

**SPARK PLASMA SINTERING OF ALUMINA REINFORCED
WITH TUNGSTEN CARBIDE-COBALT SYSTEMS**

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2019

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I, Zibani Kaisara Amos, declare and confirm that this dissertation is my own original work and appropriate credit has been given where references has been made to the work of other authors. The dissertation has not been presented or submitted to any other university for similar or any other degree award.

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A handwritten signature in black ink, appearing to read 'Z. Amos', is written over a horizontal line.

Date: 11/04/2019

CERTIFICATION

The undersigned certifies that he/she has read and hereby recommends for acceptance by the Faculty of Engineering and Technology, a dissertation titled “Spark Plasma Sintering of Alumina Reinforced with Tungsten Carbide-Cobalt Systems”, in fulfilment of the requirement for the degree of Master of Engineering in Materials and Metallurgical Engineering, in the department of Chemical, Materials and Metallurgical Engineering, Faculty of Engineering and Technology, BIUST.

Dr EN Ogunmuyiwa
Supervisor

Date: _____

DEDICATIONS

To my family.

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ABSTRACT

Alumina-based ceramic composites have attracted many research interests for several decades due to their good mechanical properties and the abundance of alumina (Al_2O_3) raw materials. This study was aimed at investigating the mechanical properties, sliding wear properties and microstructure of alumina tungsten carbide-cobalt ($\text{Al}_2\text{O}_3/\text{WC-Co}$). In this study, $\text{Al}_2\text{O}_3/\text{WC-Co}$ admixed powders were consolidated and densified via spark plasma sintering (SPS) technique at a holding time of 5 to 10 minutes. The sintering temperatures were varied between 1600 and 1800 °C. The heating rates were varied from 75 to 150 °C/min and the cooling rates were 200 °C/min and free cooling. Al_2O_3 powders were reinforced with 5, 10 and 15 vol% WC-12wt%Co. The admixed powders were consolidated to relative densities ranging from 96.5 to 99.98 % of their theoretical density. XRD was utilized for phase identification of both the sintered samples and the admixed powders. Al_2O_3 phase was present in all the samples, while WC phase was present in the composite materials, the Co phase was not identified in both the powder and sample phase match. The XRD results revealed no new phases formed either during powder milling or sintering of the samples. The microstructures of the samples were evaluated using a scanning electron microscope (SEM) equipped with an energy dispersive x-ray spectroscopy (EDS). The microstructure of the pure Al_2O_3 had an average grain size of 40 μm while the average grain size of the sintered $\text{Al}_2\text{O}_3/5\text{vol}\%(\text{WC}-12\text{wt}\%\text{Co})$ was 36 μm . It was clear that the addition of WC-12wt%Co inhibited grain growth of the Al_2O_3 matrix during the sintering process.

The hardness of the samples was measured using the Vickers hardness with a diamond indenter. Hardness of the Al_2O_3 samples was found to be lower than that of the reinforced counterparts. The increase in the composition of the additives led to an increase in the hardness of the samples. Fracture toughness was computed using the Palmqvist crack method. It was found that increasing the amount of additives significantly increases the fracture toughness. Grain refinement was postulated to have a pronounced impact on the toughness properties of the samples. $\text{Al}_2\text{O}_3/\text{WC-Co}$ systems had better wear resistance to dry sliding test as compared to pure Al_2O_3 ceramic. WC-12wt%Co has proven to be an ideal reinforcement material for Al_2O_3 with improved mechanical properties and wear properties.

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Chapter 1. Background and Motivation

Ceramics are refractory materials made from inorganic substances that have non-metallic properties, with essential components [1], [2]. Ceramic matrix composites (CMCs) are a subgroup of engineering ceramics. CMCs have drawn attention in many industries for several decades, mainly due to their potential for numerous applications including cutting tool inserts, bearings, brake disks, gas turbine components, aircraft bodies and bioceramics. CMCs have been developed to overcome the brittleness of monolithic engineering ceramics. Ceramic and ceramic composites are fabricated through milling and sintering of the powder and green compact respectively to a fully dense material. Sintering is the heating process of a powder or compact at a temperature below melting point of the main constituent, with an aim to increase powder strength by bonding together of particles and increasing densification. Sintering is carried out mainly to reduce porosity, to increase the inter-particle contact area with time, to decrease the volume of interconnected pores, to promote grain growth and to isolate pores. There are two main types of sintering processes, namely solid state sintering and liquid phase sintering, among others. There are three main stages of sintering, which include initial, intermediate and final stages of sintering. Sintering can take place in a pressurised condition or pressures-less environment. Systems for pressure assisted sintering include hot pressing (HP), hot isostatic pressing (HIP), field assisted sintering techniques (FAST) and spark plasma sintering (SPS) [3].

Alumina (Al_2O_3) is used in many applications such as cutting tools inserts and bio-ceramics owing to their superior properties, such as low density, high hardness, good chemical stability, and good high temperature properties [4]. Al_2O_3 structure consists of both ionic (Al^{3+} and O^{2-}) and covalent (Al-O) bonds existing simultaneously. However, materials with these types of bonding structure have inherently low fracture toughness. Plastic deformation in Al_2O_3 ceramics is extremely limited due to its primary bonding structure. Some studies have reported that the fracture toughness of Al_2O_3 matrix composites can be enhanced by incorporating secondary phase particles such as tungsten carbide (WC), chromium carbide (Cr_3C_2), titanium carbide (TiC), niobium carbide (NbC) or silicon carbide (SiC) [5]–[7]. Among these carbides, polycrystalline WC has attracted the most attention as reinforcement of Al_2O_3 ceramics, due to its high fracture toughness of about $4\text{--}6 \text{ MPa}\cdot\text{m}^{1/2}$ and Young's modulus of $530\text{--}700 \text{ GPa}$ [8]. In addition, WC and cobalt

have similar crystal structure (hexagonal) as Al_2O_3 . WC may thus improve the mechanical properties of Al_2O_3 composites [9].

WC is used as a secondary phase impurity to enhance the fracture toughness and hardness of monolithic Al_2O_3 ceramics. However, this ceramic systems have been reported to fail by grain pull-out during tribological applications, which is caused by poor wetting between Al_2O_3 and WC particles [10]. One of the most widely used metallic binders for WC based ceramic composites is Cobalt (Co), some other binders include iron (Fe) and nickel (Ni). Even though the addition of Co binders improves sintering process and increase toughness this binder still has some problems associated with it, (low melting point and high cost). Sintering of binderless ceramics requires high sintering temperatures (1700 - 1900 °C), however binders lower the sintering temperature because they have lower melting point than the main components of the sintered bulk. Binders are soft materials that are capable of flowing into the pores and between grain boundaries during the sintering process. They can also provide wetting between the grains of the sintered materials [11].

Alumina/tungsten carbide ($\text{Al}_2\text{O}_3/\text{WC}$) is a carbide-based composites, with a fracture toughness (K_{IC}) of about $6.1 \text{ MPa}\cdot\text{m}^{1/2}$ [4], hardness (H) of approximately 22.4 GPa [12] and high wear resistance, which makes it excellent for many engineering applications. WC is used as a toughening material and Co is used for binding due to its good wetting capabilities. The essence of Co is to increase the adhering of the WC phase to the Al_2O_3 matrix particles. The sintering in SPS is conducted at high temperature of about (1400-1800 °C) to ensure that the Co is melted [13]. Monolithic Al_2O_3 has a Young's modulus of 380 GPa and toughness of $3.2 \text{ MPa}\cdot\text{m}^{1/2}$, and WC has a Young's modulus of 530-700 GPa and a toughness of $4\text{-}6 \text{ MPa}\cdot\text{m}^{1/2}$, while WC-Co has a toughness of $12\text{-}17 \text{ MPa}\cdot\text{m}^{1/2}$ [14]. The modulus of elasticity for WC-Co vary between 330 and 400 GPa [15]. Therefore, by using the rule of mixture calculations, it is expected that the modulus of elasticity of monolithic Al_2O_3 could be increased considerably by addition of WC-12wt.%Co reinforcements. This study seeks to investigate the toughness, hardness, microstructure and dry sliding wear behaviour of $\text{Al}_2\text{O}_3/\text{WC}\text{-}12\text{wt.}\%\text{Co}$ ceramic systems fabricated by SPS.

1.1 Problem Statement

Al_2O_3 has low fracture toughness due to its atomic bonding that does not allow plastic deformation to occur easily. Al_2O_3 is widely used in cutting tool inserts, tribological applications, spark plugs insulation, biomedical and thermal protection systems, among

others. However, its application is limited due to its severe brittleness, poor durability and poor tribo-wear behaviour. Al_2O_3 is susceptible to adhesive wear due to high friction caused by high cutting speed [16]. It is well known that mechanical properties of materials are highly influenced by their microstructure, therefore Al_2O_3 ceramics have been reinforced with hardmetals to tailor its microstructure. In order to improve the properties of Al_2O_3 , reinforcements have been intensively investigated [6], [7], [17]–[20]. The addition of WC reinforcements in Al_2O_3 is well documented, but this ceramic systems still shows to be lacking in ductility. However, there is little or no adequate information on the research of $\text{Al}_2\text{O}_3/\text{WC-Co}$ systems and their mechanical properties, microstructure and sliding wear properties. This study, therefore, seeks to improve the overall performance, brittleness, fracture toughness and wear behaviour of Al_2O_3 ceramic by reinforcing with WC-12wt.%Co.

1.2 Objectives

The aim of this study is to fabricate Al_2O_3 ceramics reinforced with different volume percent of WC-12wt.%Co using SPS technique. The following objectives were employed to accomplish the aim of this study:

- Characterisation of the starting powders and milling the starting powders to finer particle size. Admixing the powders at different volume contents, i.e. 5, 10 and 15 volume percent of WC-12wt.%Co.
- Sintering and densification of Al_2O_3 ceramic powder with and without WC-12wt.%Co additives using SPS. Assessment of the mechanical properties of the composites in terms of hardness and toughness.
- Exploring the microstructure(s) and phases(s) formed before and after the consolidation of the admixed powders. Determination of the dry sliding wear behaviour/mechanisms of the sintered samples.

1.3 Hypothesis, Scope and Delimitations

This work focuses on investigation of the microstructure, mechanical properties and wear behaviour of alumina, $\text{Al}_2\text{O}_3/\text{WC-12wt.\%Co}$ ceramic systems. It is hypothesized that the addition of softer Co phase into the $\text{Al}_2\text{O}_3/\text{WC}$ systems could possibly increase their fracture toughness and improve wear properties. Co phase is expected to induce tearing during fracture toughness and it will also provide lubrication during wear of these ceramic systems.

Experiments were conducted to validate the feasibility of this hypothesis. Further experimental studies were carried out to gain a comprehensive understanding of the impact of WC-12wt.%Co on properties of Al₂O₃ ceramics. In this study Vickers hardness test was used to measure the hardness of sintered samples. Other hardness methods such as Brinell and Knoop were not exploited. The toughness of samples was measured from a Vickers indented cracked surface by means of Palmqvist crack method. The wear test were conducted through dry sliding between stainless steel balls and the sintered samples by means of ball-on-plate linear reciprocation configuration. The wear test environmental conditions in this study were dry air and ambient conditions. Factors such as temperature changes during the dry sliding test were not considered in this study.

1.4 Expected contributions

Upon completion of this study, the following is expected to be added to the body of the knowledge:

- (i) Influence of WC-12wt.%Co on fracture toughness and hardness behaviour when used as a reinforcement material in alumina ceramics.
- (ii) Effects of WC-12wt.%Co on the dry sliding wear behaviour of the Al₂O₃ ceramics.
- (iii) The influence of WC-12wt.%Co on the microstructure of spark plasma sintered Al₂O₃ ceramics.

1.5 Dissertation Layout

This dissertation has five chapters, chapter 1 outlines the introduction to the topic. The chapter includes the motivation, problem statement, objectives, scope and contributions. Chapter 2 presents a review of the recent progress of fabrication and characterisation of Al₂O₃ and its reinforcements with emphases on the WC and WC-Co cemented carbides. The review of sintering techniques and toughening mechanisms in ceramic composites is introduced.

Chapter 3 outlines the materials, equipment and experimental procedures used to carry out this study. Chapter 4 presents the results and discussions of the experimental findings of this study. Chapter 5 concludes this work and presents future directions.

Chapter 2. Literature Review

2.1 Introduction

This chapter describes the literature of alumina and alumina-based ceramic systems, their sintering methods, densification process and impurity additives. Cemented carbides (tungsten carbide-cobalt) and hardmetals (tungsten carbide) are reviewed as reinforcements for alumina in this chapter. The spark plasma sintering technique is studied as a powder consolidation method for alumina based and WC-Co ceramic systems.

2.2 Alumina ceramics

Alumina is a compound of aluminium (Al) and oxygen (O) covalently bonded together. It is produced primarily from bauxite rocks extracted through the Bayer process and it has a chemical formula Al_2O_3 . Aluminium (III) oxide is the most occurring state of this compound. Al_2O_3 crystalizes in many different polymorphous phases, namely α , γ , η , δ , θ , χ , κ and ρ . The α - phase is usually termed Corundum and is the most stable Al_2O_3 phase at room temperature. Corundum has an rhombohedral crystal lattice system, with a space group $R\bar{3}C$ at room temperature, its lattice parameters in hexagonal axes are $a = 0.4759 \text{ nm}$ and $c = 1.299 \text{ nm}$ [21].

Al_2O_3 ceramics possess excellent physical and mechanical properties, good chemical stability, and good thermal stability [22]. Al_2O_3 is a stable oxide, with strong atomic bonds, it also has good mechanical and thermal performance. Like most ceramic materials Al_2O_3 also has a high elastic modulus, satisfactory flexural strength, excellent wear and tribological properties and good refractory properties. Al_2O_3 ceramics are used in many industrial areas due to its low density (3.965 g/cm^3 about half the density of steel) as compared to other monolithic ceramics and other engineering ceramics. Al_2O_3 has a fracture toughness (K_{IC}) of approximately $3.5 \text{ MPa}\cdot\text{m}^{1/2}$, a thermal coefficient of $8.5 \cdot 10^{-6} \text{ K}^{-1}$ and its hardness value of approximately 20 GPa [23]. Highly dense Al_2O_3 with fine grains has an elastic modulus of about 400 GPa (about twice the modulus of steel) [24]. Table 1 presents a summary of properties of pure Al_2O_3 .

Table 1. Properties of pure Al_2O_3

Properties	Value
Purity	99-99.5%
Density (ρ)	3.965 g/cm^3
Crystal structure	Rhombohedral

Melting point	2072 °C
Thermal conductivity	8.5×10^{-6} /°C
Flexural strength	379 Mpa
Elastic modulus	380 Gpa
Shear modulus	152 Gpa
Bulk modulus	228 Gpa
Compressive strength	2600 Mpa
Hardness	20 GPa
Toughness	$3.5 \text{ MPa} \cdot \text{m}^{1/2}$

2.2.1 Applications of alumina ceramics

Al_2O_3 has a wide range of application owing to its excellent properties such as high hardness, high melting point, low density, good chemical stability, good corrosive resistance, good refractory properties and good biocompatibility. It is used as abrasive, due to its high hardness and good tribochemical properties. It is also used as cutting tools where friction and thermal properties are essential. Al_2O_3 is reinforced with titanium carbide to increase its thermal conductivity and with zirconium to improve its fracture toughness. Due to alumina's good tribological properties, and good chemical stability it is used in hip joint replacement. Applications of Al_2O_3 ceramics include high voltage insulators, spark plugs, electronics applications, tiles, tribology applications, and ceramics for mechanics. Al_2O_3 ceramics are used for spark plugs insulation for automobiles. Al_2O_3 is used in most electronic insulations due to its high resistivity. However, the application of Al_2O_3 ceramics is limited by its intrinsic brittleness and lack of durability like most monolithic ceramics [25].

2.3 Alumina based ceramic systems

Al_2O_3 based ceramics have been intensively investigated by many researchers with the aim of improving its fracture toughness. Different reinforcements and processing methods have been used in the production of this ceramic. Reinforcements in ceramic matrix materials are a small portion of ductile nano-particles added to ceramic materials normally to improve the strength, hardness and toughness of ceramics. Reinforcements of CMCs vary in shape, size and morphology; these reinforcements can be classified as whiskers, particulates, platelets, nano-phase, continuous and discontinuous fibres. Particulates generally mean the globular ceramic reinforcements with an aspect ratio less than about five. Particulates are cheaper and easier to acquire than other forms of reinforcements. Moreover, the composites reinforced with ceramic particles may be fabricated by

conventional ceramic processing techniques. Whiskers are dislocation-free filamentary single crystals with aspect ratios that are greater than ten. They are remarkable for their high strength, which could approach the theoretical strength of the material. Therefore, ceramic whiskers are very attractive materials for reinforcement in ceramic matrix composites to enhance the mechanical and thermal properties for high temperature and stress applications. The main toughening mechanism in whisker-reinforced ceramic matrix composites are formation of microcracks, elastic strain energy absorption, de-bonding, bridging and pull-out of whiskers and crack deflection around whiskers [26].

Nano-composites ceramics are composites consisting of nano-sized ceramics containing metallic particulates dispersed within the matrix grains and/or grain boundaries. The nano composites are said to have a great capability of improving the mechanical properties of monolithic ceramics even at high operating temperatures. Multifunctional ceramics were developed recently based on the concept of nano-composites. Polycrystalline ceramic composites can be categorised into two main groups, namely micro-composites and nano-composites. Micro-composites consist of micro sized fibres, particles, whiskers and/or particulates dispersed at the grain boundaries and within the matrix grains. These composites are said to have better fracture toughness than monolithic ceramics. Nano composites can be subdivided into four types namely intragranular, intergranular, intra/intergranular mixed and nano/nano composites [14]. Types of nano-composites are illustrated in Figure 2-1. In intragranular and intergranular nano-composites, nano-sized particles are dispersed within the matrix grain and at the grain boundaries respectively. In a realistic powder mixing the intra- and inter granular nano-composites can be obtained simultaneously. Intragranular type help by generating dislocations and pinning during the cooling down from fabrication temperatures, hence controlling the grain size and shape of the matrix. Intergranular nano dispersoids particles plays an important role in the grain boundary structure control of the oxide and nano-oxide ceramics which is postulated to play a major role in improving the mechanical properties of composites at high operational temperatures. In nano/nano composites, both phases are made of nano-sized particles. These composites were developed to overcome the problem of machinability of ceramics and are reported to have good superplasticity properties [27].

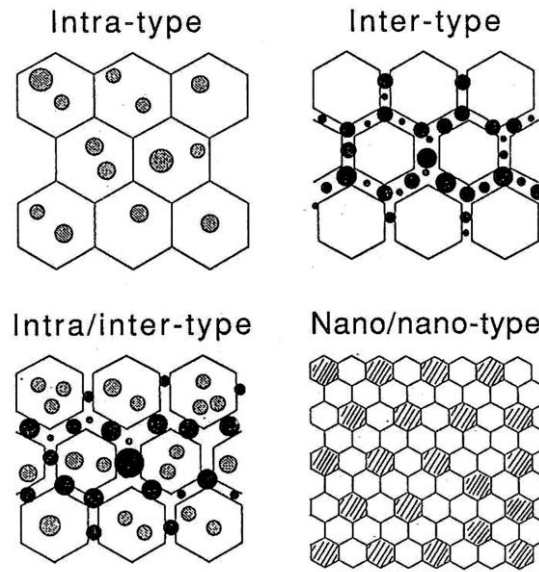


Figure 2-1. Schematic representation of ceramic based nano-composites [28]

Nano-composite systems include $\text{Al}_2\text{O}_3/\text{SiC}$, $\text{Al}_2\text{O}_3/\text{SiN}_4$, $\text{Al}_2\text{O}_3/\text{TiC}$, $\text{Y}_2\text{O}_3/\text{SiC}$. SiC has been intensively investigated as a reinforcement material for many ceramic-based composites. In the ceramic metal systems, nano-sized metallic particles are dispersed in Al_2O_3 nano-composites and sintered via spark plasma sintering [29]–[31].

It is well known that the properties of polycrystalline materials are controlled by the microstructure. Therefore, in order to obtain a reliable ceramic with better properties the grain size and grain size distribution are carefully controlled within the microstructure of ceramics. The microstructure of Al_2O_3 has been investigated by [32], these authors postulated that SPS can be used to obtain highly dense α -alumina compared to traditional powder metallurgy processing techniques. SEM was used to investigate the microstructure of WC- Al_2O_3 composite it was found that sintering temperature has a remarkable effect in grain size and microstructure of this composite. With an increase in sintering temperature from 1200 °C to 1300 °C, at a sintering temperature of 1200 °C many pores were observed with an average grain size of 2 μm .

Lin et al [33] prepared $\text{Al}_2\text{O}_3\text{-Cr}_2\text{O}_3/\text{Cr}_3\text{C}_2$ nano composites via SPS. Secondary phases were reported to procrastinate shrinkage curves of composites, it is also reported that secondary phases inhibited grain growth of Al_2O_3 . However, these phases react with Al_2O_3 if the sintering temperature is raised from 1200 to 1350 °C to form $\text{Al}_2\text{O}_3\text{-Cr}_2\text{O}_3$ solid solution. Haung et al 2010 [23] fabricated $\text{Al}_2\text{O}_3\text{-WC}$ composites using pulsed electric

current sintering. Sintering parameters employed were 1250-1750 °C sintering temperature, pressure of 60 MPa and dwell time of 4 minutes

Al₂O₃-ZrO₂ systems are preferred for applications where fracture toughness is a requirement. The ZrO₂ undergoes a phase transformation from tetragonal crystal phase to a monoclinic crystal phase at the crack tip during crack propagation. This transformation is caused by the stress field at the crack tip and it leads to material volume expansion, which causes crack arrests as the material presses against the crack tip [34].

2.3.1 Alumina-tungsten carbide ceramic systems

Composites are made from two or more constituents with significant difference in mechanical, chemical and physical properties. Ceramic matrix composites are made from ceramic material, usually reinforced with other ceramic dispersed phases with the aim to improve the microstructure, toughness and strength of monolithic ceramics and brittleness. Carbides are among the hardest engineering ceramics. Hardmetals and carbides such as WC and titanium carbide (TiC) are normally added to Al₂O₃ for cutting tool applications to increase the thermal conductivity and fracture toughness of Al₂O₃ [35].

Al₂O₃/WC has potential application in structural tools and cutting tools, however, these ceramic systems have fracture toughness lower than that of conventional WC-Co cemented carbides. The low toughness lead these ceramic systems susceptible to braking during high-speed cutting. Al₂O₃/WC systems are thermodynamically stable up to a temperature of 2000 °C [8], this allows Al₂O₃/WC composites to be sintered up to 2000°C without any chemical reaction between the Al₂O₃ and WC particles. Chen et al. (2014) [9] studied the mechanical properties of WC-Al₂O₃ ceramic systems produced by SPS. The authors used sintering temperatures ranging between 1200-1350 °C. a high hardness of 24.4 GPa was achieved and it was related to the presence of W₂C phase formed during sintering of at temperatures above 1300 °C. However sintering of this ceramic systems requires high sintering temperature to attain high densification, to solve this issue a low melting material like iron (Fe) is used as a binder [36].

2.3.2 Alumina-WC-Co systems

WC-Co are composite materials composed of tungsten carbide, ceramic bonded together with cobalt metal. The purpose of binders in cemented carbides is to hold the powder together while the material is being formed into a desired shape. Binders provide plasticity necessary for shaping process such as extrusion. The primary characteristic of binders is that they have good wettability. Co acts as a cement and provide good wetting between WC grains. WC particles dissolve into the Co phase during sintering consequently reducing the melting point of Co. The molten phase, then flows to fill pores and cavities within the sample being sintered. A WC-Co phase diagram is shown in Figure 2-2, however, for WC-Co cemented carbides the percentage of Co is kept below 20 at.%. WC-Co cements are widely used in cutting tool inserts and wear-resistant parts typically at WC-6.5wt.%Co [37] or WC-10wt.%Co [38]. Cemented tungsten carbide (WC) contains binders; the binders used for cemented carbides include Co, nickel (Ni). Cemented carbides are widely used for metalworking and high speed cutting tools [39], mainly due to their good mechanical properties i.e. toughness and hardness. Alumina is sometimes reinforced with cemented carbides, which consists of carbides and binders in the form of metallic elements. WC-Co has relatively high toughness and hardness than Al_2O_3 ceramics. WC phase is harder than Al_2O_3 phase however, this material is hard to sinter due to its high melting point. Co is used as a binder due to its good adhesive properties, it is used mainly to provide good wetting between the Al_2O_3 and WC particles during sintering. In the process, Co reduces the hardness of the Al_2O_3 /WC ceramic systems. It also has good wetting capabilities, which come in handy in the sintering of ceramic systems with different thermal conductivity.

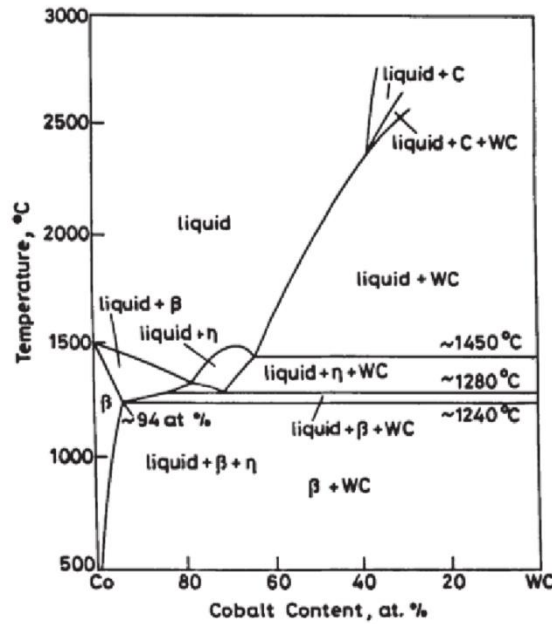


Figure 2-2. Binary phase diagram of WC-Co [40]

There is limited publication in microstructure and mechanical properties of $\text{Al}_2\text{O}_3/\text{WC-Co}$ systems. However, some studies have shown that WC-Co can contribute to the improvement in fracture toughness and hardness for alumina ceramics. The effectiveness of WC-Co on the mechanical properties of the alumina based composite is still a provocative topic. WC-Co is a composite with sufficient Co to facilitate binding/ wetting during sintering. Co also provide a well-balanced fracture toughness and hardness by altering the amount of Co in the composite. Therefore, by decreasing the amount of Co, the toughness of the WC-Co composite is also diminished. Sung et al (1994) reported that the addition of WC and Co particulates reinforcement to Al_2O_3 has a significant increase in the fracture toughness of Al_2O_3 ceramic from 2.9 to 10 $\text{MPa}\cdot\text{m}^{1/2}$ [41]. However, these authors used a different sintering technique from the one employed in this study and a sintering temperature of 1600 °C.

2.3.2.1 Mechanical properties of alumina composites

Ceramics are characterised by high hardness, high compressive strength, high elastic modulus, high strength and extreme brittleness with low fracture toughness. Understanding mechanisms of fracture and enhancement of fracture toughness of the ceramics are the two most challenging principles in these materials. These materials are highly prone to fracture and once the fracture starts, it is very difficult to contain.

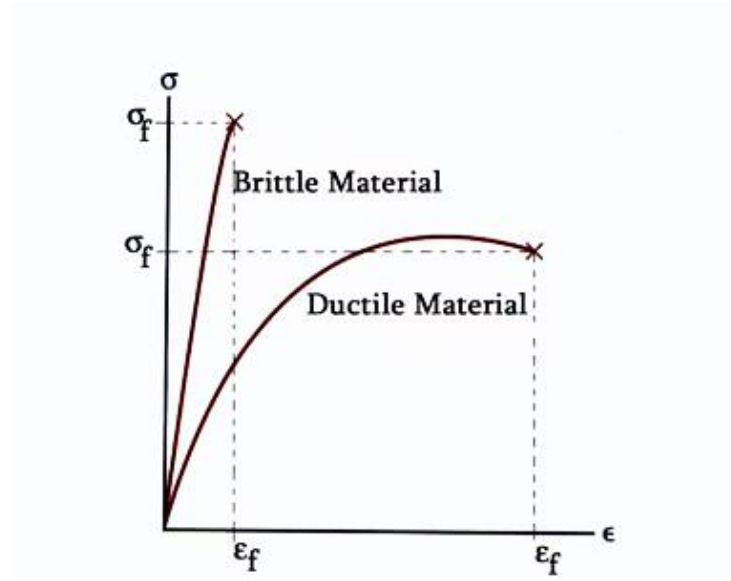


Figure 2-3 Stress, strain curve of brittle vs ductile materials

From the first principle of fracture of solid material, rupture of the inter atomic bond and consequent creation of new surfaces and enhancement of surface energy. Calculation of theoretical cohesive strength is given by

$$\sigma_{th} = \left(\frac{E\gamma}{a_0} \right)^{1/2} \quad (1)$$

Where σ_{th} is the cohesive strength, E is the modulus of elasticity, γ is the surface energy and a_0 is inter atomic spacing. The theoretical strength of the ceramic/brittle material is higher than the experimental value due to the presence of dislocation/defects. Stress concentration at the crack tip is higher than the external applied stress. The stress intensity at the crack tip is

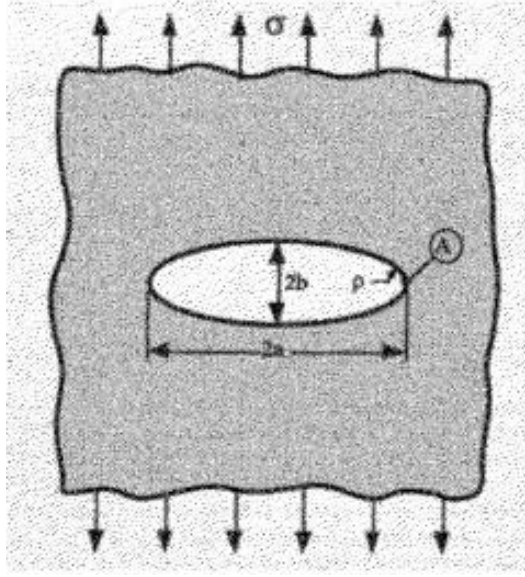


Figure 2-4 Elliptical hole on a flat plate

$$\sigma_{max} = \left(1 + 2 \sqrt{\frac{c}{\rho}} \right) \sigma = 2 \sqrt{\frac{c}{\rho}} \sigma \quad (2)$$

Where σ_{max} is the stress concentration at the crack tip, ρ is crack tip radius, c is the edge crack length, σ is the externally applied stress, σ increases as c increases or ρ decreases. Sharp cracks and long cracks will be hard to contain due to the magnitude of σ_{max} . For fracture to take place $\sigma_{max} \geq \sigma_{th}$. Therefore

$$2\sigma \sqrt{\frac{c}{\rho}} = \left(\frac{E\gamma}{a_0} \right)^{1/2} \rightarrow \sigma_c = \left(\frac{E\gamma\rho}{4a_0c} \right)^{1/2} \quad (3)$$

Assuming that $\sigma = a_0$ the critical stress becomes;

$$\sigma_{inglis} = \left(\frac{E\gamma}{4c} \right)^{1/2} \quad (4)$$

Where a_0 is inter atomic spacing and σ_{inglis} is the minimum stress required to grow a crack. Hence, the stress is more dependent of the crack length than crack tip radius and inter atomic spacing. The lower the crack length the higher the critical stress and the larger the crack tip the lower the stress required to grow a crack.

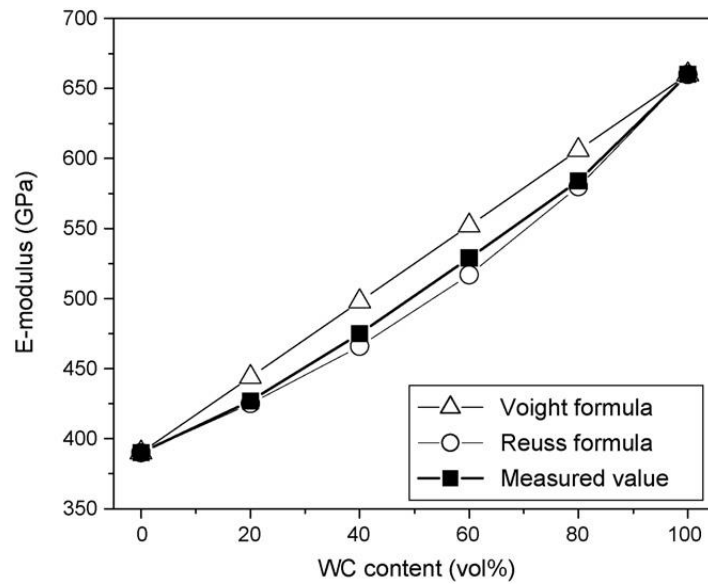


Figure 2-5 Elastic modulus of Al_2O_3 -WC composites as a function of the WC volume percent

2.3.2.2 Vickers indentation hardness of alumina ceramics

Polycrystalline materials deform by plastic or elastic or both plastic and elastic combined, however ceramics are considered brittle in general because they mostly deform elastically with little to no plastic yielding. Hardness of a material is defined as the measure of its resistance to permanent deformation. There are many hardness determining methods, including Brinell, Rockwell, Vickers and Knoop hardness test. However, the Vickers hardness test is the most widely adopted method of hardness test for advanced ceramics.

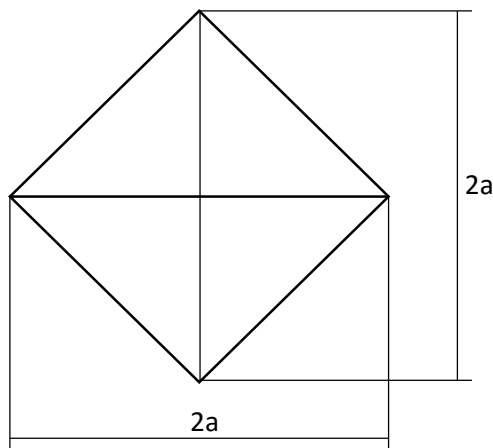


Figure 2-6. Schematic diagram of the Vickers indent showing the area of the two diagonals of the diamond indent

Diamond indentation is normally used to measure the indentation on a flat polished surface in ceramics due to their high hardness. Based on the indent size, hardness parameter is given by:

$$H = 1.854 \left(\frac{P}{d^2} \right) \quad (5)$$

Where, H is the Vickers hardness, P is the applied load and d is the average length of the two diagonals of the indent. Precautions that are considered during indentation include (1) optimisation of the applied load so that the corners of the indent are clearly visible but crack is not formed. (2) Accurately measure the indent diameter, election microscopy can be used when the diameter is in the order of micrometres. (3) Repeated measurement is considered at different locations, this is to account for material inhomogeneity.

Compressive strength of ceramics is much higher than tensile strength, typical ratio is 8:1. Failure in this type of load is more gradual than tensile loading. The elastic modulus is the same for both compressive and tensile loading. Cracks develop vertically during compressive loading, serrations during loading is associated with the spalling of the test piece. In compressive loading, the crack is formed in parallel with the loading direction. Microscopic aspects of fracture tension and compressive loading. Elastic modulus of ceramics is measured by the natural frequency of vibration of the rectangular sample when the ceramic is struck by a steel rod. The empirical formula used for elastic modulus is given by

$$E = 0.9465 \left(\frac{m f_f^2}{b} \right) \left(\frac{L^3}{t^3} \right) \left[1 + 6.858 \left(\frac{t}{L} \right) \right] \quad (6)$$

E is the elastic modulus, m is the mass of the ceramic, f_f is the natural frequency of vibration in the flexure mode, and b, t and L are the width, thickness and length of specimen respectively. This is very complex to measure in most cases a computer is used. Ultrasonic sound can be used to measure elastic modulus and Poison's ratio based on the wave velocities.

Ceramics systems do not have dislocations present during deformation, consequently there is hardly any plastic. Once the crack starts there will be a catastrophic failure. Toughness in ceramics can be enhanced by restricting the propagation of previously existing cracks. This is achievable through controlling of the microstructure at the vicinity of the crack tip. The restriction of crack propagation can be added by grain boundaries through grain boundary pinning. Also hard precipitates within a ceramic can restrict the movement of cracks. Two mechanisms of improving ceramic toughness are crack deflection and crack bridging. If alumina is reinforced with SiC whiskers the fracture toughness of the composite can be raised by up to $12 \text{ MPa}\cdot\text{m}^{1/2}$, at about 30% SiC additives. Table 2 presents a summary

of hardness and toughness of Al₂O₃, Al₂O₃/WC and Al₂O₃/WC-Co ceramic composites. The addition of 20 wt% WC increases the fracture toughness of Al₂O₃ by almost over 100% from 2.9 to 7.0 MPa·m^{1/2}. The fracture toughness and hardness values are also dependent on the method and load used for testing, densification and microstructure of the materials.

Table 2. Summary of materials and their toughness and hardness

Material	Hardness (GPa)	Toughness (MPa·m ^{1/2})	Reference
Al ₂ O ₃	12	2.9	[42]
Al ₂ O ₃ /4W	24.6±0.9		[43]
Al ₂ O ₃ /40W	24.0	4	[23]
Al ₂ O ₃ /5WC	16	3.0	[42]
Al ₂ O ₃ /10WC	19	7.0	[42]
Al ₂ O ₃ /20WC	18	7.1	[42]
90 % Al ₂ O ₃ + 10% WC+ 0% Co	18.0±0.4	4.7±0.6	[44]
90 % Al ₂ O ₃ + 9.4% WC+ 0.6% Co	17.1±0.5	5.7±0.6	[44]
90 % Al ₂ O ₃ + 9% WC+ 1.0% Co	18.1±0.7	5.5±0.4	[44]
90 % Al ₂ O ₃ + 7% WC+ 3% Co	17.6±0.5	8.0±0.6	[44]

Huang et al 2010 studied the relation of Vickers hardness and fracture toughness to the WC Volume percent as a reinforcement of Al₂O₃ ceramic. The results are shown in Figure 2-7. According to the results presented they were an increase in hardness and fracture toughness as the volume percent of WC increase. Hardness increases from approximately 19.5 to 25.5 GPa as the volume percent of WC is increased from 0 to 80%. Fracture toughness of Al₂O₃ increases from approximately 2.5 to 5.25 MPa·m^{1/2} as the volume percent of WC is raised from 0 to 80%. However, it is worth pointing out that the sintering temperature is changed after 40 vol.% WC reinforcement is reached from 1450 to 1650 °C.

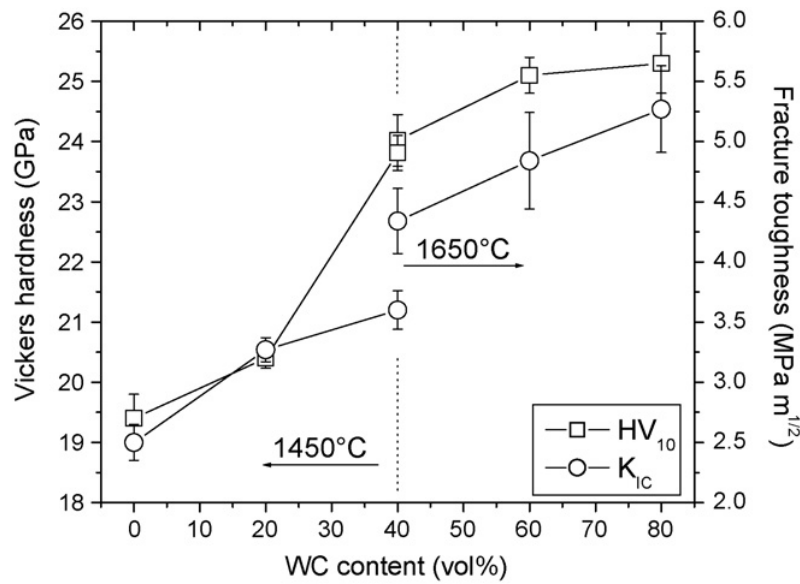


Figure 2-7 Hardness and fracture toughness of Al_2O_3 -WC composites as a function of WC volume percent

2.3.2.3 Fracture toughness of Alumina-based ceramics

Alumina is used as structural engineering ceramic applications because of its excellent mechanical properties, strength, high temperature characteristics and chemical stability. In addition, monolithic alumina is one of the most popular ceramic materials used in wear application such as cutting tools. However, the monolithic alumina is reported to be intrinsically brittle, which hinders its wider usage. The toughness of alumina can be increased by addition of hard ceramic particulate as reinforcements phases, this has shown to yield better toughness and hardness of alumina [6]. WC, SiC, TiC and Cr_3C_2 are widely used as particulate reinforcements for Al_2O_3 matrix [45]. Most of these reinforcements are reported to act as grain growth inhibitors [18], [20]. Reinforcements with higher coefficients of thermal expansion shrink throughout cooling process, which creates residual compressive stress in the matrix. Reinforcements can contribute to the toughness of ceramics in three ways, mainly crack bridging, crack deflection and reinforcement pull out. In crack bridging, crack growth is delayed by separation of fracture surface led by high-energy consumption by bridges. In crack deflection the propagating crack changes direction of propagation, this increases fracture toughness by formation of extended and twisted crack path [46]. Fracture toughness is the measure of the resistance to crack propagation of a particular material. Indentation fracture toughness is the most widely used method to determine fracture toughness of advanced ceramic materials. In excess of the critical indentation load, cracks are formed around the indentation which can be used to describe the fracture properties of

a material. The fracture indentation method has been reported in the literature since it was introduced by Lawn and Wilshaw in 1975 [47].

Numerous formulae have been developed to model the fracture toughness of ceramic materials. However, these methods have been described as load sensitive methods due to the fluctuation of the toughness with respect to the applied load. There are two main methods adopted to compute fracture toughness of engineering ceramics which are based on the crack type. Crack types that can develop during Vickers indentation test include median/ radial and Palmqvist crack as shown in Figure 2-8. Palmqvist cracks do not penetrate below the test surface, but rather are shallow extending from the indent diagonals, while median cracks from a semi-spherical shape creating a plastic zone around the penetrating crack below the indent.

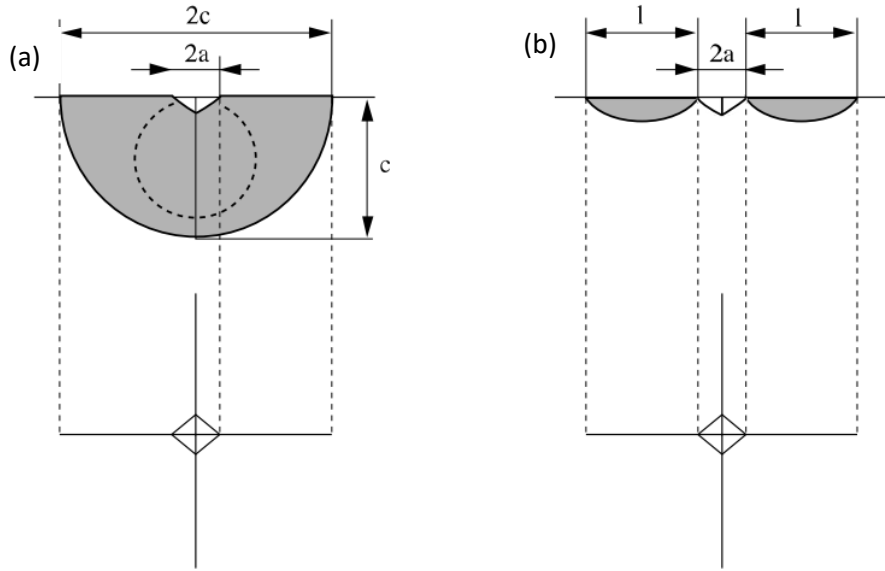


Figure 2-8. Crack types used for modelling indentation fracture toughness, (a) median crack, (b) Palmqvist crack.

The empirical formulas used in indentation fracture toughness were developed during the late 1970's and early 1980's and were considered ideal for the comparison of the toughness of ceramic and composite materials. The fracture toughness was first modelled by Lawn et al. in 1976 a median crack mode was assumed as the fracture type. The lawn formula is given by;

$$K_{IC} = \delta \left(\frac{E}{H_v} \right)^{\frac{1}{2}} \frac{P}{c^{3/2}} \quad (7)$$

Where $\delta = 0.016$ (shape factor) for a Vickers type indent, E is the elastic modulus of bulk material, H_v is the Vickers hardness, P is the applied pressure and c is the length of the

surface crack measured from the centre of the indent. In about 6 years Niihara et al. (1982) used Palmqvist crack to determine fracture toughness of advanced ceramics. The modelled formula is given by:

$$K_{IC} = 0.203 \left(\frac{c}{a} \right)^{\frac{-3}{2}} (\sqrt{a}) \cdot H_V \quad (8)$$

Where c is half crack length and a is half crack diagonal. Late Shetty et al. (1985) also defined fracture toughness using Palmqvist crack as given by equation below;

$$K_{IC} = 0.0899 \left(\frac{HP}{4l} \right)^{0.5} \quad (9)$$

Where l is the length of the indentation crack. Both the lawn, Niihara and Shetty are still applied in the determination of fracture toughness of advanced ceramics. The selection of the empirical formula for determination of fracture toughness is based on the type of crack and nature of ceramic (i.e. carbides, nitrides and oxides). However, both these methods are applicable to Al_2O_3 ceramic materials and have been used by many authors [48]–[50]. However, this formula assumes single crack propagating from the edge of the diamond indenter and away from it, which is not always the case with experimental cracks. The Rockwell hardness test is also used in fracture toughness testing of relatively softer materials (i.e. ductile metals and polymers). Toughness of hard and brittle materials can be enhanced by doping with hard particles or soft impurities depending on the intended application. These impurities may have an effect on the toughness mechanisms of the matrix material.

2.4 Spark Plasma Sintering of Al_2O_3 Ceramics

Sintering is a process by which a loosely bonded and highly porous ceramic powder is transformed into a strongly bonded monolithic mass with the removal of inter-particulate pores. The advantages of sintering are that it lowers excess energy associated with the free surfaces of the fine powders. Lowering of surface energy can be obtained by reduction of the surface area is done by coarsening of particle size of the fine powder. And also by formation of grain boundaries, or solid/solid interface (low energy) from a solid/vapour interface (high energy). SPS is capable of producing ceramic samples at low sintering temperature with densities nearly close to that of theoretical density and have minimal grain growth.

Ceramics have a high melting point and therefore require high temperature to melt and cast like metals and alloys, which is energy consuming. Sintering is one of the most common steps and a unique phenomenon in manufacturing of ceramic materials. Ceramics are also brittle and cannot be forged easily due to low to no plastic deformation. Sintering provides an alternative and useful process for the shaping and consolidation of ceramics. Ceramic raw materials are available in powder forms produced by chemical synthesis, or by grinding of the bulk naturally occurring minerals. If the powder is given sufficient activation energy, the powder tends to lose the excess energy associated with their free surfaces, which is an advantage in the sintering process. Furthermore, powders have a higher surface area than lumpy minerals; therefore, they tend to lose excess free energy. Conventional sintering methods were used to fabricate nano composites, these include;

- (i) Pressure-less sintering
- (ii) Hot pressing
- (iii) Hot isostatic pressing.

SPS has been eminent for its faster and more efficient sintering abilities, which occurs due to the combined action of heating processes such as Joule heating, spark plasma discharge, electrical diffusion, and plastic deformation of sintered material [51]. SPS is a field assisted processing technique, it has received high appreciation over the last three decades, SPS has been utilized by many authors as a fabricate technique for ceramics and ceramic composites [52]–[54]. SPS have been developed as a densification method for producing dense materials at a relatively lower temperature and in a shorter period of time compared to the conventional sintering techniques. SPS employs D.C voltage, large electric currents and high pressure to produce a fully dense material within a few minutes. The benefits of SPS are short processing time, fewer processing steps, a near net shape and elimination of the need of sintering aids. In 1990, Sumitomo Heavy Industries Ltd. established the first commercial spark plasma sintering system. SPS is a uniaxial pressure-assisted synthesis and processing technique, which employs low voltage and high current from the beginning to the end of the sintering process under low atmospheric pressure. SPS seems to be similar to hot pressing (HP) method, but it is regarded as a fast sintering method and heating mechanism, effects of electric field and electric current, and ways of heat transfer to the sample show differences. In HP, the sample is heated by a radiator furnace, whereas in SPS, the Joule effect caused by a pulsed direct current (typically a few thousand

amperes and a few volts) provides the primary heating source. In the SPS technique, very high thermal efficiency can be achieved. The sample and die-punch rod assembly (mostly graphite) are directly heated with a pulsed direct current (DC) which passes through graphite punch rods, powder and dies simultaneously under a uniaxial pressure. Typically, external heating elements are not used in a conventional SPS system. Heating is achieved by way of a pulsed (on/off) DC. Moreover, application of on/off direct current generates sparks plasma, Joule heating and an electric field diffusion effect. In addition, on/off DC current form local high temperature states and cause vaporization and melting of the powder surfaces and promote sintering. This induces enhanced neck formation around contact area and improved densification [55]. A basic configuration of an SPS experimental setup is shown in Figure 2-9.

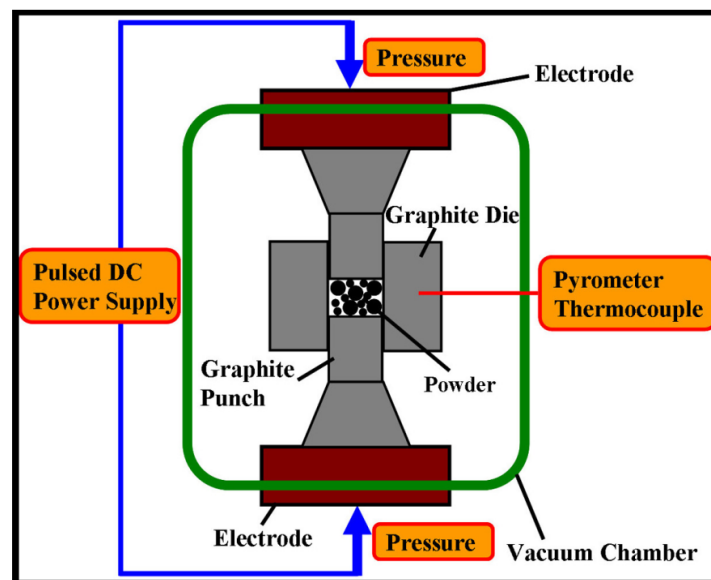


Figure 2-9. Basic configuration of a Spark Plasma Sintering technique [1]

Spark plasma sintering has been used in the fabrication of many ceramic systems and other metallurgical powders. However, there is limited literature available in the SPS parameters and phase transformation and properties of $\text{Al}_2\text{O}_3/\text{WC-Co}$ systems via SPS. Ceramics are first consolidated into green compact and sintering temperature about 50% to 80% of the melting temperature of the material. The melting temperature of Al_2O_3 is 2073 °C and sintering is carried out at about 1400 °C to 1650 °C. Kim et al 2004 [56] fabricated alumina by spark plasma sintering at 1150 °C. Grain growth of pure alumina was reported to have a significant dependence on the heating rate, applied pressure and loading schedule. Full densification was reported to occur by grain boundary sliding into the defects. Borrell et al 2012 studied the specific effects of SPS on the microstructure and mechanical

properties of pure Al_2O_3 . The authors reported that SPS generates residual strain concentration at the grain boundaries to restrain crack growth resulting in an increase in fracture toughness.

SPS has been widely used for various productions of Al_2O_3 ceramic systems, including $\text{Al}_2\text{O}_3/\text{WC-Co}$ [57], $\text{WC-Al}_2\text{O}_3$ [4], $\text{Al}_2\text{O}_3\text{-TiC}$ [58], $\text{BaTiO}_3/\text{Al}_2\text{O}_3$ [59] Aman et al 2011 [32] prepared $\alpha\text{-Al}_2\text{O}_3$ ceramics using SPS technique and the kinetics were investigated at different sintering stages. The authors reported that highly dense and fine polycrystalline Al_2O_3 material is achievable with SPS provided short sintering time is maintained compared to conventional sintering methods. The sintering kinetics are also reported for materials sintered at different heating rates, sintering temperature and holding time. The heating rates are reported to have a strong influence on the mechanisms of sintering kinetics. At low sintering temperature densification is favoured by low heating rate, this is claimed to trigger grain boundary diffusion mechanism. It is also reported that plastic yield might lead to densification at the early stages of sintering. Pure Al_2O_3 is claimed to have grain coarsening at temperatures above 1150°C , due to the surface diffusion sintering kinetics. It is also reported that at high sintering temperature densification is much lower for low heating rates, due to grain boundary sliding and power law creep. At the high heating rate lattice diffusion and grain boundary sliding are reported to be the most dominant sintering kinetics.

Lee et al. (2016) evaluated the microstructural evolution and mechanical properties of alumina sintered via spark plasma sintering (using Dr. Sinter SPS-515S, Japan). Phase transformation of Al_2O_3 was monitored at 1100 and 1600°C and a densification $> 99\%$ theoretical density was attained at 1600°C for ultra-fine grain $\alpha\text{-Al}_2\text{O}_3$.

2.4.1 Densification and Coarsening during sintering

Loosely bonded particle consists of a solid/vapour interface provided by the pores in between the particles. Particle growth is the coarsening process, which happens with bigger particles growing at the expense of the small particles. Here the overall surface area reduces and there is no chemical bonding-taking place, hence the strength of the material does not change. Coarsening reduces the surface energy due to surface area change reduction [60].

Densification is when the loosely bonded powder changes configuration and becoming a strongly bonded powder. In case of densification, grain boundaries are formed and pores are eliminated from the powders and the material becomes very dense. During densification,

the material gains strength and the specific surface energy $\Delta\gamma$ changes due to the change in the nature of the surface (solid-vapour surface to solid-solid surface). Coarsening and densification can proceed at the same time. If coarsening takes place first without densification sintering process cannot be able to reduce pores or densification is not feasible after coarsening [60].

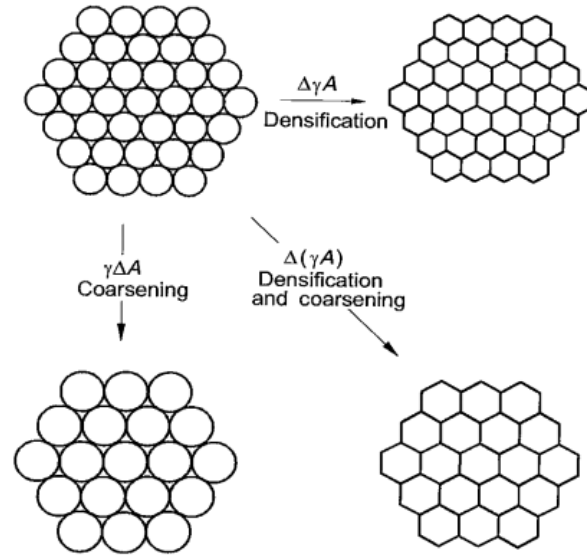


Figure 2-10. Schematic illustration of coarsening and densification behaviour [2]

There are two main types of sintering process are solid state sintering and liquid phase sintering. Solid state sintering involves direct particle-to-particle contact and vapour phase from pores. Liquid phase sintering involves a liquid phase and solid phase, the liquid phase is used as an adhesive at high temperature to adhere solid particles together. In both types, bonding takes place [60].

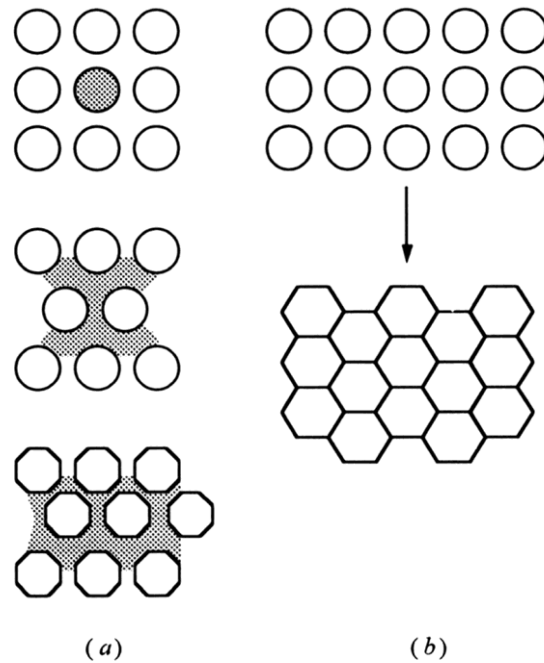


Figure 2-11. Schematic representation of (a) liquid phase sintering and (b) Solid state sintering processes [61]

In the solid state sintering, there is no melting of the particles only densification and grain growth remove pores. In liquid phase sintering the composite, consist of powders one with high melting point and another with low melting point. During high temperature, sintering the low melting point particles will melt into a liquid phase. The liquid phase in this case can fill the vapour phase/ pores this will form a bond and high strength [62].

2.4.2 Mass transport

The primary mechanism involved during sintering is the movement of atomic species from one lattice site to another takes place during sintering. Solid-state diffusion is the most important mechanism of mass transport, vapour phase transport takes place under certain conditions. Diffusion takes place in the crystal structure from one site to another. Capillary flow (viscous flow) of liquid is also an important mechanism, particularly in the liquid phase sintering process.

A global driving force for mass transport is associated with the lowering of free energy through elimination of excess surface energy. Mass transport is the local driving force at the atomistic level due to changes in the surface area. As the primary driving force for diffusion is the concentration gradient and that of the vapour phase transport is the gradient of vapour pressure, it is necessary to understand how these gradients are set up at the local level. In

order for vapour phase transport to occur there should be a difference in vapour pressure at two points (different sites) for diffusion to take place. Curvature of the particle surface plays the most crucial role in realising these gradients.

Point defects such as vacancies plays the most pivotal role in the diffusion mechanism of mass transport. Diffusion takes place in solids mainly by the presence of point defects mainly vacancies. Vacancy gradient can be established during the diffusion process. In addition to the dependence of its concentration on temperature and impurity content, it is also dependent on the curvature of the solid surface at the local level. Mostly point defects are created at high temperature and activation energy is provided for the creation of the defects mainly by heating the material. Creation of defects lowers the free energy of the system, therefore defects are having an exponential temperature dependence hence, and defects can be created by increasing temperature. Increasing impurities of different valence can also increase vacancies. Change in curvature also leads to changes in vacancy concentration at the surface. Therefore, it is necessary to understand the variation of the vacancy concentration and the vapour pressure as a function of curvature of the solid in a systematic manner.

Sintering process can be divided into three distinct stages based on the geometrical changes that the simple undergoes during the sintering process. Initial stage, contact area increases by neck-growth from 0 to 0.2 and the relative density is up to a maximum of 65%. Intermediate stage, this is the longest stage of sintering during which the relative density changes from 65% to 90 %. The final stage of sintering begins when the continuous pore gets separated into a large number of isolated pores, which may be lenticular in shape if they are along the grain boundaries or nearly spherical if they are away from the grain boundary. Sintering kinetics are different during different stages of sintering. Types of vacancy diffusion rate mechanisms in sintering are lattice diffusion, grain boundary diffusion and surface diffusion. Lattice diffusion is given by:

$$\frac{x}{r} = \left[\frac{64\gamma_{SV}V_{MX}^2 D_{ambi}}{kT} \right]^{\frac{1}{4}} t^{\frac{1}{4}} \cdot r^{-\left(\frac{3}{4}\right)} \quad (10)$$

Grain boundary diffusion

$$\frac{x}{r} = \left[\frac{192\gamma_{SV}V_{MX}^2 \delta_{gb} D_{gb}}{kT} \right]^{\frac{1}{6}} t^{\frac{1}{6}} \cdot r^{-\left(\frac{2}{3}\right)} \quad (11)$$

Surface diffusion

$$\frac{x}{r} = \left[\frac{225\gamma_{sv}V_{MX}\delta_s D_s}{kT} \right]^{\frac{1}{5}} t^{\frac{1}{5}} \cdot r^{-\left(\frac{4}{5}\right)} \quad (12)$$

δ_{gb} and δ_s are the grain boundary width and surface thickness respectively. D_{ambi} is the ambipolar diffusion coefficient for the compound MX expressed as $D_{ambi} = \frac{D_M D_X}{D_M + D_X}$, D_{gb} and D_s are the diffusion coefficients along the grain boundary and the surface respectively. The activation energy of the surface is lower than the grain boundary activation energy, which is also lower than the lattice activation energy. Hence, surface diffusion is dominant at lower temperature, while lattice diffusion is dominant at highest temperature. However, surface and grain boundary diffusion are preferred for smaller particle sizes. Lattice diffusion dominates for larger particle size at longer times and high temperatures. Picture activation energy for different diffusion mechanisms. Viscous flow mechanism of sintering also takes place as a form of sintering and mass transport. The pores are filled up by the flow of viscous mass. Viscous flow is in between solid state sintering and solid/liquid sintering. The linear shrinkage of viscous flow is time dependent and is expressed as

$$\frac{\Delta L}{L_o} = \frac{3\gamma_{sv}}{4\eta} t \quad (13)$$

Where η is the viscosity of the softened mass. $\Delta L/L_o$ is the linear shrinkage expression. The relationship between density and linear shrinkage is η , t is time of sintering, which is equivalent to a volumetric strain rate.

$$\rho = \frac{\rho_o}{(1 + \Delta L/L_o)^3} \quad (14)$$

Where ρ_o is the relative density. The densification can be determined by $(1/\rho)$ (dp/dt) . During the final stage of sintering pores are eliminated and Coarsening of particles takes place, which might lead to abnormal grain growth, during this stage average grain size increases with time. Ostwald ripening is whereby the pores are trapped within the large grains. Coarsening of particles is given by;

$$\frac{dr}{dt} = A_r(P_{av} - P_r) = \frac{2A_r V_{MX} P_{flat} \gamma_{sv}}{kT} \left(\frac{1}{r_{av}} - \frac{1}{r} \right) \quad (15)$$

Particles smaller than r_{av} shrink at the expense of larger particles. Where dr/dt is the change in particle radius with respect to time, P_{av} is the partial pressure and r_{av} is the critical

particle size. Factors that influence the solid state sintering includes; temperature, vapour pressure, diffusion coefficient, initial particle size, particle size distribution, the presence of agglomerates, green density, uniformity of initial microstructure, atmospheric conditions, concentration and nature of impurities, sintering aids and dwell time. Surface energy and dihedral angle of solid -vapour interface

2.4.2.1 Surface energy and dihedral angle of solid/liquid interface

Sintering of the solid particles can take place in the presence of a liquid phase, it, the corresponding dihedral angle (Ψ) is less than 180° . The equilibrium conditions are given by:

$$\gamma_{gb} = 2\gamma_{sl} \cos \frac{\varphi}{2} \quad (16)$$

During grain growth, the liquid phase is removed from the solid/liquid interface and the grain boundary becomes the solid-solid interface. Other variations of sintering are high pressure sintering, reactive sintering, microwave sintering and SPS. SPS relatively new technique, apply pressure and at the same time apply very high d.c voltage so that at local level they are relatively less sparks created the temperatures goes very high at the surface due to high surface energy of sparks is generated at the surface.

During sintering, there is volumetric shrinkage and densification. Pores are reduced when particles get closer to each other. The volume is reduced and the mass remains unchanged hence, the densification process. In addition, pore volume and size reduction can take place. There is a significant enhancement of mechanical strength. Also, if there are no enough particles to pin the grain boundaries, grain coarsening can take place at high temperature due to prolonged exposed to high thermal energy.

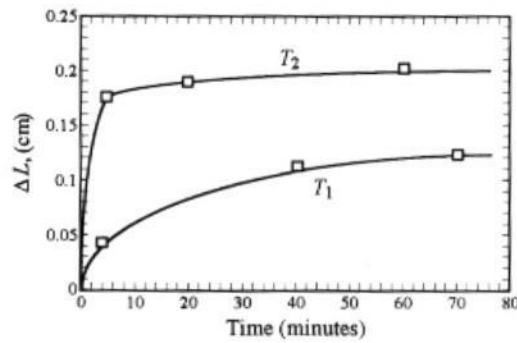


Figure 2-12 Typical shrinking vs time curve during sintering

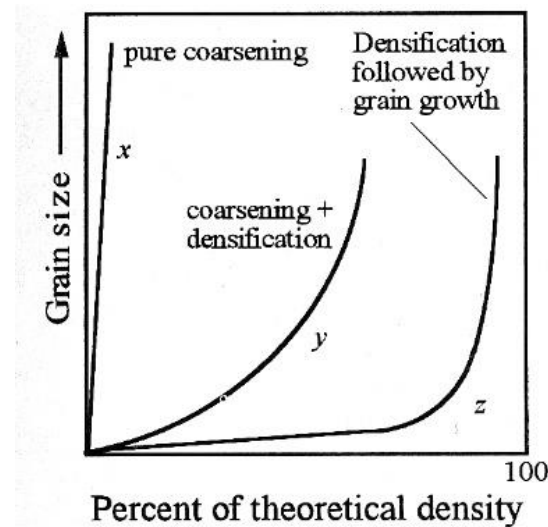


Figure 2-13 Coarsening and densification behaviour during sintering

Pure coarsening no densification, but rapid grain growth relative to the starting powder particle size. Densification followed by grain growth, theoretical density increases rapidly without much of grain growth and then grain growth follows after. Coarsening + densification takes place at the same time. Initial configuration/green compact before firing, Coarsening increases both grain size and grain size at the begging of the sintering process. If densification takes place first, pore size will reduce with a slight increase in grain size and then grain growth will take place.

2.5 Wear behaviour of alumina ceramics

Wear resistance is the ability of a material to withstand mechanical or chemical-mechanical abrasion. Ceramics are used in tribological application such as, gas turbine engines, cutting tools, roller and slid bearing hip replacements [1], [63], [64]. Wear is known to reduce the performance and damages the parts in contact. It is normally reduced by

lubrication between the two parts in contact and surface coatings are sometimes applied to improve the tribological properties. Sliding wear test with dynamic loading is normally observed to study the coefficient of friction, wear volume and wear rate for most ceramics [65], [66]. Roy et al. (2007) conducted a comparative analysis of the wear properties of fine and coarse-grained alumina ceramics. Sliding wear without lubrication tests were carried out using a pin-on-disc configuration wear test. The authors claimed that coarse grained alumina with 4 µm average grain sized had lower wear resistance than fine grained alumina with an average grain size of 0.45 µm. Furthermore, the authors stated that small grain sized alumina had compacted layer suffering from mild abrasion while the coarse-grained alumina had extensive cracking which led to delamination and flaking of the surface layer resulting in brittle fracture on the sliding surface. Similar behaviour was reported by Ajayi and Ludema (1988) [67]. Wear rate can be calculated using the following equation

$$Wr = \frac{k_{abr}P_n}{3H_V} = \left(\frac{k'}{2\pi R} \right)^{1/2} l^{3/2} \delta^{1/2} \quad (17)$$

Where k is Wear is a deformation process whereby one material surface removes material from another materials' surface by mechanical means (i.e. rubbing). Rubbing together of two or more surfaces creates friction and induce heat to the material verified by Newton's third law. Archard developed sliding wear test model, Archard's wear equation postulates that the volume worn away per unit sliding distance and the load defines the wear rate, W_r . The wear depth can be evaluated related to the wear rate, sliding distance and contact pressure. The modified Archard's equation is given by;

$$\frac{V}{\delta} = W_r \frac{F_N}{H} \quad (18)$$

Which reduces to;

$$W_r = \frac{V * H}{F_N \delta} \quad (19)$$

Where V is the wear volume in mm³, δ is the total sliding distance in m, F_N is the normal load (N), H is the hardness of the worn surface and W_r is the wear rate. However, wear volume is calculated by

$$V_f = l_s \left[R_f^2 \arcsin \left(\frac{W}{2R_f} \right) - \frac{W}{2} (R_f - h_f) \right] + \frac{\pi}{3} h_f^2 (3R_f - h_f) \quad (20)$$

Where l_s is stroke length, R_f is wear tract radius at the two ends of the wear track, W is the wear width and h_f is wear depth. In this work, the test pieces are small and only linear

reciprocating test is possible. The temperature of the test piece and test material are important in the analysis in terms of high speed cutting tools, however, this was not conducted due to the limitations of the equipment used in this study.

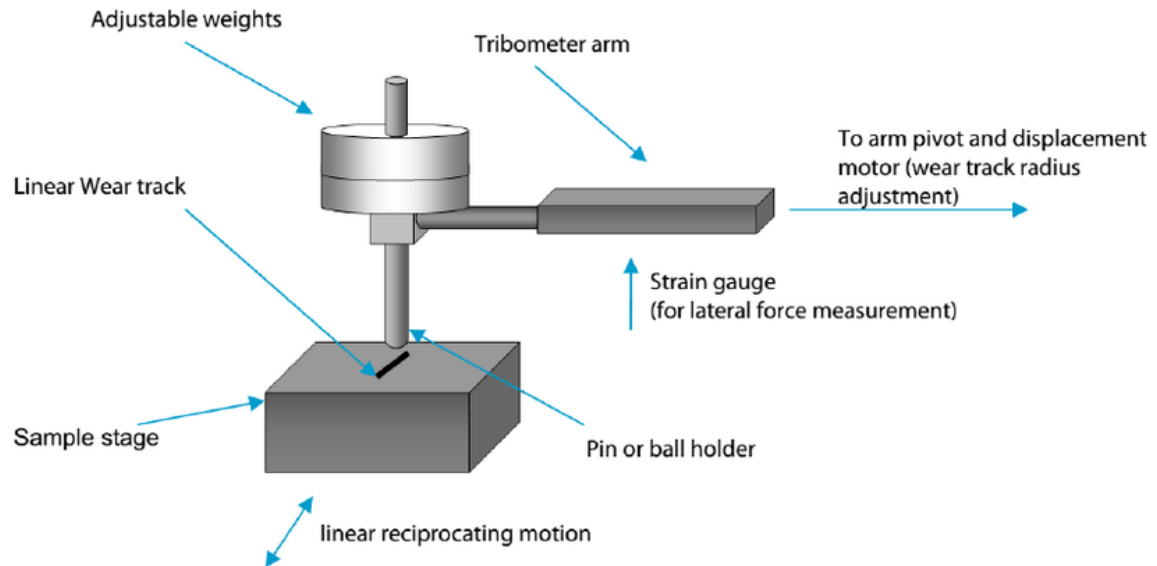


Figure 2-14. Schematic representation of a pin-on-plate or ball-on-plate sliding wear test setup

Hsu et al (1991) [68] investigated dry sliding test on alumina at low speed and elevated temperature (800 °C) under dry air, water and paraffin conditions. Wear contour maps were used to describe the wear mechanisms dominate within a region. The authors reported a high wear at high temperature and high sliding speed for the Al_2O_3 . The authors further reports that the use of fluids introduces a protective thin film to the slid surfaces. Monolithic Al_2O_3 showed intergranular, intragranular and grain pull-out fracture at high wear test. Later Xiong et al 1997 [69] reported that the wear properties of alumina are strongly dependent on the test configuration; the authors used a rounded pin to test the effects of grain size on the wear behaviour of alumina. They reported that at a fine-grain size, there is high wear and at a coarse-grain size, the wear of alumina is low. The authors further reported that the wear mechanisms in fine-grains are more dominated by grain-pull-out mechanisms, microchipping and abrasive wear mechanisms and in coarse-grained material is dominated by plastic deformation of the material grains. Grain pull-out causes the materials to chip off or break, which is not desirable in cutting tools inserts and tribological applications, this could be the issue of poor wettability between Al_2O_3 particles. Therefore there is a need to reinforce Al_2O_3 with hardmetals (WC) and binders (Co) for strengthening and toughening of this ceramic systems for wider industrial applications.

Chapter 3. Materials and Experimental Methods

3.1 Introduction

This chapter describes the materials, equipment and experimental methods used in the microstructural and the phase characterisation of pure Al_2O_3 and $\text{Al}_2\text{O}_3/\text{WC}$ -12wt.%Co composites consolidated via Spark Plasma Sintering (SPS) technique. The procedures employed in the investigation of mechanical properties, hardness, fracture toughness as well as wear mechanisms of the sintered materials.

3.2 Materials

Commercial available alumina (Al_2O_3) powder, with 99.5% purity, was acquired from Alfa Aesar GmbH & Co.KG, and it was used as the matrix (main constituent) material. Tungsten carbide (WC) powder (with 99% purity) and cobalt (Co) powder (with 99.998% purity) were also supplied by Alfa Aesar GmbH & Co.KG and used in this study as reinforcement materials. Table 3 shows powder properties as supplied.

Table 3. Powder properties as supplied.

Powder	Density g/cm^3	Purity (%)	Mesh size	Melting point $^{\circ}\text{C}$	Molecular weight (g/mol)
Al_2O_3	3.965	99.5	-270+325	2045	101.96
WC	15.63	99	-100+270	2870	195.86
Co	8.92	99.99	45	1495	58.933

Reinforcement's volume fraction of 5, 10, and 15% were selected for the powder consolidation. The selection of the reinforcements was governed by the volume percent of the binder (Co) required for a liquid phase sintering (LPS) regime [70]. The compositions of the fabricated composites are shown in Table 4 in terms of volume percentages, weight fractions.

Table 4. Composition of selected samples

Sample number	Component Vol. %			Component weight fraction %		
	Al_2O_3	WC	Co	Al_2O_3	WC	Co
1	100	0.0	0.0	100.000	0.000	0.000
2	95	4.4	0.6	83.980	14.098	1.922
3	90	8.8	1.2	71.290	25.265	3.445
4	85	13.2	1.8	60.980	34.338	4.682

3.3 Equipment

3.3.1 Particle size analyser

Mastersizer 3000 laser diffraction particle size analyser (by Malvern Instruments Ltd, UK) was used to characterise the starting powders and the milled powders. Mastersizer 3000 applies the Mie theory and the Fraunhofer model to measure the particle size and calculate the particle size distribution based on the scattering of laser light as it diffracts from a particle. The assumption made by the Mie theory in calculating of particle size is that all particles are of a spherical shape [71]. The technique of laser diffraction is based on the principle that particles passing through a laser beam will scatter light at an angle that is directly related to their geometric size i.e. larger particles scatter at low angles, whereas small particles scatter at high angles [72]. The Mastersizer 3000 laser diffraction particle size analyser can analyse powder samples of particle sizes ranging between 0.1 and 1000 μm . It has a voltage of up to 10 kV for fast recording and measuring time of as low as 5 seconds background measurements and 5 seconds analysing time. Mastersizer 3000 has two measurement cells, namely Hydro EV and Aero; Hydro EV unit uses automated wet sample dispersion, while Aero M unit is a manual dry powder dispersion. Hydro EV has an ultrasonic sound which helps with separation of agglomerated particles. Figure 3-1 shows the Mastersizer 3000 system setup.



Figure 3-1. Mastersizer 3000 particle size analyser setup

3.3.2 Planetary ball miller

The supplied powders were milled using a planetary ball milling machine (RETSCH PM 400) prior to sintering. The RETSCH PM 400 utilises high centrifugal forces to grind

small particles (micron-size) to finer particles (nano-size range), the PM 400 has a sun wheel to grinding jars speed ratio of up to 1:-3, which is sufficient to break covalent bonds between a hardmetal and a brittle material. The grinding in the RESTCH PM 400 is known as colloidal grinding. It has four grinding stations, each station have a milling capacity of up to 500 ml, and it also has a high milling speed of up to 400 rpm. The RESTCH PM 400 used in this work is shown in Figure 3-2. The maximum feed particle size is 10 mm. Depending on the material properties a final fineness down to 1 μm can be achieved with dry milling. Moreover, a final fineness below 0.1 μm up to a nano-size range can be achieved by wet milling.



Figure 3-2. Planetary ball milling machine: Retsch PM 400 MA-type

3.3.3 Tubular mixer

Mixing of powders were performed in a tubular mixer, model TURBULA-T2F by Glen Mills. The tubular mixer set up is shown in Figure 3-3. It has a mixing capacity of up to 2 litres depending on the mixing container used and a maximum weight of 10 kg. The container is supported by rubber clamps and belt and eccentric gear are used to drive the container. The rotation speed is adjusted by shifting the position of the belt on the 5-step pulley. A major advantage of using this mixer is the excellent homogeneity of powder

mixing with different densities and particle sizes; due to multidirectional rotation, translation and inversion according to the geometric theory by Schatz [73].



Figure 3-3. Tubular mixer setup, manufactured by Glen Mills

3.3.4 Sintering machine

Powder consolidation were performed using a spark plasma sintering machine model FCT Systeme GmbH, Germany. The equipment setup is shown in Figure 3-4. The equipment employs various die sizes ranging from 20 to 100 mm in diameter during sintering. Sintering temperatures of up to 2200 °C and a uniaxial pressure of 50 MPa are achievable in the FCT Systeme GmbH sintering equipment. Heating is accomplished by pulsed DC power supply and/or induction heating, however, induction heating is mostly utilised in larger samples with a diameter of above 30 mm to minimise the temperature difference across the sample.



Figure 3-4. FAST/SPS sintering equipment (model FCT Systeme GmbH, Germany)

3.3.5 Metallographic sample preparation

3.3.5.1 Sand blasting equipment

Sand blasting of the sintered samples were performed in a MAC-AFRIC sand blaster shown in *Figure 3-5*. This was done to remove excess graphite from the surface of the samples. The MAC-AFRIC sand blaster has a nozzle size ranging from 4 to 7 mm. It is connected to an air compressor with an air pressure of 2.75 bar (275 kPa) to enable the projection of sand at very high speed.



Figure 3-5 Sand blaster machine setup

3.3.5.2 Grinding and polishing machine

Grinding and polishing of the sand blasted samples were performed using the MP-1B grinding and polishing machine manufactured by MRC. The MP-1B grinder is shown in Figure 3-6, two samples can be manually polished simultaneously using this grinder. Cylindrical samples are preferred for manual grinding and polishing. MP-1B is capable of rough grinding, fine grinding, rough polishing, and fine polishing. MP-1B has a single disc for grinding/polishing. The machine uses a grinding/polishing disk with a diameter 230 mm, with the rotation speed range from 50 to 1000 rpm. The machine is equipped with a water cooling system which can help cool samples during rough grinding and prevent overheating and damage of the metallographic structure.



Figure 3-6. *MP-1B* grinding equipment

3.3.6 X-ray diffraction (XRD)

Powder and sample phases identification were carried out using the Empyrean X-ray powder diffractometer (XRD) by PANalytical. XRD equipment set up is shown on Figure 3-7. The PANalytical Empyrean machine can load up to sixty samples, twenty in each rack. It has a high scanning speed and the step size of up to 0.2 °/min and 0.01 °, respectively. Powder samples are preferred but solid samples with cylindrical shape and a high of about 3 mm can also be scanned successfully.



Figure 3-7 XRD PANalytical Empyrean machine

3.3.7 Optical micrography

Polished samples were examined by optical microscope (Reichert Microscope, Austria) and JEOL JSM-7100F Field emission scanning electron microscopy (FE-SEM). *Figure 3-8* shows a setup for SEM used in this study. JSM-7100F has a multi-modal and multi scaled microscopic analysis capability. It has a scanning resolution up to 1.2 nm at low voltage (kV), and up to 200 nA probe current, small probe diameter even at large probe current, 129 eV resolution silicon drift detector (SDD) for X-ray Energy Dispersive Spectroscopy (EDS). It has better grain resolution with high definition backscatter electron imaging. Up to four linear images can be viewed simultaneously using this equipment.



Figure 3-8 JEOL JSM-7100F, the SEM equipment setup

3.3.8 Density measurement equipment

Densities of sintered samples were measured using a laboratory liquid density meter. Densities of sintered samples were measured using an OHAUS balance for density determination. This is shown in Figure 3-9. The equipment is designed to an accuracy to 0.0001 g/cm^3 . The balance software includes a built-in reference density table for water at temperatures between $10 \text{ }^{\circ}\text{C}$ and $30 \text{ }^{\circ}\text{C}$. It calculates water density based on the water temperature value entered. Once the necessary weights have been determined, the density of the sample is displayed in g/cm^3 on the application screen. Users can print out a detailed report with weight in air, in liquid, water temperature, density type and other related information.



Figure 3-9. The OHAUS density measuring equipment

3.3.9 Universal hardness tester

Sample hardness was measured using a Universal hardness tester model FH-002-0001 manufactured by Tunis Oslesis shown in Figure 3-10. The equipment is capable of performing most types of hardness testing, including Vickers, Brinell, Vickers depth (HVT), Brinell depth (HBT), Rockwell and Knoop hardness. The tester meets the ASTM, ISO-EN, DIN and JIS testing standards. It has a test load ranging from 500 g to 125 kg, the diamond indenter has an indentation angle (2θ) of 136° ($\theta = 68^\circ$). However, Vickers hardness is desired for hardness testing of brittle materials, including, ceramic/hard-metals [74]. Vickers hardness uses a diamond indenter pin, which is placed on the sample test surface, and load (dead weight) is applied during the test to create an indent. The Vickers hardness test is also used to measure the material toughness by forcing the indent crack to grow beyond the diamond indent geometry.



Figure 3-10. Universal hardness tester model FH-002-0001 manufactured by Tunis Oslesis

3.3.10 Wear testing machine

A universal tribometer (by Rtec instruments) used in this study is shown in Figure 3-11. The universal tribometer uses modular designs ranging from nano, micro, and macro scale. It is able to test samples at a nano to a macro range. It is designed to meet the testing standards including ASTM, DIN, and ISO. Tests that can be performed by this universal tribometer includes wear, scratch, indentation, and imaging. Test forces that can be applied in this machine are in a range of nano N to 5000 N, up to 10000 rpm rotational speed is achievable with most test modules.



Figure 3-11. Universal tribometer equipment by (Rtec)

3.4 Experimental Procedures

3.4.1 Powder Particle characterization

Particle size distribution of the starting powder was characterized using the Mastersizer 3000E (MAZ3010) by Malvern instruments. A pinch of powder was dispersed in a distilled water for a hydro EV test, performance verification standard operating procedure (PV-SOP) was performed to check for instrument optical fidelity. Obscuration was set between 8 and 15% for the hydro dispersion test and 0.1 to 6% for the aero dispersion test. The refractive index of the Al_2O_3 was taken as 1.7460 [75] and the absorption index as 0.03 to 0.08 %v/v [76]. 1000 ml beakers were filled with water to about 800 ml mark and a pinch of powder was added into the beaker for powder particle dispersion.

3.4.2 Milling

Milling was performed on a planetary ball milling machine (Restch PM 400) for 8 hours at 400 rpm and 40 minute cycle; 30 minutes running time and 10 minutes break time intervals. The breaks were performed to reduce heating effects caused by friction during milling. The ball to powder weight ratio (BPR) was maintained at 10 grams of balls to 1 gram of powder (BPR ratio 10:1) [77]. Al_2O_3 milling balls with small diameters (3 to 10 mm) were used for milling in an Al_2O_3 milling jar. Approximately 60 % of the jar volume is filled with milling balls, in most cases where a ball to powder weight ratio is high $\geq 10:1$.

This BPR ratio was chosen as the ideal ratio, in order to allow enough vacancy/space between the powder particles and between powder particles and milling balls for an optimized milling efficiency. Two jars were used simultaneously with the aim of balancing the machine and avoiding damage of machine and powder. Separate milling was carried out to avoid segregation of heavier powder and to avoid damaging/ wear-off, of milling balls due to difference in particle hardness. Milling of Al_2O_3 powder was performed in an Al_2O_3 jar, using sintered Al_2O_3 milling balls and ethanol as the milling liquid. The milled powders were hot dried in a laboratory oven at 100 °C for 10 hours to vaporise the milling liquid [78].

3.4.3 Mixing

Mixing was performed for 120 minutes, with the addition of 5 sintered alumina balls to reduce particles from agglomerating with each other and/or coagulating to the surface of the container. The speed of the mixer was set to 101 revs per minute. Mixing was performed to ensure even dispersion of the reinforcement within the Al_2O_3 matrix powder. Milled and mixed powders were analysed by XRD and SEM for the possibility of foreign elements and to check for powder homogeneity.

3.4.4 Samples consolidation procedures

SPS sintering consisted of six steps, namely vacuuming, pressing, jump-heating, heating, holding at maximum sintering temperature and cooling stages. The vacuuming and pressing stages were carried out at ambient temperature. On the vacuuming stage, the pre-pressing uniaxial pressure was kept at 34 MPa (10 kN force). The purpose of jump heating was to elevate the processing temperature from ambient temperature to 260 °C, since the pyrometers can only read temperatures from 260 °C and above. A uniaxial pressure of approximately 48 MPa (using a general pressure, force and area relation, 15 kN force at 20 mm diameter) was applied to the powder during the pressing, jump heating, heating and cooling processes. The vacuum was maintained at 0.6 kPa during the entire sintering processes. The heating rate varying from 75, 100 °C/min to 150 °C/min was employed to heat the samples from 260 °C to 1600 or 1750 or 1800°C [79] and a cooling rate of 200 °C/min. The holding temperatures range from 1600 °C to 1800 °C. The dwell time at holding temperature was maintained for 5 and 10 minutes for all samples and the pressure was kept

at 48 MPa. The total sintering time ranged between 60 minutes and 80 minutes per sample, depending on the length of vacuuming stage.

Figure 3-12 shows the sintering profiles of the samples sintered at 1750 °C and at a heating rate of 75°C/min with holding time of 5 minutes and a cooling rate of 200 °C. Al₂O₃ and Al₂O₃/WC-12wt.%Co composite powders were densified via SPS process, using a graphite die of 20 mm diameter. The same heating rate of 75 °C/min was used to heat the samples from 250 °C to 1800 °C as shown in Figure 3-12, giving a heating time of 15 minutes and 24 s. The SPS machine uses water-cooling system to cool the samples.

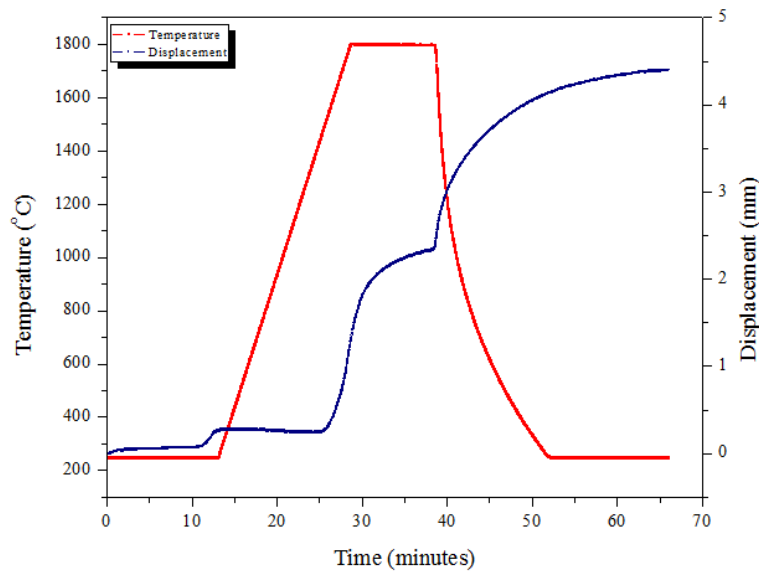


Figure 3-12 Sintering profile of Al₂O₃/5vol.%(WC-12wt.%Co)

3.4.5 Metallographic Sample preparations

A sand blaster (by MAC-AFRIC) was used to remove graphite from the sample surfaces. Wearing off of the samples was avoided at all cost by constantly checking the sample for surface cavities caused by the blasting. The standard time for sand blasting was 30 seconds at an air pressure of 0.34 MPa.

The grinding and polishing procedures are summarised in Table 5. Samples were ground using an opposite movement to the disk rotation, applying force from the fingers to maintain a good contact between the sample and the surface. The samples' orientation was changed every 60 seconds by a 90 degree angle to get an even polished surface. Once the scratches of the previous disk were overwritten completely by the new disc, it was safe to move on to the next size disc with low roughness. Lubricants were used to dissipate the heat generated

during polishing and grinding water was preferred for the rough stage (220 μm) other lubricants with suspensions were used at later stages of finer grinding and polishing.

Table 5 Grinding and polishing procedure

Process	Grinding	Final grinding	Final polishing
Base/ surface	MD-Piano	MD-Plan	MD-Chem
Grit/ suspension size (μm)	220	9	0.04
Lubricant	Water	DiaPro Plan	Oxide Polishing - S suspension
Speed (rpm)	300	300	150
Force (N)	180	100	50
Time (min)	5 - Until flat	4	1

3.4.5.1 XRD

Powder and sample phases were analysed using a PANalytical Empyrean X-ray powder diffractometer (XRD) with a scanning angle between 5.0 and 90.0 $^{\circ}$ (2θ) using copper tube X-ray source of K_{α} radiation (with wavelength $\lambda=0.1541874$ nm) at a generator voltage of 30 kV. Generator current of 40 mA and a LynxEye energy dispersive strip detector. The scanning speed and the step size were 0.08 $^{\circ}$ /min and 0.02 $^{\circ}$, respectively. Highscore Plus software (by PANalytical) was used to carry out the phase match of the samples to that found in International Centre for Database Data (ICDD). It was used for the background correction of the X-ray patterns, profile fitting and $K_{\alpha 2}$ stripping correction.

3.4.5.2 SEM

After polishing samples, they were rinsed with distilled water and dried in a laboratory microwave at 100 $^{\circ}\text{C}$ for 1 hour to remove the moisture from the pores. It is very difficult to chemically etch Al_2O_3 samples and therefore, thermal etching is preferred [80]. Thermal etching has the risk of grain growth if the samples are etched at very high temperature for a longer time. The samples were thermally etched at a temperature of 1450 $^{\circ}\text{C}$ for 12 minutes at a heating rate of 30 $^{\circ}\text{C}$ /min. in a furnace The purpose of thermal etching was to reveal the grain boundaries. Samples were then carbon coated using a Q150T ES (by Quorum), at 60.3 nm thickness to make its surface conductive. Without carbon coating the primary electron produced by the cathode in the SEM will accumulate at the surface of the samples and secondary electron from the surface of the samples will not be easily detected. Once the fully polished samples were prepared, they could be put into the vacuum chamber and inserted into the chamber of the SEM once fully pumped. The high efficiency In-lens SE

detector was used for high contrast surface imaging. An accelerating voltage of 5kV was used for the majority of the images reported in this thesis. Magnifications vary across images taken, but most were in the range of 1 k to 20 k. The characterization of the reinforcement-matrix interface, morphology and the crystal structure of the composite were observed in an optical microscope and FE-SEM. Average powder particle size and elemental analysis were performed for all sintered samples using a FE-SEM. The average grain size was measured using linear interpolation (ASTM4 E112 standard test method) of the polished sample [81]. More than 100 grains per image were taken into account in the calculations. SEM was employed to reveal the microstructure of the sintered samples and the starting powder. EDS was used to identify the chemical elements present in the sample and starting powders.

3.4.6 Density

Bulk density was measured in this study using the Archimedes' Principle, after sanding off the graphite layer and polishing. The bulk density measurements were performed by measuring mass of sample in air, mass of sample in water and water displaced by the sample. The bulk density was then converted to relative density by dividing its value with the calculated sample density (ratio of the bulk density/calculated density) and then expressed as a percentage. Calculated density was determined by the rule of mixtures using equations below;

$$\rho_c = \frac{1}{\left(\frac{w_{Co}}{\rho_{Co}} + \frac{w_{WC}}{\rho_{WC}}\right)} \quad (21)$$

In general,

$$\rho_c = \frac{1}{\sum_{i=1}^n \left(\frac{w_i}{\rho_i}\right)} \quad (22)$$

Where ρ_c , ρ_f and ρ_m are the densities of composite, reinforcement and matrix respectively and w_f and w_m are the masses of reinforcement and matrix respectively. The calculating of the density using volume fraction is given by the following equation;

$$\rho_c = \rho_f V_f + \rho_m V_m \quad (23)$$

In general, $\rho_c = \sum_{i=1}^n \rho_i V_i$, where V_f and V_m are the volume fractions of reinforcement and matrix respectively. All density measurements have been performed for at least seven times, to improve the statistical significance of the results. Porosity was studied to evaluate

its significant effect on the mechanical properties of the composites. Percentage porosity was determined by:

$$\% \text{ Porosity} = \frac{\text{Geometric density}}{\text{Theoretical density}} * 100 \quad (24)$$

3.4.7 Mechanical Characterisation

3.4.7.1 Hardness

Hardness tests were carried out using a universal hardness tester as discussed in subsection 3.3.9. The tests were performed at ambient conditions. Measuring conditions for the Vickers hardness, H_v values, where an application of 0.5, 1, 10, 20, 30 and 50 kgf load for 10 s, and the standard specification ASTM E92-72 [82]. The diagonals of each indentation were measured using an assistance of an optical microscope. A minimum of five measurements was conducted on each sample at different points for better results and average values recorded. The sample hardness was calculated from the equation given by:

$$H_v = \frac{2F \sin \frac{136^\circ}{2}}{d^2} \quad (25)$$

Hence, for Vickers hardness the equation reduces to,

$$H_v = 1.8544 \frac{F}{d^2} \quad (26)$$

Where F is the load in kgf and d is the arithmetic mean of the two diagonals d_1 and d_2 in mm.

3.4.7.2 Fracture Toughness

The fracture toughness was measured using the micro-indentation method. The reported toughness values are the means and standard deviations of five independent measurements. The fracture toughness was calculated from the length of the radial cracks of the indentation test using a formula developed by Anstis et al [83]–[85]

$$K_{IC} = 0.016 \left(\frac{E}{H} \right)^{1/2} \left(\frac{P}{C^{3/2}} \right) \quad (27)$$

Where 0.016 is a constant for Vickers produced radial cracks, E/H is the ration of young's modulus to hardness, P is the peak load and C is half length of the radial crack. To estimate the indentation fracture toughness (K_{IC}), a load of 20 kgf and above was applied to the sample for 15 s. Vickers indentations were performed on the surface of the samples, to produce Palmqvist cracks, from which the indentation fracture toughness was obtained by the method previously reported by Niihara [86].

3.4.8 Friction coefficient and wear testing

A universal tribometer was used to test the wear resistance and coefficient of friction (CoF) of the sintered material. The CoF of investigated samples were obtained online via a computer- based data system by the variation in tangential force recorded during wear tests. In a sliding wear test, both load and speed are applied to a surface of a sample in contact with a pin or ball. The pin is placed on the material of which its wear properties are to be determined and a speed, force and time are selected as test parameters. An optical microscope is then used to examine the wear depth, width and wear volume. Pin on disk configuration with the linear reciprocating motion was used for wear test at ambient conditions, with minimal vibration and noise. The wear test conditions are shown in Table 6. The counter specimen was a ball made from ball bearing steel 52100 of hardness 66 Rockwell C [87].

Table 6. Sliding wear test parameters and environmental conditions

Test parameter	Value
Normal load	30, 50,70 and 100 N
Linear sliding speed	3 mm/s
Total sling time	3 minutes
Wear track length	3 mm
Acceleration	0.1 m/s ²
Atmosphere	Air tested
Ambient temperature	21 °C
Atmospheric pressure	994 mbar
Humidity	41%

The wear rate was calculated using the following equation:

$$W_r = \frac{\Delta m}{d} \quad (28)$$

Where, W_r : is the wear rate in (mg/m), Δm : is weight loss in mg, d is sliding distance in (m). A wear coefficient was used to categories resistance to contact wear. Lubrication was not used to prevent the complication of thermochemical effects during the wear test. The

real geometry and shape of the worn-out areas were explored via the optical microscope, and SEM analyses. Thus, wear variables observed using wear scar geometry were given as follow: wear depth, wear width, wear track radius, and wear stroke length.

The test configuration employed a ball on plate setup. The worn tracks were analysed using SEM and optical microscope to investigate wear mechanisms.

Chapter 4. Results and Discussions

4.1 Introduction

This chapter highlights the results gathered through the experiments conducted for this study. It also presents the discussions of experimental findings with respect to the aim of this study.

4.2 Powder particle characterization

Particle size is very important in powder consolidation, as it has an impact on the final grain size of the product. Consequently, it is necessary to evaluate the starting powder particle size and distribution. Laser diffraction technique is the most commonly used methods of measuring particle size distribution (PSD) [88]. Particle size distribution based on volume of particles and average particle size of the starting powders is shown in Table 7, obtained from a Mastersizer 3000 laser diffraction particle size analyser. Two types of test were conducted using a wet dispersion cell and a dry cell unit for comparison of results. The results were analysed and captured through the Mastersizer 3000 software (Version no. 3.63).

Poor wetting was suspected between water and the Co powder measurements during PSD test, to minimise the error multiple reading were taken both with and without ultrasound. Moreover, Co was supplied as rough mesh due to its high market value in its powder form; this can have a significant influence on the results due to poor particle uptake to the cell for testing. For Al_2O_3 and WC wet powder particle dispersion showed smaller particle size than dry powder particle analysis, this is postulated to be poor powder flow in the dry powder test which causes agglomeration. It is worth mentioning that all the powders had one most dominant peak. The powder is not perfect for sintering at this particle size and distribution due to the following assumptions;

- (i) The powder is too rough; therefore, densification will be delayed, due to slow mass transport and few mass transport mechanisms in large particles. Mechanisms of mass transport in large particles occur mostly by surface diffusion, volume diffusion and grain boundary diffusion [89].
- (ii) Larger grains will grow with the expense of small grains during sintering hence coarsening will take place leading to less densification due to pore trapping between the grains and within large grains. Coarsening is caused by inter-particle

diffusion when particles have non-uniform particle distribution which results in neck formation [62].

- (iii) There is also a low surface area if particles are large/ micron size range, wetting of particles will be poor this may reduce the reactivity of the powder [60].

Al_2O_3 powder had an average particle size of 13.0 in a wet powder particle dispersion. The average particle sizes for $\text{Al}_2\text{O}_3/5\text{vol}\%(\text{WC}-12\text{wt}\%.\text{Co})$, $\text{Al}_2\text{O}_3/5\text{vol}\%(\text{WC}-12\text{wt}\%.\text{Co})$, and $\text{Al}_2\text{O}_3/5\text{vol}\%(\text{WC}-12\text{wt}\%.\text{Co})$, were 16.0, 16.3 and 16.2 respectively.

Table 7. Particle size distribution of wet dispersed and dry tested admixed powders

Test Method	Powder	Size (μm)		
		Dv ₁₀	Dv ₅₀	Dv ₉₀
Wet dispersion	Al_2O_3	1.9	7.0	26.1
	$\text{Al}_2\text{O}_3/5\text{vol}\%(\text{WC}-12\text{wt}\%.\text{Co})$	1.8	12.2	36.6
	$\text{Al}_2\text{O}_3/10\text{vol}\%(\text{WC}-12\text{wt}\%.\text{Co})$	1.6	12.1	35.2
	$\text{Al}_2\text{O}_3/15\text{vol}\%(\text{WC}-12\text{wt}\%.\text{Co})$	1.4	12.5	36.7
Dry powder	Al_2O_3	2.1	7.2	25.7
	$\text{Al}_2\text{O}_3/5\text{vol}\%(\text{WC}-12\text{wt}\%.\text{Co})$	2.0	12.3	36.5
	$\text{Al}_2\text{O}_3/10\text{vol}\%(\text{WC}-12\text{wt}\%.\text{Co})$	2.3	12.1	35.4
	$\text{Al}_2\text{O}_3/15\text{vol}\%(\text{WC}-12\text{wt}\%.\text{Co})$	2.2	12.2	36.7

The powder has a tendency of sinking to the bottom and agglomerate [90] during testing, which affects obscuration. This was minimised by continuing to stir at a very high speed (with angular velocity of 2900 rpm) and by allowing more background and data recording time from 10 s and 10 s background measurement and data recording times for 20 s and 60 s background measurement and data recording times respectively.

4.3 SPS Powder consolidation

Milled powders were oven dried at 100°C for 12 hours to evaporate the milling medium (ethanol). Dried powders were admixed with the weight fractions shown in Table 8 and transferred to graphite dies. Reinforcing additives were added at a volume fraction of 0, 5, 10 and 15%, however the ratio of WC (carbide) to Co (binder) was kept constant at a weight fraction of 88% WC to 12% Co for all the sintered materials. This was to enable sufficient wetting capability of Co additive between WC particles and Al_2O_3 matrix during sintering. The weight fraction of Co additive was below 5 wt.% for all samples to avoid flowing of the excess liquid phase out of the sample during sintering, but also enough to provide good

wetting of WC + Al₂O₃ particles. Pure Al₂O₃ samples were produced as reference samples and compared with the reinforced sintered materials.

Table 8. Chemical composition of selected ceramic systems

Composite	Component weight fraction %		
	Al ₂ O ₃	WC	Co
1	100.00	0.00	0.00
2	83.98	14.10	1.92
3	71.29	25.27	3.45
4	60.98	34.34	4.68

The admixed powders were consolidated at 1600, 1750, and 1800°C, with a heating rate of 100 °C/min, in an argon atmosphere, under a uniaxial pressure of 48 MPa and holding time of 5 and 10 minutes. Using a hybrid SPS/FAST sintering machine (model FCT Systeme GmbH, Germany). The temperature was controlled by an optical pyrometer inside the graphite punches. Sintering profiles were obtained from the SPS machine for analysis.

During SPS, the displacement of the lower punch reflects the densification process of the samples, this was automatically recorded by the operating software. The sintering profiles for the samples sintered at 1600, 1750 and 1800°C are shown in Figure 4-1, comprising of temperature, time and displacement. They are two graphs in each image; the temperature-time profile graph plotted in red colour and the displacement-time profile graph in blue colour. The temperature-time profile is similar for all samples. The displacement-time profile is slightly different in all the samples. This could be explained by the shrinkage behaviour of samples at different temperatures, the applied pressure on the powder compact, the difference in thermal conductivity and expansion, and/or by the availability and quantity of the liquid phase. For all of the tests, before the starting of densification of the powders, the displacement increases opposite to the shrinkage direction due to the thermal expansion of the compacted samples and the punches. The displacement then becomes positive nearly when the temperature reaches the maximum sintering temperature. For all samples sintered at 1800°C the densification starts at 1800°C and for samples sintered at 1600°C densification starts at 1600°C and lastly for samples sintered at 1750°C densification starts at 1750°C. Addition of WC-12wt%Co have proven to have no effect on the densification temperature of the samples. A large displacement is shown in Al₂O₃/5vol%(WC-12wt%Co) sample profile, with up to 4.5 mm compared to other samples. However, they are no significant trend or correlation between the additive composition and the displacement of the samples.

At 1000 °C the cooling rate decreases for all the samples, at this point the steepness of the cooling curve reduces. Rapid (free) cooling is evident in all the sintering profile graphs. It is also evident that during cooling the displacement elevates by almost over 1.75 mm. This was hypothesized to be due to the shrinkage of the samples as it loses thermal kinetic energy. In addition, some of the liquid phase, (Co) solidifies causing even more shrinkage of the samples. The applied pressure was increased from 34 MPa at the vacuuming stage to 48 MPa at the pressing stage and kept constant until the final stage. However, the maximum value was reached before the sample reaches a temperature of 250 °C. The power used gradually increases from the jump heating process to the end of the heating process.

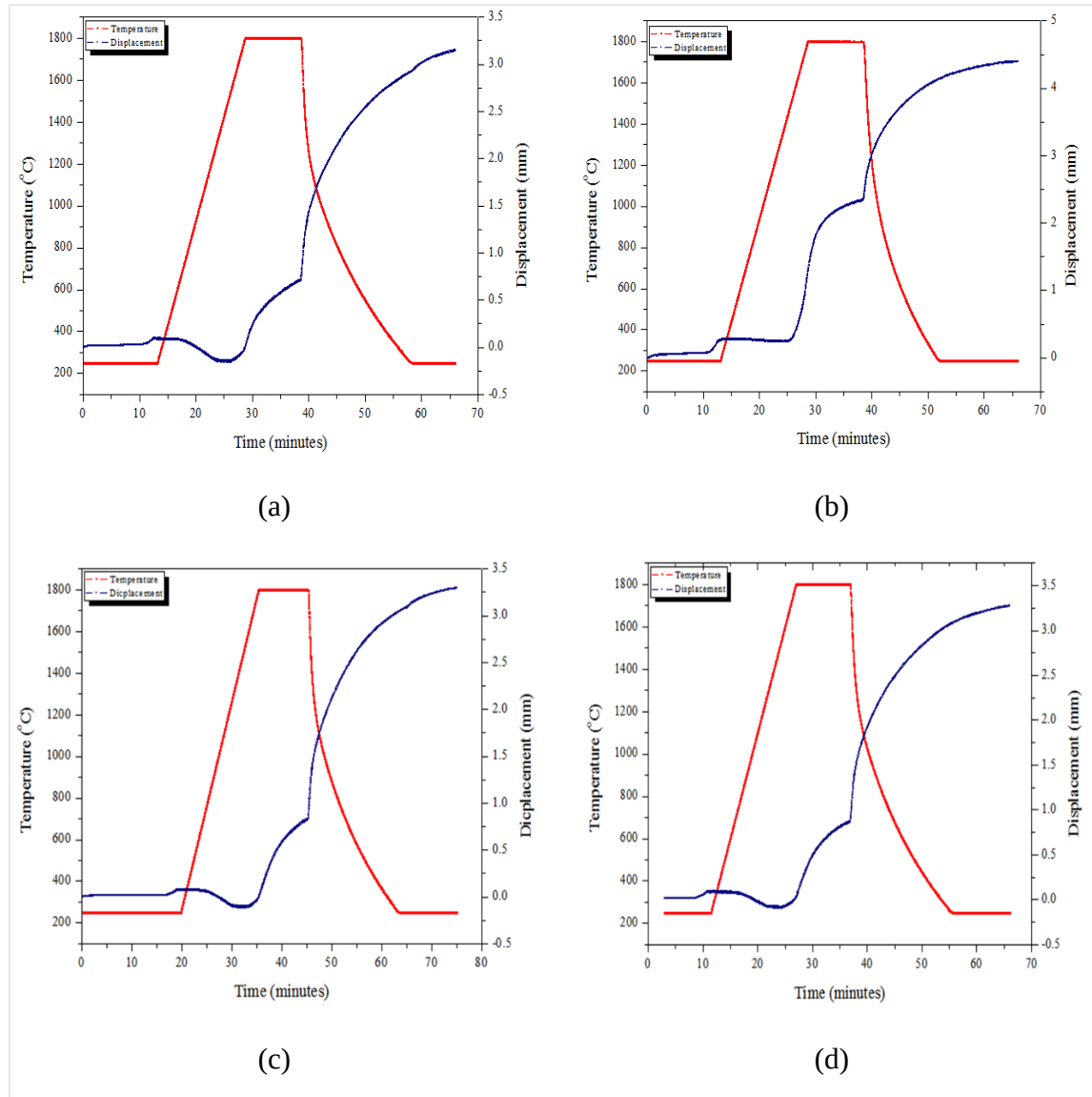


Figure 4-1. Spark plasma sintering profiles illustrating temperature and displacement against time of (a) Al_2O_3 , (b) $\text{Al}_2\text{O}_3/5\text{vol}\%(\text{WC}-12\text{wt}\%\text{Co})$ (c) $\text{Al}_2\text{O}_3/10\text{vol}\%(\text{WC}-12\text{wt}\%\text{Co})$, and (d) $\text{Al}_2\text{O}_3/15\text{vol}\%(\text{WC}-12\text{wt}\%\text{Co})$ samples

4.4 Relative density

Figure 4-2 shows the relative density against sintering temperature, the actual density of the composite may divert from the measured density due to the potential contaminants from the milling process and the reaction of the graphite sheets to the sample surface during sintering. The influence of dwell temperature was investigated while maintaining other sintering conditions constant. The powders were consolidated at 1600 °C, 1750 °C, and 1800 °C at a heating rate of 100 °C/min and at 1750 °C at a heating rate of 75 °C/min. The porosity of the samples sintered at 1750 °C and 1800 °C is acceptable. Cooling was automated and very rapid to inhibit grain growth and abnormal grain growth.

Sintering at temperatures higher than 1600 °C melts the Co phase, Co phase was the chosen binder due to its good wetting ability with the WC phase [70]. Sintering in the liquid phase state significantly improve densification process by mechanisms of mass transport of the liquid phase. The liquid Co phase flows to fill the pores in between the particles, forming new grain boundaries. Co phase provides wetting between WC and Al₂O₃ particles. Wetting also increases the ability of the WC particles to coagulate with the Al₂O₃ matrix during sintering. Good wetting is reported to lead to poor de-bonding during crack propagation [57].

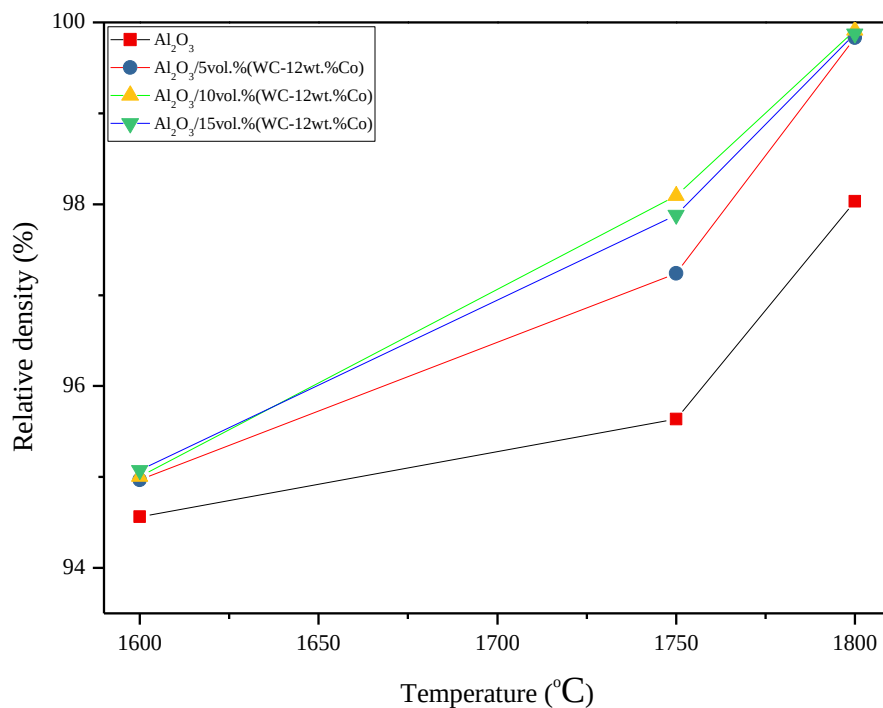


Figure 4-2 Relative density (%) against sintering temperature /°C of samples

Maintaining a pressure of 48 MPa at 1800 °C seemed to be destructive to the die and punches. The relative density of un-doped Al₂O₃ was found to be relatively low as compared to the reinforced ceramic. Keeping every parameter constant. *Santanach et al.* (2011) [24], achieved a 99.2 % TD when sintering a fine powder of Al₂O₃ powder of 0.14 µm at 1300 °C, with a heating rate similar to the ones used in this study, and a cooling rate of 100°C/min. However, this was not possible in this work due to the difference in other sintering condition i.e. particle size, sintering pressure, dwell time and sintering equipment used in this study. The calculated densities of the samples are listed in Table 9. The theoretical densities for

Al₂O₃, WC, Co were taken as 3.97, 15.63 and 8.86 g/cm³ respectively, as reported from the literature [91], [92]

Table 9. Theoretical densities and relative densities of sintered ceramic systems

Composite	Calculated density (g/cm ³)	Theoretical density (%)
Al ₂ O ₃	3.97±0.001	99.92±0.03
Al ₂ O ₃ /5vol.%(WC-12wt.%Co)	4.47±0.003	99.91±0.07
Al ₂ O ₃ /10vol.%(WC-12wt.%Co)	4.99±0.001	99.99±0.01
Al ₂ O ₃ /15vol.%(WC-12wt.%Co)	5.51±0.002	97.48±0.04

The highest theoretical density is achieved in the both the three composite consolidated at 1800 °C at a heating rate of 100 °C/min with a total average sintering time of 1 hour: 30 minutes. The highest recorded value of relative density for Al₂O₃ sample was below 98% at a sintering temperature of 1800 °C. In LPS pores isolated at the grain boundaries can be filled with either nano particles or by liquid phase. However, there is rapid material transport in LPS which is postulated to cause grain coarsening [14].

Pure alumina was sintered in a solid-state sintering regime; it required a relatively high sintering temperature between 1750 and 1800 °C to obtain theoretical densification of above 97%. Moreover, the relative density of the materials does not show any correlation relative to the sintering temperature. The effect of heating rate on the relative density was investigated at sintering temperature of 1750 °C. A slow heating rate of 75 °C/min coupled with controlled cooling at 200 °C/min, were compared to a slightly higher heating rate of 150 °C/min. It was found that the relative density was reduced slightly at higher heating rate and 100% densification was achieved through controlled cooling and slow heating rate. Figure 4-3 shows the effect of heating rates on the density of samples. The densification is affected by sample size and heating rate, Olevsky et al. (2013) [93] showed that at 300°C/min samples with larger diameters will have poor densification features than samples with small diameter (< 40 mm) and low heating rates of about 100 °C/min. The compaction of the pure Al₂O₃ was low with relative density of 95.6%. The difference in relative density for Al₂O₃/WC-12wt.%Co composite is well above 96%, but they seem to be high porosity in the composite with low reinforcements vol.% namely Al₂O₃/5vol.%(WC-12wt.%Co). Faster heating rates do not allow the powder to be compacted at a low temperature, but

rather the powder is heated faster, making the necking process to be suppressed, which can promote grain coarsening.

The porosity of un-doped Al_2O_3 was high, high porosity can be brought about by large powder particle sizes with complex shapes. Larger particle sizes have low surface area, therefore, they will be low points of contact at the beginning of sintering. However, this can promote grain growth/ coarsening without a significant powder compaction. Lower porosity was recorded on the $\text{Al}_2\text{O}_3/10\text{vol.}\%(\text{WC}-12\text{wt.}\%\text{Co})$ and $\text{Al}_2\text{O}_3/15\text{vol.}\%(\text{WC}-12\text{wt.}\%\text{Co})$ at all sintering temperatures, this can be a result of the high volume of reinforcements and binder phase. The binder volume percent is also assumed to be high enough to fill the pores between the grain of the sample and good wetting between Al_2O_3 and WC particles is assumed to increase bonding between the particles.

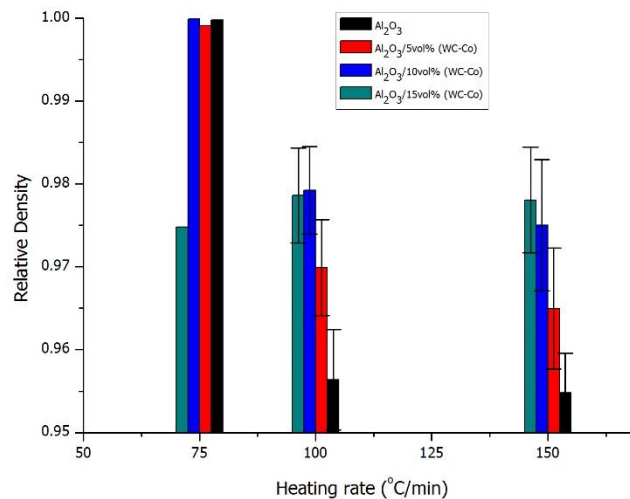


Figure 4-3 Relative density against heating rate at 1750 °C

For pure solid state sintering like in pure Al_2O_3 samples, densification of the powder particles may occur by local plastic deformation at the particle contact points, if the yield strength at that particular temperature is reached by the application of external pressure. The most dominant densification mechanism is through grain boundary diffusion. Controlled cooling yielded the highest density of up to 99.99% TD for most of the samples produced as compared to free cooled samples.

4.5 Phase characterization

Phase match was determined by the analysis of the XRD patterns by the investigation of peaks. XRD patterns of Al_2O_3 powder are shown in Figure 4-4. The peaks were compared

to the reference powders of similar structure in the XRD software. The crystal structure of the starting Al_2O_3 powder is characterized as rhombohedral Al_2O_3 , and there is no redundant peak to be detected XRD patterns for this powder.

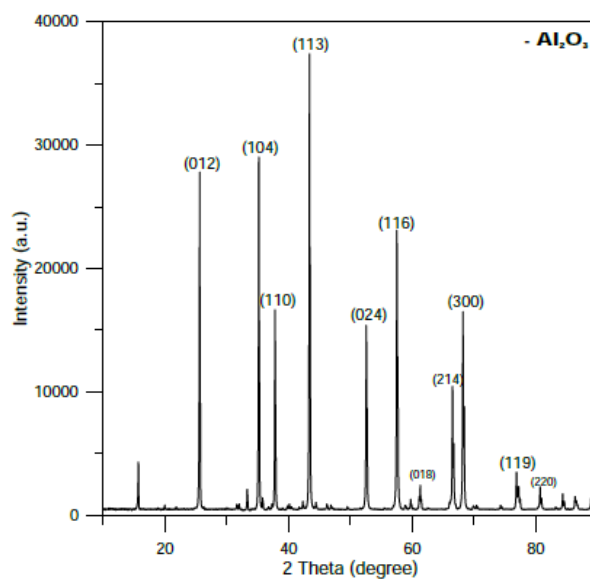


Figure 4-4 XRD pattern of alumina powder

The XRD patterns of WC powder are shown in Figure 4-5. The starting WC powder was characterized using XRD for identification of phases present. The results show that WC with a hexagonal close packed crystal structure is the present phase in the powder, the XRD patterns do not show the presence of any unwanted phase.

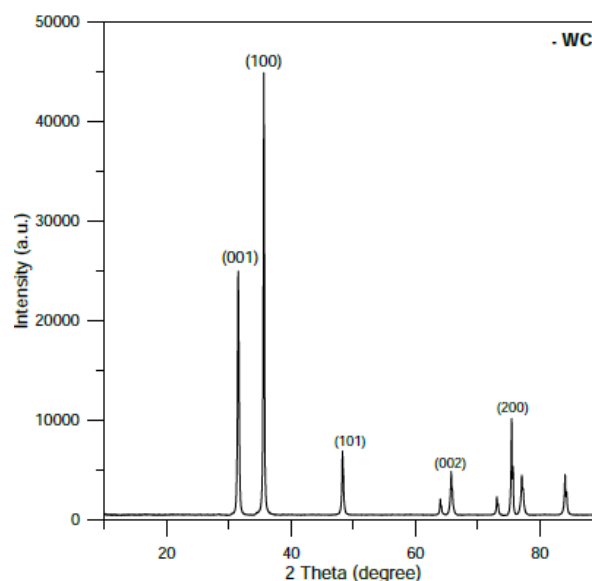


Figure 4-5 XRD pattern of WC powder

The XRD results for Co powder are illustrated in Figure 4-6. The patterns observed in this powder resemble that of an amorphous phase with too much background noise. This might be caused by the coarse nature of the powder particle, and this might affect the scanning results by causing noise in the analysis due to the open spaces between the particles. Moreover, cobalt powder has a few peaks, which makes it even more difficult to analyse with background noise. Moreover, the correction of background noise lead to the creation of new small peaks.

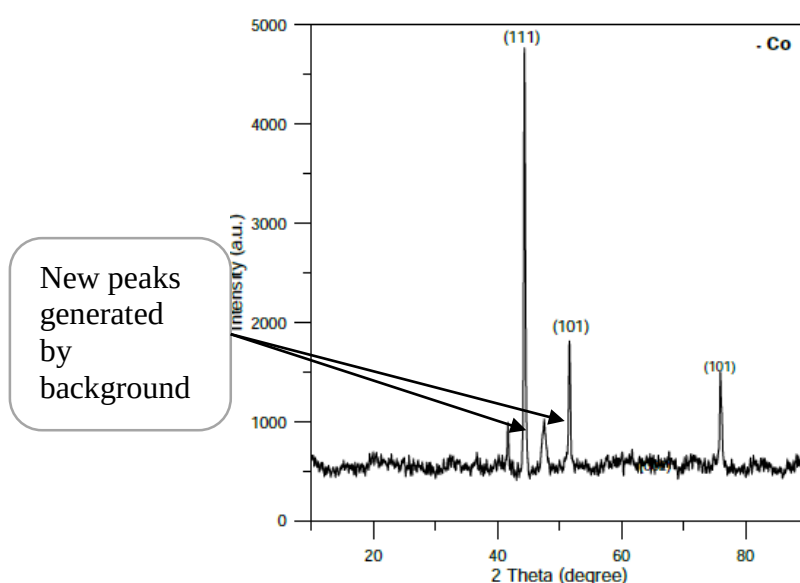


Figure 4-6 XRD pattern of Co powder

Figure 4-7 shows the XRD patterns of the powders used for production of sample materials. Al_2O_3 XRD patterns matched with the reference XRD patterns known as the

Al_2O_3 (corundum). WC patterns concurred with the reference XRD patterns for WC found in the XRD software; Highscore plus. Co X-ray powder diffraction patterns corresponded with the reference XRD patterns for Co. The WC powder had high inter-planar spacing value than other powders. Al_2O_3 patterns have more crystallographic planes than other powders while Co has lowest crystallographic plane. The crystallinity of the Co is presented to be partially amorphous, this might be caused by either moisture on the powder or the particle size and roughness of the powder that lead to the scatter of the refracted x-ray beams. Background correction of the Co powder patterns leads to the formation of new peaks at 2θ values between 40° and 50° . Figure 4-7 shows milled admixed powders, there is no reaction of phases present after the milling of WC powder. WC and Al_2O_3 phases are present in all the $\text{Al}_2\text{O}_3/\text{WC-Co}$ samples. There is no sign of impurities in the XRD patterns of powders after milling.

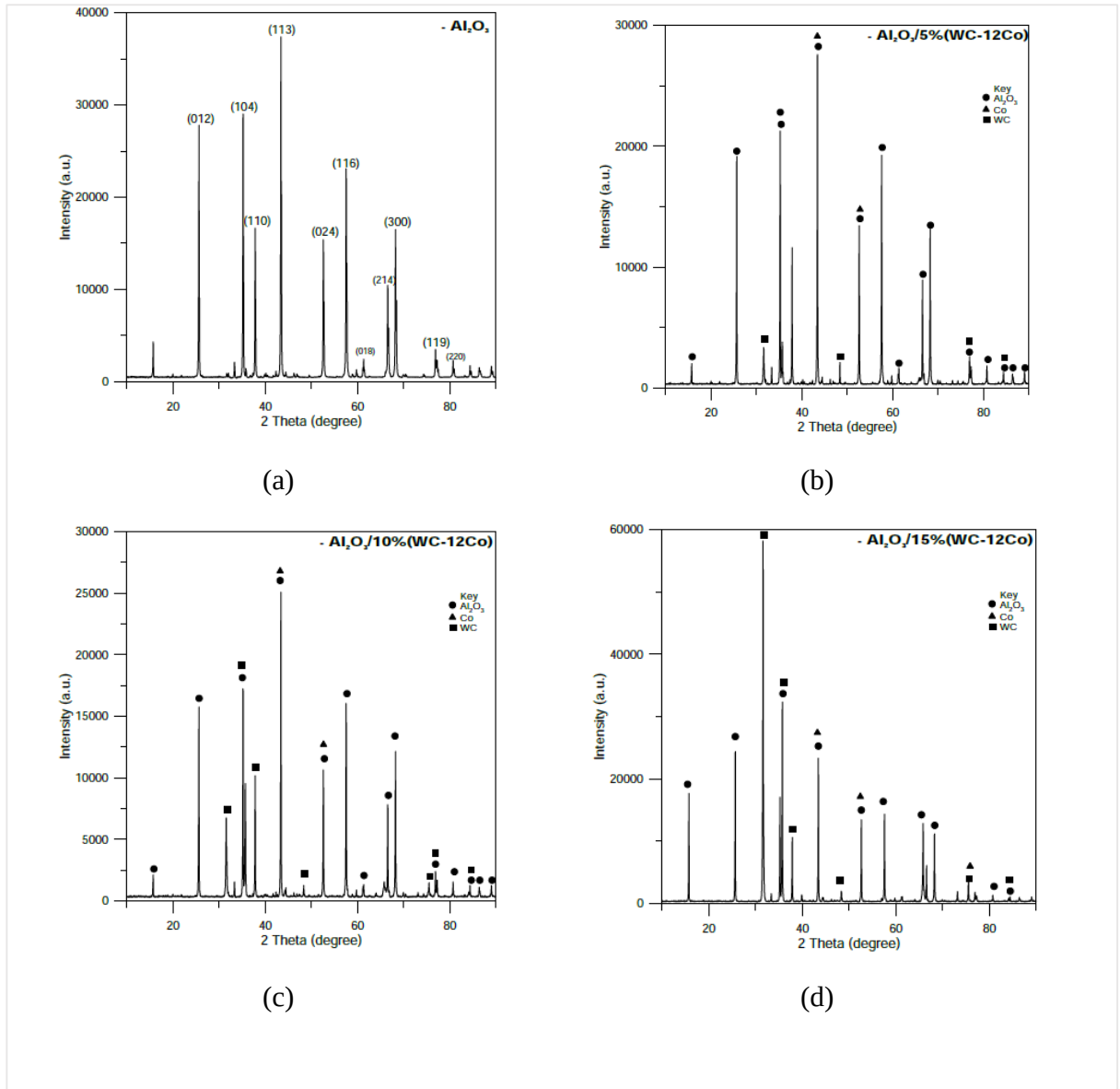


Figure 4-7. XRD patterns of; (a) Al_2O_3 , (b) $\text{Al}_2\text{O}_3/5\text{vol}\%(\text{WC-12wt}\%\text{Co})$, (c) $\text{Al}_2\text{O}_3/10\text{vol}\%(\text{WC-12wt}\%\text{Co})$, (d) $\text{Al}_2\text{O}_3/15\text{vol}\%(\text{WC-12wt}\%\text{Co})$ powders

Figure 4-8 shows the XRD patterns for the sintered bulk samples, the patterns show that Al_2O_3 , WC phase was present within the bulk samples for 5, 10 and 15 vol% additives. The XRD patterns indicate that there is no phase change in the Al_2O_3 sample after sintering. However, in all samples, Co phase is absent which coincides with results acquired from EDS spectrum. This might be the fact that Co phase evaporated during sintering and thermal etching at very high melting point. In addition, the diminutive amount of Co additives might have been the cause of its absence and it might have been imbedded within the grains during densification.. It is also clear that the peak intensity of the WC within the admixed powders increases with the increase in volume percentage of WC-12wt.%Co reinforcements. The inter-planer spacing increases with the increase in the vol.% of the reinforcements. In all the

powders and samples, the alpha Al_2O_3 phase was the only available phase in the alumina, and the WC phase was observed in the composites with no secondary phases.

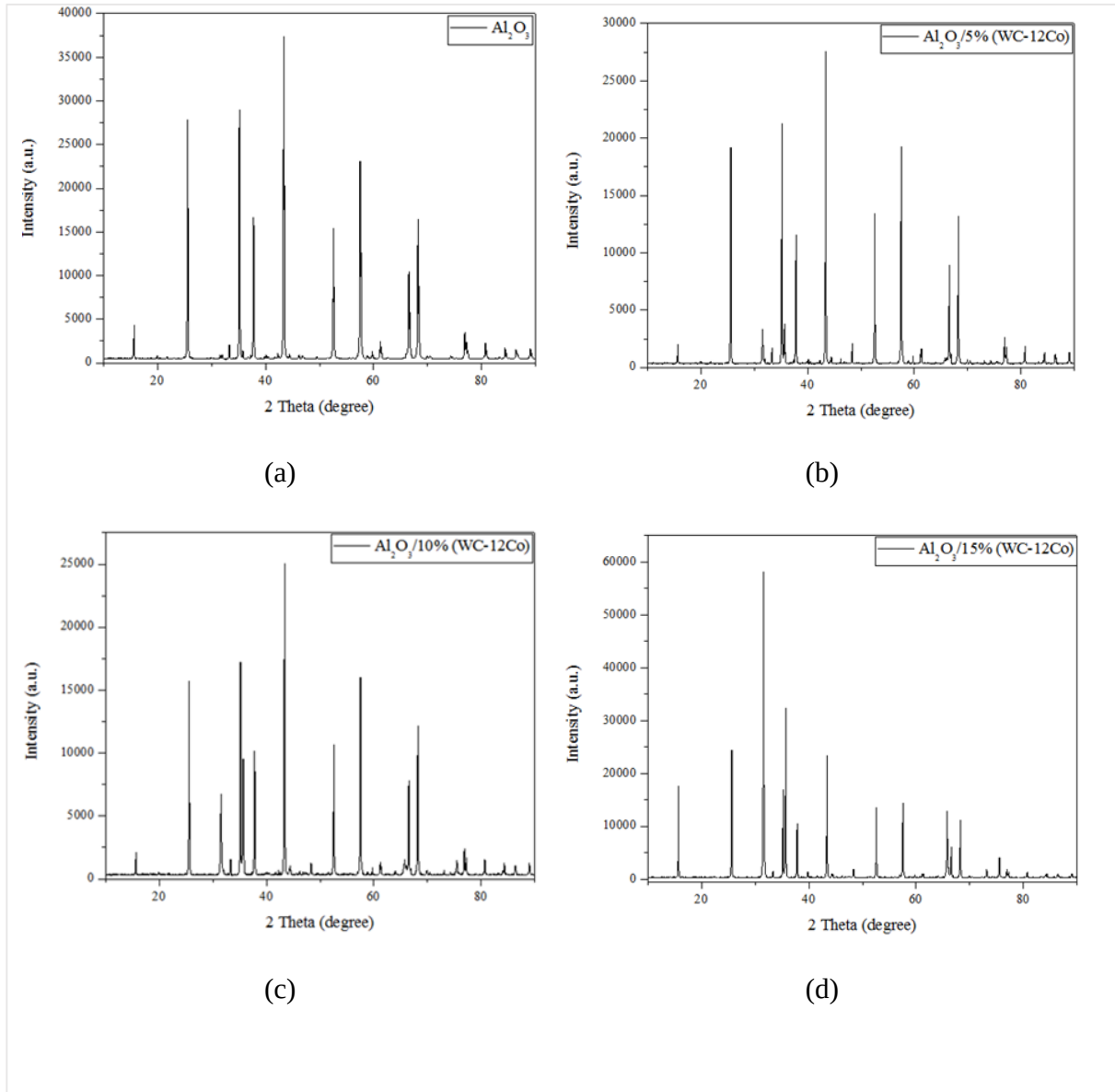


Figure 4-8. XRD results of (a) Al_2O_3 , (b) $\text{Al}_2\text{O}_3/5\text{vol}\%(\text{WC-12wt}\%\text{Co})$, (c) $\text{Al}_2\text{O}_3/10\text{vol}\%(\text{WC-12wt}\%\text{Co})$ and (d) $\text{Al}_2\text{O}_3/15\text{vol}\%(\text{WC-12wt}\%\text{Co})$ samples sintered at 1750 °C

4.6 Microstructure Analysis

Secondary electron imaging of pure $\text{Al}_2\text{O}_3/10\text{Vol}\%(\text{WC-12wt}\%.\text{Co})$ sample is shown in Figure 4-9. In the SEM, secondary electrons have low energy; they leave the surface of the sample and move towards the collector with positive potential, and interact with the secondary electron detector and the signal is used to create the secondary electron image. The sample was thermally etched to melt the low melting point grain boundaries. It is clear that the grains are of an irregular shape. No secondary phases (i.e. W_2C) were present from

the EDS analysis at an accelerating current of up to 25 kV and probe current ranging between 5 and 10 mA.. Samples were thermally etched in a high temperature furnace from 30 to 1450 °C at a heating rates of 30°C/min from 30 to 650°C and 10 °C/min from 650 to 1450 °C/min and a holding time of 12 minutes. The samples were then carbon coated to make their cross-sections and surfaces conductive.

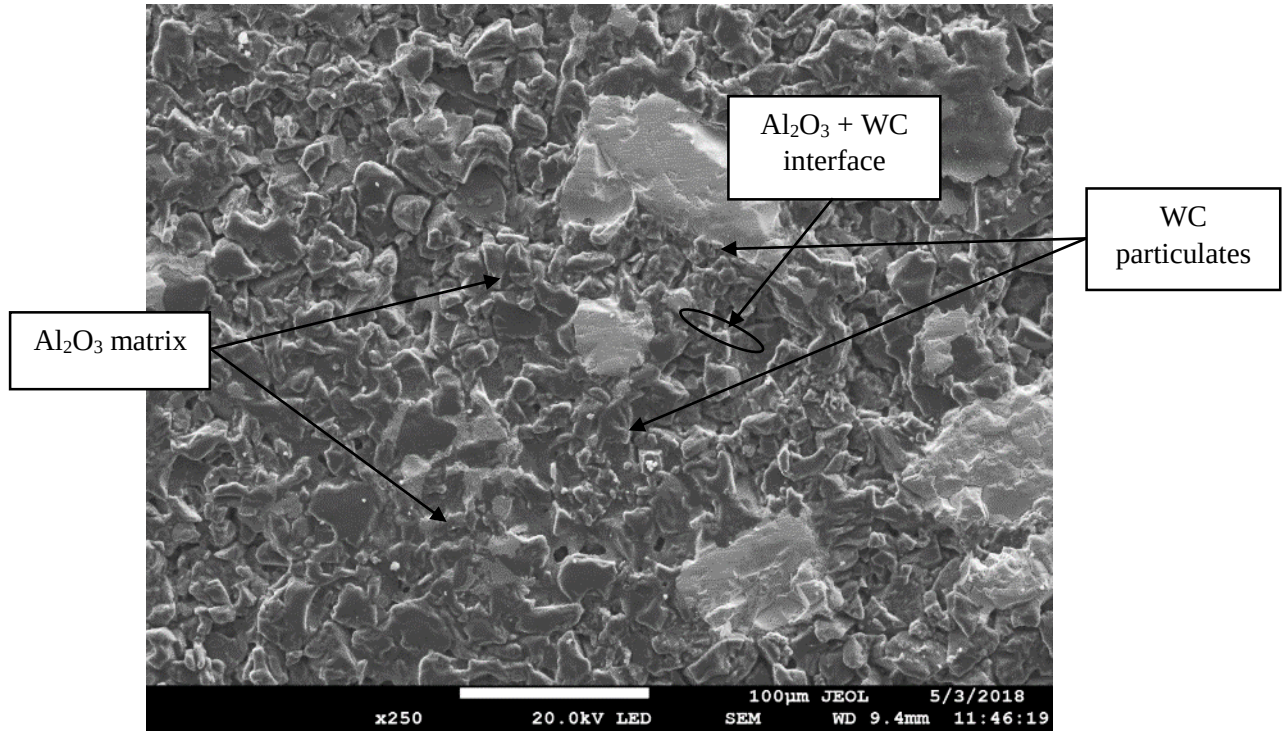
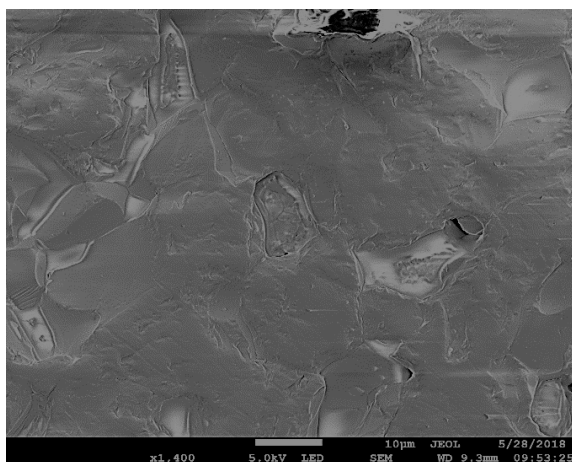


Figure 4-9. SEM secondary electron scatter micrograph of Al_2O_3 -10vol.%(WC-12wt%Co) before thermal etching

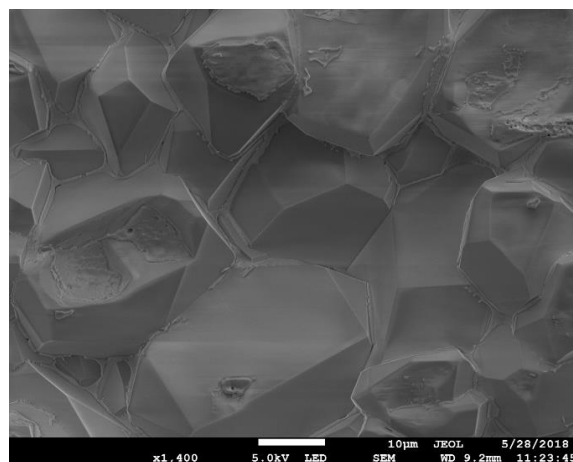
Sites that appeared to be porous contained high amounts of Co phase as analysed by the EDS software. The Al_2O_3 /WC interface contained a significant amount of Co phase as it was expected to act as a wetting agent between the Al_2O_3 phase and WC particles.

W_2C phase is extensively reported in the literature when bulk WC is fabricated at high temperature [12], [94], [95], when Al_2O_3 is admixed with WC. This is due to the high thermodynamic stability of W_2C phase at high temperatures and it is also postulated that they were decarburization at the powder surface caused by a reduction process and burning of the carbon from graphite sheets. However, in the present work W_2C is not observed, this is postulated to be caused by fast sintering time not giving the sample enough time to decarburise. This phase is unwanted due to its inferior properties such as low hardness, low modulus of elasticity.

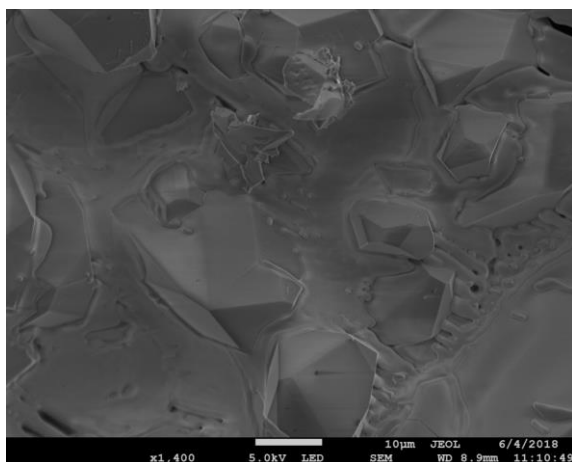
Figure 4-10 shows micrographs of thermally etched samples at 1450°C for 12 minutes dwell time. The figure shows the microstructures of two sample Figure 4-10 (a) Al_2O_3 sample and Figure 4-10 (b) $\text{Al}_2\text{O}_3/5\text{vol}\%(\text{WC-Co})$. Both the samples show irregular shaped grain structures with non-uniform microstructure. There is no significant grain growth within the composite samples, this proves the grain size retention capabilities of the spark plasma sintering technique. The SPS is a fast powder consolidation technique, which helps in grain retention by not allowing abnormal grain growth to occur. The microstructure of Al_2O_3 show high number of pores, which are visible on the thermally etched surface. This sample has less densification than the $\text{Al}_2\text{O}_3/5\text{vol}\%(\text{WC-12wt}\%\text{Co})$ sintered with the same parameters. The effects of thermal etching show that with high volume additives, more material melt this is due to high grain boundaries, materials and melting of the low melting point phases. The grain boundary and the melted grains show a high content of W and C as compared to the grains region.



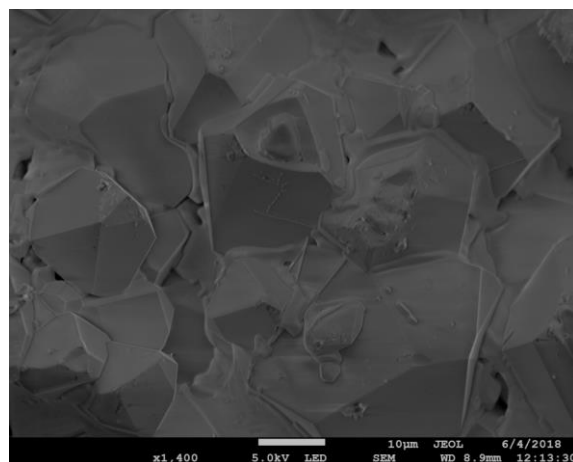
(a)



(b)



(c)



(d)

Figure 4-10. Microstructure of thermally etched (a) Al_2O_3 (b) $\text{Al}_2\text{O}_3/ 5\text{vol}\%$ (WC-12wt%Co), (c) $\text{Al}_2\text{O}_3/ 10\text{vol}\%$ (WC-12wt%Co), (d) $\text{Al}_2\text{O}_3/ 15\text{vol}\%$ (WC-12wt%Co) sample

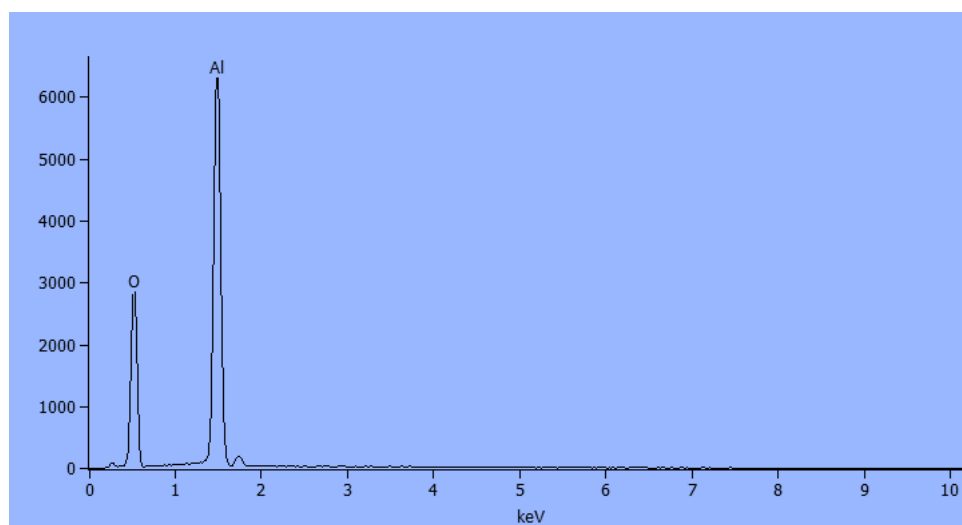


Figure 4-11. EDS results of Al_2O_3 sample sintered at 1750°C

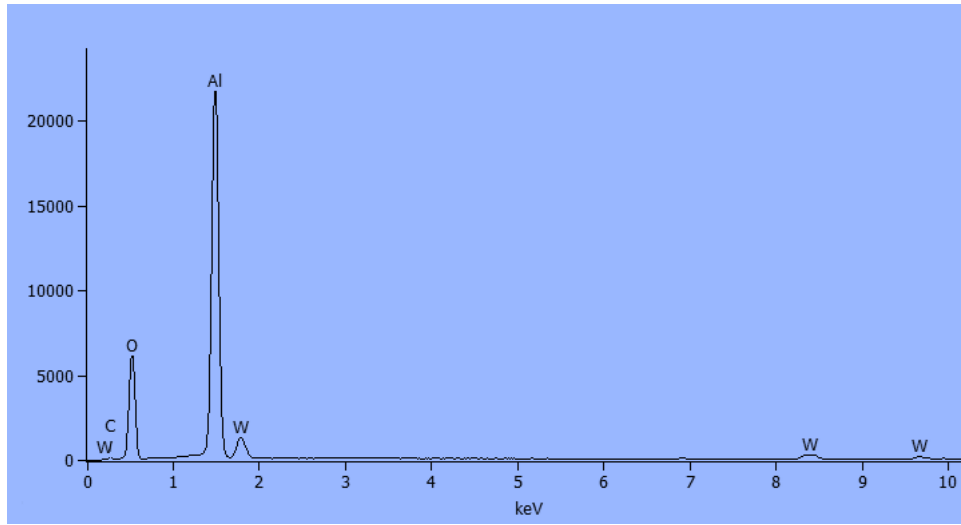


Figure 4-12. EDS spectrum of $\text{Al}_2\text{O}_3/5\text{vol}\%(\text{WC-Co})$ sample sintered at 1750°C

Table 10. Chemical composition of Al_2O_3 sintered samples

Chemical symbol	Weight %	Atomic %
O	50.52	63.26
Al	49.48	36.74
Total	100.00	100.00

Table 11. Chemical composition of $\text{Al}_2\text{O}_3/5\text{vol}\%(\text{WC-12wt.\%Co})$ sintered sample

Chemical symbol	Weight %	Atomic %
C	2.67	4.68
O	4.886	64.14
Al	38.62	30.06
W	9.84	1.12
Total	100.00	100.00

Large grains in the Al_2O_3 sample shows that there was an abnormal grain growth during the sintering process. Pure Al_2O_3 is hard to etch after high temperature thermal etching its microstructure is still not clear. They might have been grain growth during thermal etching due to a significant temperature for microwave sintering. Etching was carried out in the

presence of air, and the oxide layer might have been affected by excess oxygen in the air, making it even more difficult to etch.

The average grain size was calculated by the linear interpolation method developed by Nelson and Wurst [96], describe in Chapter 3. The average grain size for Al_2O_3 sample was $40 \pm 5 \mu\text{m}$, for $\text{Al}_2\text{O}_3/ 5\text{vol}\% (\text{WC}-12\text{wt}\%\text{Co})$ it was $36 \pm 5 \mu\text{m}$. There is a visible even suspension of the WC particles across the Al_2O_3 matrix, and the grain size distribution is heterogeneous across the sample. The main source of error for measuring grain size and evaluating grain size distributions from micrograph images is in the assumption that the grains are spherical therefore shape factor is necessary. Microstructure of alloyed Al_2O_3 shows the development of nano-cracks, this might have been caused by the difference in thermal expansion between the WC and Al_2O_3 phase and by the melting and solidification of the Co phase, which can cause high shrinkage of the sample.

Figure 4-13 shows the relationship between the grain size and relative density of samples. It is clear that the relative density increases linearly with the increase in the grain size. However, addition of WC-12wt%Co has shown to suppress grain growth in the Al_2O_3 composite. Hence, maximum densification can be achieved if the grain are inhibited from growing. Al_2O_3 has high grain growth and full densification (>98% TD) was not achieved due to the coarseness of the starting powders.

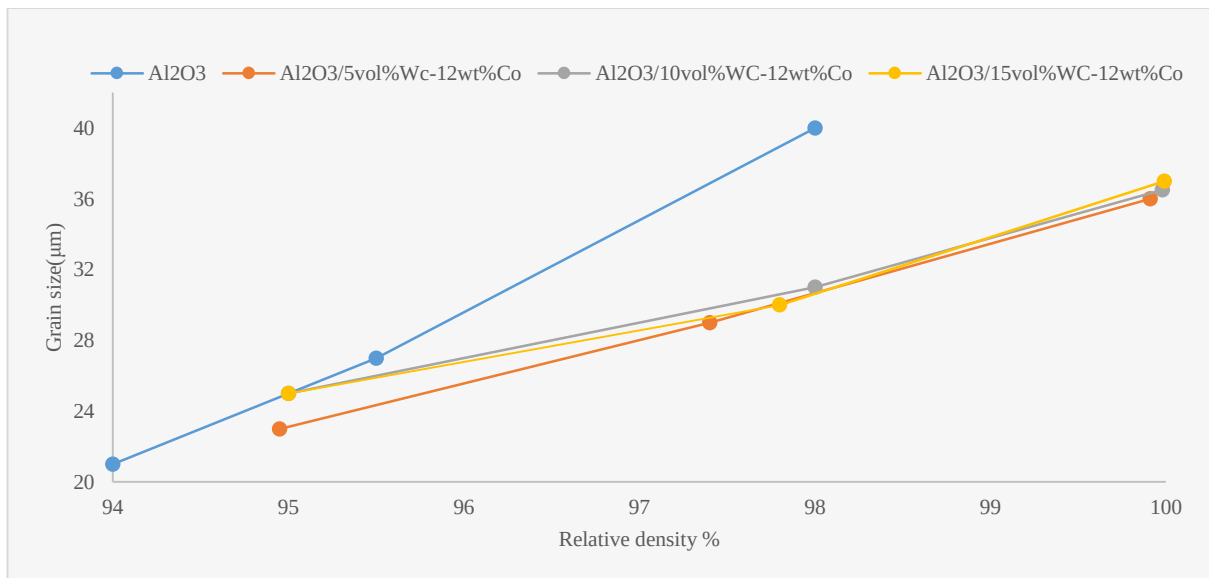


Figure 4-13. The relationship between grain size and relative density of sintered samples.

EDS results are for $\text{Al}_2\text{O}_3/ 5\text{vol}\% (\text{WC}-12\text{wt}\%\text{Co})$ and Al_2O_3 samples are shown in Figure 4-11 and Figure 4-12 respectively. According to Mosely's law, the lightweight

elements will emit X-rays of the K line series only, moderate elements will emit L and K series lines while denser elements will emit X-rays of M series or L and M series. These conditions will be acceptable when the accelerating voltage is in the range of 15-20 kV.

The accelerating voltage was taken up to 15.0 kV for analysis of the live SEM image via EDS software and the probe current was kept at 6 mA. High acceleration voltages above 25 kV made it difficult to analyse the samples due to charging effect on the sample surface. Therefore, samples needed to be coated with carbon, which will affect the results and their analysis, as carbon was one of the elements contained within the sample. Two series of lines detected by the EDS software were K (for O, Co, C, and Al elements) and M (for W element) shown in Figure 4-11. Therefore, O, Co, C and Al are lightweight elements and W is a heavy element as described by the Moseley's law. The spectrum peaks match with the reference peaks as those mentioned in the periodic table of elements. There is a tendency of the absence of Co phase from the whole sample analysis, however, point analysis show some Co phase present generally located in between the grains, in the pore like structure and even trapped within the grains of the Al_2O_3 matrix. The absence of Co phase might be due to the effect of background noise, and/or the small energy of the Co phase caused by its diminutive quantity. For the Al_2O_3 pure sample shown in Figure 4-12, there is hardly any other elements besides O and Al. However, there are traces of the Si element in the polished samples. Si traces might have been introduced during milling using sintered alumina balls, or by oxide polishing using silica suspensions or the impurities from the powder itself.

Good wetting capabilities between the WC particulates and Al_2O_3 matrix was observed between the 10 and 15 vol% (WC-12wt%Co). On the 5vol% WC-12wt%Co, there are signs of de-bonding of the particles upon excessive thermal etching of the samples. Table 12 shows elemental analysis of Al_2O_3 /5%vol%(WC-12wt%Co) composite sintered at 1800°C. The composition was determined by point and shoot method, which zooms in the specific area of analysis to the composition of a specific feature in the sample's microstructure. The microstructure analysed is shown in Figure 4-10 (b), the samples were thermally etched to reveal the grain boundaries by partially re-melting the lower melting point regions. Lighter grains are made of Al_2O_3 as only the oxygen and aluminium elements are present in this region. The molten phase or droplets contain all the components, which means that this region was a mixture of all the powders. There was no detection of Co phase in the darker grains only O, Al, C and W elements were present. The grain boundary region, part 1, part 2 and triple points (in Table 12) did not have the cobalt element the Co might have been

evaporated during thermal etching, or the Co phase may have been transported and trapped into the pores during sintering or reacted to the molten phase during thermal etching. High amounts of Co elements are found in darker pore sites with up to 60.54 wt%. This is not a good sign as the Co is expected to be at the WC-Al₂O₃ grain boundaries for wetting/adhesion of the particles. Large amounts of Co in the pores can also weaken the properties of the composites by introducing residual stress in the sample during cooling due to the difference in the thermal expansion of the elements. On the other hand, this might be the primary cause of high densification of the samples, the Co was in a liquid phase, which made it easy to flow into the pores than micron sized Al₂O₃ and WC particles.

Table 12. EDS point and shoot analysis of chemical composition obtained from Al₂O₃/5 vol%(WC-12wt%Co)

Composition (wt.%)	C	O	Al	P	Co	W
Molten phase	2.38	20.97	0.40	-	16.56	59.69
Lighter grain	-	50.22	49.78	-	-	-
Dark grain	3.37	28.32	6.53	-	-	61.77
Light grain boundary	2.44	30.77	17.81	-	-	48.98
Pore (dark)	-	13.74	23.94	-	60.54	1.78
Dark grain boundary	3.06	27.34	10.64	-	-	58.96
Triple point grains + molten phase	3.01	30.76	7.67	-	-	58.56
part 1	3.49	31.72	25.48	-	-	39.32
Part 2	3.50	34.73	16.18	-	-	45.58
Part 3	2.93	23.10	4.30	-	5.65	64.02
Part 4	3.35	33.84	6.97	0.35	-	55.49

4.7 Hardness

Hardness of the sintered material composites was determined by the Vickers hardness indentation test with a diamond indenter. Measurements were performed on polished and thermally etched samples. The hardness values of the samples were performed using a load of 10 kgf (98.1 N) (Hv₁₀), for a dwell time of 15 s, a standard test procedure for testing hard-metals and ceramic composites, which is frequently reported in literature [97]–[99]. The Five hardness measurements were made and the average was calculated and recorded. The Vickers hardness indentation method is destructive, it leads to surface deformation of the sample and causes stress concentration around the indent point this is sometimes called

surface deformation zone. This can lead to a change in mechanical properties of the sample. It is caused by deformation pile up and primary shear bands induced by compressive stresses underneath the indent this will normally cause temporary increases in hardness around the indented area for most materials.

The hardness values of samples are presented in Figure 4-14. Al_2O_3 sintered at 1600 °C at a heating rate of 100 °C/min had the lowest hardness, this might have been caused by the porous nature of the sample. The hardness of samples sintered at this temperature increased with the increase in the quantity of additives. Hardness of samples were highly dependent on the porosity and sintering temperature and has nonlinear dependence on the quantity of additives in the sample. The hardness of the samples increased with the increase in the amount of additives for similar sintering parameters. The high hardness value was recorded on the $\text{Al}_2\text{O}_3/15\text{vol.}\%(\text{WC}-12\text{wt.}\%\text{Co})$ sample at 23 GPa. These values of hardness are acceptable for cutting tools applications. For all the samples, the hardness, increased gradually with increase in vol.% of additives.

The hardness value measured near the reinforcement particles (WC) showed a hardness of 25 GPa, which is approximately 9 % higher than the hardness value of the matrix. The grain boundaries have the lowest hardness value, which might be caused by high stress concentration caused by dislocation pile up. Dislocation pile up can take place during the production of samples as a result of mechanical pressing of the sample. The hardness was dependent on the position of indent relative to the phases of the composites.

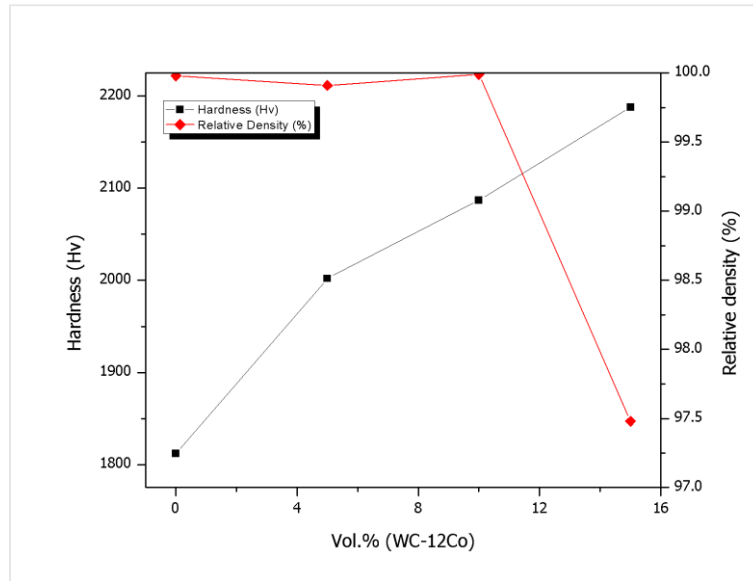


Figure 4-14. Hardness and relative density against composition of samples sintered at 1750 °C, 48 MPa, heating rate of 75 °C/min, in a nitrogen atmosphere

The hardness, increased significantly with the increase in sintering temperature for a specific composite. It also show a dependence on the volume percentage of WC-12wt%Co additives. The hardness of 18.75 ± 1.25 GPa was obtained for the overall Al_2O_3 samples.

4.8 Toughness

Toughness of samples was evaluated using the Palmqvist principle on macro indented samples. Loads of 10 to 20 kgf was applied to the sample for 15 s, to create a propagating crack on the polished sample surface and cross section. The crack length and diamond indenter diagonals were recorded and used to calculate the resistance of the sample to fracture (K_{IC}). The variations of toughness and the composition of the samples are shown in Figure 4-15. The fracture toughness of the samples increases with the increase in temperature and volume of the additives. However, it is worth mentioning that the K_{IC} does not have a linear dependence on sample and composition. This behaviour can be closely related to the densification of samples. To calculate K_{IC} the elastic modulus of the material needs to be known and in this work it is calculated using the Voigt-Reuss bounds suggested by Hsieh and Tuan (2005) [100]. This method is independent of the microstructure of the composite material. This relation was the most suitable due to the fact that it incorporates the features of large particle reinforcements $\gg 0.1 \mu\text{m}$. Elastic modulus of WC-12wt%Co was taken as 495 GPa from Chawla et al (2003) [101]. The elastic modulus of Al_2O_3 was taken as 375 GPa as from the supplier. Therefore, using the upper bound of the rule of mixture, the modulus of the composites becomes 381, 387 and 393 GPa for 5, 10 and 15 vol% additives

respectively. However, these moduli is only applicable for samples with 98% TD densification and above, to compensate for the effect of porosity on the elastic modulus.

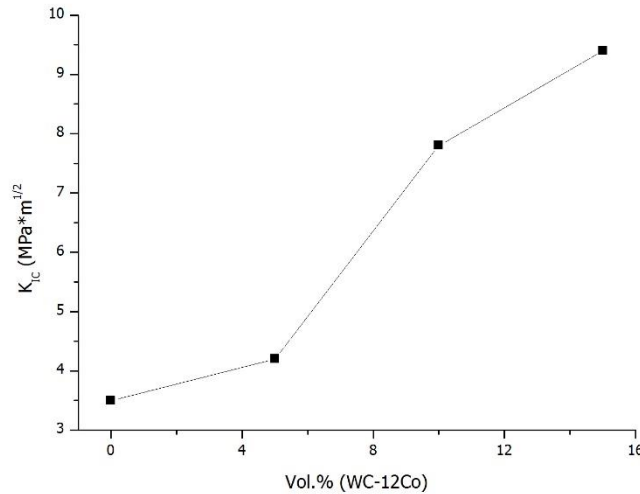


Figure 4-15. Toughness of samples sintered at 1750 °C with a heating rate of 75 °C/min

Intergranular fracture is the most dominate fracture mode. However, formation of new independent cracks (crack jump) was observed in samples with low volume percent additives. The increase in fracture toughness was presumed to be a result of plastic deformation of the ductile dull grain boundaries containing higher amounts of Co metal phase. Plastic deformation of this region absorbs more energy during fracture leading to tearing of the plastic zone at the crack tip forming microcracks and blunting the crack, stopping it from growing. However, the addition of Co particulates should be limited to avoid diminishing other properties of the composites such as high melting point, high hardness, good chemical stability.

4.9 Wear resistance and coefficient of friction

The wear rate of Al₂O₃ and Al₂O₃/WC-12wt%Co composites sliding against steel ball at a speed of 3 mm/s were investigated. At first, the wear rate increased with increase in sliding velocity. Then wear rate decreased with increase in load. When sliding against hard materials, the friction coefficient and wear rate showed the same variation trend. Smaller coefficient of friction may result in smaller friction force, then the wear effects on ceramic disk are weakened, and thus the wear rate is reduced. This may probably be responsible for the same variation trend of coefficient of friction and wear rate. Similar trends were recorded by *He et al.* (1997) [66]. The CoF of Al₂O₃ ceramics sintered at low applied force have large

fluctuations with sliding time, while the average coefficient of friction fluctuations has the smaller ranges for Al₂O₃ ceramics sintered at 1750 °C. For 30 N applied load after 3 min of the sliding time, the coefficient of friction for Al₂O₃ sample was 0.6, while for Al₂O₃ ceramics with 5, 10, 15 vol.% of WC-12wt%Co were 0.4, 0.3 and 0.3, respectively. The value of CoF decreases with an increase in applied force. By comparison, the CoF for Al₂O₃ ceramics is higher than that of reinforced composites, for samples sintered with the same parameters. The CoF of Al₂O₃ rises faster at the start of the wear test and then remains almost constant through the whole test. Whereas, the CoF of Al₂O₃/5vol%(WC-12wt%Co) starts low with a relatively lower increase than Al₂O₃ counterpart.

Table 13. Coefficient of friction, sliding distance and applied force of sintered samples

Material	FN (N)	Sliding distance (m)	CoF
Al ₂ O ₃	30	0.18	0.60
	50	0.18	0.40
	100	0.18	0.20
Al ₂ O ₃ /5%(WC-Co)	30	0.18	0.40
	50	0.18	0.30
	100	0.18	0.20
Al ₂ O ₃ /10%(WC-Co)	30	0.18	0.30
	50	0.18	0.20
	100	0.18	0.20
Al ₂ O ₃ /15%(WC-Co)	30	0.18	0.30
	50	0.18	0.20
	100	0.18	0.18

High hardness AISI 52100 alloy steel was used to make scratches to the polished surface of the samples and varying the normal load from 10 to 100 N, without lubrication. AISI 52100 steel is a tool steel widely used in mechanical components as bearing or extrusion tool. It is used in application where high hardness, wear and fatigue resistance are demanded. Some of its important properties include elastic modulus of 210 GPa, bulk density of 7.81 g/cm³, hardness of 848 Hv which is lower than hardness of Al₂O₃.

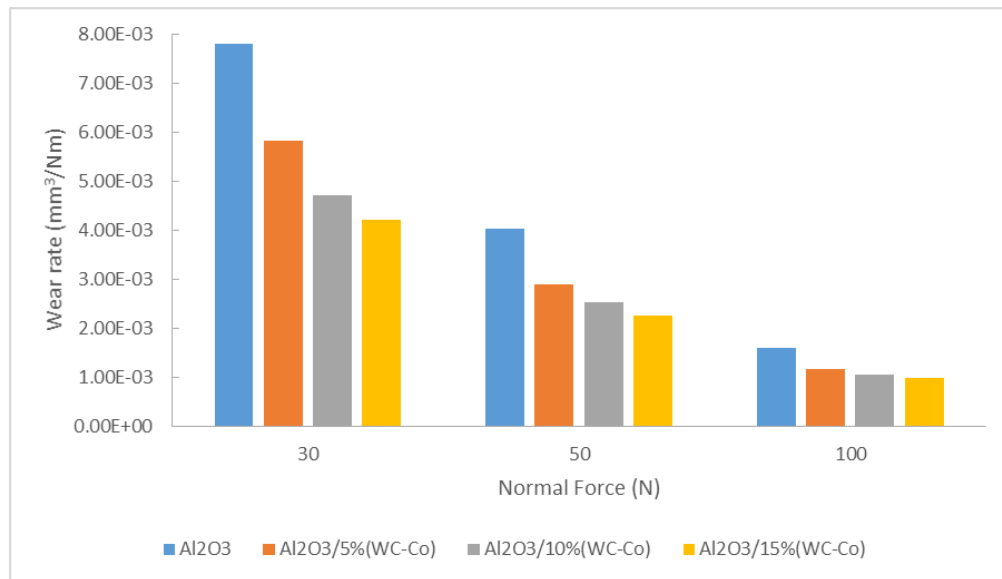


Figure 4-16. Wear rate and normal applied force of sintered samples

4.9.1 SEM Characterisation of Wear Track

Wear track geometry was analysed using optical microscopy. Worn surfaces were investigated under a scanning electron microscope (SEM) equipped with an energy dispersive spectroscope (EDS). Furthermore, wear debris and severe wear were perceived or identified, evidently in all the wear tracks of all the samples. Scratches were evaluated using the optical microscope to analyse wear volume and wear rate. The samples wear further analysed using an SEM equipped with EDS to analyse the wear debris and the chemical composition in the wear debris. However, the worn surfaces were articulated by spherical dent shapes in all the samples. Figure 4-17 shows wear volume and wear depth of alumina sample sintered at 1750°C. Wear volume of $2.2563 \times 10^{-2} \text{ mm}^3$ with a wear depth of - 5.656 μm and width (Δx) of 754.941 μm were observed.

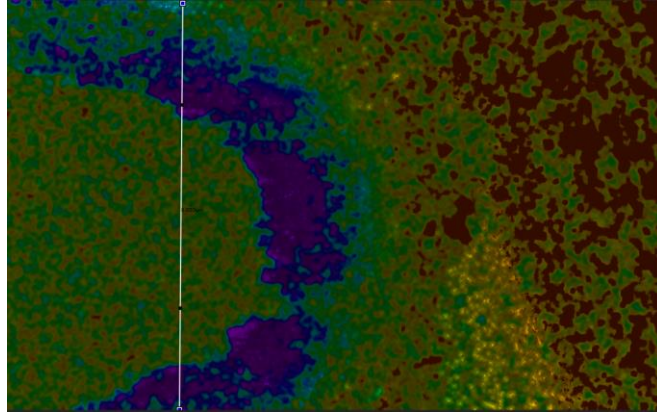


Figure 4-17. Wear surface of alumina tested at 30N

Figure 4-18 shows wear volume and wear depth of alumina sample sintered at 1750°C. Wear volume of $4.70088 \times 10^{-2} \text{ mm}^3$ with a wear depth of $-8.877 \text{ }\mu\text{m}$ and width (Δx) of $967.808 \text{ }\mu\text{m}$ were observed.

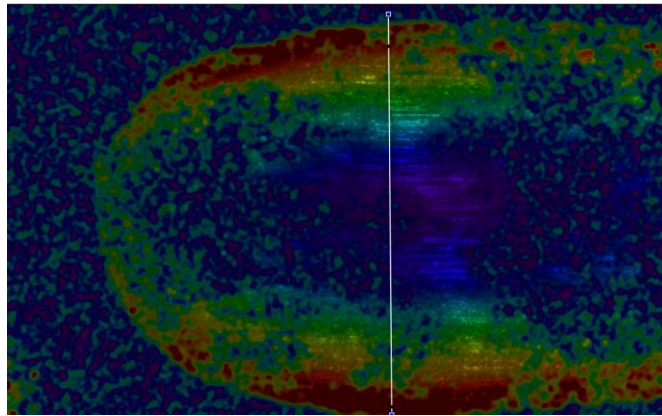


Figure 4-18. Wear surface of alumina tested at 50N

Figure 4-19 shows wear volume and wear depth of alumina sample sintered at 1750°C. Wear volume of $6.435626 \times 10^{-2} \text{ mm}^3$ with a wear depth of $-5.033 \text{ }\mu\text{m}$ and width (Δx) of $1049.781 \text{ }\mu\text{m}$ were observed.

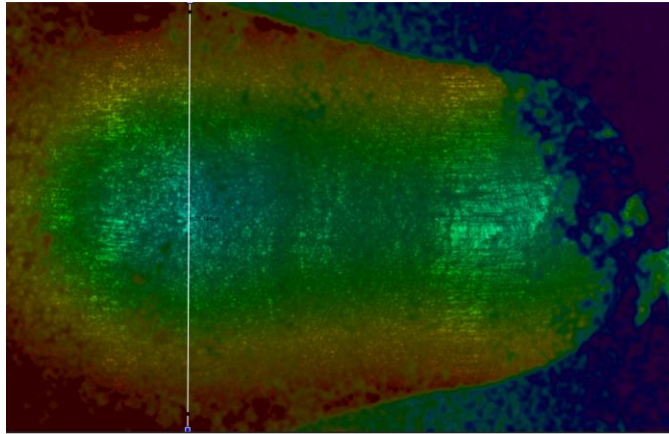


Figure 4-19. Wear surface of alumina sample tested at 70N

Figure 4-20 shows wear volume and wear depth of alumina sample sintered at 1750°C. Wear volume of $8.53179 \times 10^{-2} \text{ mm}^3$ with a wear depth of $-1.1132 \text{ }\mu\text{m}$ and width (Δx) of $880.765 \text{ }\mu\text{m}$ were observed.

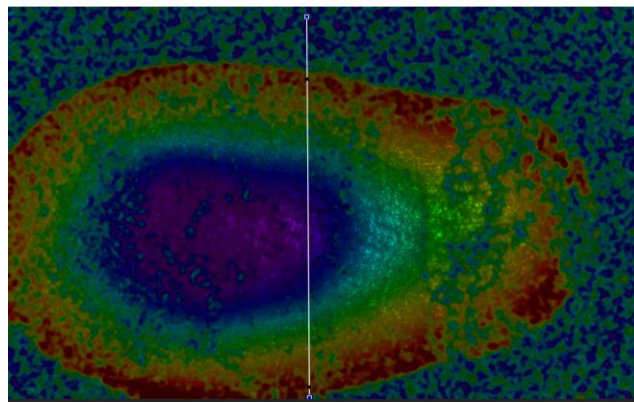


Figure 4-20. Wear surface of alumina tested at 100N

The wear volume increases with increase in normal load. However, there was no correlation between depth and width of the scratches. The measurement of the wear volume and depth was challenging, which led to a deviation in the actual values. The error was minimized by locating the part of the scratch where the volume was damaged the most and the scratch had to fit into the screen at 10X optical zoom. Another problem faced during wear volume measurements was the poor contrast of the image due to low light.

The chemical composition of the wear debris was analysed by EDS and the wear mechanism was analysed by SEM. The images from the SEM were analysed to identify wear type, Figure 4-21 shows wear debris of alumina sample sintered at 1750 °C and tested at 30 N applied force. Adhesive wear was assumed from the SEM image analysis. More material is whipped off during wear, scratch load. This was observed for all the samples

sintered at this temperature. Whereas for samples sintered at a 1800 °C abrasive wear was observed.

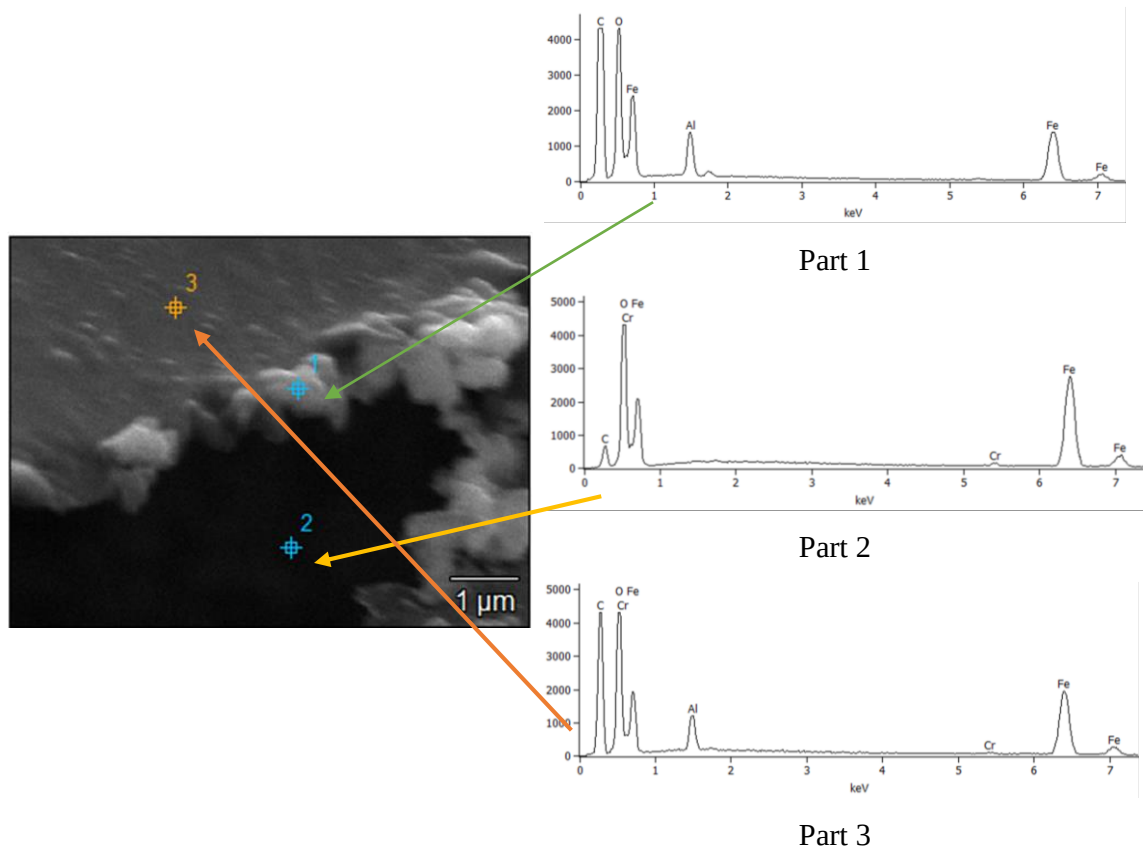


Figure 4-21. Wear debris and EDS analysis of alumina sample sintered at 1750 and tested at 100 N normal load.

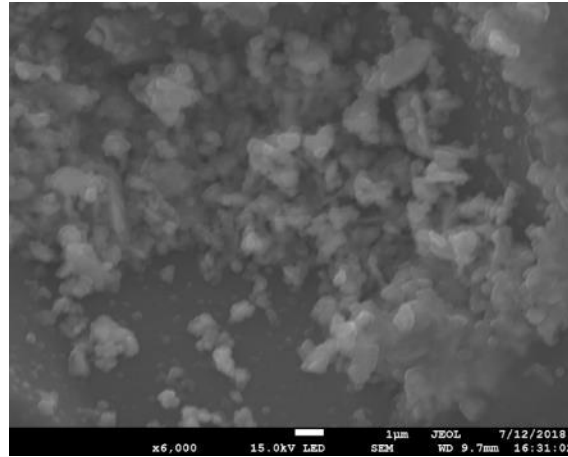


Figure 4-22. Worn surface of Al_2O_3 sample

Figure 4-23 shows crack Intergranular crack developed during wear test at high load 100 N.

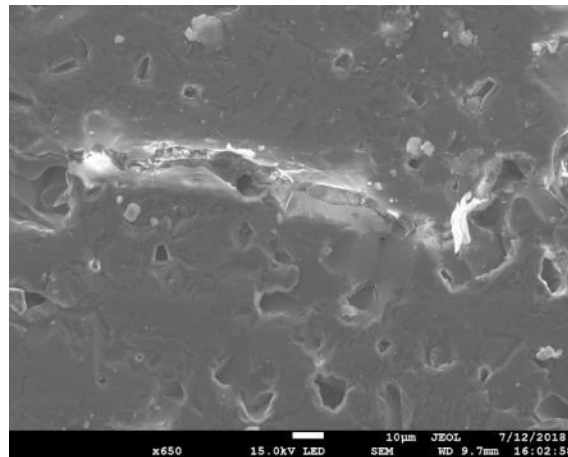


Figure 4-23. SEM image of wear tested Al_2O_3 sample

The elemental quantification of the worn surface shows high iron and carbon contents. This is due to the hard nature of the alumina composites. Therefore the wear debris contains some wear ball test material.

Coefficient of friction and wear resistance were investigated using a pin on plate configuration with linear reciprocating motion. The wear track was examined using optical microscope Micrographs were used to study the wear mechanisms involved during the ball on disk wear test. The coefficient of friction of the Al_2O_3 and $\text{Al}_2\text{O}_3/\text{WC-Co}$ composite materials obtained by the pin-on-plate was investigated.

The friction coefficient was lower in Al_2O_3 than in composite material. However, the wear rate was higher in Al_2O_3 than in composites. This is assumed to be brought about by metal adhesion layer, which was formed by the chemical reaction between Al_2O_3 and iron

oxides. The rough surface layer and lack of adhesion was assumed to yield very high CoF. Adhesive wear was the most dominate wear mechanism observed in this test, while abrasion and chipping (reinforcement pull-out) were considered the main wear mechanisms in these tests due to sliding against metal ball.

Chapter 5. Conclusions and Suggestions for Future Work

5.1 Introduction

This chapter presents the conclusion of this study. The overview of the study is presented, highlighting the results that support the main objectives of this study. The chapter concludes with potential future directions, elaborating methodology to be undertaken to improve the significance of the findings and further investigation into $\text{Al}_2\text{O}_3/\text{WC-Co}$ systems for better mechanical and wear properties.

5.2 Conclusions

This Masters dissertation was aimed at investigating tungsten carbide-cobalt as reinforcement additives to alumina with improved fracture toughness and wear resistance properties. The research encompasses the fabrication and characterisation of $\text{Al}_2\text{O}_3/\text{WC-Co}$ composites consolidated via spark plasma sintering (SPS). It also involves an intensive comparison of microstructure, mechanical properties and wear resistance of Al_2O_3 with the $\text{Al}_2\text{O}_3/\text{WC-Co}$ composites. Pure alumina Al_2O_3 and Al_2O_3 reinforced with tungsten carbide-cobalt of volume percentages 5, 10, and 15 were consolidated via SPS, with a uniaxial pressing of 48 MPa at 1600 °C, 1750 °C and 1800 °C, for a holding time of 5 and 10 minutes. The ratio of WC to Co was kept constant at WC-12wt%Co. It was found that increasing the reinforcements increased the densification of Al_2O_3 up to 10% reinforcements for temperatures below 1800 °C. Sintering temperature and reinforcement compositions have a remarkable influence on the densification of the composites. Full densification > 99.8% TD was achieved at 1800 °C sintering temperature for all the composites, while for un-doped Al_2O_3 only up to 99.9% TD was possible. Grain coarsening was postulated to be a major factor in low density of Al_2O_3 , this caused grain growth without a significant densification which lead to pore being embedded in the grains and at the grain boundaries. On the other hand, the additives WC particles acted as grain boundary pinning to restrict Al_2O_3 grain from growth, which lead to grain size retention. In addition, Co particles melted and acted as a wetting, adhesive between the WC particles and Al_2O_3 matrix. This leads to good bonding between the two phases, which helps to stick the particles together to avoid debonding of the material during use.

The young's modulus was calculated by a simple rule of mixture method these values were 375, 381, 387 and 393 GPa for Al_2O_3 , $\text{Al}_2\text{O}_3/5\text{vol}\%\text{WC-12wt}\%\text{Co}$,

$\text{Al}_2\text{O}_3/10\text{vol}\%(\text{WC}-12\text{wt}\%\text{Co})$ and $\text{Al}_2\text{O}_3/15\text{vol}\%(\text{WC}-12\text{wt}\%\text{Co})$ respectively. The Al_2O_3 composite has shown a good combination of hardness, fracture toughness and tribo-wear properties. There is an increase in hardness with an increase in additives, however the correlation showed a linear increase in hardness of materials sintered at 1800°C . The increase in hardness is associated with grain retention during sintering for doped Al_2O_3 and relative density of the material. Al_2O_3 had low densification and it's also hard low hardness compared to other ceramic composites of similar sintering parameters, with higher densification.

The fracture mechanism observed in the un-doped Al_2O_3 sample was mostly intergranular. This is assumed to be caused by de-bonding of the weaker grain boundaries compared to the grain of Al_2O_3 . This will yield low fracture toughness value, as they will be less obstacle to obstruct crack growth. Moreover, intergranular, intergranular and crack bridging were found to be the main fracture mechanisms in the sintered samples. In addition to these forms of fracture new crack formations were found in fractured samples, this could lead to more ductile material as the stress intensity along the propagating crack tip lowers due to the formation of these new cracks. Adhesive wear was the most dominant wear mode for all the samples.

The powder was milled and then examined for new phase using XRD, they are no phase transformation during milling. After powder consolidation, samples were also examined using XRD for new phase and possible reactions during the sintering process. It was found that no new phases were formed during this process. This is a good thing because the material is capable of attaining full densification if no new phases are formed which can have negative features that might end up having undesirable effects on the mechanical properties of the composites.

5.3 Suggestions for Future Work

Despite the progress made through this experimental investigation, more work is still to be conducted on these ceramic systems. The time available for sample powder milling and drying, consolidation and study using SEM was limited. More detailed study of the milled powder to nano-size range will be the beneficiary in studying the effects of reinforcement's quantity, heating rate, cooling rate and holding temperature on the microscopic properties and mechanical properties of the $\text{Al}_2\text{O}_3/\text{WC-Co}$ ceramic systems. The results of this study represent the microstructural and mechanical characteristics of Al_2O_3 matrix reinforced with

WC-12wt%Co additives at a volume percent of 0, 5, 10 and 15. The following methods are recommended corresponding to the conclusion presented in this work.

- In this study the composition was varied from 5 vol.% to 10 vol.% and 15 vol.% and the samples are sintered in a liquid phase sintering (LPS) state. The new material can be sintered in a solid state sintering (SSS) conditions by varying the sintering parameters. The composition can also be varied from 1 vol.% to 15 vol.% reinforcements for better analysis of optimal composition.
- The ratio of the reinforcement was fixed at WC-12 wt.% Co, leading to too much Co liquid phase at higher reinforcement content say 15vol%(WC-12wt.%Co). Therefore, liquid phase can be reduced by finding the proper wt.% of Co at high volume percent additive.
- Longer milling time at lower milling speed may be used to achieve homogeneously dispersed nano-particles of additives within the matrix.
- The sliding wear properties of the composites may be tested. Transition electron microscopy (TEM) may be used to characterise the microstructure of samples for comparison of the materials microstructure from SEM. TEM should also be used to study the admixed powders.
- The digital image correlation can be applied to study the invisible cracks that propagate from an indent. Furthermore, electron backscattered diffraction can be used to observe the orientation of the microcracks and grains in the sample microstructure for better understanding of toughening mechanisms in the samples.
- Use of finer powder in the range of <100 nm, and high uniaxial pressure of up to 100 MPa, might yield high densification of >99.99 % TD at low temperature.
- The pin on disk configuration, temperature changes during dry and lubricated sliding wear test and other wear situation can be employed to further investigate the wear properties of the samples.
- The tribo-wear properties of samples can be studied by varying the tribo-wear test conditions.

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