

Investigation and Processing of 3D-polycrystalline Diamond Material

Master's Dissertation

prepared by

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DEDICATION

**I HEREBY WOULD LIKE TO DEDICATE THIS RESEARCH TO MY LATE
GRANDFATHER. THANK YOU FOR YOUR LOVE, SUPPORT AND CONTRIBUTION
THROUGHOUT MY UPBRINGING.REST IN PEACE**

DECLARATION

I Sibusiso Ngwenya student no. 473663 declare hereby that this work done in this research is my work. It is submitted for the degree of Masters of Science in Engineering to the University of Witwatersrand. It has not been submitted before for any degree or examination to this University or any other.

Sibusiso Ngwenya (473663)

ABSTRACT

The purpose of this work was to manufacture three dimensionally-structured polycrystalline diamond materials (3D PCD) with the aim of improving the resistance to wear of the polycrystalline diamond by crack deflection toughening induced by residual stresses. A further aim was to correlate the measured property with the microstructure of the material, to better understand how 3D PCD material concepts might be employed to improve material performance in application.

To achieve this, samples were made with composite spherical bilayer granules of grade 2 (mean grain size approximately 2 μm) and grade 22 (mean grain size approximately of 22 μm) diamond powder. The granules had a core/rim structure with the core comprising of grade 22 and the rim of grade 2 fabricated by granulation technique. The average volume fraction of the core versus the rim was 0.51. These granules were compacted and sintered on a 13 wt% cobalt tungsten carbide substrate under high pressure and high temperature (HPHT) conditions by a liquid infiltration and sintering process. Samples were then characterized by X-ray Diffraction, Scanning Electron Microscopy and Energy dispersive X-ray Spectroscopy. The fracture toughness of the material was measured, as well as its wear resistance by turning test methods. The fracture toughness of the resulting material was measured to be 7.02 ± 0.61 , with an improved wear resistance and better wear scar morphology when compared to samples made with only 2 μm diamond powders. Evidence of crack deflection was found without any loss of abrasion resistance. The crack deflection was caused by the presence of residual stresses generated within the matrix and the

dispersed phase, courtesy of the difference in thermal properties of the granule constituents. Samples made this way showed an improvement in wear resistance.

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LIST OF SYMBOLS

HPHT-High Pressure High Temperature

PCD-Polycrystalline Diamond

Hv-Vickers Hardness

m_w - Wet mass

m_d -Dry Mass

ρ -Density

c-Crack length

d-Diameter

K_{IC} -Fracture Toughness

E-Elastic Modulus

wt%-weight percentage

σ_{res} - residual stress

T-temperature

α - thermal expansion coefficient

ν - Poisson's constant

1. INTRODUCTION

1.1 Background and Motivation of Research

Ultra-hard materials can be classified or defined as materials that are extremely hard, with Vickers hardness greater than 40 GPa. The mechanical and physical properties of such materials make them unique and attractive in wear applications. To date many of these ultra-hard materials are intensively used in cutting and drilling applications in the manufacturing and oil and gas drilling industry. The interest in ultra-hard materials is attributed to their properties of high hardness, excellent compressive strength, excellent shear resistance, significant fracture toughness, high melting point, high chemical inertness and high thermal conductivity^[1].

The main ultra-hard material commercially used at present in the oil and gas industry is polycrystalline diamond (PCD).

PCD is made through a liquid phase sintering process, involving the sintering of diamond fine powders with the aid of a liquid metal, typically Co, Fe or Ni. Figure1 shows the resulting microstructure of a typical PCD material. The black phase is diamond, the grey phase is cobalt, left over from the liquid phase sintering process and the bright phase is WC contamination.

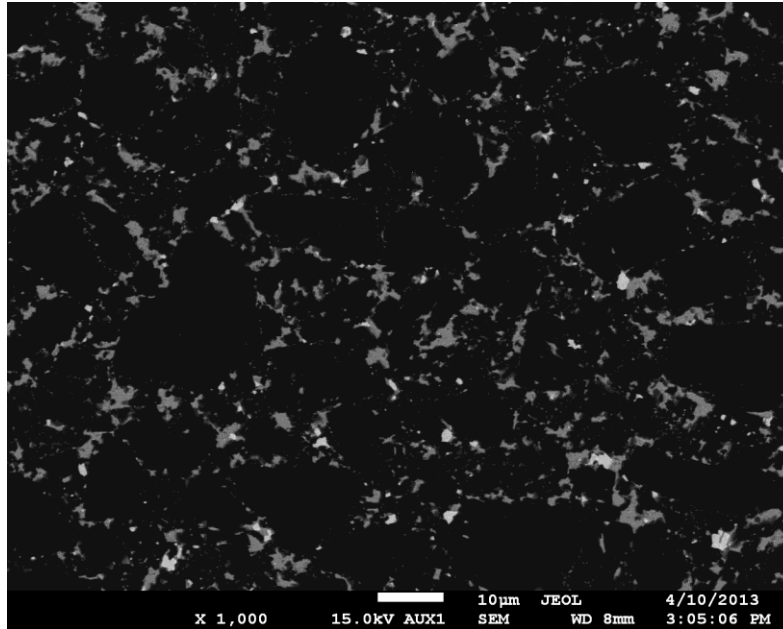


Figure 1: Microstructure of PCD, obtained by Scanning Electron Microscopy

Materials belonging to this family have excellent properties, such as very high hardness, and thermal conductivity as well as high compressive strength and chemical inertness; however they tend to fail by chipping. As a consequence the life span of the cutters used for oil and gas drilling and which have PCD as the main cutting component is reduced, thereby reducing the tool life and ultimately increasing operational cost.

Wear can be defined as the amount of material loss experienced during the grinding of that material against another surface. In the abrasive industry wear resistance is important and critically determines the efficiency and behavior of the tool. Therefore, finding ways of improving the wear resistance in such tools is of great importance. Shown in Figure 2 are sintered PCD -WC prototypes used in oil and gas drilling applications. Shown in Figure 3 is a Drill Bit tool with PCD cutters brazed onto it.



Figure 2: PCD syndrill cutter used in Oil and Gas drilling



Figure 3: PCD Drill bit tool used for Oil and Gas drilling

Although PCD cutters possess exceptional hardness and wear resistance, the continuous drive of the industry to ever-more demanding applications gives rise to situations in which even these exceptional materials experience rapid wear. A typical wear mode experienced by these tools is spalling and chipping. Both of these wear modes are fracture related behaviour and ultimately lead to the failure of the tools in application. During such processes, PCD fragments of various sizes are broken off, resulting in accelerated wear of the remaining part of the table, and consequent failure of the cutter. As a result the penetration rate of the drill bit is drastically reduced, resulting in productivity losses and unacceptably frequent replacement of the tools.

Therefore investigating the reasons and causes for PCD cutters chipping and spalling is imperative in order to find ways of reducing these behaviors when drilling. It is known that fracture related phenomena are dependent on the internal structure of the material undergoing fracture. Thus, modifying the internal structure of the PCD table in such a way as to deliberately engineer specific types of fracture within specific regions of the PCD table should ultimately contribute to the improvement of the performance of the tools in application. This strategy is referred to as 3D PCD, since the intention of this work is to modify the 3-dimensional structure of the PCD table so as to control the failing behaviour mentioned previously. Such structures were made and subsequently analyzed for their wear and fracture behaviour.

The central hypothesis is to produce a 3D strategy that entailed designing and producing a PCD material in a way that introduces non-uniformed residual stresses in the microstructure. This inhomogeneity of local stresses can interfere with crack propagation causing crack deflection and possibly branching, thereby toughening the material and improving wear resistance.

The 3D PCD composite materials generated and studied in this work were made using two different diamond grades. These were Grade 2 (meaning grain size approximately 2 μm) and Grade 22 (meaning grain size approximately of 22 μm) diamond powders. The PCD table was made by sintering granules comprising a diamond powder core-rim structure. A freeze granulation (core material), followed by fluidized bed granulation (rim material) process was used to achieve the above-mentioned core-rim structures (Section 3.2.2). It is expected that different grain size PCD will contain significantly different amounts of cobalt (residue of the liquid phase sintering process, see paragraph liquid phase sintering in section 2.3. As a result, different grades of PCD will have different thermal expansion coefficients, which will generate residuals interfacial stresses between the two phases on cool down after sintering. It is these residual stresses that are expected to cause crack deflection, thus increasing the toughness of the resulting, composite PCD.

Due to the cost of diamond, the above process was first developed on the model materials of alumina and titanium carbonitride composite. Specifically, the cores were made out of alumina through a freeze granulation and freeze drying process, followed by the deposition of the rim titanium carbonitride through a fluidized bed granulation process.

1.2 Scope of Research

The scope of this work began with a development of a technology for producing spherical bilayered granules of different materials. Thereafter, with the bilayered granules, produce a bulk composite material by sintering. This served as a training procedure, which later was applied in the production of the 3D PCD material.

This dissertation has 7 chapters. Chapter one (the current chapter) is the introduction. Chapter two gives the overview of the literature. Chapter three describes the experimental method used to make the samples. Chapter four gives results of the work done and the analysis of the samples made. Chapter five is the discussion of the results obtained. Chapter six contains the conclusions and finally Chapter seven gives the references.

2. LITERATURE SURVEY

There are two distinctive natural allotropes of carbon with different crystalline structures. These forms are known as diamond and graphite. Both of these allotropes have the same chemical structure but different physical properties. Diamond is a form of carbon formed under high pressure and high temperature. Diamond occurs naturally and can also be synthesized in the laboratory under high pressure and high temperature. The bonding and arrangement of the carbon atoms in diamond is the key to the excellent properties of this material.

2.1 Diamond

Diamond is a high pressure crystalline form of carbon which has two distinct crystallographic structures, hexagonal and cubic ^[1]. The cubic structure is the more common of the two. The arrangement of carbon atoms in this structure is such that the atoms form a tetrahedral network of sp³ hybridized C-C covalent bonds with an inter-atomic distance of 1.544 Å. This structure comprises two interpenetrating face-centered cubic lattices with a unit cell dimension of a=3.567Å.

The covalent bond between the carbon atoms is extremely strong and is characterized by the small length of 0.154 nm and bond energy of 711 kJ/mol ^[1]. The stacking of the face-centred interpenetrating cubic lattices is of the ABCABC sequence with the origin of the plane at 0,0,0 and $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$ positions as shown in Figure 3. Due to the symmetry and the tetrahedral (sp³ hybridization) bonding system, the diamond structure is isotropic and is denser than that of

graphite. Diamond is a metastable form of carbon polymorph and has excellent properties at room temperature (Table 1). These properties together with the slow conversion of diamond to graphite make diamond an excellent material for many industrial applications especially in abrasive, cutting and drilling industries ^[1]. Figure 4 shows the atomic structure of diamond.



Figure 4: Schematic structure of cubic diamond with carbon atoms Sp^3 hybridized forming a tetrahedral bonding network ^[1]

Table 1: Physical properties of Diamond and Graphite^[1]

Properties	Diamond	Graphite
Density (g.cm ⁻³)	3.52	2.09-2.23
Thermal conductivity (Wm ⁻¹ K ⁻¹)	600-1000	>-25-470
Thermal expansion (°C ⁻¹)	0.8±0.1x 10 ⁻⁶	1.2-8.2 x10 ⁻⁶
Hardness (GPa)	56-102	7-11
Elastic modulus(GPa)	1050	8-15
Unit cell (Å)	a=3.567	a =2.461 , c =6.708

2.2 Graphite

There are other forms of carbon allotropes; graphite is by far the most common of them. Graphite has the same chemical composition but different structure compared to diamond and therefore different physical properties. This material is soft, due to the arrangement of carbon in its structure. The structure of graphite consists of a succession of layers parallel to the basal plane of the hexagonally linked carbon atoms ^[1]. The distance between the carbon atoms in such a plane is 1.42 Å, and between successive sheets is 6.69 Å. Figure 4 shows the sheets of carbon atoms stacked in the hexagonal closed packed way, leading to the hexagonal crystal symmetry of graphite. The bonding between carbon atoms is covalent and sp² hybridized in the plane, whereas between the planes, the sheets are held together by weak Van der Waals forces ^[1]. The stacking sequence of these parallel layers is ABABAB.

The Van der Waals bonds holding the graphite carbon sheets together, make graphite weak, allowing for easy glide of adjacent basal planes against each other. This therefore makes graphite

not suitable for applications where diamond is used ^[1]. Figure 5 shows the atomic structure of graphite.

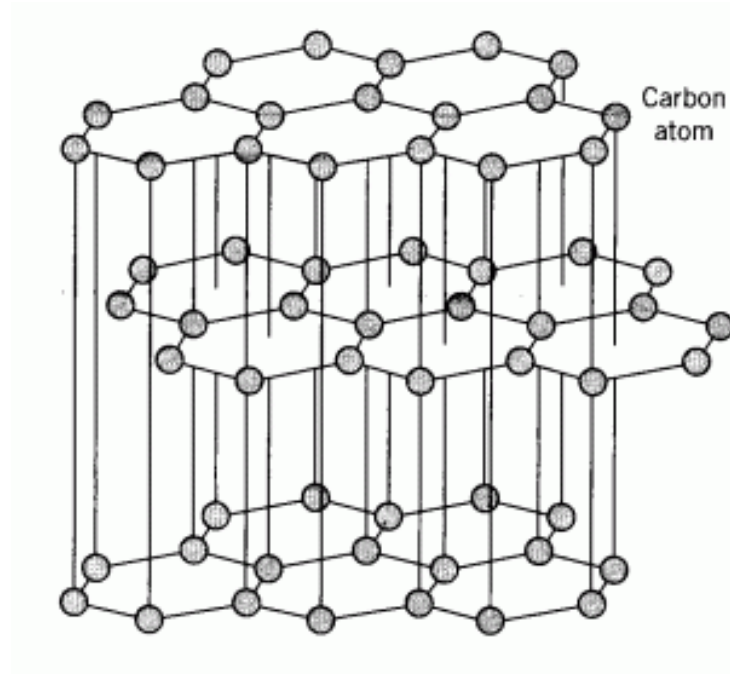


Figure 5: Schematic structure of stacked of carbon atoms forming graphite sheet ^[1]

2.3 Polycrystalline Diamond

Polycrystalline diamond (PCD) is a synthetic diamond material derived from diamond and is used in rock drilling, cutting and machining applications. This material is made by a liquid phase sintering process, using diamond powders and a sintering aid, typically cobalt. PCD is classified as ultra-hard due to its very high hardness. These materials also possess other excellent properties that set them apart from other ultra-hard materials. These include sufficient fracture toughness, excellent wear resistance and very high elastic constants. Many of the materials belonging to the PCD family have applications in abrasives industries. When the intended application is oil or gas drilling PCD is made into a cutter which is brazed onto a tool bit which is used to perform the drilling action. During processing diamond powder is sintered onto a Co-cemented tungsten carbide (WC) substrate by liquid infiltration using a belt type or anvil cubic press ultra-high pressure apparatus ^[2]. During this process, the liquid Co sintering aid is infiltrated onto the diamond powder compact, thus facilitating and promoting densification as well as diamond-diamond bonding. The amounts of cobalt infiltrated vary with the grain sizes of diamond sintered. Coarser grain diamond plastic deform more than the fine grain diamond during sintering. This allows rearrangement of particles which leads to lower porosity than that of fine grain diamond. Therefore, during sintering lower residual amounts of cobalt wets the coarser grain layer.

The high pressure and high temperature (HPHT) parameters commercially used range from 5-7 GPa in pressure and 1500°C-2000°C in temperature ^[3]. These conditions allow the diamond compacts to sinter and densify forming a polycrystalline solid mass, which can be processed into different tool shapes. The amounts of cobalt infiltrated vary with the grain sizes of diamond

sintered. Coarser grain diamonds undergo plastic deformation more than the fine grain diamond during sintering. This allows rearrangement of particles which leads to lower porosity than that of fine grain diamond. Lower residual amounts of cobalt infiltrate through the coarser grain layer, conversely to fine grain layer.

Most of the conventional sintered PCD compacts are sintered through the addition of metallic liquid phase sintering aid. These are transition metals such as cobalt, nickel and iron. Of these metal solvents, cobalt is the most commonly used additive ^[4]. This is because cobalt is the most suitable binder for WC due to its high carbon solubility. The same property is critical for the efficient diamond liquid phase sintering process ^[3,4]. However, there are other unconventional non-metallic sintering agents which are also used for PCD fabrication. These catalysts are alkaline earth metal carbonates, such as CaCO_3 , MgCO_3 and SrCO_3 ^[5]. Ueda et al. ^[5] investigated these carbonates and have discovered that they behave differently from cobalt when used as PCD liquid phase sintering aids. They enhance the sintering ability and prevent graphitization of diamond crystals by suppressing diamond oxidation. The role of the metal and non-metal catalysts in PCD sintering is to promote and catalyze direct bonding of the diamond grains and to keep the constituents bound together.

The finished compacts are round disks comprising a thin layer of sintered PCD bonded to a cemented tungsten carbide substrate. The thickness of the diamond table ranges from 0.5mm-4mm and the diameter of the disk, range from 12.5mm-50mm ^[4].

One of the major problems encountered when using PCD tools is their phase instability at high temperatures. At temperatures exceeding 800°C cobalt catalyzes the conversion of diamond to graphite ^[4,5]. This process is called graphitization. Graphitization is detrimental to the cutter as it

compromises the desired PCD properties, thus decreasing the tool life of the cutter. This can be avoided either by decreasing the cutting speeds employed or by increasing the PCD table's thermal stability by various means. Graphitization results in local weakening of the PCD structure, leading to small chips being removed from the cutting edge. This process is called chipping and results in the cutter tool life decreasing significantly ^[5, 6].

Because of the graphitization of PCD cobalt-sintered PCD tools cannot be employed at temperatures above 800°C. In addition, cobalt-tungsten carbides and cobalt-solid solution form at elevated temperatures. This occurs since cobalt has a high affinity for carbon.

In a study done by *Molinari et al.* ^[6] it has been shown that graphitization of diamond is induced by both high temperatures and oxidation, and is catalyzed by cobalt. In this study the authors proved that the deterioration of the properties of PCD is attributed to the formation of graphite, some of which dissolves into cobalt forming a solid solution. By adding low amounts of tin (Sn), the authors observed that this additive inhibited graphitization and prevented cobalt-carbon solid solution from forming. The protective action of tin was attributed to its strong affinity for oxygen which prevented the oxidation of diamond at high temperatures. Based on this study it was concluded that the root cause of chipping of Co-sintered PCD is its thermal instability and its sensitivity to an oxidizing atmosphere ^[6].

Thermal instability also induces residual stresses within the grain boundaries and initiates micro-cracks that propagate easily, thus causing chip formation. This happens because of the compromised PCD structure due to the partial conversion of the PCD phase to graphite ^[6]. This phase transformation is associated with a volume expansion caused by the difference in density between the two phases.

Another important stress factor playing a major role in the life of the PCD cutter table is the residual stresses caused by the difference in thermal expansion coefficient of PCD, tungsten carbide and cobalt sintering aid. This produces typically compressive residual stresses in the PCD table and very high shear stresses at the interface of diamond and the substrate. These stresses are acquired during cooling from sintering temperatures to room temperature ^[7]. *Paggett et al.* ^[8] measured these stresses and found that there are micro and macro residual stresses. The micro stresses were found present in the cemented WC substrate. This was due to the mismatch in the coefficients of thermal expansion between the binder and the tungsten carbide. Thermal macro-stresses were present in the PCD table as well as in the substrate composite. These too are due to the large mismatch of the thermal expansion of the PCD and the substrate. During cool down after sintering the PCD thermally contracts less than the substrate. Therefore, compressive stresses are generated in the PCD layer and tensile ones in the substrate. The differential contraction was reported to generate a bending moment associated with the asymmetry of the PCD layer and the substrate system which subsequently causes a stress gradient to develop through the thickness of the cutter ^[7, 8].

Tze et al. ^[9] also reported that stresses in the diamond phase were compressive and can be as high as 1.4 GPa. Simultaneously large tensile stresses of the order of 500 MPa are induced within the cemented carbide substrate. During drilling the rock-cutting action generates loads on the cutter which translate into externally applied cutting stresses. The residual stresses combined with externally applied stresses during drilling could lead to tool failure. The principal stresses (compressive and tensile) are mainly in the radial and axial directions with prominence in the axial direction ^[9]. It is imperative that the axial stresses are minimal, particularly if they are

tensile. Such stresses can be detrimental to the cutter resulting in large PCD flakes that easily break off. On the other hand, compressive stresses in this direction are advantageous, since they can suppress the effect of externally applied tensile stresses acting along the same axis.

The offset of these stresses induces shear stress near the specimen edge at the interface between the diamond and carbide substrate ^[9]. Although shear stress at the PCD-substrate interface can be very high, very strong bonding has ensured that in modern cutters delamination at this point no longer occurs. Also, shaped interface designs, innovated by the cutter manufacturing companies, have further helped suppress this mode of failure ^[10]. Cutting stresses generated during the rock-cutting action, combined with residual stresses, are reported to generate cracks at the cutting tip, early in the life of the cutter. These cracks are almost parallel to the PCD – substrate interface, but at a shallow angle to the PCD table top. They can propagate underneath the table top, aided by cyclic repeated external stresses caused by the cutting action until they become critical and remove a large piece of the PCD table, thus causing early deterioration of the cutter.

Smooth Wear and *Gross failure* have also been reported as other modes of PCD tool failure. This was reported by *Tze-Pin et al.* ^[9] in their study of wear and failure mechanism of PCD compacts used on drill bits. During laboratory rock-cutting tests and field operations they observed tool failure by smooth wear and gross failure. Smooth wear occurs by individual diamond grains being polished away by combinations of high mechanical and thermal loads ^[11,12]. Very high local temperatures are generated by friction at the point of contact between the cutter and individual quartz/rock grains. These local high temperatures damage the diamond by promoting graphitization or oxidation. This results in a progressive and rapid removal of the diamond without causing it to fracture in a macroscopic sense ^[12].

In gross fracture, the crack nucleates on the curved (edge of cylinder) surface of the PCD table of the cutter and propagates towards the centre removing a circular chip with a fracture surface that is plane and normal to the cutting tool table. This damage occurs when the formation changes and the bit runs into a hard assembly of rocks. *Tze-Pin et al.* ^[9] found that this mode of failure is only attributable to mechanical overload. This conclusion was arrived at on the basis of the short period of time in which the fracture occurs.

In addressing this problem, an approach of producing a material from plurality of granules having a core-rim structure as shown in Figure 6 was proposed. When these structures are sintered together they form a PCD material that will have two phases distributed throughout its volume. It is therefore visualized that the resulting PCD will have a number of interfaces (Figure 7), to form the boundaries between different residual stresses inherited during cooling after sintering. These stresses will act as crack deflectors. This should give rise to a better, more crack propagation-resistant PCD, thus helping to address the problems described above.

2.4 Residual Stresses

The residual stresses in PCD cutters are generated during cooling from sintering temperatures. These stresses are largely due to the mismatch of thermal expansion coefficients of the various components out of which the cutter is made. Specifically, cobalt, the binder commercially used in PCD synthesis has a higher thermal expansion co-efficient ($16.8 \times 10^{-6} \text{K}^{-1}$) than diamond ($4.5 \times 10^{-6} \text{K}^{-1}$). Cobalt therefore contracts faster during cooling than diamond, thus inducing tensile stresses caused by the constraints of the diamond skeleton. It is known that the cobalt content in PCD varies with diamond grain size, specifically increasing with decreasing value of that parameter^[13,14]. It is therefore expected that the thermal expansion coefficient of PCD will be a decreasing function of diamond grain size. In a composite PCD material made out of two or more different grades of PCD, it is expected that, during cooling after sintering, residual stresses are set up, caused by different rates of contraction for these different grades during this process. In a simplistic model of two strips of PCD, of different grain size, bonded together, the fine grain PCD would go in tension during contraction caused by cooling and the coarse grain PCD would go in compression. The situation is more complex in a composite PCD material, comprising a matrix of Grade A and inclusions of Grade B PCD, but the basic principle of tensile and compressive stresses being set up in the material will still apply. Such residual stresses will affect the propagation of a crack advancing through such a material, causing it to deflect, thus improving the fracture toughness of the material^[13,14].

2.5 Toughening techniques

Ceramic materials are inherently hard and strong due to the nature of the mainly covalent bonding system present in their structure^[15,16]. The same strong bonds that give ceramics their

hardness and strength also inhibit dislocation flow in these materials. This, as a result reduces the usual crack blunting that happens in ductile materials, thus making ceramics particularly brittle [15,16]. The resulting low fracture toughness is often a limiting factor in the applicability of ceramics in various challenging industrial processes and systems. Therefore various ways of improving the fracture toughness of ceramics have been used over the years [16, 17,18]. These include crack arrest, crack bridging, frictional toughening, transformation toughening and crack deflection [17, 18]. Crack deflection is the toughening mechanisms that this work seeks to use in improving the fracture toughness of PCD. Crack deflection occurs when a crack tip encounters inhomogeneity in the microstructure or local stresses in the material. These inhomogeneities are generally caused by impurities, porosity, dislocations and local stresses [19].

In multiphase material where there are residual stresses caused by thermophysical properties mismatch, crack deflection is expected to occur [17, 18,19]. This effect is also expected to occur in the case of multiphase PCD, made into a 3D architecture through the sintering of diamond powder granules comprising two grades of diamond particles, arranged in a core-rim structure, as shown in Figure 5 below. It is expected that, when these granules are sintered, a dual phase composite will result, comprising a matrix made from the sintering of the rim material into one continuous phase, with the core diamond particles sintered into particulate inclusions within this matrix, as shown in Figure 6. The residual stresses generated in the resulting materials were calculated with the aid of a mathematical model generated by *Selsing et al.* [20] using the formula given in in eq. (1) below.

$$\sigma_{res} = \frac{\Delta\alpha(\Delta T)}{\frac{1+v_m}{2E_m} + \frac{1-2\nu_p}{E_p}} \quad (1)$$

Where σ_{res} is the residual stress in the dispersed particle, at the matrix-particles surface interface, $\Delta\alpha$ represents the difference between the thermal expansion co-efficient of the matrix and the secondary phase ($\Delta\alpha = \alpha_m - \alpha_p$), if $\Delta\alpha$ is negative the secondary phase is under tension and if $\Delta\alpha$ is positive it is under compression; E is the elastic modulus and ν is the Poisson's ratio. The subscripts “m” and “p” represent the matrix and the dispersed phase. ΔT ($T_o - T_{ref}$) is the difference between the temperature where relaxation of residual stresses occurs (1000°C) and room temperature (T_o). Table 4.4 has the parameters used to calculate internal stresses present in the 2/22 μm PCD. The corresponding stresses in the matrix are given by eq. 2 and 3 below ^[20,21]

$$\sigma_r = -\sigma_R(a/r)^3 \quad (2)$$

$$\sigma_t = \frac{1}{2} \sigma_R \left(\frac{a}{r}\right)^3 \quad (3)$$

Where: σ_r , is the radial stress component, σ_t is the tangential stress component, σ_R is the stress inside the cobalt phase and r is the radius. a is the radius at the interface.

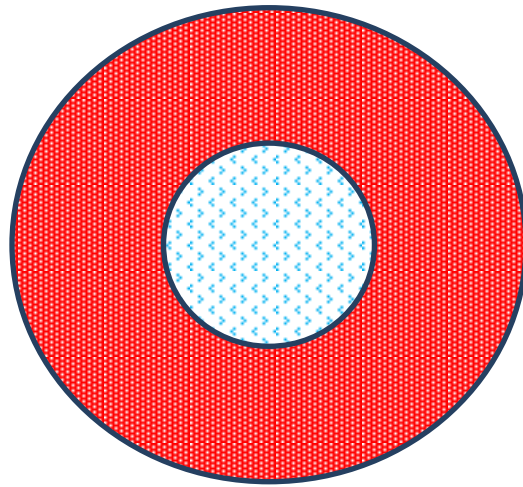


Figure 6: Schematic drawing of the Bilayered (core-rim) diamond granule

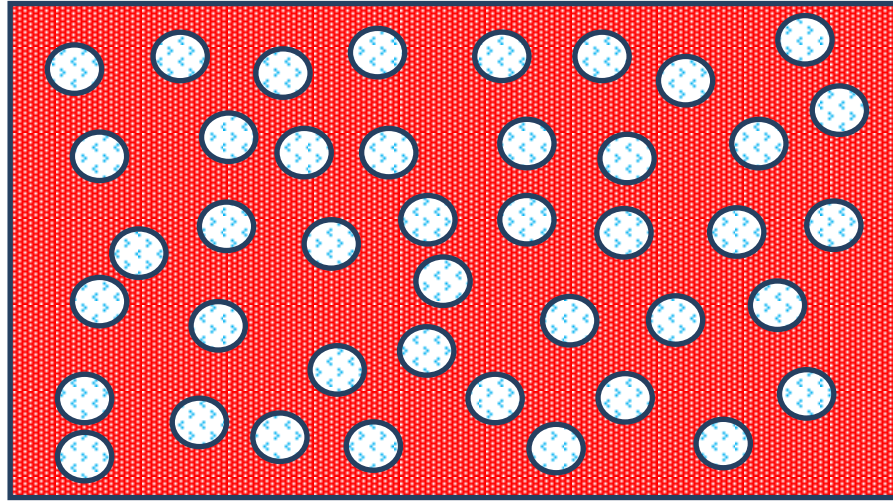


Figure 7: Schematic drawing of a sintered bulk PCD with a plurality of interfaces

It is known that structures of the above type cause crack deflection and thus increase the fracture toughness of the resulting ceramic^[21]. Therefore, it was proposed to make PCD comprising two phases, each from a different grade of PCD, the difference originating from different diamond powder particle sizes used to make the core and the rim of the starting granules, as shown in Figures 6 and 7 above. The resulting PCD (which we will refer to as 3D PCD) will be characterised for density, phase composition, microstructure, and fracture behaviour and wear resistance.

Diamond powder is very expensive and sintering requires very costly ultrahigh pressure sintering techniques. Therefore, the techniques for making the two-phase composites were first developed on a model material made out of Al_2O_3 and $\text{Ti}(\text{CN})$. Chapter 3 below gives the experimental techniques used to make the composite materials, Chapter 4 gives the results obtained, Chapter 5 contains the discussion of these results and Chapter 6 gives the conclusions.

3. EXPERIMENTAL METHODOLOGY

3.1 Introduction

This chapter describes the experimental procedures used to do this work as well as the preparation, manufacture, testing and characterization of the alumina, titanium carbonitride and diamond powders. A trial run using $\text{Al}_2\text{O}_3\text{-Ti(CN)}$ was first performed as a training procedure to prepare for the actual processing method of making 3D PCD material. This section is divided into two parts, the first part being the alumina-titanium carbonitride and the second part diamond.

3.2 Alumina – titanium carbonitride

3.2.1 Materials and preparation

Alumina powder (AKP50) obtained from Sumitomo Chemical Co. Ltd., with average particle size of 0.1-0.3 μm was used together with organic solvents obtained from Glassworld & Chemical Suppliers Cc. In addition, titanium carbonitride powder obtained from American Elements Co. Ltd with average of 10-20 μm . Figure 8 and 9 shows the particle size distribution of the two powders mentioned.

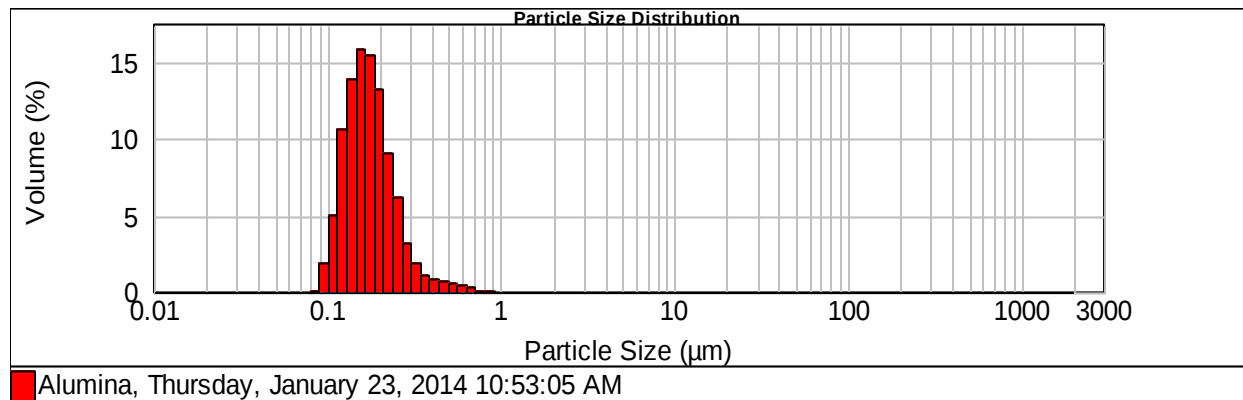


Figure 8: Particle size analysis of AKP50 Alumina

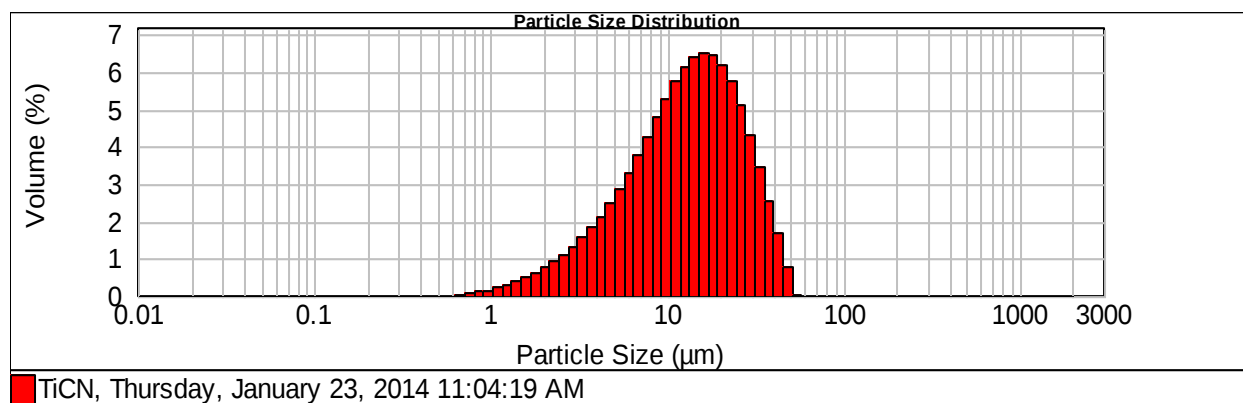


Figure 9: Particle size analysis of TiCN

Table 2: Materials and organic solvents

Material	Supplier
Alumina powder	Sumitomo Chemical Co. Ltd
Polyvinyl Alcohol	Glassworld & Chemical Suppliers Cc
Glycerol	Glassworld & Chemical Suppliers Cc
TiCN	American Elements Co. Ltd
Epoxy resin	IMP Innovative Solutions (Pty) Ltd

A slurry mixture using the materials shown in Table 2 was prepared. In a 200 ml beaker. 13.3 g of polyvinyl alcohol was weighed and poured followed by the addition of 1.5 g of glycerol. Using a graded glass cylinder, 5ml of de-ionised water were measured and added to the mixture. This was mixed with a magnetic stirrer until homogenous. In the same mixture, 100 g of alumina powder was added followed by an addition of 100 ml of de-ionised water. The slurry was mixed for 1 hour prior to granulation. The stirring speed used was 500 rpm.

3.2.2 Granulation: Freeze and Fluidized Bed granulation

This section describes the two granulation techniques used to make spherical bi-layered granules of alumina with titanium carbonitride(obtained from American Elements Co. Ltd) as a coating layer. The first technique was freeze granulation. In this technique the alumina core of the bi-layered granule was made. The second technique used to make the composite granules was fluidized bed granulation, where the alumina core granules were coated with titanium carbonitride slurry.

Freeze Granulation

The alumina granules were made by using the setup shown in Figure 8. The process entailed placing the beaker with the slurry next to the spray chamber containing liquid nitrogen as shown in the image. One end of the tubing was inserted into the slurry and connected through peristaltic pump to the spray nozzle which was inserted in to the spray chamber. The granules were made by spraying and atomising the slurry into granules in the liquid nitrogen. The sprayed droplets were thus frozen solid. The frozen granules were then dried in freeze dryer. Figure 9 shows schematically of the process. The freeze dried granules were then used to extract the target granule size range of 125-212 μm by sieving.

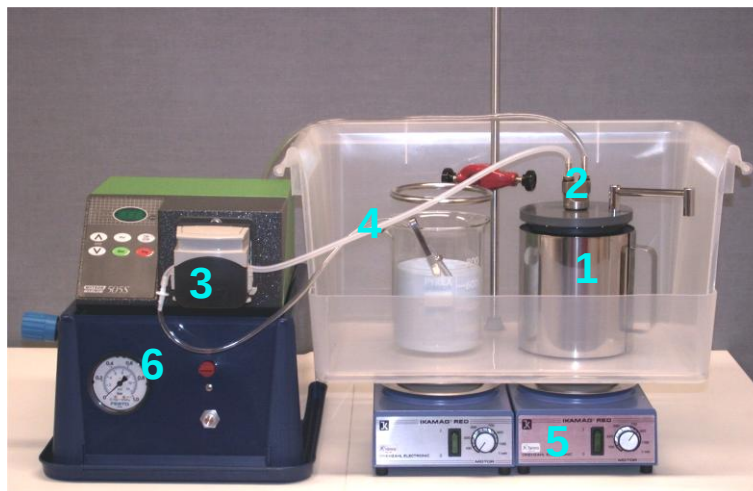


Figure 10: LS2 Freeze granulator with components (1) Spray Chamber (2) Spray Nozzle (3) Peristaltic Pump (4) Slurry Feed tube (5) Magnetic Stirrers (6) Air Pressure control ^[23]

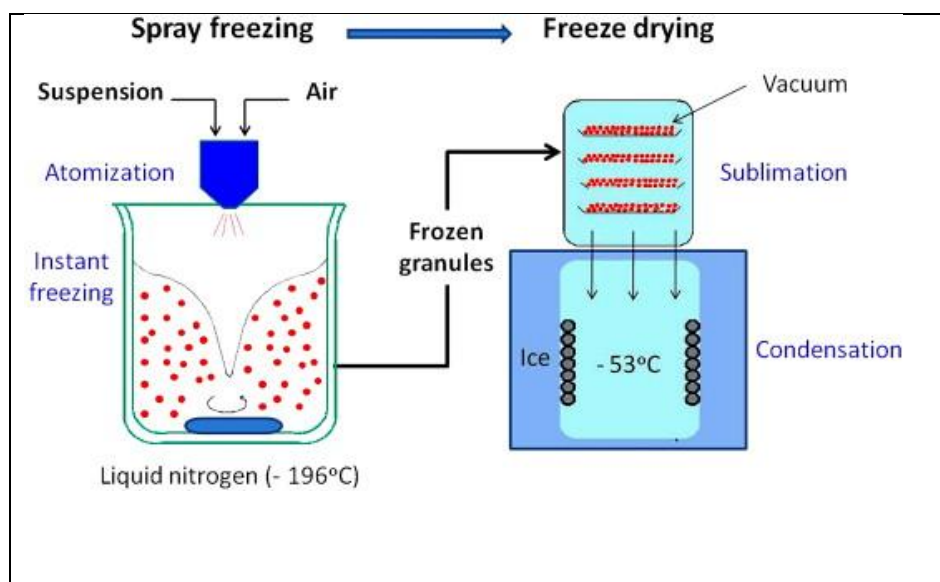


Figure 11: Schematic Image Freeze granulation and Freeze drying of granules ^[24]

Fluidized Bed Granulation

In a separate beaker, a solvent-based slurry of titanium carbonitride with 13.3 g of polyvinyl alcohol with the addition of 1.5 g of glycerol binder and 100 ml distilled water was prepared prior to coating. This was done by first weighing the 13.3 g of polyvinyl alcohol in a beaker. In the same beaker a 1.5 g of glycerol was added. 100 ml of distilled water was then poured into the 500 ml beaker. The same process used for the alumina slurry was also followed to make the titanium carbonitride slurry. The mixture was stirred with a magnetic stirrer at 500 rpm for 1 hour.

A Glatt Fluidized Bed machine shown in Figure 13 was then used for coating the alumina granules with the titanium carbonitride slurry. In this process the freeze granulated alumina granules previously prepared with the size range 125-212 μm were placed inside the bed chamber of the Glatt machine. Inside the chamber the granules were suspended by warm air

flowing vertically from underneath the chamber as shown in Figure 12. The titanium carbonitride was then fed into the chamber by a spraying action. This spraying action coated the suspended alumina granules. The composite granules were then dried and removed from the Glatt fluidized bed machine shown in Figure 13. The granulator operating parameters used are shown in Table 3.

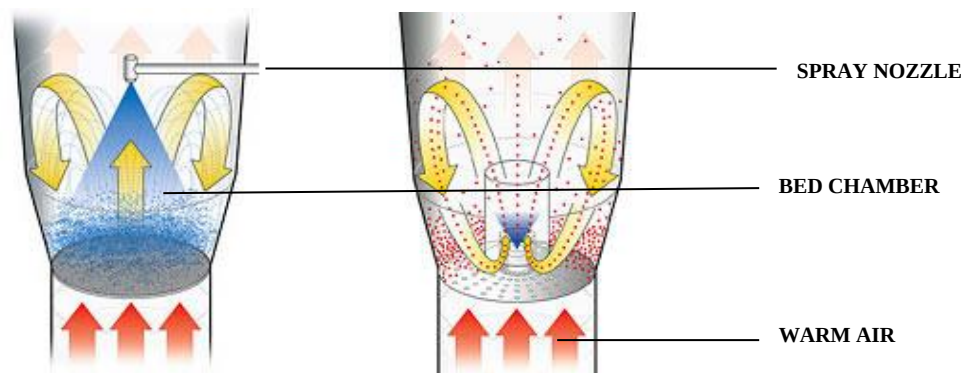


Figure 12: Fluidize bed granulation process ^[25]



Figure 13: Glatt Fluidize Bed granulation equipment

Table 3: Glatt Fluidize Bed parameters used

Fluidized Bed chamber temperature	40° C
Nozzle pressure	0.5 bar
Slurry flow rate	3 rpm
Air Flow	90 m ³ /h
Time	15 mins

After coating, a few of the granules made were cold mounted onto an epoxy resin obtained from IMP Innovative Solutions (Pty) Ltd. These granules were mounted on a flat surface of epoxy the polymer, to allow grinding and then polishing. Grinding was done with a LECO GP20 GRINDER while polishing with a LECO GP20 POLISHER machine. Grinding was done though subsequent treatments with 400, 800 and 1200 mesh emery paper pads. The sample was then rinsed with water and dried, and polished with a 6 µm, followed by a 1 µm diamond polishing pads.

3.2.3 Binder removal

The composite coated granules were placed onto an alumina refractory boat which was then placed in a tube furnace. The aim of this operation was to remove the organic binders used for granulation. The atmosphere used was 10% hydrogen with argon as balance. The heat treatment profile is shown in Table 4.

Table 4: Heat treatment profile for binder removal

Profile	Temperature (°C)	Time (hours)
Ramping	20°C to 600°C	2
Stationary	600°C	3
Cooling	600 to 25°C	natural

3.2.4 Spark Plasma sintering

Densification of granules was done in a FCT SP D 5 Spark Plasma Sintering furnace. The sintering temperature used was 1800°C with an applied pressure of 35 MPa. A temperature upramp rate of 150°C/min was used. The samples were sintered in vacuum for 5 minutes. In this process ceramic particles densify and form a bulk solid material.

3.3 PCD

A process similar to the one used in making alumina titanium carbonitride granules was also followed in making diamond-diamond granules. In this case, grade 22 diamond powders was used to make the core of the bi-layered granules, with grade 2 diamond powder used to make the rim of these structures. Different organic binders to those used in the training procedure were used for diamond granules preparation..

3.3.1 Materials and preparation

In a 200 ml beaker, solvent based slurry of grade 22 diamond powder was prepared with a similar procedure as mentioned in section 3.2. However the organic binders used were not the same. Due to the propriety nature of the information concerning the binders used, no details

concerning their composition will be given here. The slurry was mixed for 1 hour by stirring at 500 rpm. Table 5 gives the information on the components used to make the diamond composite granules.

Table 5 Diamond powder and binder used

Material	Average particle size	Supplier
Diamond powder(grade 2)	2 μ m	Element 6 (Pty) Ltd
Diamond powder(grade 22)	22 μ m	Element 6 (Pty) Ltd
Organic binders batch X332	-	Element Six Proprietary information.

3.3.2 Granulation

A similar procedure similar to the one described in section 3.2.2 was followed in making the diamond granules. After making the bi-layered granules, they were screened by sieving. The targeted granule size range was 250-212-125 μ m.

3.3.3 Pre-sintering preparation

Due to the nature of diamond, sintering of PCD was done following the method described Ringwood et al ^[25]. The advantage of this method was that it allowed better packing density of the diamond also the cobalt binder filled the voids thereby promoting inter diamond- diamond bonding. This method entails sintering a diamond powder onto of tungsten carbide-cobalt substrate.

2 g of diamond bi-layered granules were placed into 18 mm outer diameter (OD) niobium cups followed by placing a WC-13% Co substrate with the outer diameter of 17.9 mm upside down

into the same cup, on top of the diamond charge. There were 20 samples prepared this way and then placed in a Balzers vacuum furnace for 15 hours in an air atmosphere. The optimum temperature used was 370° C, at which temperature all organic binders evaporated and were totally removed from the diamond

3.3.4 Out-gassing

Samples were then placed in a TORVAC vacuum furnace (Figure 14) to remove all unwanted gases and impurities that might oxidize the diamond before sintering. Samples were out-gassed for 10 hours at 1050° C. After out-gassing the cups were encapsulated in titanium cups and sealed by Electron Beam welding.



Figure 14: Torvac equipment used for removing unwanted gases

3.3.5 Sintering: High Pressure High Temperature (HPHT)

All samples were sintered on 13wt%Co-WC substrates. The sintering was done at high pressure and high temperature conditions using a belt type apparatus ^[26, 27]. The high pressure capsule

used for the sintering experiments is shown in Figure 15. The pressure used ranged between 5-6 GPa with temperature between 1400° C and 1500° C. Complete densification was achieved and the samples did not have any unsintered areas. The sintering was in accordance to the Element 6 diamond sintering standard. For comparison purpose samples of 22 μm PCD were also sintered.

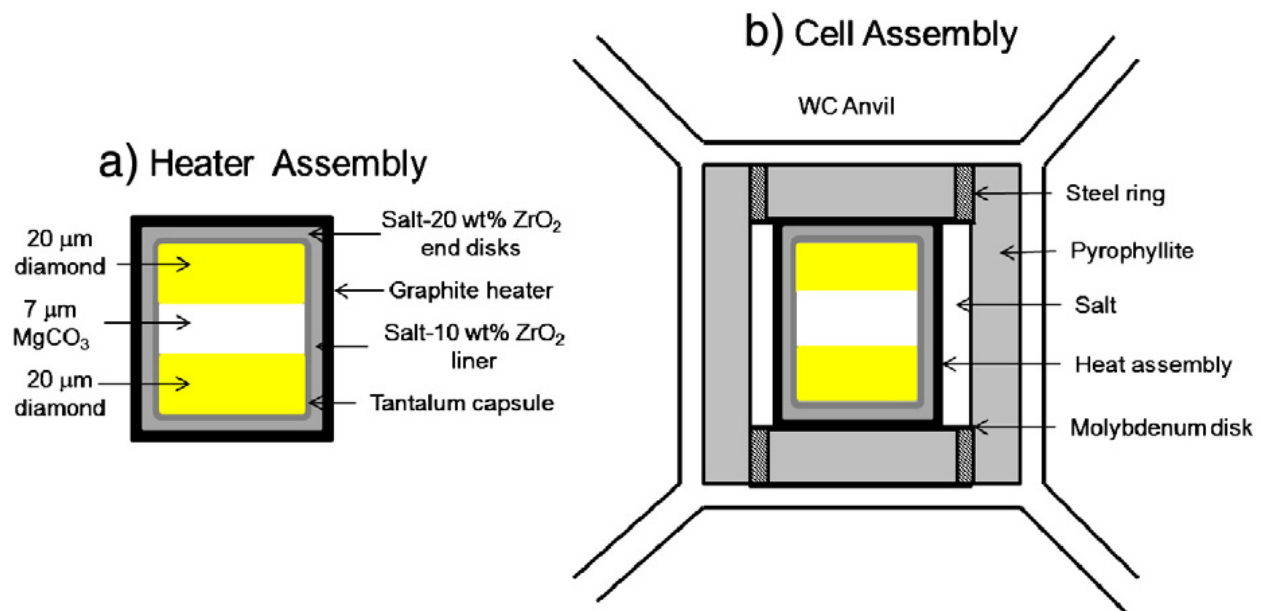


Figure 15: Example of cubic press used to sinter PCD specimen ^[26,27]

3.3.6 Materials preparations after sintering

Prior to characterization, samples were subjected to various preparation processes such as cutting, lapping, grinding and polishing.

Alumina-Titanium carbonitride

Before cutting, $\text{Al}_2\text{O}_3\text{-Ti(C,N)}$ samples were sand blasted to remove any contamination from their surface after sintering. They were then cut using a Streuers Socotom-10 into two halves. The fresh, cross-sectional surfaces were then ground using diamond paper. This operation was carried out using a LECO GP20 GRINDER machine. Subsequently the samples were polished on the LECO GP20 POLISHER machine. The polishing started with 6 μm , followed by 1 μm polishing pads with the required lubricant liquids. The samples were then microscopically inspected to determine the amount of material removed and ascertain that the polishing achieved was of the required quality.

PCD

PCD samples after sintering still had niobium and titanium cups used during sintering attached to them; these cups were removed by Outer diameter (OD) grinding and lapping. This was done to expose the sintered PCD and prepare the samples for characterization.

Prior to characterization PCD samples were cut by EDM (Electrical Discharge Machining) to expose and reveal the cross sectional area. Samples were then polished for microstructural analysis. This was done according to the Element 6 standards.

3.4 Characterization

In this section a brief description of the characterization techniques used to analyse the samples is given.

3.4.1 Density

The density of the samples was determined by the Archimedes principle. A piece of sample was weighed to obtain the dry mass (m_d) and then suspended in water and weighed while suspended. The recorded mass was the wet mass (m_w). Measurements were done twice with the average mass taken and used to calculate the density. The volume of the sample was calculated by subtracting the dry mass from the wet mass: The density was then calculated using equation 2. Table 6 shows the densities of the component materials used to make the composites studied in this work.

$$\text{Volume displaced} = m_d - m_s$$

$$\rho = \left(\frac{m_d}{m_d - m_s} \right) \rho_{\text{solvent}} \quad [28] \quad (4)$$

Table 6: Theoretical density of materials

Material	Density(g.cm ⁻³)
Alumina	3.99
Diamond	3.52
Cobalt	8.90
Tungsten carbide	15.63
TiCN	5.09

3.4.2 X-ray Diffraction

X-ray diffraction analysis was performed using Xpert Pro model XRD diffractometer. The parameters employed to get the required traces are given in Table 7:

Table 7: X-ray Diffraction parameters used

Tube type	Cobalt
Voltage	40 kV
Current	40 mA
2 Theta range	20-100
Step size	0.02 °

3.4.3 Scanning Electron Microscopy

Scanning Electron microscopy images and Energy Dispersive X-ray Spectroscopy results were obtained using OXFORD INCAPENTA-FETX3 JEOL JSM 7500F Field Emission Scanning Electron microscope.

3.4.4 Hardness testing

The hardness of the sintered samples was measured by using a Crayford Kent Vickers limited Macro hardness machine. The load used was 30 kgf with indentation and crack length measured using an optical microscope with 200X magnification.

The Vickers hardness was determined using Equation 3:

$$H_v = 1.8544 \frac{P}{d^2} \quad [29] \quad (5)$$

Fracture Toughness was calculated using Anstis Equation 4:

$$K_{IC} = 0.016 \left(\frac{E}{H_v} \right)^{1/2} \left(\frac{P}{C^{3/2}} \right) 1000 \quad [29] \quad (6)$$

Where **d** is the average length of the diagonal measured in millimeters, **P** is the force applied in Newton. **E** is the elastic modulus of the sample in MPa, **H_v** is the hardness of the materials and **C** is the crack length in millimeters.

3.4.5 Fracture toughness

The Brazilian test ^[30, 31] was used to measure the fracture toughness of the PCD samples. The preparation of samples for this test entailed Electron Discharge Machining (EDM), which was used to separate the PCD disc from the substrate. The extracted PCD discs were laser cut into smaller ones with an average diameter of 8.5 mm and average thickness of 1.75 mm. A notch of 4mm length and depth of 1 mm was inserted into the discs by laser cutting. Samples were then tested according to the Brazilian test ASTM standard for fracture toughness using an Instron 5500R Universal tester. Fracture toughness of PCD samples were calculated using equation 7 below. Images of the Brazilian disks samples are shown in Figure 16.

$$K_{1C} = 0.016P(k/(1-k) (1-0.6038k+ 1.672k^2 -1.698k^3)t(3.14R)^{1/2} \quad [32] \quad (7)$$

Where: P is the fracture load; t is the specimen thickness; R is the radius of the specimen; k is the ratio (2a/D) of the notch length to the specimen diameter D.



Figure 16: PCD specimen disk prepared for Brazillian Test

3.4.6 Elastic properties

The elastic properties of the samples were measured by Pulse echo ultrasonic technique using a Krautkramer USIP 12 with a longitudinal probe frequency of 50 Hz. The elastic properties measured were elastic modulus, shear modulus, bulk modulus and Poisson's ratio.

3.4.7 Paarl granite and Vertical Borer Test

PCD samples were tested for wear by PGT (Paarl Granite Test). These samples were locked into a sample holder and tested by machining a Paarl granite rock bar until failure of samples. The amount of rock removed was measured per grinding pass of the PCD cutter until failure. This test was done for 10 minutes. Due to the intellectual property associated with this test, testing

parameters used will not be disclosed. A vertical borer test is a test similar to Paarl Granite Test, but more aggressive. A similar procedure was followed to do this test.

3.4.8 Crack propagation

In order to analyse crack propagation, a crack was introduced in the sample by carefully placing the sample in between two steel rollers (Figure 17). Crack initiate in the PCD table by squeezing the two rollers against the sample. To avoid the crack propagating through the entire sample, the process was stopped when the crack initiated. The purpose of pre-cracking the PCD sample was to qualitatively study crack propagation and to observe any evidence of crack deflection. The pre-cracked sample was then analysed by SEM.

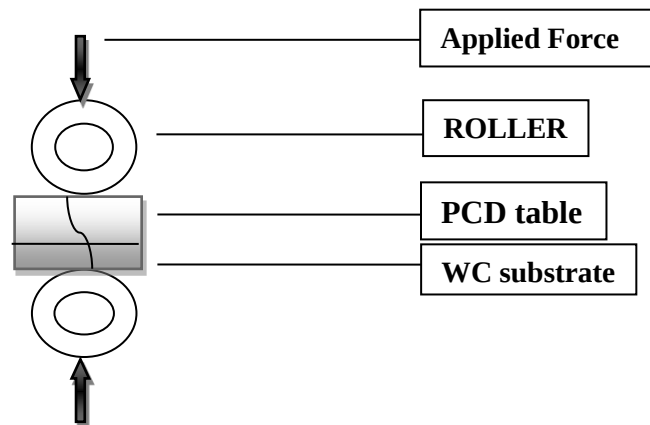


Figure 17: Sketch showing pre-cracking of PCD Specimen

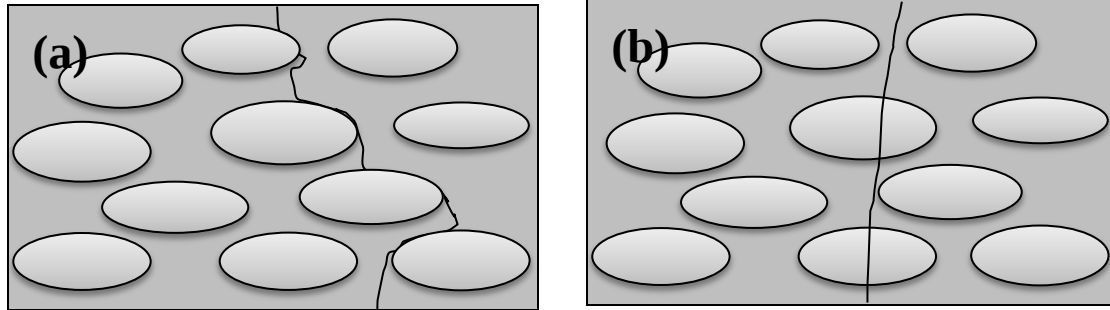


Figure 18: Schematic sketch showing (a) Crack deflecting away from the dispersed phase
(b) Crack propagating through the dispersed phase

4. RESULTS

In this Chapter, all the results of the work done for both the alumina-titanium carbonitride as well as for diamond are presented.

4.1 Alumina- titanium carbonitride

Figure 19 shows, the spherical alumina granules made by freeze granulation with size range of 125-212 μm . The granules were then coated with titanium carbonitride slurry using a Glatt Fluidize bed granulation machine. Figure 20 shows the coated alumina particles with some of the alumina visible in the core. The overall size range of the granules was 200-300 μm . In order to observe the bi- layered structure and expose the cross-sectional area, granules were mounted onto an epoxy polymer resin. The polymer resin was ground using 400 and 600 μm diamond mesh grinding discs on LECO GP20 GRINDER machine and polished using a 6 μm polishing pad on a LECO GP20 POLISHER long enough to be able to see the cross-sectional area under the microscope. Figure 20 shows the images of the granules after coating and also after ground to reveal their core-rim structure.

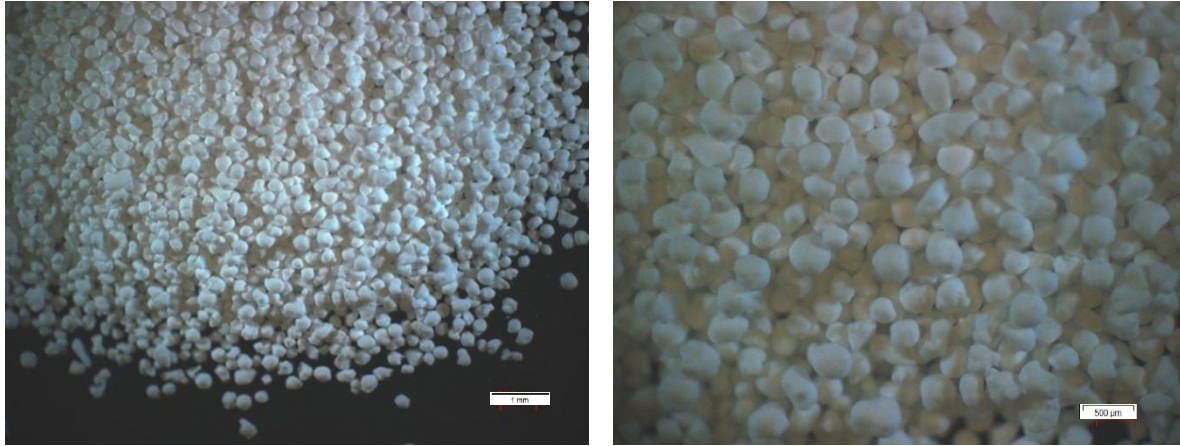


Figure 19: Optical images of alumina (core)

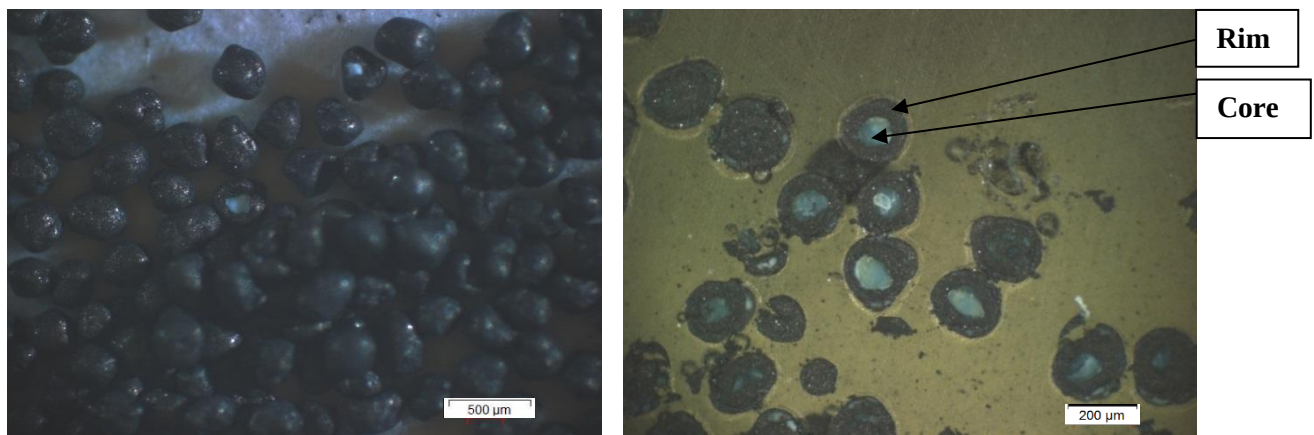


Figure 20: Optical images of coated alumina(white) titanium carbonitride(dark)

The average volume fraction of the core of the granules was calculated and estimated to be 0.14 (Table 8). To achieve this, granules were progressively ground and polished until reaching the centre. This was modelled by geometric calculation. Only five granules were used for this calculation.

Table 8: Radius and Volume fraction of granules

Inner radius (μm)	Inner Volume (μm^3)	Outer radius (μm)	Overall Volume (μm^3)	Vol (in)/Vov
122	7.60×10^6	240	5.79×10^7	0.13
119	7.06×10^6	232	5.23×10^7	0.13
125	8.18×10^6	223	4.65×10^7	0.17
123	7.79×10^6	243	6.01×10^7	0.13
Average				0.14

Figure 21 shows SEM images of the microstructure and morphology of the compacted sintered granules. The sintering was done by using spark plasma sintering at 1800°C and 35 MPa. Dwell time was 5 minutes. From the images, it is evident that the material thus made is a composite with two phases. The light phase is the titanium carbonitride which forms a continuous (matrix) phase throughout the sample. The dark phase is alumina, which is dispersed across the sample. The density of the sample was measured to be 4.75 g/cm^3 using Archimedes principle. To confirm the composition of each phase, the sample was analysed using Energy Dispersive X-ray Spectroscopy (EDS) analysis.

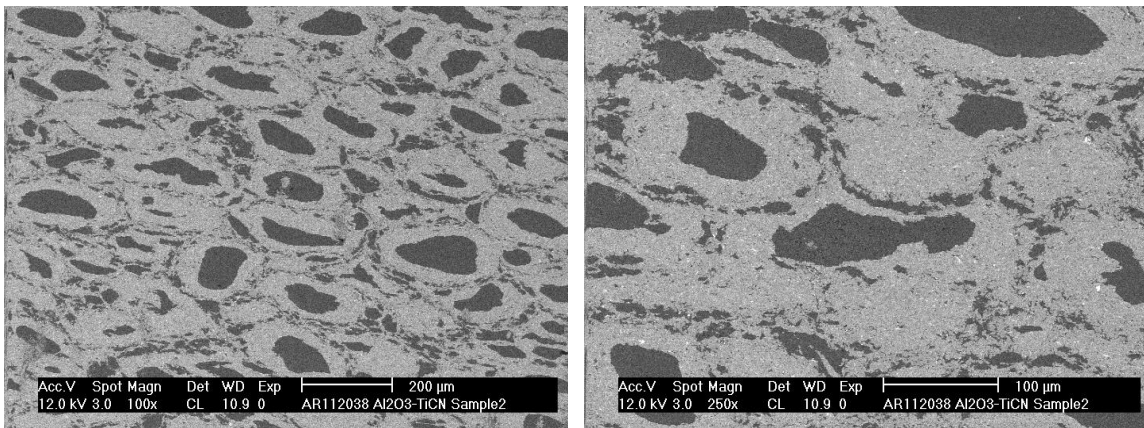


Figure 21: Scanning Electron images of sintered of Alumina titanium carbonitride specimen

The EDS results, shown in Figure 22 show the composition of the dispersed and matrix phases. From the spectrum of the dispersed phase, the component elements are aluminium and oxygen. There is no contamination in this phase. On the other hand the continuous phase is composed of titanium, carbon and nitrogen as well as other (contaminant) trace elements. To further understand the nature of these phases, the sample was analysed using powder X-Ray diffraction (XRD).

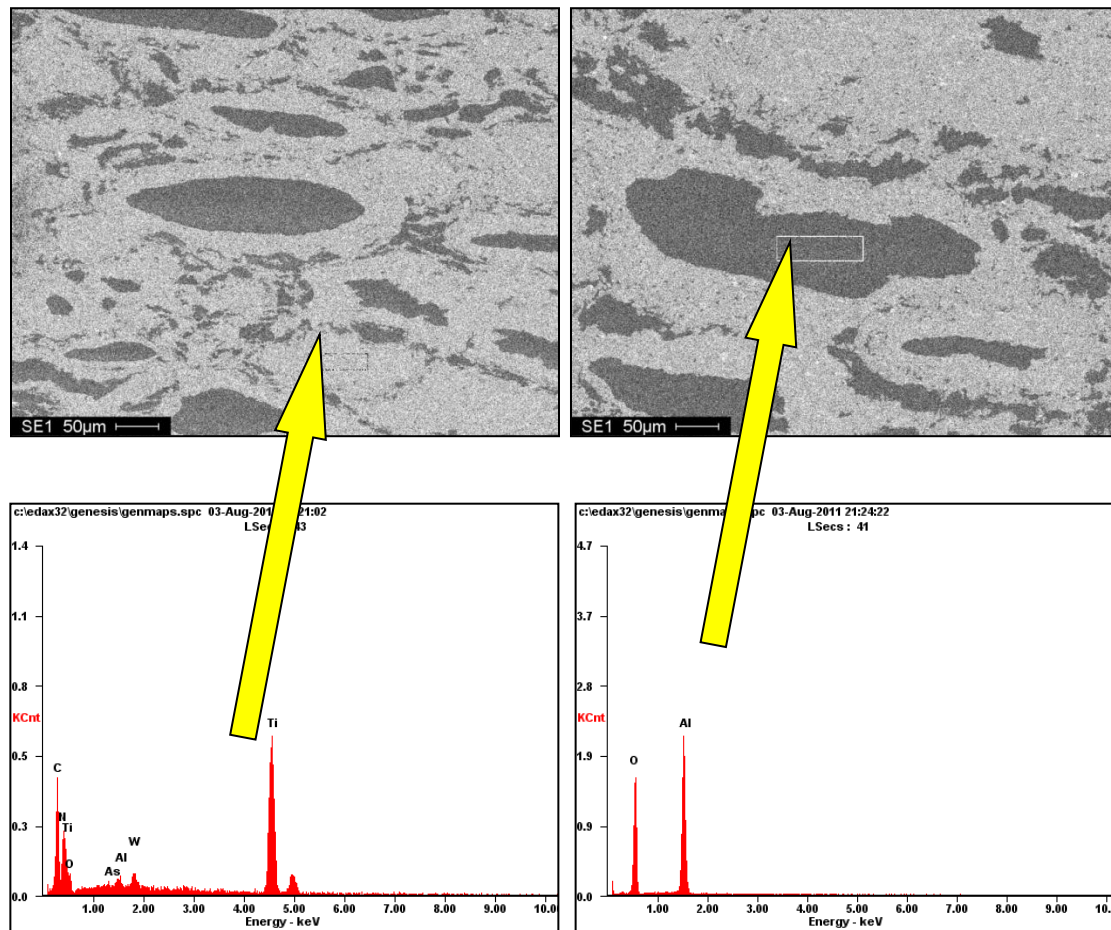


Figure 22: Energy Dispersive X-ray Spectroscopy results of sample showing the chemical composition of each phase

Figure 23 shows is the XRD analysis trace of the $\text{Al}_2\text{O}_3\text{-Ti(C,N)}$ composite. This trace shows two phases present in the sample, those being alumina and titanium oxide-carbide-nitride. This result is in agreement with the results obtained with EDS and SEM.

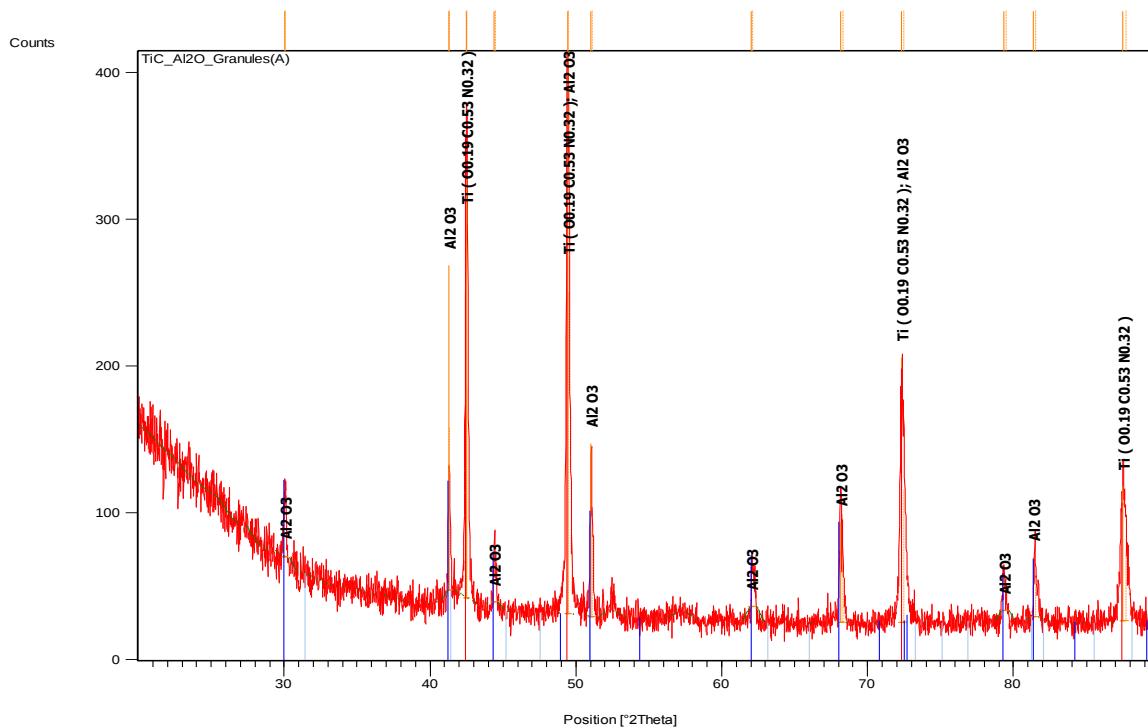


Figure 23: X-ray Diffraction results of specimen showing the phases composition

Table 9: XRD results

Ref. Code	Compound Name	Chemical Formula
00-050-0681	Titanium Oxide Carbide nitride	$\text{Ti(00.19C 0.53 N 0.32)}$
01-075-1865	Aluminum Oxide	Al_2O_3

The density of the sample was measured using the Archimedes principle. This was found to be **4.75 g/cm³**. The hardness of the sample was measured using the Macro Vickers hardness indentation method. The load used was 30 kgf. The number of indents done on the sample was 8. These indentations were done randomly across the sample.

The average hardness of alumina/titanium carbonitride sample was **1751 ± 33 MPa**.

Furthermore, the fracture toughness of the sample was also measured. This was done by measuring the crack length of each crack that occurred after Vickers indentation. Equation 9 was used to calculate the value of this property. The average fracture toughness calculated for this material was **8.0 ± 1.40 MPa.m^{0.5}**. From the analysis of the cracks generated it was seen that the cracks propagated through both the materials.

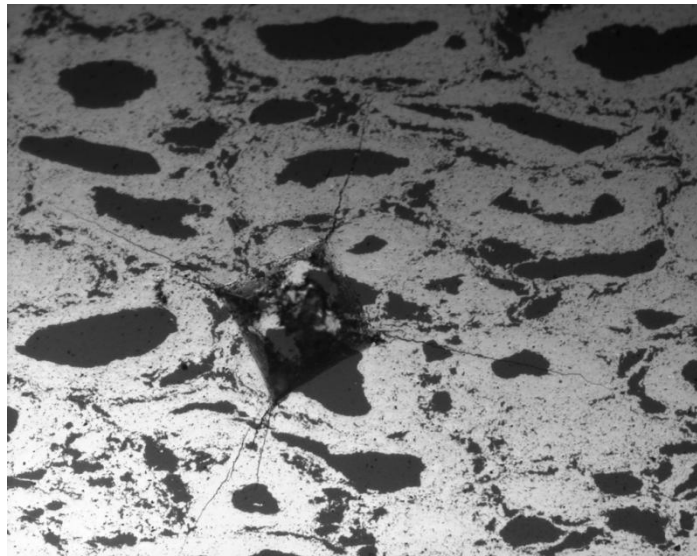


Figure 24: Cracked image of Titanium carbonitride

4.2 PCD

Figure 21 shows the bi-layered diamond granules after fluidized bed granulation. The size of the granules ranges from 300-600 μm . The core of the granules was made from grade 22 diamond powder (22 μm); while the coating layer was made from grade 2 diamond powders (2 μm). Similarly to the work done with the alumina, the 22 μm diamond was made into granules by freeze granulation and coated by 2 μm diamond powder to make 2/22 μm bi-layered diamond granules.

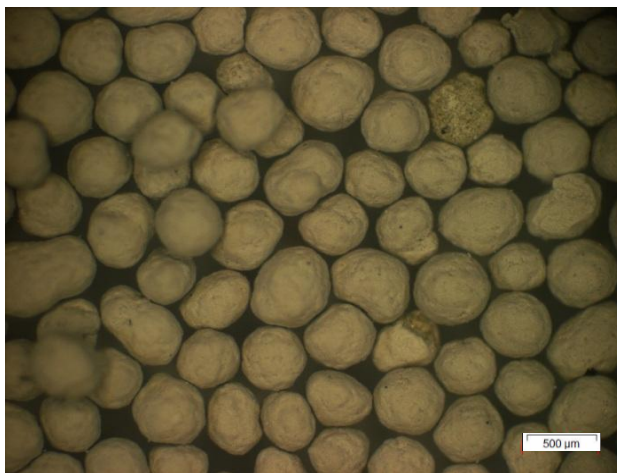


Figure 25: Optical image of bilayered diamond granules after granulation

The granules were cold mounted into epoxy resin to reveal their cross sectional area. This allowed the removal of the surface of the granules to expose the two layers by grinding and polishing. Figure 26 shows the granules examined under a light microscope. As shown in the image the granules are made out of two different grades diamond powders, as indicated by the different appearance of the core and rim of the capsule. The core is composed of 22 μm diamond powder and the rim of 2 μm diamond

powder. The average volume fraction of the two grades of diamond of granules was determined by progressive grinding, polishing, observing and measuring the change in the diameters of their inner and outer parts until the center of the granules was reached. During each grinding and polishing process the inner and outer diameters were measured to a point where the outer diameter did not change. This was achieved by mounting the granules at the same depth on an epoxy polymer resin.

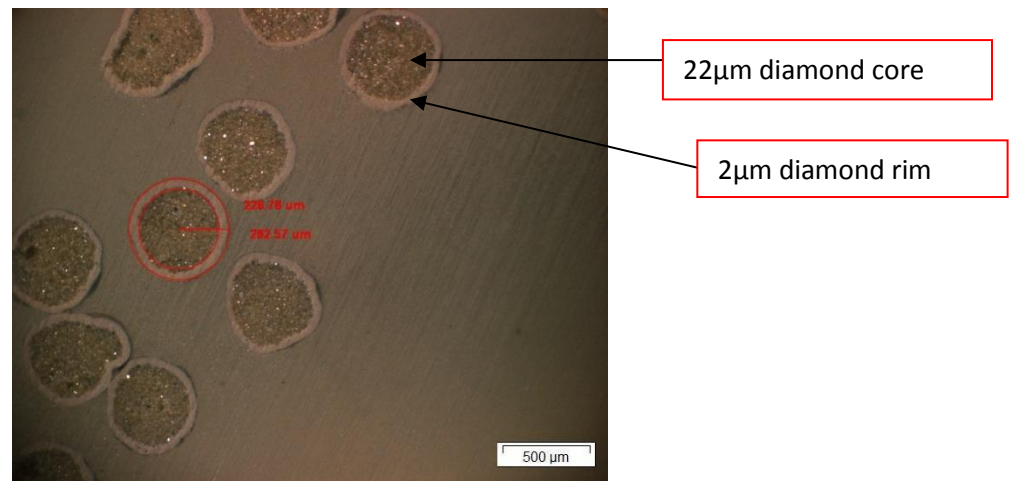


Figure 26: Cross sectional of diamond granules

Table 10 shows the parameters as well as the inner and outer diameter of granules after successive grinding at 10 seconds intervals. This is also shown in Figure 27.

Table 10: Grinding and Polishing of granules at 10 seconds intervals

Grinding time(sec)	Polishing time (sec)	Inner diameter (μm)	Overall diameter(μm)
(a) 10	10	156	564
(b) 10	10	228	564
(c) 10	10	316	564
(d) 10	10	398	564
(e) 10	10	446	564
(f) 10	10	340	440

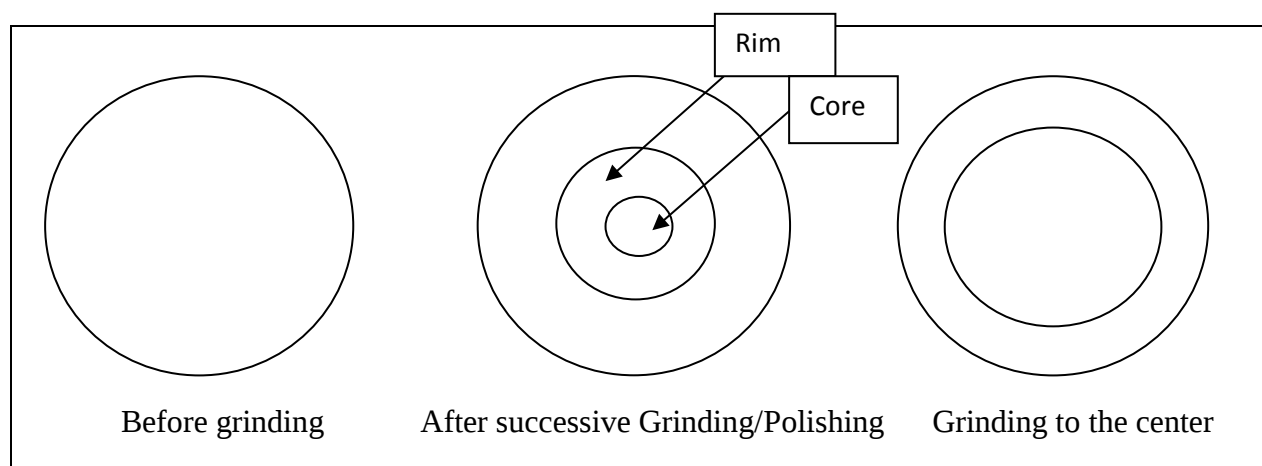


Figure 27: Schematic sketch illustrating how the bilayered granules were grounded expose the two layer

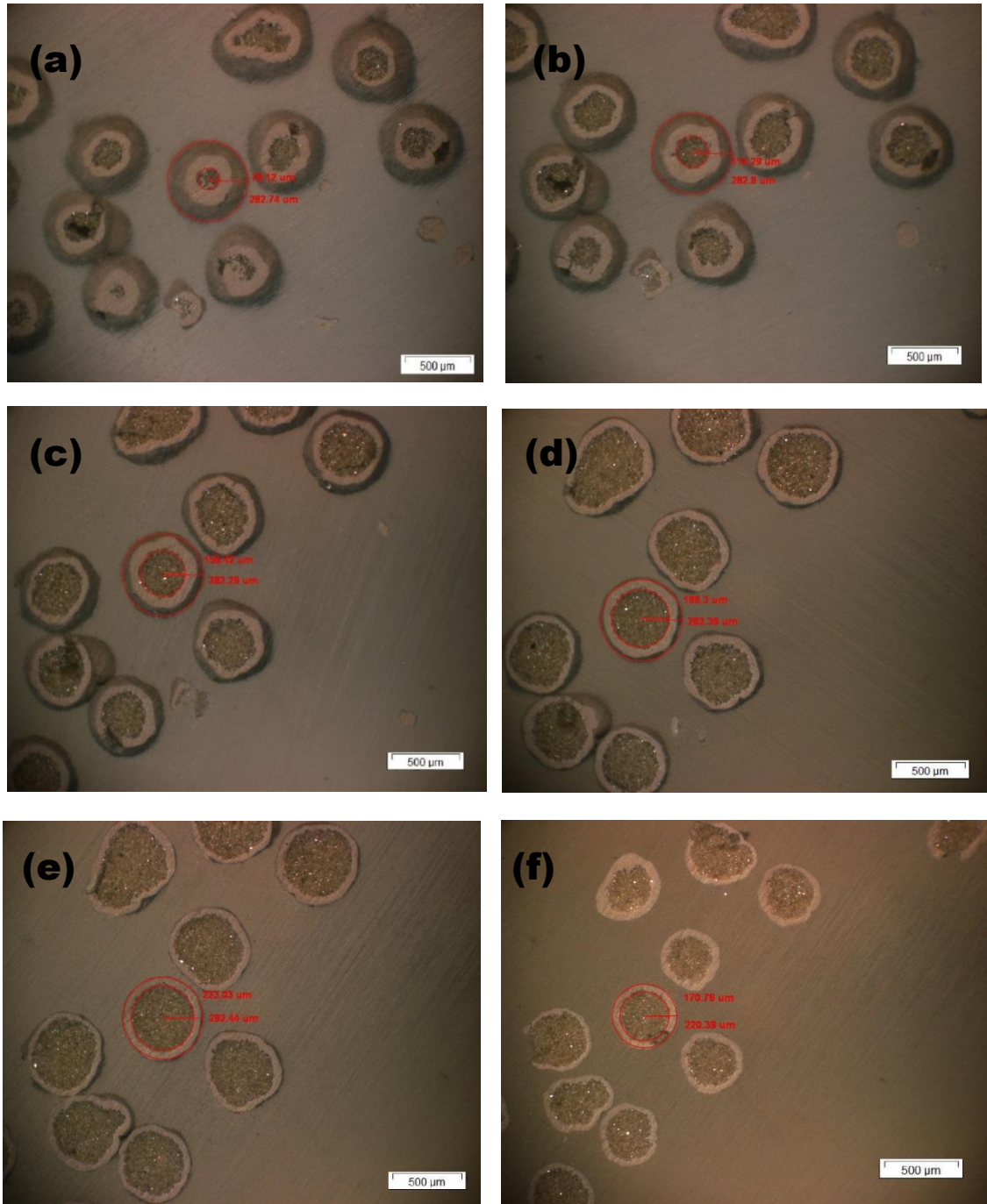


Figure 28: Diamond bilayered granules images from (a)-(f) showing cross sectional area grounded to the centre of the granules

Table 11 shows the measured dimensions of the ground and polished granules. With this data it was possible to calculate the core volume fraction of each granule measured. The average volume fraction of the core part of the granules was 0.51.

Table 11: Dimension and Volume fraction of each granule

Core radius (μm)	Vol. of Core (μm^3)	Overall radius (μm)	Vol. Overall (μm^3)	Vcor/Vov
228	4.96×10^7	282	9.39×10^7	0.53
225	4.77×10^7	278	9.0×10^7	0.53
233	5.03×10^7	294	1.06×10^8	0.50
226	4.84×10^7	284	9.59×10^7	0.50
average				0.51

Samples were sintered at HPHT conditions as described in the section 3.35. After sintering the samples were lapped and the outer diameter ground to remove the niobium and titanium encapsulation cups. The resulting sintered PCD samples are shown in Figure 29. The outer diameter of the sample was measured to be 16.12 mm and the thickness of the PCD table 2.63 mm.

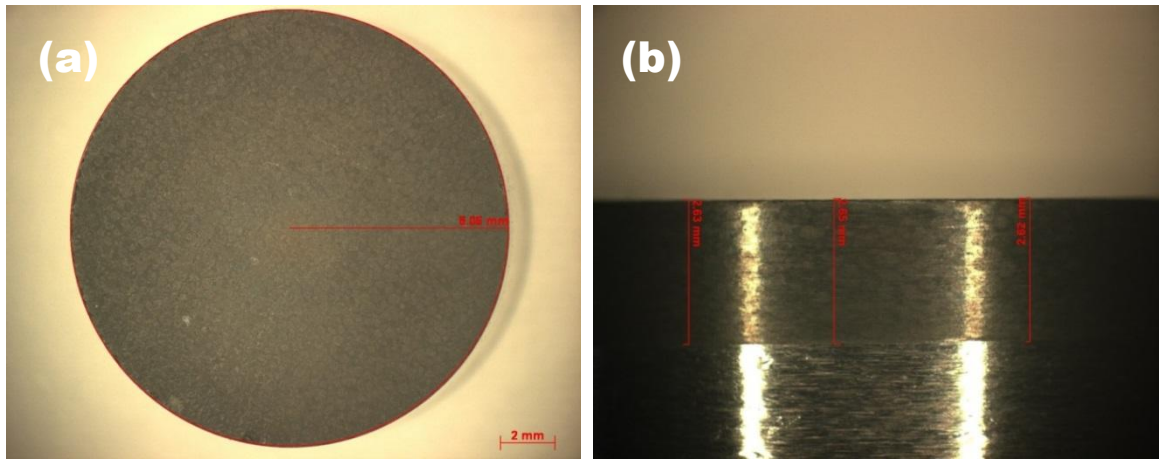


Figure 29: Sintered PCD units (a) Top view (b) Side view

In order to analyze the microstructure of the PCD table, samples were EDM cut and the cross section of the one resulting sample was polished as described in Paragraph 3.3.6. Figure 29 shows an optical micrograph of such a polished surface. The two PCD phases are clearly seen.

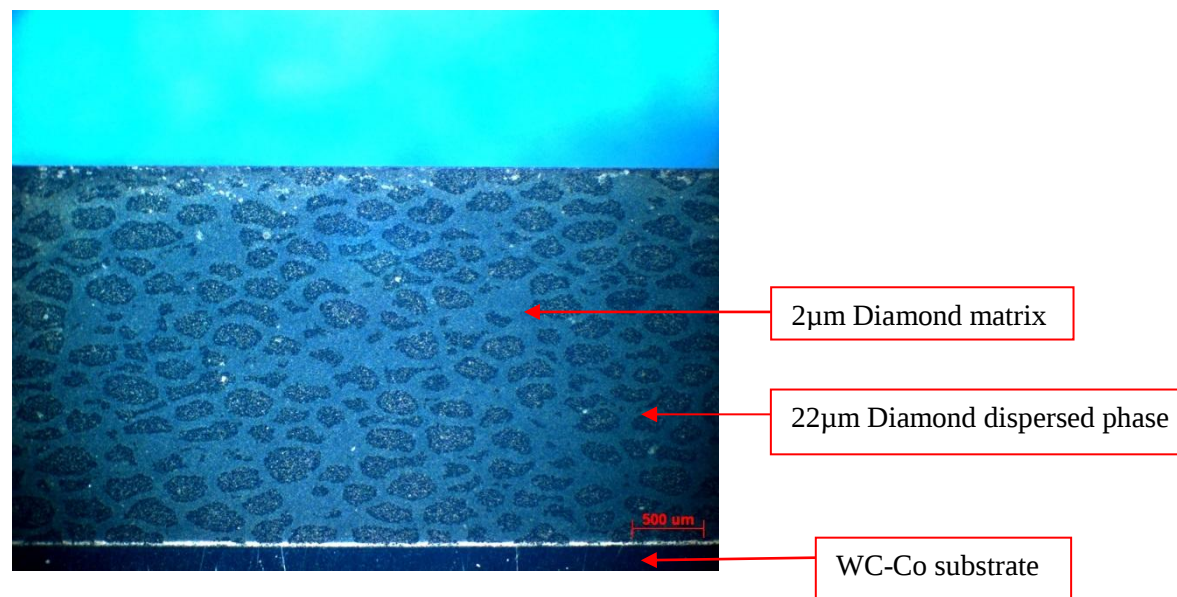


Figure 30: PCD table showing the two phases distributed homogenously in the specimen

SEM analysis of the PCD allowed the study of the microstructure in detail, as shown in Figure 31. A good distribution of the coarse grained diamond cores has been attained. Figure 32 and Figure 33 show the two phases in the materials.

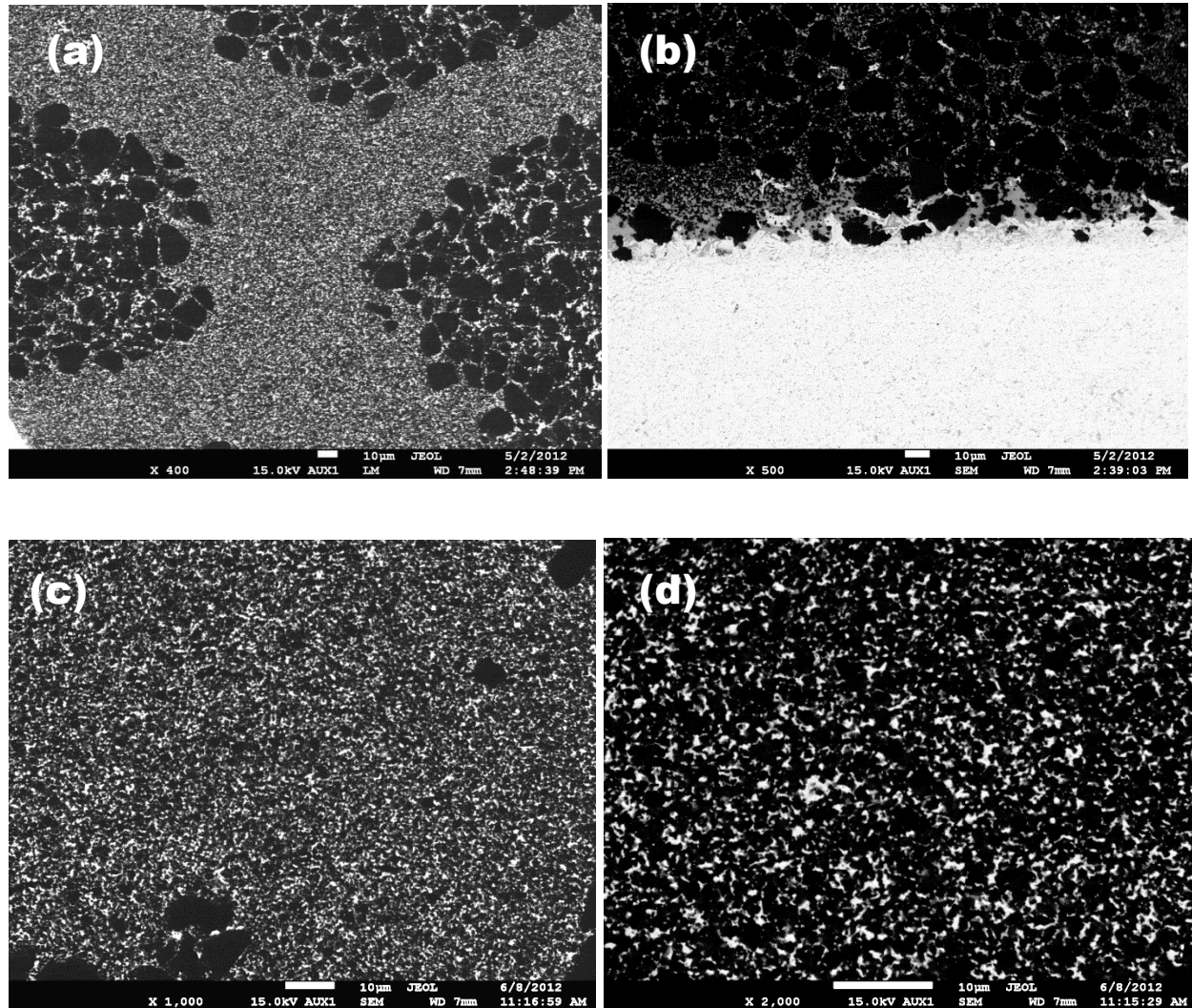


Figure 31: Scanning Electron Microscope PCD image showing (a) matrix and dispersed phases (b) interface of WC and PCD table (c) the matrix phase and (d) the dispersed phase

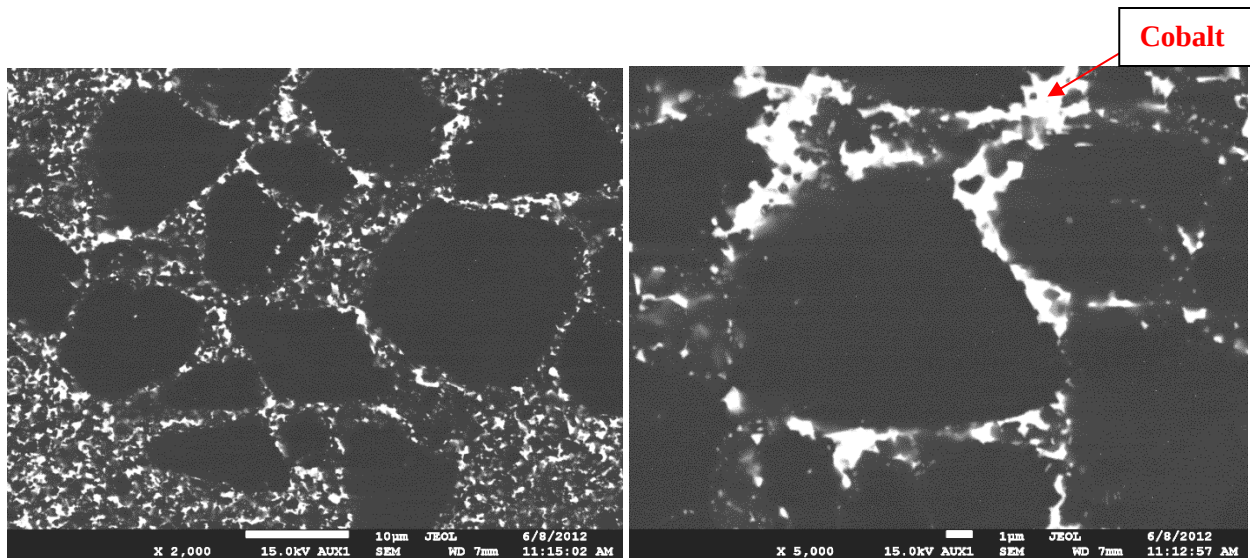


Figure 32: Scanning Electron Microscope images showing the dispersed phase with larger grains

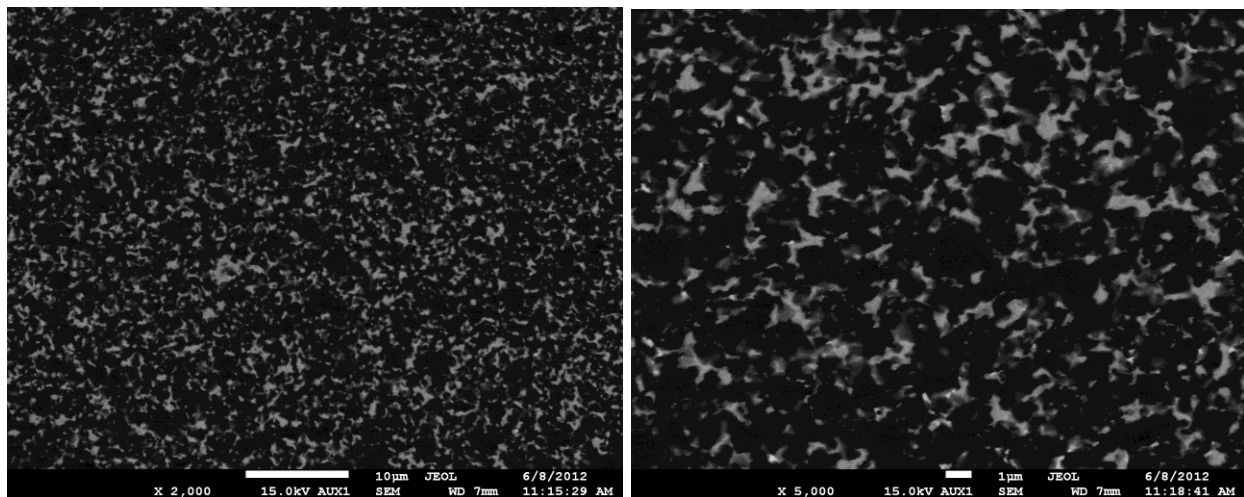


Figure 33: Scanning Electron Microscope images showing the matrix with small grains

XRD analysis was carried out on the sample surface after lapping without polishing. These results are shown in Table 12. The phases present in the sample were: cobalt, tungsten carbide, diamond, cobalt carbide and tungsten carbide. Cobalt was not present as an element but compounds (Figure 34) residual cobalt.

Table 12: XRD results

Compound name	Chemical formula	Crystal System	Space group
Cobalt tungsten carbide	$\text{Co}_3\text{W}_3\text{C}$	Cubic	F3m3 E
Diamond	C	Cubic	Fd3m
Cobalt carbide	CoC_x	Cubic	P43m
Tungsten carbide	WC	hexagonal	P6m2

- CoC_x is solid solution of cobalt with carbon

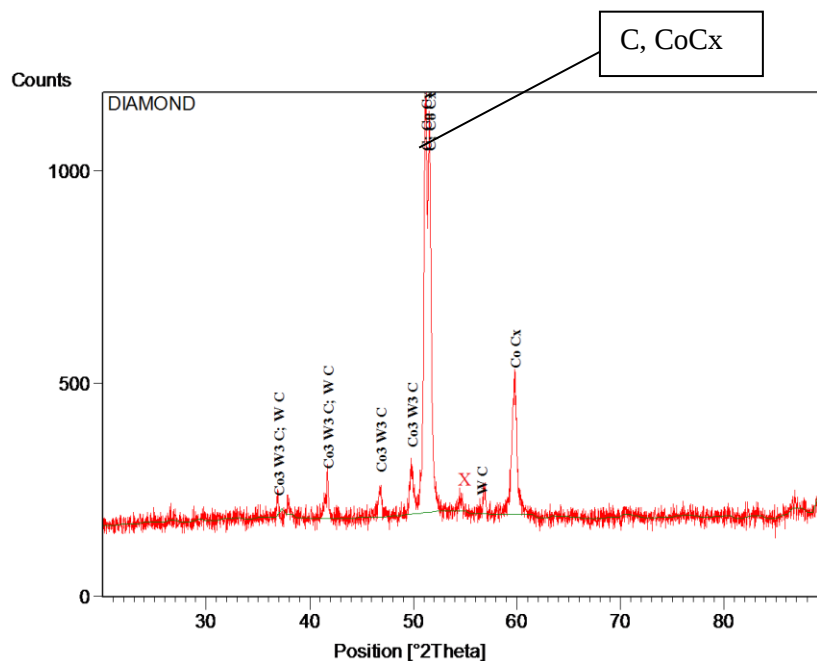


Figure 34: XRD spectrum of sample determined by X-ray diffraction

In order to examine the fracture behaviour of the granule-based PCD, a controlled crack was introduced in a sintered PCD sample. The crack was carefully introduced into the sample by placing it, while still attached to its substrate, in between two rollers. A force was slowly applied by hand, squeezing the PCD. A crack was observed initiating in the WC substrate and propagating into the PCD table. The force was carefully applied and controlled to prevent the crack propagating through the sample. The images in Figures 35 show the pre-cracked sample observed with an optical microscope. SEM images shown in Figure 36 show the behaviour of the crack in both phases. It can be seen that the crack was deflected as it was propagating through the sample, progressing preferably through the coarse grained part of the PCD and in the matrix it did not deflect. This deflection was due to the inherited different residual stresses of the two phases. The crack was observed deflecting when it entered the dispersed phase especially where there was cobalt. No deflection was seen to occur in the matrix phase.

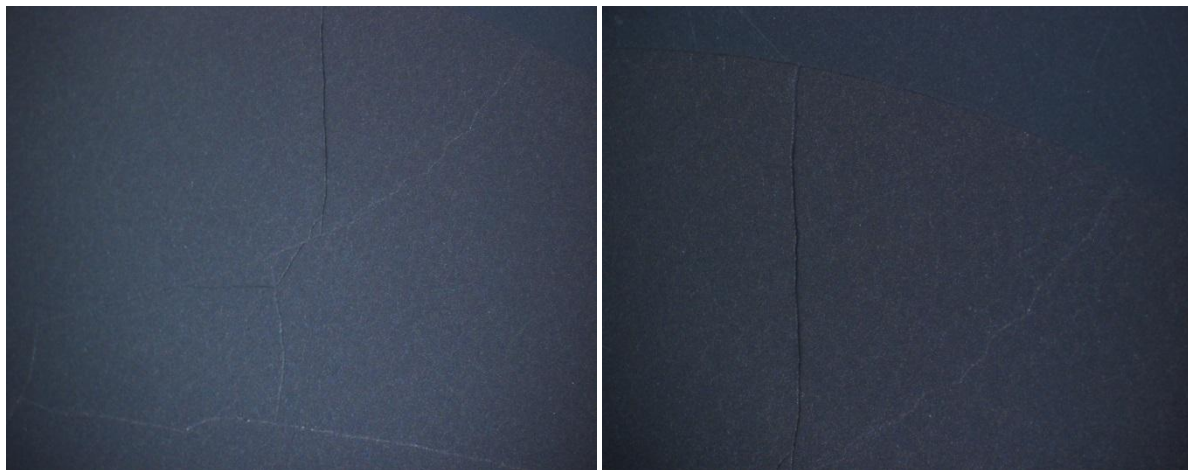


Figure 35: Pre-cracked PCD sample before SEM characterization

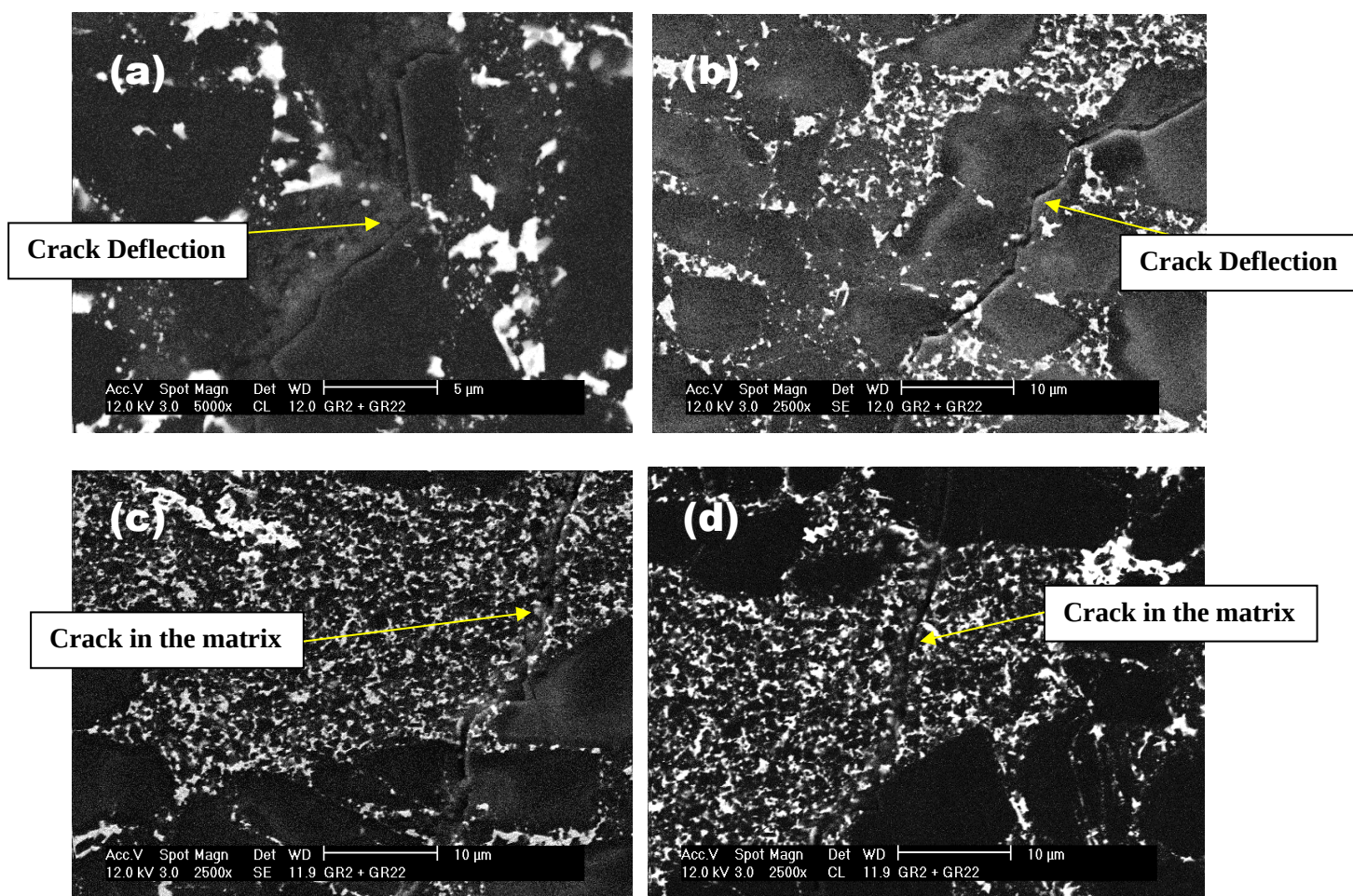


Figure 36: Scanning Electron Microscope images showing (a) & (b) crack deflection inside and outside the dispersed phase (c) & (d) crack propagating in the matrix phase

To further characterize the sample, the mechanical properties of the samples were measured.

This was done for the granule-based, as well as for the 22 μm PCD. In the case of the 2 μm grain PCD property data was obtained from Element Six (Pty) Ltd. The elastic modulus of 22 μm PCD was approximated.

The fracture toughness of samples was measured and compared to other types of PCD. The results are shown in Figure 34. From these results, it is seen that 2 μm PCD had a higher fracture toughness compared to the 22 μm and the composite 2/22 μm PCD material. The attributive

factors in the variation of the fracture toughness are the amount of cobalt as sintering additive and the particle sizes of the diamond crystals. It was expected that the 2/22 μm PCD would have a fracture toughness between that of the 2 and 22 μm PCD materials. This was not the case; the reason could be inhomogeneity of residual stresses in the sample.

Table 13: Summary of Elastic properties of PCD sample

	2 μm PCD	22 μm PCD	2/22 μm PCD
Density(g/cm^3)	4.43	3.95	4.09
Poisson's ratio	0.203	0.10	0.11
Shear modulus(GPa)	372	469	445
Elastic modulus(GPa)	894	1220	991
Bulk modulus (GPa)	502	437	427
K_{IC} (fracture toughness)$\text{MPa}\cdot\text{m}^{1/2}$	8.5 ± 0.4	8 ± 0.5	7 ± 0.6

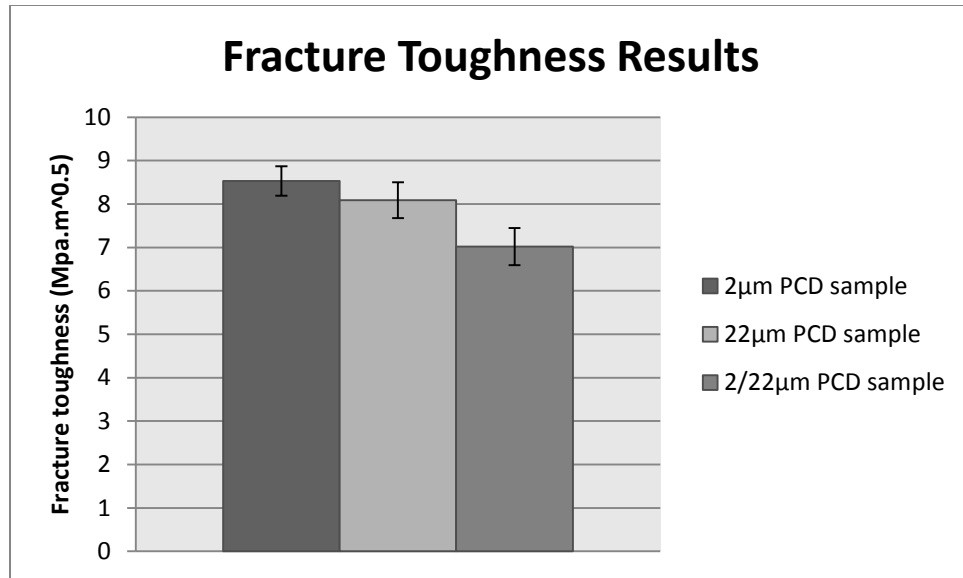


Figure 37: Summary of Fracture Toughness of sample

Using the equations presented in section 2.4 it was possible to calculate and estimate the residual stresses in the sample and more specifically in the dispersed phase. Table 14 shows the parameters used to calculate stresses inside the dispersed phase. The radial stress in the dispersed coarse-grained phase at the particle-matrix interface was estimated to be ± 511 MPa (i.e. tensile). On the other hand, using eq. 2 the residual radial stress in the matrix is compressive, while the tangential stress is tensile. As a result, the crack was drawn to and preferably propagated through the dispersed phases. This was indeed observed in the SEM images presented in Figure 36 where the crack preferentially propagated inside the dispersed phase.

Table 14: Parameters and Values used to calculate residual stresses

Parameter	Value & units
Sintering Temperature	1500 °C
Ambient temperature	25 °C
Thermal expansion coefficients of grade 22 diamond disperse phase	$4.1 \times 10^{-6} \text{ K}^{-1} [^{**}]$
Thermal expansion coefficient of grade 2 diamond matrix	$4.8 \times 10^{-6} \text{ K}^{-1} [^{**}]$
Elastic Modulus of 2 µm PCD	894 GPa ^[33]
Elastic Modulus of 22 µm PCD	1220 GPa ^[33]
Poisson ratio of 2 µm PCD	0.2 ^[33]
Poisson ratio of 22 µm PCD	0.1 ^[33]

[**]- These values were measured at Netsch-Novartis, Germany. Work commissioned by Element Six

From the images in Figure 36 the crack propagated straight through the matrix without any deflection but as soon as it enters the dispersed phase it began to be deflected. At the particle-matrix interface the stresses are tensile; this is the cause of the change in direction of crack propagation. ; this however had a negative effect on the fracture toughness. From literature ^[43] it is known that wear resistant of PCD composite is inversely proportion to the particle size. The larger the particle size of making the PCD the lower the wear resistance and vice versa. On the other hand, fracture toughness of PCD has been found to be increase with larger particle size. This therefore means that the wear resistance and fracture toughness has an antagonistic effect on the PCD ^[43]. With this in mind it was expected that the sample will have a relatively better wear resistance and also fracture toughness. However, that was not the case. The material produced in this work had coarse grained cores and fine grained matrix. It was expected that the wear

resistance as well as fracture toughness would improve in comparison to single phase PCD materials. However this was not the case. In a multiphase material, when $\Delta\alpha < 0$ the matrix is under hoop compression around the dispersed phase cracks tends to deflect away from the dispersed phase, thereby increasing fracture toughness by increasing crack length. Conversely when $\Delta\alpha > 0$ the dispersed phase is under tension, while the matrix is under hoop tension around the dispersed second phase inclusions, in which case the is attracted to the dispersed phase. The latter was the case for the material produced in this research. This can be explained by the increasing function of crack length and fracture toughness which stipulates that as crack path length increases fracture toughness also increases.

With the crack not deflecting away from the dispersed phase but towards it, it was expected that the fracture toughness of the composite diamond material would be low because the crack is not deflecting away from the dispersed phase but propagates through both phases. The exception here is that when inside the dispersed phase the crack deflects. The composite material made had a fracture toughness of $7.0 \pm 0.6 \text{ MPa.m}^{1/2}$ which was lower than that of the unimodal samples (2 μm and 22 μm PCD) of $8.5 \pm 0.4 \text{ MPa.m}^{1/2}$ and $8.1 \pm 0.5 \text{ MPa.m}^{1/2}$ respectively (Figure 34). The fracture toughness of this material was expected to be between those of the unimodal samples since it was composed of both diamond grades. This was not the case due to the effect of the inhomogeneity of stresses and the secondary phase being under tension.

To further characterize the granule-based PCD, samples were wear tested using two different types of turning tests. The two methods used were the Paarl Granite Test (PGT) and the Vertical Borer test. In these techniques only 22 μm PCD sample was used to compare with the composite 2/22 μm PCD sample. Due to the difficulty in sintering 2 μm PCD because of defects these

samples developed, it was decided not to test this material, but compare with Quadmodal and Tristar PCD samples

Figure 38 shows the Paarl granite test results of the two cutters made from the two materials being compared. As can be seen, composite 2/22 μm performed much better than the 22 μm PCD. Also shown in Figure 39 are sets of Paarl Granite test results for Quadmodal and Tristar PCD materials which were included for comparison's sake. Quadmodal PCD is a material comprising grade 4, grade 12, grade 22 and grade 30 with ratio 5:10:20:65 respectively; Tristar PCD comprises grade 2, grade 4, grade 6 and grade 22 with ratio 5:16:7:44:28 respectively. As can be seen from Fig. 38 and 39, 2/22 μm PCD performed, within the error, equally well as the Quadmodal PCD material.

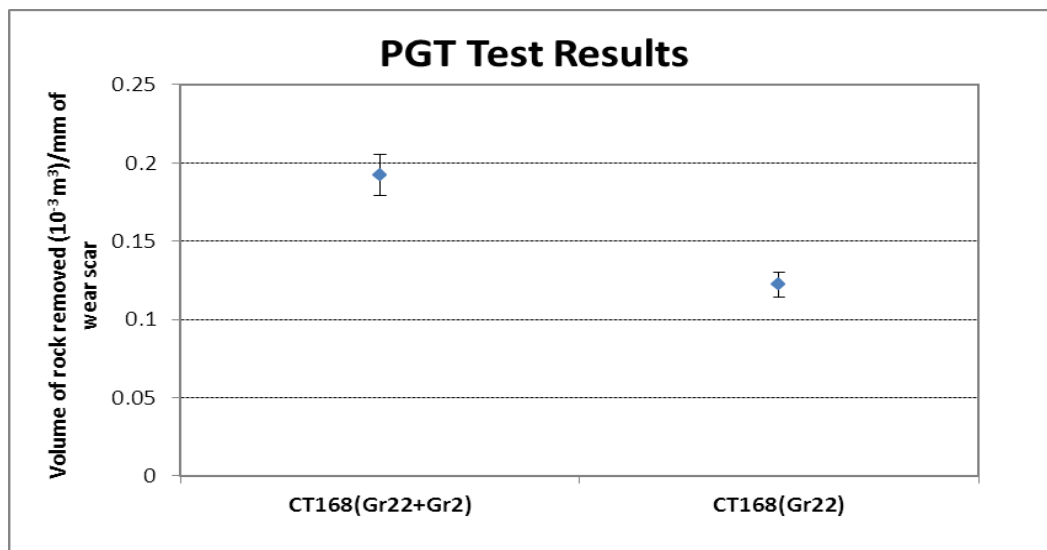


Figure 38: Paarl Granite Test results of composite (2/22 μm) sample and grade 22 μm PCD sample

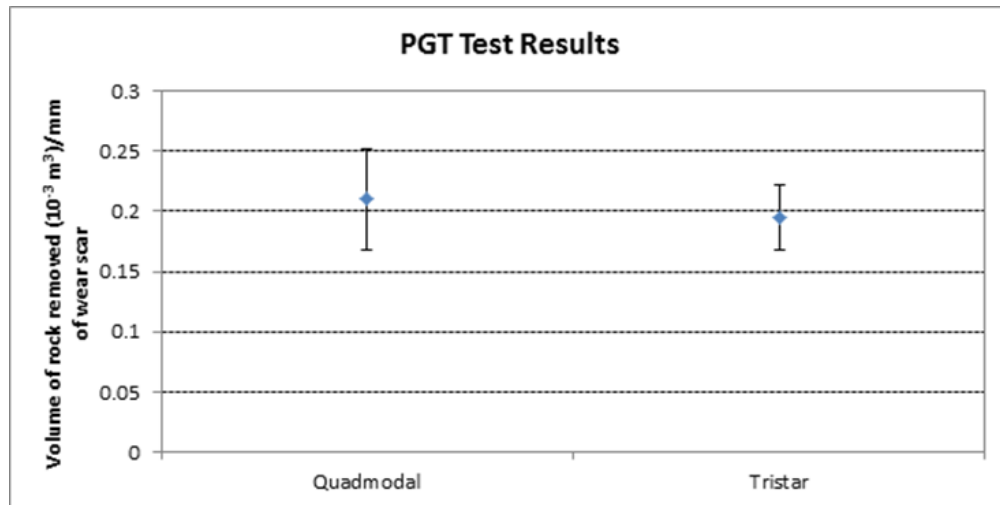


Figure 39: Paarl Granite Test results of composite Quad modal sample and Tristar PCD sample

The second turning test method used to test the PCD cutters was the Vertical Borer. This technique is similar to the Paarl granite test except it is more aggressive. Similarly to Paarl granite test, all four samples were tested and their performance was compared. The results of the samples are shown in Figure(s) 40 & 41. The total wear scar of the samples was compared to the length of cutting. Also the wear scars are presented in Figure 42. If one compares the size of the wear scars generated for equal distance travelled, we find that the 2/22 μm PCD performs equally well as the best performing of the other three grades, namely Tristar. It therefore follows that our composite PCD has the best combination of results in Paarl Granite and vertical borer tests. This means that this PCD is the most versatile of the 4 grades tested and considered here.

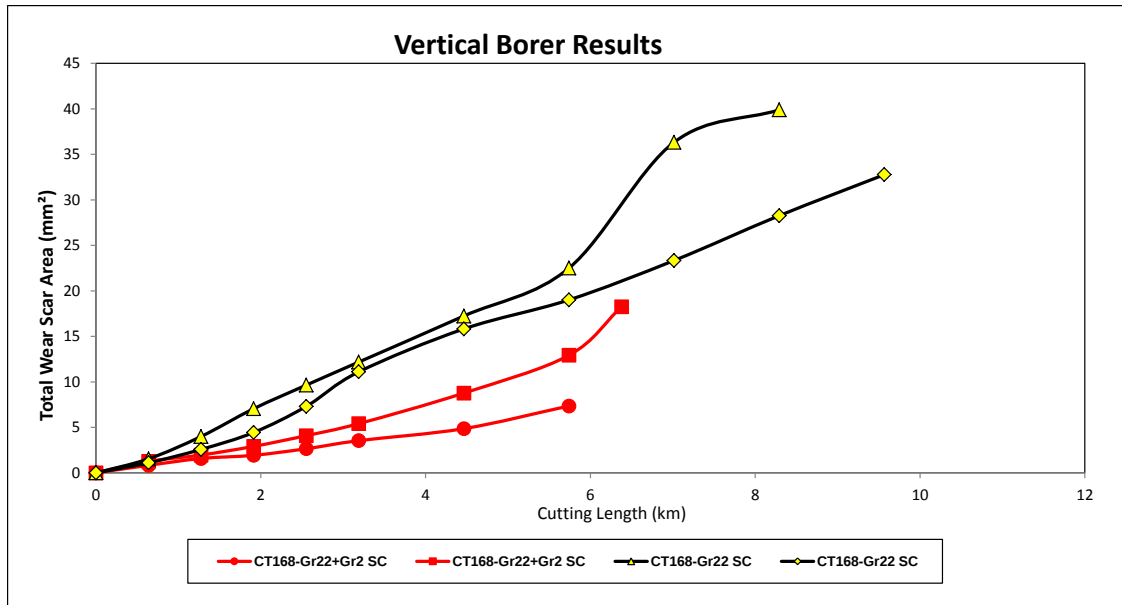


Figure 40: Vertical Borer results of the composite ($2/22\mu m$) sample and the grade $22\mu m$ PCD sample

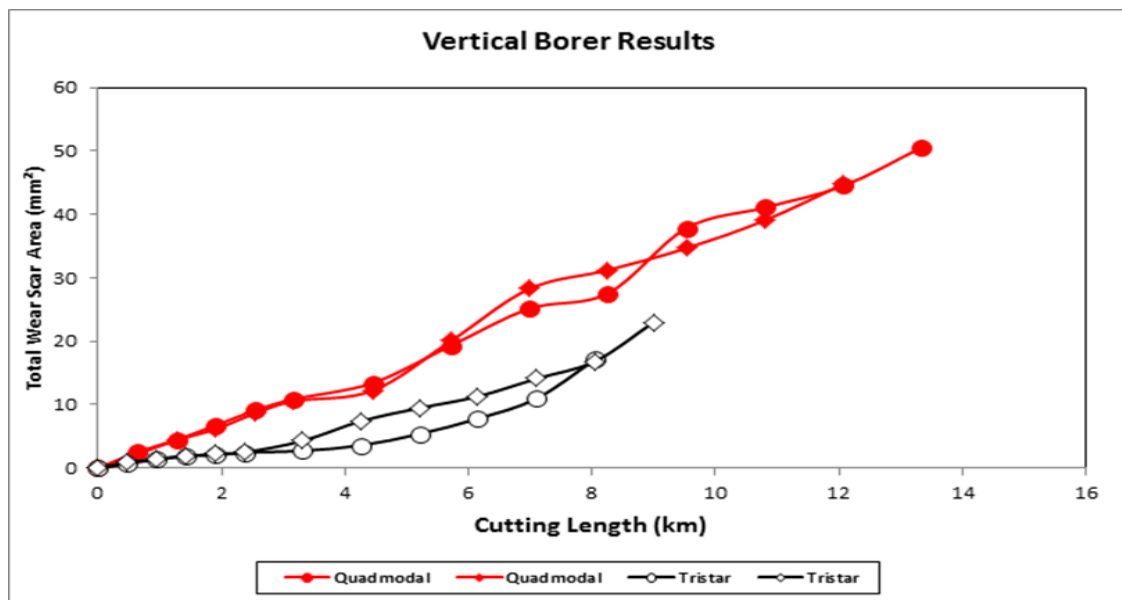


Figure 40

Figure 41: Vertical Borer results of the Quadmodal and Tristar PCD samples

Figure 42 shows the images of the composite (2/22 μm), 22 μm PCD, Quadmodal PCD and Tristar PCD samples with each showing the wear scar after successive grinding.

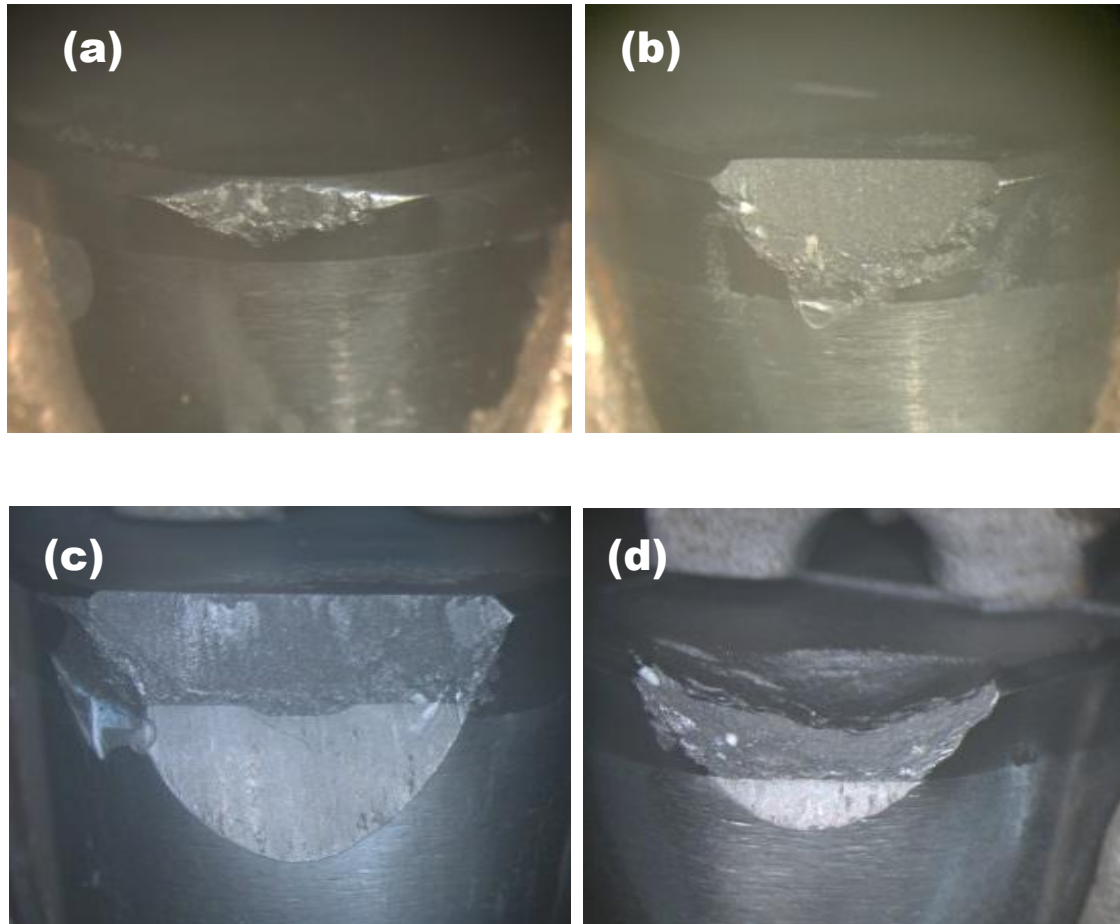


Figure 42: Optical images of the wear scar of (a) composite (2/22 μm) PCD (b) 22 μm PCD (c) Quadmodal PCD and (d) Tristar PCD sample(s)

5. DISCUSSION

The purpose of this work was to manufacture three dimensionally-structured polycrystalline diamond materials (3D PCD) with the aim of improving the resistance to wear of the material by crack deflection toughening induced by residual stresses. This work began by first producing alumina carbonitride composite material mimicking the work later would be done with diamond.. In this chapter, results of the work done on both alumina and diamond are discussed.

5.1 Alumina – titanium carbonitride

The work began by making alumina carbonitride by granulation technique. From the results present in section 4.1 Figure 17 and Figure 18, it is evident that making bi-layered granules is possible both with freeze granulation and Fluidized bed granulation. The core was made of alumina and coated with a layer of titanium carbonitride. The granules were pressed and sintered to form a bulk composite material with a matrix and a dispersed phase. The SEM images shown in Figure 19 confirm this result. The matrix was composed of titanium carbonitride which appeared white in appearance and the alumina which was the dispersed phase which appeared dark when observed under the Scanning Electron Microscope. This is to be expected from the difference in atomic numbers involved. . Both phases were well homogenised and distributed fairly within the material. The two phases were evaluated and determined by X-ray diffraction. The XRD traces show the presence of alumina and Ti (C, N). EDS analysis of the micrographs obtained confirms that the dispersed phase is Al_2O_3 , while the matrix is seen to be Ti(C,N).

There was little contamination of tungsten in the Ti (C, N) phase. This is seen on the EDS results given in Figure 22.

The density of sintered composite was 4.75 g/cm^3 , which is lower than the theoretical density of 4.93 g/cm^3 which was determined by equation 4. The reasons for this could be incomplete densification of the sample during sintering.

The hardness of the sample was measured to be 1751 MPa with a standard deviation of 33 high standard deviation indicates that there was some inaccuracy when measuring this property. This could have been due to human error, associated with the determination of the length of each the diagonals of the indented diamond shape on the sample, or, most probably, caused by the presence of two phases in the material tested. The hardness was measured by indentation, which could have sampled either the matrix, the dispersed phase, or parts of both at any given measurement. The fracture toughness of the sample was $8.0 \text{ MPa.m}^{0.5}$ with a standard deviation of 1.40. There was no crack deflection observed. The crack propagated straight through both phases as schematically shown in Figure 24. This meant that the residual stresses present were not high enough to cause crack deflection. Characterization was not done beyond what have been mentioned on the alumina carbonitride composite samples.

5.2 PCD

Through the successful processing, manufacture and characterization of the alumina-titanium carbonitride composite ceramics, a clear understanding of the technologies involved in making core-rim granules and the resulting composite ceramics was obtained. A similar procedure was followed in making the diamond bi-layered granules. The organic binders used for this

fabrication proved to be suitable and relatively easy to remove after granule formation. From the results shown in Figure 22 the granules had the desired spherical shape and the two diamond constituents. This is clearly seen in the cross sectional area of the granules shown in Figure 23. Sintering of the granules was done successfully with the samples being completely densified without any defects.

Each sintered PCD cutter was ground and lapped to outer diameter of 16.12 mm and thickness of 2.63 mm as this was the desired specification for characterization.

To observe the macrostructure and microstructure, optical microscope and scanning electron microscopy were used for analysis. From the images of presented in Figure 27,28 and 29 it is clear that the PCD made was dense and free of any defects. The micrographs obtained revealed the presence of two phases composing the sample. Similarly to the alumina-titanium carbonitride samples, there were two phases, one continuous and the other dispersed. The continuous phase was made from the diamond on the rim of the granules and the dispersed phase from the diamond of the core when the diamond granules were pressed together during sintering. The grain size of the matrix was approximately 2 μm and the grain sizes of the dispersed phase 22 μm . Evidence of this is seen in SEM images presented in Figure 27, where the matrix has fine grains and the dispersed phases coarse grains. The sample was well sintered with no defects such as soft spots (partially sintered areas). The two phases were well homogenized throughout the sample. This can be seen in the optical image shown in Figure 27. The matrix had a large amount of cobalt due to the large surface area of the 2 μm powder. This phase appeared lighter due to its large cobalt content. This is attributed to lower packing density of the fine diamond (2 μm diamond grade). The converse of this is seen in the dispersed phase. To further characterize this material, semi quantitative analysis of samples was carried out. Energy Dispersive X-ray

spectroscopy (EDS) was the technique used to determine the composition of each phase. The results found once more confirm the large cobalt content in the matrix and lower content in the dispersed phase. Traces of oxygen were found in the dispersed phase and dismissed as contaminant. EDS technique was limited in studying the phases in which these elements appeared.

To understand the nature of the phase's present in the sample, X-ray diffraction was used. As expected, prominent diamond peaks were observed, corresponding to the diamond predominant standard peaks known. Other phases detected in the XRD trace were: cobalt tungsten carbide, cobalt, tungsten carbide and cobalt carbon solid solution which appeared as CoC_x on the XRD spectrum. This was confirmed by comparing XRD results of PCD obtained from the Element 6 database.

Mechanical properties of samples were measured and compared with the Element Six 2 μm PCD standardized sample as well as the 22 μm PCD sample. The properties measured were density, Poisson's ratio shear and bulk modulus as well as fracture toughness. It was expected that the composite PCD sample would have properties that are in between the 2 μm PCD and 22 μm PCD sample.

The density of the composite PCD sample was 4.09 g/cm^3 which when compared to the other densities of the 2 μm PCD sample and 22 μm PCD sample was in between the two densities which were 4.43 g/cm^3 and 3.95 g/cm^3 respectively. This was expected and is indicative of the fact that the samples sintered and densified into solid PCD relatively well.

The values of Poisson's ratio, Young's , shear and the bulk moduli of the composite PCD sample, as expected were in between those of the two other (unimodal) materials. This was not the case for the fracture toughness.

The fracture toughness of the composite PCD had a lower K_{Ic} value comparable to that of unimodal samples i.e. 2 μm and 22 μm samples (Table 13). The results shown in Table 13 represent the antagonist effect of wear resistance and fracture toughness on the material. The wear resistance of this sample improved significantly by crack deflection seen in Figure 33 furthermore the results of the turning tests (Paarl granite and vertical borer) showed this improvement. Therefore it is logical that the fracture toughness would be compromised, but even though compromised it was not significantly reduced. This meets the objective set in this work to engineer and produce a 3D PCD with an improved wear resistance while maintaining relatively better fracture toughness. The wear resistance improved by crack deflecting in to the sample thereby delaying reaching critical crack length and fracture off the sample. This was induced by local stresses that were deliberately introduced by the way the material was designed. Crack deflection occurs as a result of inhomogeneity at the crack tip. This inhomogeneity can be local stresses, impurities and defects. In this case the local stresses are the source of this deflection. From the results, the crack was seen propagating easily through the matrix but as soon it entered the dispersed phase it began to deflect. The explanation for this span from the local stresses estimated in this phase. This deflection can be attributed to both the stresses and the large grain size off the dispersed phase. The sudden change in local stresses puts a strain in the crack tip and forces it to find an alternative route to propagate. The large grain size on the other hand is soft compared to fine grain. This therefore increases the energy the crack required to propagate by, thereby deflect the crack. This result has shown an improvement in wear of the sample. The

estimated tensile stress was 511 MPa calculated by equations 1, 2 and 3 with the parameters presented in Table 14. This value was compared to that obtained by Dzepina^[13, 14] which was 755 MPa .

The wear resistance of samples was measured by turning methods i.e. PGT and Vertical Borer. Due to technical problems encounter when sintering the 2 μ m PCD samples, only the 22 μ m and 2/22 μ m PCD samples were tested. To compare with, Quadmodal and Tristar PCD was tested. Results from the Paarl granite test showed that the 2/22 μ m composite material had a better performance than 22 μ m PCD sample but performed more or less the same as both Quadmodal and Tristar (Figure 38 and 39). The vertical borer results showed the 2/22 μ m composite PCD wears relatively better than Tristar, Quadmodal and 22 μ m unimodal PCD (Figure 41 and 42). The images of the wear scar of the samples are shown in Figure 42. This illustrated that the 3D concept had a positive impact in the wear resistance of the material.

6. CONCLUSION

The purpose of this work was to manufacture three dimensionally-structured polycrystalline diamond materials (3D PCD) with the aim of improving the resistance to wear of PCD by crack deflection toughening induced by residual stresses. A further aim was to correlate the measured properties with the microstructure of the material, to better understand how 3D PCD material concepts might be employed to improve material performance in application.

Based on the results, the 3D concept proved to be effective in improving wear resistance while maintaining relative sufficient fracture toughness. Engineering and designing the PCD material by deliberately inducing inhomogeneity of residual stresses was a success. Crack deflection caused by the various residual stresses proved to improve the wear resistance and wear scar development. The composite PCD made had the best combination of results on the Paarl Granite and the Vertical Borer test, when compared to the vastly successful commercial grades of Quadmodal and Tristar Grades.

For future work it is recommended that PCD made with granules featuring a core-rim structure where the core has a thermal expansion coefficient higher than the rim is explored. It is expected that such a material would have a different crack propagation mechanism and consequent different fracture toughness.

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