastic modulus (696GPa) than Ni (207 GPa) [1992Scu]. The low elastic modulus in the 3.5M sample sintered at 1280°C was as a result of poor densification (Figure 7.10), because elastic modulus increases with reduction in sample porosity [1995Ban].

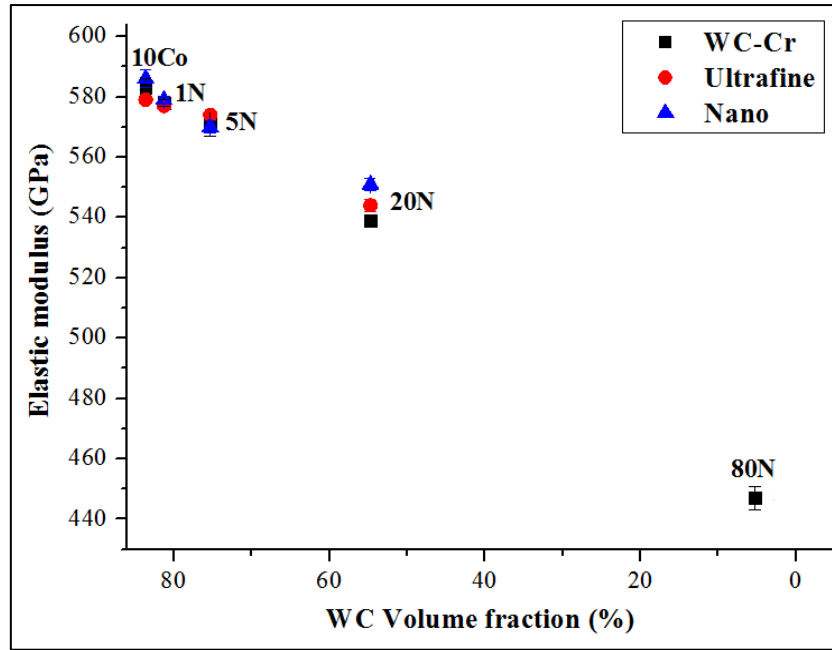


Figure 7.9. Effect of WC volume fraction on elastic modulus in WC-NbC-Co samples.

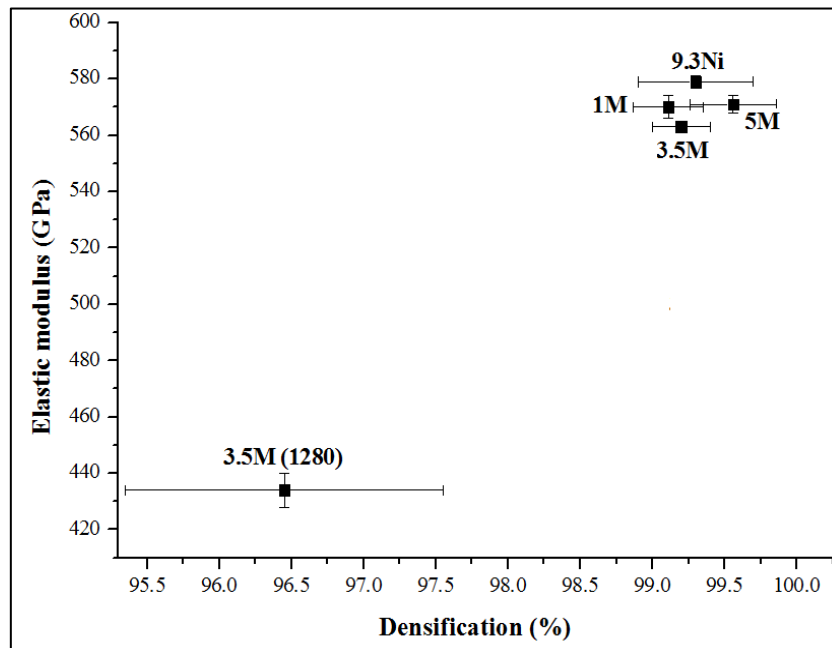


Figure 7.10. Effect of densification on elastic modulus for WC-0.5Cr₃C₂-9.3Ni (wt%), with TiC and Mo₂C additions.

7.8 Magnetic saturation

Liquid phase sintered WC-0.5Cr₃C₂-10Co (wt%) had the lowest magnetic saturation than all the spark plasma sintered samples (Table 5.20), because of the high sintering temperature and presence of the liquid phase during sintering that enhanced WC solubility in the (Co),

increasing the amount of W in (Co) [1975Bro, 1997Luy]. High additions of NbC (≥ 10 wt%) to WC-0.5Cr₃C₂-10Co (wt%) produced by SPS resulted in increased magnetic saturation, with 80 wt% having the highest value (Table 5.20). This reduction was attributed to formation of (Nb,W)C solid solution that reduced the amount of W in the (Co) binder [2008Hua1].

7.9 Transverse rupture strength

The liquid phase sintered compositions had higher TRS than the spark plasma sintered compositions, of which the WC-0.5Cr₃C₂-10Co (wt%) had the highest value followed by WC-9.3Ni (wt%) produced from nano WC (Table 5.21). The higher TRS of the liquid phase sintered samples was due to thicker and better distributed binder pools [1998Upa] and lower residual stresses because of the slow cooling rate after sintering [2008Zha]. The larger WC grains in LPS WC-9.3Ni (wt%) (Figure 5.12 (b)) than in LPS WC-0.5Cr₃C₂-10Co (wt%) sample (Figure 5.1 (a)) could have acted as internal defects that could have prematurely initiated the fractures [1975Luy], slightly lowering the TRS. The higher TRS was also attributed to the presence of Cr₃C₂, that prevents the fcc to hcp transformation of the Co binder, improving the ductility of cemented carbide [1986Cha]. The liquid phase WC-0.5Cr₃C₂-10Co (wt%) had also had a higher TRS than the similar composition sample produced by SPS due to the higher sintering temperatures that increased the W and C solubility in the (Co), increasing the stability of the tougher fcc allotrope [1976Rud, 1985Yi]. The higher residual stresses due to rapid cooling after SPS also reduced the TRS [2008Zha]. All grades of SPS WC-9.3Ni (wt%) had lower TRS than LPS and SPS WC-0.5Cr₃C₂-10Co (wt%), because of poorer binder distribution (large uniformly distributed binder pools) that acted as internal defects [1975Luy, 1998Upa]. The lower binder amount in the WC-9.3Ni (wt%) also lowered the TRS, since TRS decreases with reduction in amount of binder [1998Upa]. The TRS decreased with increased sample hardness (Figure 7.11) due to the residual stresses from the rapid cooling after SPS, reduction of Ni binder amount and additions of NbC, TiC and Mo₂C [1998Upa]. Increased addition of cubic carbides (NbC, TiC and Mo₂C) to plain WC-cemented carbides reduces the TRS [1998Upa]. The TRS increased with increased K_{1C} (Figure 7.12), because TRS is a combination of shear strength, compressive strength and tensile strength, and thus is a general measure of the toughness of the sintered cemented carbide [1998Upa].

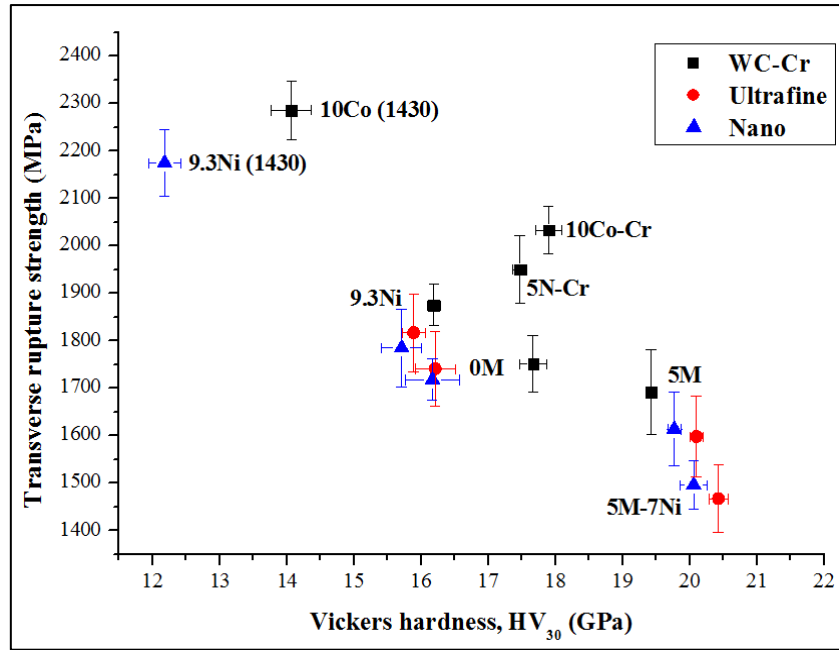


Figure 7.11. Relationship between Vickers hardness and transverse rupture strength.

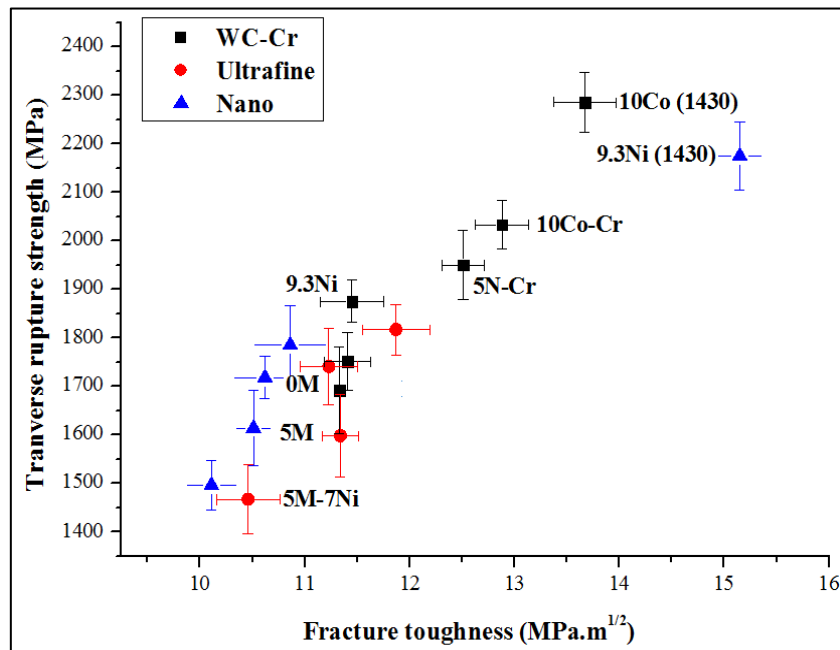


Figure 7.12. Relationship between transverse rupture strength and fracture toughness.

7.10 Sliding wear resistance

7.10.1 Samples sliding wear due to 100 Cr 6 steel ball

The liquid phase sintered WC-0.5Cr₃C₂-10Co (wt%) (10Co (1430)) had a wider wear track than both the spark plasma sintered WC-0.5Cr₃C₂-5NbC-10Co (wt%) (5N-Cr) and WC-

5Mo₂C-6.25TiC-7Ni (wt%) (5M-7Ni-u) samples, indicating greater wear [2002AST]. However, the difference in worn volume loss between 5N-Cr and 5M-7Ni-u samples was not clear from the optical images (Figure 6.1 (b) and (c)), because their wear tracks had almost the same width. Thus, laser confocal microscopy for 3D topographic mapping of the wear track was conducted to measure the actual worn volume within the tracks (Figures 6.2 and 6.3). Optical microscopes can only focus on a single optical plane at any point in time (focal plane), limiting accurate depth measurements [1999Pad]. Thus, when the focal plane was at the top surface the sample, the width of the track could be accurately measured but the depth was not possible. However, light from the laser confocal scans over the wear track touches every point from the highest to the lowest points, and the deflection of the light back to the detector, as the sample is scanned is then used plot the 3D topography [2013Mur]. The 3D topographic maps and wear track profiles of the wear tracks for 10Co (1430) and 9.3Ni (1430) samples (Figure 6.2) showed a wider wear track and greater wear (Table 6.1). This was attributed to the slightly lower binder content [1975Bro, 1976Lar] and the use of a Ni binder in the 9.3Ni (1430) sample [1987Pen, 2004Bon]. Compared to cobalt, nickel has a more ductile austenitic structure which reduces loss of WC grains by extruding outwards to replace the eroded binder between the WC grains, improving the wear resistance [1987Pen]. Most of the volume loss in the 10Co (1430) sample was on the both edges of the track due to the accumulation of wear debris (from fragmentation of carbide grains) near the edge of the wear track, increasing the friction and material removal [2011Sha]. Conversely, for the 9.3Ni (1430) sample, wear was mostly in the track, and this was attributed to slight downward displacement of the WC grains due to extrusion of the ductile Ni binder under the action of high localized stress from the Hertzian contact pressure [1985Las]. The reason why some of the samples were worn on the edge of the tracks and others at the centre, even though they had similar compositions and mechanical properties is still not quite clear. This is because wear is dependent on several variables such as contact geometry, oxygen availability, load, speed, surface roughness, material surface compositions and temperature [1989Hsu]. The dependence on this large number of variables makes it difficult to reproduce similar wear track profiles [1989Hsu].

Spark plasma sintering improved the wear resistance, with all grades of WC-9.3Ni (wt%) (9.3Ni) having a lower wear rates than the 9.3Ni (1430) sample (Figures 6.3-6.5 and Table 6.1). This was because of the increased hardness [1953Arc, 1976Lar] of the finer WC grains (Table 5.6). The lower worn volume in the 5N-Cr sample compared to nano, ultrafine and

submicron 9.3Ni and WC-6.25TiC-9.3Ni (wt%) (0M) samples (Figures 6.1-6.4 and Table 6.1) was due to its higher hardness (Tables 5.8-5.13). Further additions of up to 5 wt% Mo₂C and reduced Ni binder to 7 wt% significantly improved the wear resistance, resulting in the 5M-s, 5M-7Ni-u and 5M-7Ni-n samples having the lowest sample wear rates (Figure 7.13). This was because of increased hardness [1953Arc, 1976Lar] through WC grain refinement (Figures 5.13, 5.14 and 5.20) and improved Ni distribution with Mo₂C additions [1980Roe, 1999Yao, 2013Gen1].

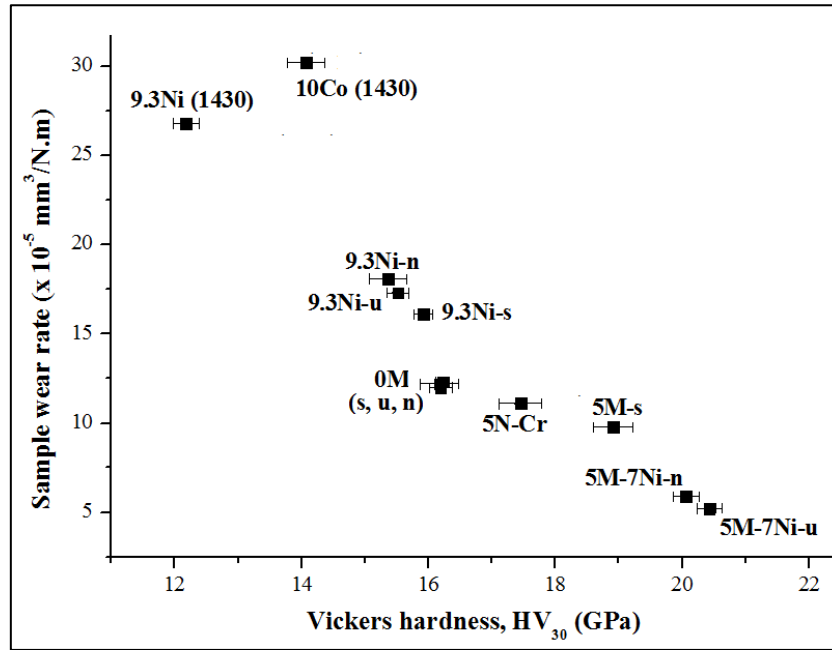


Figure 7.13. Variation of sample wear rate with Vickers hardness from the 100 Cr6 steel balls.

7.10.2. Wear on 100 Cr6 steel balls

The optical images of the 100 Cr6 steel balls after sliding wear tests on 10Co (1430), 5N-Cr and 5M-7Ni-u samples (Figure 6.6) showed that the 10Co (1430) sample had the smallest wear scar, while the 5M-7Ni-u had the largest wear scar, with large scratches and pull-out. This was attributed to higher ball wear by the 5M-7Ni-u sample than the 5N-Cr and 10Co (1430) samples [2002AST]. This was confirmed by the microstructures of the wear tracks (Figure 6.7), which showed the present of iron oxide debris tribolayers, explaining the pull-out in the steel balls wear scars (Table 6.2) [1958Mur, 2000Eng2, 2008Kum]. The 5M-7Ni-u sample had more iron oxide debris than the 5N-Cr, while none was observed on the wear track for the 10Co (1430) sample, because the ball wear rate (BWR) increased with increase in sample hardness (Figure 7.14) [2002AST]. The significantly higher hardness of the 5M-

7Ni-u (20.33 ± 0.49) and 5N-Cr (17.47 ± 0.47) samples than the 100 Cr6 steel ball (~ 7 GPa) [2008Kum] caused abrasion of the steel ball surface by the harder cermet asperities, resulting the formation of iron debris [2008Kum]. For this reason, the BWRs increased with increased sample hardness.

The coefficient of friction (μ) graphs (Figure 6.11) had similar profiles for approximately the first 10 m (first stage), consisting of rapid increase in μ . In second stage, the 10Co (1430) sample had a steeper increase than the other samples. This was followed by a plateau stage for the all samples, apart from the 5N-Cr sample which had a slight increase before the steady state. Instabilities were observed in the steady-state plateau stage, particularly for the 10Co (1430) and 5M-7Ni-u samples. The rapid increase in μ during the first 10 m of the wear test was because of the polishing effect at the ball and sample interface, smoothing the wear track by ploughing away at the surface asperities, increasing the interaction between the mating solids, and the interlocking asperities increased the friction [1981Eva, 2008Kum]. Generally, friction during wear is as a result of three main components, deformation of interlocking asperities, adhesion and abrasion (ploughing) [1981Eva]. Initially, when two surfaces are in sliding contact, friction increases due to deformation of interlocking asperities, so as to eliminate the obstacles between them (smoothing). In the case of adhesion, force is required to shear the adhesive bonds formed at the interface during sliding, increasing the friction force [1981Eva]. Abrasion or ploughing occurs when the asperities of one body are much harder than the other, resulting in scratches (grooves) or cuts on the other surface, increasing the friction [1981Eva]. The gentle slope in the second stage of the μ curves were due to smoothing of the wear track with continued deformation of asperities [1996Bhu, 1999Bhu]. The plateau stage was due to the smooth surfaces, after the elimination of asperities [1996Bhu, 1999Bhu]. The instabilities during the plateau stages, particularly for the 10Co (1430) and 5M-7Ni-u samples were attributed to the continuous breaking and regeneration of the ball/sample contact interface by trapped wear particles, slightly reducing the friction [1996Bhu, 1999Bhu]. The slight increase in μ between the second and third stages of the 5N-Cr sample curve could possibly be a result of a trapped wear particle that was ejected from the ball/sample interface, increasing the friction [1996Bhu, 1999Bhu].

The μ reduced with increased sample hardness, with the LPS samples having the highest value and the 5M-7Ni-u sample having the lowest (Table 6.2 and Figure 7.15). This was attributed the formation of the iron oxide tribolayer that acted as a lubricant, reducing the friction [1958Mur, 2000Eng2, 2008Kum], explaining the reduction in μ with increased 100

Cr6 steel ball worn volume (Figure 7.15). This was confirmed by the PCD sample that had the highest tribolayer amount and the lowest μ . The PCD sample also had the highest amount of iron oxide tribolayer (Figures 6.9 and 6.10), because it experienced a higher Hertzian pressure from its significantly higher modulus of elasticity (~ 1000 GPa) [Element Six S.O.P] than the WC-cemented carbides (from 560-590 GPa) [1985Las].

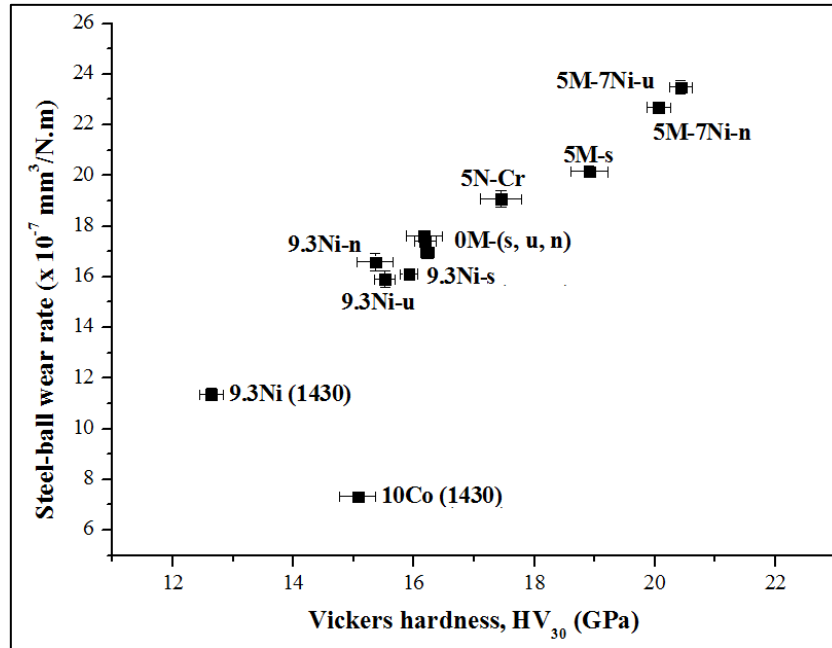


Figure 7.14. Comparison between the steel ball wear rate and the samples' Vickers hardness.

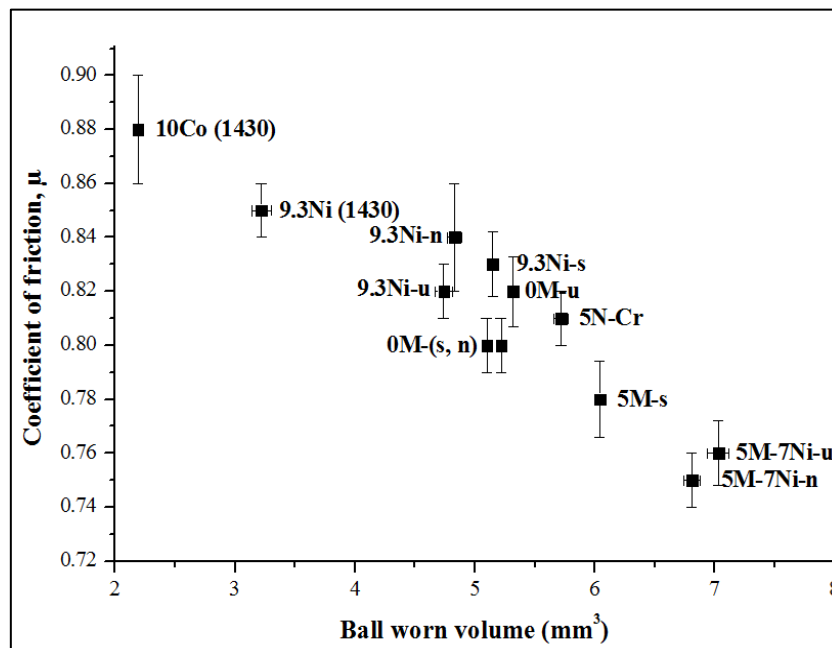


Figure 7.15. Variation of coefficient of friction with ball worn volume.

7.10.3. Sample wear due to silicon nitride (Si_3N_4) balls

The optical image of the 10Co (1430) sample had a slightly wider track than both 5N-Cr and 5M-7Ni-u samples (Figure 6.12), although the difference in width of the track between the 5N-Cr and 5M-7Ni-u samples was not discernable. Thus, laser confocal microscopy was used for samples the wear track analyses. The 10Co (1430) sample had a wider wear track and greater wear than the 9.3Ni (1430) sample (Figure 6.13 and Table 6.3), and this was attributed to the slightly lower binder content [1975Bro, 1976Lar] and use of the Ni binder [1987Pen, 2002Bon]. Scanning electron microscope images of the 10Co (1430) sample showed depressions and fragmentation on the wear track. The depressions were due to the Hertzian pressure that was high enough to cause yielding of the Co binder below the wear track, resulting in the WC being shifted below the wear surface [1985Lar, 2004Pir]. The formation of depressions increases with increased binder amount [2004Pir]. The fragmentation was due to abrasive ploughing of the exposed WC grains [1979Lar] by the harder Si_3N_4 ball (hardness of $\sim 15.7\text{GPa}$) [2003Yun], through gross plastic deformation [1979Lar].

The SPS 9.3Ni-n sample had a slightly lower wear rate than the 9.3Ni (1430) sample (Figures 6.13 (b) and 6.14 (b)) and Table 6.3) because of its higher hardness (Tables 5.11-5.13) [1958Mur, 1976Lar] due to SPS. The 5M-7Ni u and 5M-7Ni-n samples had the lowest sample wear rates (Figure 7.16) due to the refined microstructure [1993Kea, 1996Jai] and lower binder content [1973Lar], resulting in significantly higher hardness ($>20\text{ GPa}$) (Tables 5.11-5.13) than the Si_3N_4 ball. The wear track for the 5N-Cr sample mainly had scratches (Figure 6.17), and fragmentation of WC grains around large (Co) binder pools and between the WC continuous skeleton (Figures 6.17 (b) and (d)) (shown by the arrow). The Co binder was preferentially extruded, especially from large binder pools, increasing the number of asperities capable directly pulling out the binder, to continue the process [1973Lar, 1985Lar]. This leads to compressive stresses in the WC grains, caused by the difference in contraction between the WC and Co during cooling to relax, leading to WC fragmentation [1985Lar, 1998Upa]. The wear track for the 5M-7Ni-u sample had fewer scratches that were thicker than those in the 5N-Cr sample, because of its better wear resistance, due to the finer microstructure and lower binder content. No pull-out of TiC grains in the 5M-7Ni-u sample (Figure 6.18) indicated good bonding during the short sintering period [2004Pir]. Transgranular crack propagation between WC grains on the wear track due to the Hertzian stress (2.17GPa) (Table 6.4) [2004Pir] was only observed in the 5M-7Ni-u sample (Figure

6.18 (c) and (d)) (between the arrows), because of low K_{IC} from the lower Ni binder content [1975Bro, 1990Spi].

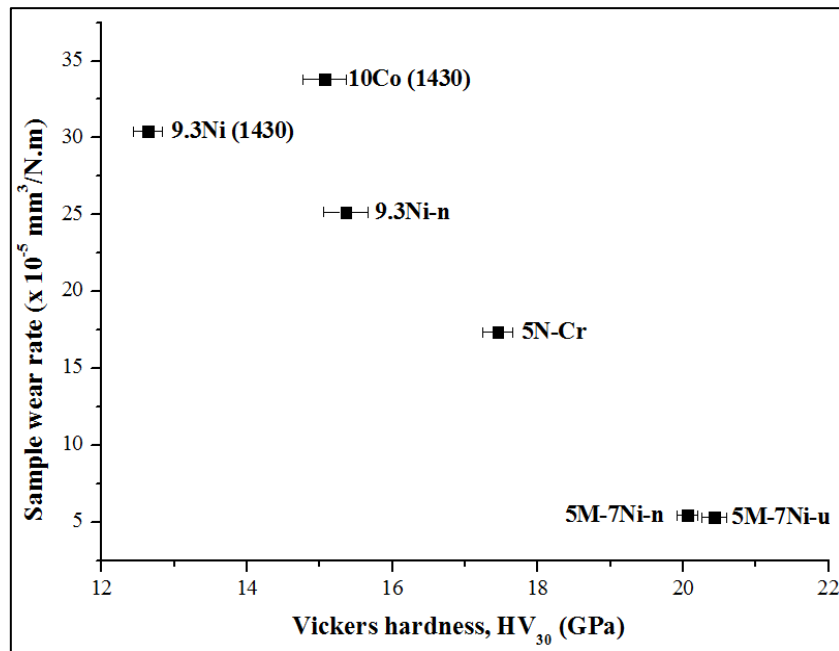


Figure 7.16. Variation of sample wear rate with sample Vickers hardness from the Si_3N_4 balls.

7.10.4 Wear on silicon nitride (Si_3N_4) balls

The 5N-Cr and 5M-7Ni-u samples had larger wear scars than the 10Co (1430) sample (Figure 6.15), with the 5M-7Ni-u sample having the largest diameter, and thus the highest ball wear rate (Figure 7.17). The ball worn volume and ball wear rate increased with increased sample hardness (Figures 7.17). The liquid phase sintered samples (10Co (1430) and 9.3Ni (1430)) had lower hardness than the Si_3N_4 ball, resulting in plastic deformation of the cemented carbide surface and elimination of surface asperities [2004Pir], explaining the absence of scratches on the surface (Figure 6.16). The 5N-Cr and 5M-7Ni-u samples had higher hardness than the Si_3N_4 ball, and hence acted as abrasive bodies, wearing the balls [2002AST]. This increased the friction, due to three-body abrasion from the breakup of asperities from the balls and the cemented carbides [1999Bhu], leading to scratches on the wear track (Figures 6.17 and 6.18). The μ increased with increased sample hardness due to this reason (Figure 7.18). The 5M-7Ni-u wear track had fewer scratches than the 5N-Cr sample and no fragmentation of WC grains, because its higher hardness improved the wear resistance.

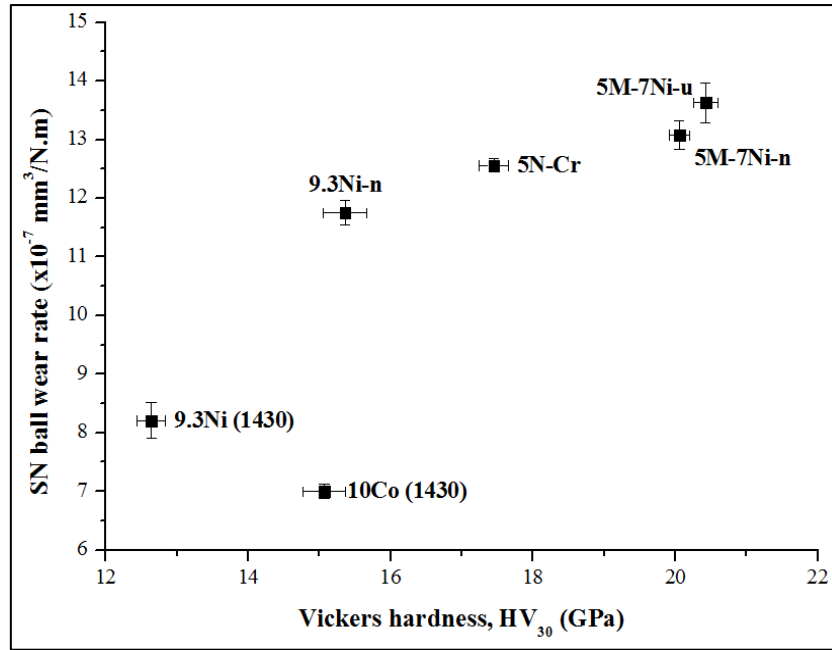


Figure 7.17. Variation in Si_3N_4 ball wear rate with sample hardness.

The coefficient of friction graphs had similar profiles, rapid increase for approximately the first 10-15 m, followed by a slight drop and then a plateau stage (Figure 6.19). The rapid increase stage was because of the polishing effect at the ball and sample interface, smoothing the wear track by ploughing away at the surface asperities, increasing the friction [1981Eva, 2008Kum]. As the wear process continued, the wear track became smoother, due to elimination of asperities, reducing the number of obstacles to overcome, and decreasing the μ until a steady state (plateau stage) was reached [1981Eva, 2008Bon].

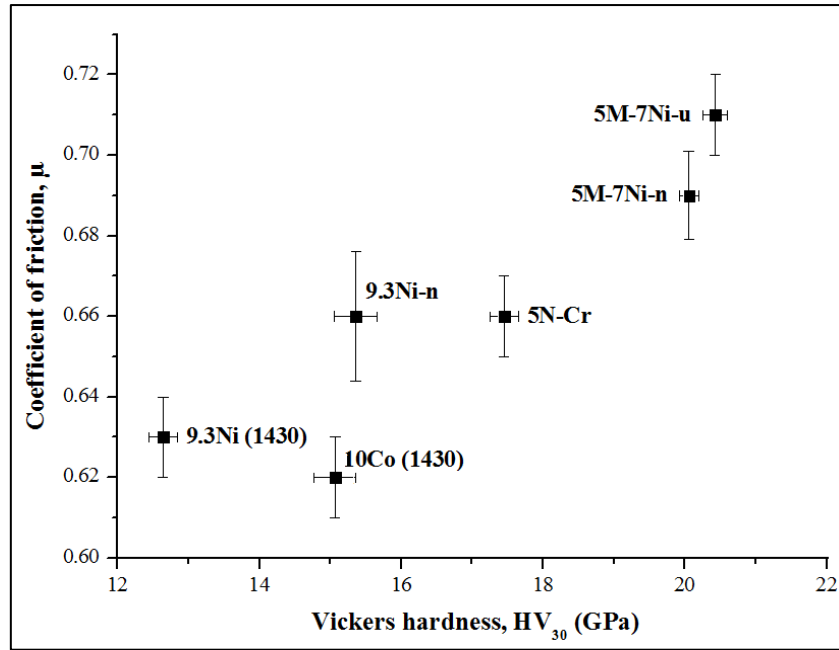


Figure 7.18. Variation of coefficient of friction from the Si_3N_4 balls with sample Vickers hardness.

The Si_3N_4 balls resulted in a higher Hertzian pressure and had lower ball wear rates than the 100 Cr6 steel balls (Tables 6.2 and 6.4). The higher Hertzian pressure was because of Si_3N_4 balls' higher modulus of elasticity (~320 GPa) [1996Bob, 2009CSM] than the 100 Cr6 steel balls (~200 GPa) [1999BS, 2009CSM], as Hertzian pressure increases with increased modulus of elasticity [1953Rad]. The Si_3N_4 balls had generally lower ball wear rates and higher sample wear rates (Figure 7.19) than the 100 Cr6 steel balls, due to silicon nitride's higher hardness, giving better wear resistance [1953Arc, 1976Lar]. The Si_3N_4 balls gave slightly higher sample wears rates than the 100 Cr6 steel balls for both 5M-7Ni samples than the other samples (Figure 7.19), even though Si_3N_4 is a more abrasive material, indicating the 5M-7Ni samples had very good abrasion wear resistance.

7.11 Thermal shock and impact resistance

Optical images of the 10Co (1430) and 5N-Cr insert cutting edges due to milling at a cutting speed (v_c) of 40 m/minute and a depth of cut of (a_p) of 1mm, showed negligible flank wear (VB), but the 5M-7Ni-u insert had a VB of 287.7 μm (Figure 6.20). This was confirmed by the SEM images of the 5M-7Ni-u insert (Figure 6.25) that showed the fractured surface of the cutting edge. Most of the fractured cutting edge was covered by Ti-6Al-4V which stuck onto the insert during milling and some carbon from the taping that was used to protect edge from further damage after the test.

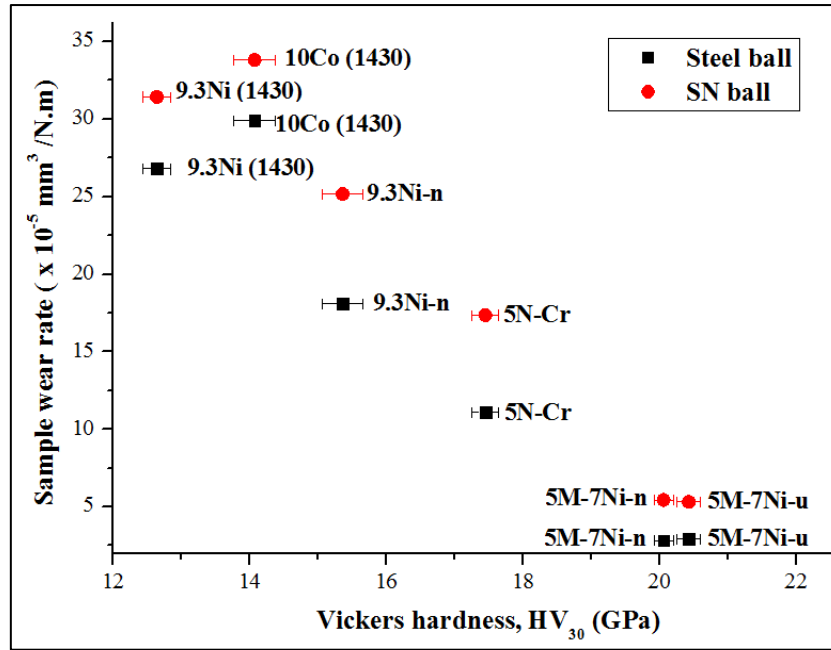


Figure 7.19. Comparison of sample wear rates from 100 Cr6 steel (Steel) and Si₃N₄ (SN) balls and their variations with Vickers hardness.

However, higher magnification of the fractured surface showed the fragmentation of WC grains with interconnected microvoids (~1µm diameter) between them (indicated by arrows in Figure 6.25 (f)), indicating to ductile fracture [1975Hah, 1988Sig]. In the initial stages of ductile fracture, microvoids nucleate preferentially at the WC/binder interface, due to the high interface energies (low fracture energy) and the incompatibility strains (pile-up of dislocations) [1975Hah]. These microvoids grow with increased plastic deformation, and begin to connect (coalescence), facilitating fracture of the sample [1975Hah, 1988Sig]. The flank wear was caused by the rapid changes in temperature (thermal shock) and the impact between the workpiece and insert at the cutting edge [1989Boo, 1999Gu]. The fracture of the 5M-7Ni-u insert's cutting edge was attributed to the lower binder content (7 wt%) compared to 5N-Cr and 10Co (1430) inserts (10 wt%), since resistance to ductile fracture increases with increased amount of binder phase [1988Sig]. The 5M-7Ni-u also had the highest flank wear rate (FWR), although it experienced a lower average resultant force and similar thermal variation per second to the 10Co (1430) insert (Table 6.5). This was as a result of the 5M-7Ni-u inserts lower TRS and fracture toughness (K_{IC}) compared to the 5N-Cr and 10Co (1430) inserts (Figures 7.20 and 7.21), since thermal shock and impact resistance increase with increased TRS and K_{IC} [1955Gur, 1968Kre]. After ~100 seconds, significant increase in resultant force occurred rapidly (inflection) in the 5M-7Ni-u insert (Figure 6.32), which was not observed in the other two inserts (Figures 6.30 and 6.31). The inflection was due to

increased flank wear (VB), which resulted in blunting of the cutting edge, increasing the cutting force because of increased shear area [1993Pra]. The 10Co (1430) insert experienced higher resultant cutting forces than the 5N-Cr and 5M-7Ni-u (before the inflection point) (Table 6.5 and Figure 6.31), because of its lower hardness and higher toughness. This resulted in a blunt cutting edge, due to deformation at the cutting surface, increasing the cutting forces [1993Pra]. The graphs for the 5M-7Ni-u (Figure 6.28) and 5N-Cr (Figure 6.29) inserts had points of rapid increase and decrease of resultant force (spikes) every ~30 seconds, which were not present for the 10Co (1430) insert (Figures 6.30 and 6.31). These spikes were the points at which the inserts would re-engage the workpiece after a complete length of cut, and were the points of maximum impact. From Figure 6.30, the 10Co (1430) insert did not have these spikes because of the high TRS of the insert. The 5N-Cr insert experienced the lowest resultant forces (Figures 6.29 and 6.31), leading to the lower thermal variation per second (Table 6.5), because of its hard cutting edge, good TRS and K_{1C} (Figures 7.20 and 7.21).

Increased v_c to 60 m/minute while maintaining the same a_p , increased the VB in all three inserts, the 10Co (1430) insert had the lowest VB (66.2) μm , followed by the 5N-Cr insert (144.8 μm), while the 5M-7Ni-u insert had the highest VB (314.9 μm) (Figure 6.21). The VB increased due to increased cutting forces as a result of increased impact (from 5 to 7 collisions per second with the workpiece) and higher thermal variations per second (Table 6.5) [1987Sol, 1999Gu]. Similar to the 5M-7Ni-u insert cutting edge (Figure 6.25), most of the fractured cutting edge of the 5N-Cr insert was covered by Ti-6Al-4V and some protective carbon tape debris (Figure 6.26). The 5N-Cr fractured surface from a v_c of 60 m/minute was smaller than the 5M-7Ni-u insert milled at a v_c of 40 m/minute (Figure 6.25), resulting in a lower VB, although a higher cutting speed was used. This was because of the higher binder amount which improved the resistance to ductile fracture [1988Sig], as well as the high TRS and K_{1C} . The effect of the lower TRS and K_{1C} of 5M-7Ni-u was also observed in Figure 6.33, in which an inflection was observed after ~25 seconds of milling, indicating blunting of the cutting edge (cutting edge failure), due to flank wear. No inflections were observed in the graphs for the 5N-Cr (Figure 6.34) and 10Co (1430) (Figure 6.35) inserts. Blunting of the 5M-7Ni-u inserts cutting edge increased the cutting force required [1993Pra], resulting in higher average resultant force (Figure 6.32) and FWR than the other inserts (Table 6.5).

Increase of the v_c to 75 m/minute and the a_p to 2 mm significantly increased the VB for all samples (Figure 6.22), because of increased cutting force [1987Sol, 1999Gu]. The 5M-7Ni-u

insert's cutting edge was completely damaged (catastrophic failure), resulting in the highest VB of 707.5 μm (Figure 6.22), while the liquid phase sintered 9.3Ni (1430) and 10Co (1430) inserts had the lowest VB (Figure 6.23). This was confirmed by the SEM images of the 10Co (1430) cutting edge, which showed smaller fractured surfaces (Figures 6.27 (a) and (b)) than both the 5N-Cr and 5M-7Ni-u inserts, although a higher cutting speed (75 m/minute) and longer depth of cut (2 mm) were used. Although Ti-6Al-4V and protective carbon tape debris had covered the cutting edge, disconnected cracks parallel to the insert cutting edge were observed (indicated by arrows in Figure 6.27). The cracks occurred due to increased mechanical impact as a result of the high cutting speed (9 collisions with the workpiece per second) [1999Gu]. The cracks were parallel to the cutting edge because the insert was subjected to dynamic stresses in the normal direction to the cutting edge [1999Gu]. Although all the inserts experienced similar thermal variations per second (Figure 6.32), the 5M-7Ni-u insert had the highest average resultant force and FWR, followed by the 5N-Cr insert (Table 6.5). This was because of the lower TRS and K_{1C} of the two spark plasma sintered samples [1955Gur, 1968Kre]. The 10Co (1430) insert experienced slightly higher resultant forces and had a slightly higher FWR than 9.3Ni (1430) (Table 6.5, Figures 6.36 and 6.37), because of the Ni binder's higher resistance to ductile fracture [1986Sig, 1988Sig]. Cobalt's stacking fault intersections [1988Sig] and volume change due to fcc-hcp phase transformation [1977Luy] increase the amount of micro-voids, reducing the resistance to ductile fracture [1988Sig]. Nickel has no α - β phase transformation [1987Pen] and high stacking fault energy prevents the microvoid nucleation through stalk fault intersection [1986Sig, 1988Sig]. The highest flank wear occurred at the point furthest from the cutting edge nose, irrespective of the type of insert or cutting speed (Figures 6.20-6.23). This is because that part of the cutting edge experiences the highest stresses and the material cut by that point had been work hardened by previous cuts [2002Lui, 2003Jun].

The PCD inserts tested at cutting speeds of 60 and 150 m/minute using an a_p of 0.5 mm (Figure 6.24) showed increased VB with increased v_c . The PCD insert used at a v_c of 60 m/minute had a higher FWR than the 10Co (1430) and 9.3Ni (1430) inserts, even though a shorter a_p of 0.5 mm was used (Table 6.6). The higher FWR in the PCD insert was attributed to the lower TRS and K_{1C} of the PCD (~ 1480 MPa [Element Six S.O.P] and ~ 5 MPa.m^{1/2} [2002Zha]). The damage of the PCD insert emphasized the aggressive nature test method used. Increased v_c from 60 m/minute to 150 m/minute resulted in higher resultant forces (Figures 6.38 and 6.39), thermal variations per second and FWR (Table 6.6), due to increased

impact with workpiece and higher cutting force due to blunting of the cutting edge. This was evident from the variation in resultant force with time graphs (Figures 6.38 and 6.39), in which the inflection point for the inserts milling at a v_c of 60 m/minute was at ~25 seconds, while at 150 m/minute it was at ~12.5 seconds.

Generally, the sample wear rate reduced with increased sample hardness (Figure 7.19), showing that the abrasion resistance during sliding wear increased with WC grain size refinement and reduction of the binder amount. Sliding wear is normally studied in the context of metal cutting using turning processes [1997Kia]. Thus, the good performance of the 5M-7Ni SPS samples in the sliding wear test with both balls is an indication of possible turning applications for the compositions. Although the LPS samples had the lowest hardnesses, they had the lowest FWRs because of their very good TRS and K_{1C} (Figures 7.20 and 7.21) that improved their thermal shock and impact resistance. During face milling, flank wear increases due to several mechanisms, of which mechanical fatigue (impact) and thermal fatigue (thermal shock) mechanisms are key [1999Gu]. Hence, due to the high strength, toughness and low FWRs under aggressive milling conditions of the LPS samples, they show promise for heavy interrupted face milling applications. Overall, the SPS 5M-7Ni samples had the best abrasion wear resistance, and the LPS inserts had the best thermal shock and impact resistance.

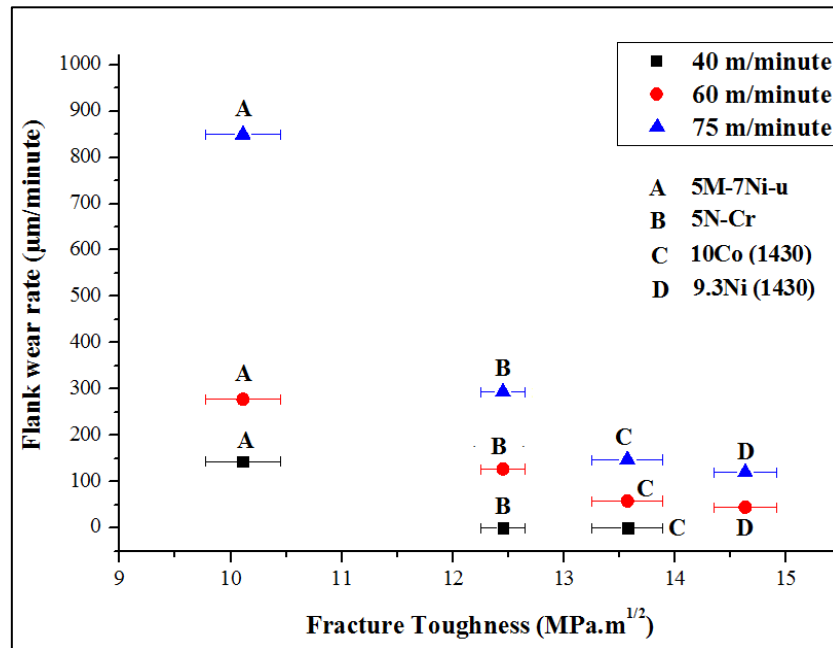


Figure 7.20. Comparison between insert flank wear rate and fracture toughness.

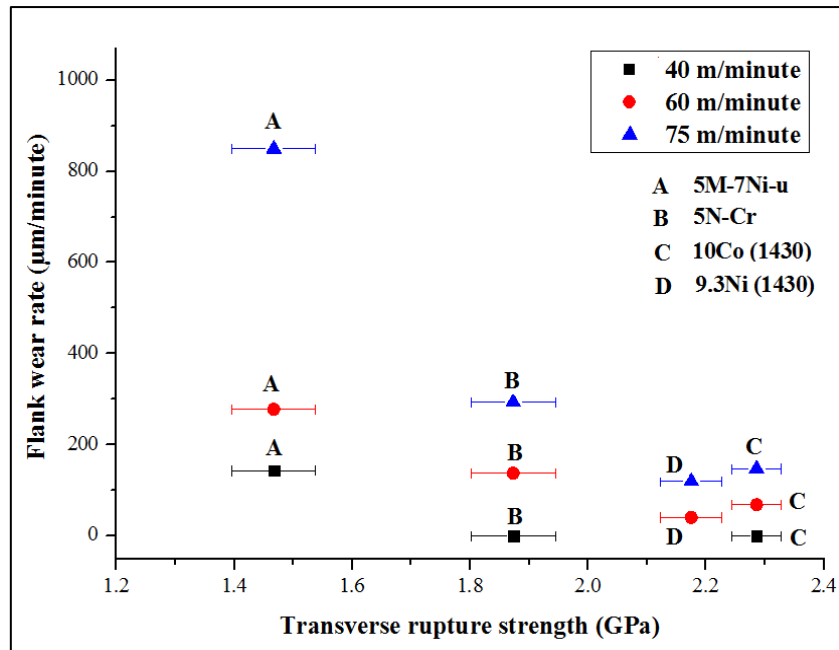


Figure 7.21. Comparison between insert flank wear rate and transverse rupture strength.

Chapter 8: Conclusions and Recommendations

8.1 Conclusions

The use of WC-Co milling balls gave a more homogenous Co distribution between the WC particles than steel balls, and reduced the milling time. This was due to the higher density of the WC-Co balls which increased milling energy and resulted in better ball distribution. Increased ball to powder ratio from 3:1 to 6:1 was required to achieve good mixing for milling the nano and ultrafine WC powder samples. For the reduction in WC grain size from 1 μm to 0.8 μm (submicron) and 0.4 μm (ultrafine), significantly higher ball to powder ratios (10:1 and 15:1) and longer milling times (19 h and 30 h) were required.

All SPS WC-Co and WC-Ni cemented carbides had good densification (>99% theoretical density), affirming the ability of SPS to produce dense cemented carbides with temperatures significantly below the sintering temperatures normally employed and with shorter sintering dwell times. Additions of NbC to WC-10Co (wt%) inhibited densification during SPS in the nano, ultrafine and submicron grades, and thus higher sintering temperatures and pressures were required. The SPS WC-0.5Cr₃C₂-10Co (wt%) and WC-9.3Ni (wt%) samples had higher hardnesses than the similar samples produced by LPS, due to the finer WC grains. However, the liquid phase sintered sample had higher fracture toughness (K_{1C}) and transverse rupture strength (TRS) because of the more homogenous binder distribution and lower residual stresses from the slower cooling rates after sintering. Grain growth of up to 0.8 μm occurred in the SPS WC-10Co (wt%) sample produced from nano (0.1 μm) and ultrafine WC starting powders because of rapid grain growth from grain coalescence. Minor additions of up to 5 wt% NbC to WC-10Co (wt%) gave a good combination of hardness, fracture toughness and modulus of elasticity. Higher additions of NbC reduced the mechanical properties, irrespective of starting WC grain size, due to the reduction in WC volume fraction, lower solubility of NbC in Co and poorer wetting of NbC by Co compared to WC.

Higher sintering temperatures and pressures were required to achieve good densification of the WC-Ni cemented carbides than the WC-Co cemented carbides, because of the poorer wetting of the WC by Ni and the lower solubility of WC in Ni compared to Co. Spark plasma sintered WC-9.3Ni (wt%) had finer WC grains and poorer distributed Ni binder pools than liquid phase sintered WC-9.3Ni (wt%), resulting in higher hardness, but lower K_{1C} and TRS. The LPS WC-0.5Cr₃C₂-10Co (wt%) sample had a higher TRS than the LPS WC-9.3Ni (wt%) sample, due to the larger WC grains which acted as defects. Slight grain growth was observed

in the WC-9.3Ni (wt%) sample produced from submicron WC starting powders after SPS, but grain growth to up to 1 μ m occurred in the nano and ultrafine grades. Additions of TiC and Mo₂C to WC-9.3Ni (wt%) inhibited densification during SPS, necessitating higher sintering temperatures and pressures to achieve good densification. The titanium carbide addition slightly improved the hardness, while further additions of 0.5-5 Mo₂C (wt%) significantly increased the hardness, with 5 wt% giving the highest hardness. The increased hardness in the nano and ultrafine grades was due to good grain growth inhibition and improved wetting of WC by Ni, while in the submicron grades, it was because of improved wetting of WC by Ni. The WC-5Mo₂C-6.25TiC-9.3Ni (wt%) ultrafine grade had a higher hardness than the nano grade WC-5Mo₂C-6.25TiC-9.3Ni (wt%) due to higher driving force for grain growth in the nano WC powders and poorer distribution of micron Mo₂C during milling. Further hardness increases with a slight reduction in fracture toughness was achieved through the reduction of the binder proportion from 9.3 wt% to 7 wt%, giving much higher hardness than the LPS and SPS WC-Co compositions. All the WC-Ni compositions had good modulus of elasticity values above 560 MPa, which were comparable to both LPS and SPS WC-Co compositions.

All the SPS samples had higher resistance to sliding wear than the LPS samples using both the Si₃N₄ and 100 Cr6 steel balls, which was attributed to their higher hardness as a result of their refined microstructures. The resistance increased with increased sample hardness with the WC-5Mo₂C-6.25TiC-7Ni (wt%) ultrafine and nano grades having the highest resistance. The ball wear rates also increased with increased sample hardness, since the higher hardness samples acted as the abrasive body on the balls. The LPS WC-9.3Ni (wt%) sample had higher abrasion resistance than the LPS WC-0.5Cr₃C₂-10Co (wt%) sample because of the slightly lower binder content and Ni binder's better wear properties. The LPS samples had the highest thermal shock and impact resistances, shown by their higher TRS and K_{1C}. The WC-0.5Cr₃C₂-5NbC-10Co (wt%) sample had a good hardness, from SPS and the addition of NbC and Cr₃C₂ grain growth inhibitors, as well as good fracture toughness and TRS, from the high binder amount and good wetting of WC by Co. These resulted in a good combination of sliding wear, thermal shock and impact resistance in the WC-0.5Cr₃C₂-5NbC-10Co (wt%) sample. The ultrafine grade WC-5Mo₂C-6.25TiC-7Ni (wt%) sample had the lowest thermal shock and impact resistance because of its poor K_{1C} and TRS.

8.2 Recommendations

- 8.2.1 To improve the mechanical properties of the WC-NbC-Co cemented carbides with high NbC additions, a different binder with better wetting of NbC is required. Alternatively, if possible, other additives to improve the wetting behaviour should be investigated and introduced. Lower NbC additions gave good mechanical properties, but to further improve the hardness of the nano and ultrafine grades, even better grain growth inhibition is required. This can be achieved by better milling techniques such as use of precursor/chemical deposition methods which could achieve uniform distribution of the grain growth inhibitors between the fine WC grains.
- 8.2.2 Spark plasma sintering, addition on TiC and Mo₂C and use of nano and ultrafine WC powders significantly improved the mechanical properties. However, to further improve these properties, better grain growth inhibition is required by the use of precursor/chemical deposition methods. The K_{1C} and TRS can be improved by optimising the Ni binder amount (increasing the binder amount without significantly reducing the hardness) and the introduction of an additional annealing step during cooling after sintering, to help reduce the retained thermal stresses. These two modifications should improve the thermal shock and impact resistance.
- 8.2.3 For good mechanical properties using SPS and ball milling, the finest possible WC grain size used should be in the ultrafine range (approximately between 0.4 µm - 0.5 µm).
- 8.2.4 The ultrafine and nano 5M-7Ni grades are recommended for further testing as turning tools for Ti alloys, steels and cast irons, because of their high hardnesses, very good abrasion resistance during sliding wear and good chemical stability due to TiC addition.

- 8.2.5 The LPS WC-Co and WC-Ni grades are recommended for further testing as tools for interrupted face milling of Ti alloys, because of their high strength, thermal shock and impact resistance.
- 8.2.6 The 5N-Cr sample had a good combination of hardness, thermal shock, sliding wear resistance and impact resistance, and thus is recommended for applications where both light turning and milling processes are required.

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APPENDIX: OUTPUTS FROM THIS WORK

PUBLICATIONS

1. R.M. Genga, L.A. Cornish, G. Akdogan, E. Herselman, L. Bergstrom and F. Akhtar, Properties of SPS Manufactured Tungsten Carbides with an Alternative binder, Microscopy Society of Southern Africa (MSSA), ISBN 0-620-35056-3, 40 (2010) 66.
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PRESENTATIONS AND CONFERENCES

1. Powder Metallurgy Association of South Africa (PMA), South Africa. (2010-2013).
2. 10th International conference on the Science of Hard Materials, Cancun Mexico, (2014).

AWARDS

1. Powder Metallurgy Association of South Africa (PMA) Best Student Presentation (2010).
2. Powder Metallurgy Association of South Africa (PMA) Best Student Presentation (2012).
3. DST/NRF Centre of Excellence in Strong Materials Best Student Presentation (2013).
4. 1st runner up in the Institute of Materials, Minerals and Mining (IOM3), National Young Lecturer's Competition (2013).
5. Faculty of Engineering and Built Environment, "Prof S. Luyckx Postgraduate Prize", for the postgraduate student who has made an outstanding contribution to the fields of hard metals or powder metallurgy (2014).