

Study of Grain Boundary Character in WC-Co

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Statement of Originality

I declare that this thesis is entirely my own work. Any contributions to it from others are acknowledged and referenced accordingly.

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Abstract

Cemented carbide tools are used in applications demanding high hardness and toughness. However, fracture during operation of WC-Co tools is deleterious for tool performance and lifetimes. Interfaces in WC-Co, especially the WC grain boundary network are crucial for mechanical properties as crack path is mostly intergranular. Therefore, it is beneficial to gain knowledge about the WC boundaries. This will in turn allow for grain boundary engineering (GBE) of WC-Co tools with superior performance and lifetimes.

To achieve this, firstly, WC grain boundaries have been examined using wedge loaded double cantilever beam (DCB) fracture tests. Since the literature review of WC-Co revealed that $\Sigma 2$ twist boundaries are the most abundant boundary type, these have been studied with DCB tests. Ideal $\Sigma 2$ twist boundaries (perpendicular to the surface) for fracture testing have been identified from electron backscatter diffraction (EBSD) data acquired from a WC-10wt%Co sample and processed via a custom MATLAB script working in MTEX. The fracture energy of $\Sigma 2$ twist boundaries has been compared to cleaving the lowest energy plane (type II $\{10\bar{1}0\}$) in a WC single crystal. Fracture energies of $3.59 \pm 0.30 \text{ Jm}^{-2}$ and $7.04 \pm 0.36 \text{ Jm}^{-2}$ were measured for cleaving $\Sigma 2$ twist boundaries and type II $\{10\bar{1}0\}$ planes respectively. This results in a few conclusions. Firstly, fracture energy measured for type II $\{10\bar{1}0\}$ plane is in agreement with the values ($7.25\text{-}7.33 \text{ Jm}^{-2}$) reported from the literature using density functional theory calculations. Secondly, the fracture energy of $\Sigma 2$ twist boundaries being half that of the type II $\{10\bar{1}0\}$ planes is consistent with the observation that most of the fracture path in WC-Co is intergranular.

As a complementary study, grain boundary character distribution (GBCD) analysis of the most abundant boundaries ($\Sigma 2$ boundaries and $\Sigma 13$ boundaries) in WC-Co was performed. This analysis is based on Rohrer et al.'s five parameter GBCD analysis [1]. Furthermore, the effect of chromium doping on WC boundary populations of a chromium doped sample (WC-10wt%Co-1wt%Cr) was examined and compared with an undoped WC-Co (WC-10wt%Co) sample. It was found that the area fraction of $\Sigma 2$ boundaries increased by a factor of 3 (from 5% to 15% area fraction) with chromium doping. Area fraction of $\Sigma 13$ boundaries was not measured quantitatively owing to low boundary counts. However, qualitative analysis indicated that $\Sigma 13$ boundary population declined with doping. Finally, it was deduced that the fraction of $\Sigma 2$ and $\Sigma 13$ were more frequent when examining exclusively WC/WC boundaries compared to looking at all possible WC grain boundaries. This observation held true regardless of doping.

Interestingly, all further DCB tests performed at $\Sigma 2$ twist boundaries on the chromium doped sample, WC-10wt%Co-1wt%Cr failed. This corresponds with the increased fraction of $\Sigma 2$ twist boundaries on the chromium doped sample. It was thus hypothesised that chromium doping alters the boundary

chemistry of $\Sigma 2$ twist boundaries which in turn reduces the grain boundary energy (increasing the $\Sigma 2$ twist boundary population) and thus increases the fracture toughness of the $\Sigma 2$ twist boundary.

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List of Publications and Conferences

Publications

- EMMANUEL, M., GAVALDA-DIAZ, O., SERNICOLA, G., M'SAOUBI, R., PERSSON, T., NORGRÉN, S., MARQUARDT, K., BRITTON, T.B. and GIULIANI, F., 2021. Fracture energy measurement of prismatic plane and $\Sigma 2$ boundary in cemented carbide. *JOM*, **73**(6), pp. 1589-1596. Available from: <https://doi.org/10.1007/s11837-021-04638-6>.
- GAVALDA-DIAZ, O., LYONS, J., WANG, S., EMMANUEL, M., MARQUARDT, K., SAIZ, E. and GIULIANI, F., 2021. Basal plane delamination energy measurement in a Ti₃SiC₂ MAX phase. *JOM*, **73**(6), pp. 1582-1588. Available from: <https://doi.org/10.1007/s11837-021-04635-9>.

Conferences

- Measuring the fracture energy of WC grain boundaries; poster presentation at ECI, Malaga, Spain, 2019.
- Analysis of strength and grain boundary character in polycrystalline WC-Co; poster presentation at EUROMAT, virtual conference, 2021.
- Grain boundary character distribution of WC-Co cutting tools; poster presentation at RMS|Virtual EBSD, virtual conference, 2022.

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List of Abbreviations

AM	Additive Manufacturing
APT	Ammonium Paratungstate
BS	Band Slope
BIB	Broad Ion Beam
CCD	Charge Coupled Device
CN	Chevron Notch
CSL	Coincidence Site Lattice
CIP	Computer Integrated Polarization Microscopy
CI	Confidence Index
DRIE	Deep Reactive Ion Etching
DAXM	Differential Aperture X-Ray Microscopy
DHP	Displacement Head Piezo
DCB	Double Cantilever Beam
EDM	Electrical Discharge Machining
EBSD	Electron Backscatter Diffraction
EBSP	Electron Backscatter Pattern
ECD	Equivalent Circle Diameter
EBT	Euler-Bernoulli Beam Theory
FCC	Face Centred Cubic
FEA	Finite Element Analysis
FFT	Fast Fourier Transform
FSSS	Fisher Sub Sieve Grain Size
FIB	Focused Ion Beam
GBCD	Grain Boundary Character Distribution
GBE	Grain Boundary Engineering
GBPD	Grain Boundary Plane Distribution
HCP	Hexagonal Close Packed
HIP	Hot Isostatic Pressing
IQ	Image Quality
IF	Indentation Fracture
IPF	Inverse Pole Figure
LEM	Lawn-Evans-Marshall
LEFM	Linear Elastic Fracture Mechanics

LPS	Liquid Phase Sintering
MAD	Mean Angular Deviation
MFP	Mean Free Path
MRD	Multiples of Random Distribution
PIG	Penning Ion Gun
SEM	Scanning Electron Microscope
SNR	Signal to Noise Ratio
SC	Single Crystal
SENB	Single Edge Notch Bend
SEPB	Single Edge Pre-Cracked Beam
SEVNB	Single Edge V-Notched Beam
SSS	Solid State Sintering
SPS	Spark Plasma Sintering
3DXRD	Three-Dimensional X-Ray Diffraction Microscopy
TBT	Timoshenko Beam Theory
TEM	Transmission Electron Microscope
TRS	Transverse Rapture Strength
$\Sigma 2$ B	$\Sigma 2$ Twist Boundary

Introduction

Cemented carbides are important composite materials in the manufacturing industry, with applications in mining, drilling and cutting. Their composite structure is made of two interpenetrating constituent phases: WC (hard phase) and Co (soft phase). This results in an exceptional combination of high hardness and toughness compared to other hard materials. Yet, performance and lifetimes of WC-Co tools is limited because of fracture and wear. In this study, the fracture aspect of this problem has been explored.

Bulk toughness of WC-Co has been studied with a variety of macroscale fracture tests such as single edge notch beam (SENB), DCB, double torsion and Palmqvist indentation fracture tests. Bulk toughness values of 8-26 MPam^{1/2} (91-961 Jm⁻²) have been measured for WC-Co depending on cobalt content and carbide grain size [2]. The high toughness of WC-Co is possible due to the main toughening mechanism, the formation of the multiligament zone. In a multiligament zone, crack surfaces are held together by cobalt ligaments along fracture paths impeding crack growth. However, fracture in ceramics is facilitated by the weakest link of the microstructure. Given that most of the fracture path has been shown to be intergranular with respect to carbide grains, the aim of this work is to investigate the WC boundaries.

The effect of microstructural features such as WC boundaries in WC-Co fracture is lacking within the current literature. The WC boundaries have been studied in two ways in this work. Firstly, fracture properties i.e., the fracture energy of the most abundant WC boundary ($\Sigma 2$ twist) in WC-Co has been measured using DCB tests. Secondly, grain boundary statistical analysis via Rohrer et al.'s five parameter GBCD analysis has been performed to determine the area fraction of the $\Sigma 2$ and $\Sigma 13$ boundaries. In both cases, a standard (WC-10wt%Co) and a chromium doped (WC-10wt%Co-1wt%Cr) WC-Co sample were used. Hence, the study also investigated the effect of chromium doping on $\Sigma 2$ twist boundary fracture energy and the populations of $\Sigma 2$ and $\Sigma 13$ boundaries.

Structure of the Thesis

Chapter 1 reviews the literature on WC-Co. This includes details on the manufacture of WC-Co and WC-Co microstructure. Additionally, the effect of parameters such as WC grain size and cobalt content on mechanical properties (hardness, toughness and transverse rupture strength) has been reported. Furthermore, room temperature fracture tests performed on WC-Co from other studies has been discussed here.

Chapter 2 delves into the theory and practical means for quantifying fracture toughness/energy. The theory segment is dedicated to looking at the different approaches (energy balance and stress field) for quantifying fracture toughness. The experimental segment reports on the macro and micro scale fracture tests available for fracture toughness measurements.

Chapter 3 is dedicated to examining the merits of using DCB tests as a micromechanical test of choice to measure fracture energy as well as presenting the theory behind extracting fracture energy values from DCB testing.

Chapter 4 explains Rohrer et al.'s five parameter GBCD analysis.

Chapter 5 presents sample production routes used to manufacture the samples (WC-10wt%Co and WC-10wt%Co-1wt%Cr) and details on the material characterisation techniques used in this work.

Chapter 6 in essence is an extended methods chapter. The chapter covers the theory, implementation and verification of the process used to identify ideal (perpendicular the surface) $\Sigma 2$ twist boundaries necessary for DCB testing. It also includes the challenges and lessons learned from performing DCB tests on WC-Co.

Chapter 7 reports on the procedure for measuring the fracture energy values from DCB test videos and the error analysis performed on the test data. A discussion on the merits of using DCB tests to measure the fracture energy of the $\Sigma 2$ twist boundaries is also presented. Finally, this chapter presents and analyses crack paths in successfully fractured DCBs as imaged via TEM.

Chapter 8 examines the effect of chromium doping in WC-Co with regards to changes in $\Sigma 2$ and $\Sigma 13$ boundary populations. Furthermore, discussions about the implications of chromium doping for boundary chemistry, grain boundary energy and boundary fracture toughness are presented here. Additionally, grain size distribution and texture of WC-Co samples investigated in this project are also provided in this chapter.

Chapter 9 summarises the work carried out in this project and provides possible avenues for future work extending from this project.

1 Cemented Carbide

1.1 Introduction

Cemented tungsten carbide (WC-Co) is a particle reinforced matrix; hard tungsten carbide (WC) particles (hard phase) embedded in a ductile cobalt matrix (binder phase). 'Cemented' refers to WC particles having been encapsulated in the binder phase [3]. The term hard metal is used interchangeably with WC due to its high hardness relative to other metals. French chemist, Henri Moissan was the first to synthesise WC in the 1890s [4]. In the 1920s, researchers at Osram Studiengesellschaft combined WC with a ductile matrix to produce cemented tungsten carbide [4]. Its original use was to replace diamond in the nozzle tip of extruders employed for drawing tungsten filament for manufacturing incandescent lamps. High hardness and wear resistance combined with high fracture toughness makes it unique among most materials. It is an engineering material of choice due to resisting harshest conditions such as corrosion, high temperature, high compressive loads and severe abrasion. It is primarily made use of in applications involving abrasive wear such as rock and earth drilling for mining, wear resistance coatings and metal cutting [5]. Additionally, cemented carbide also finds non-industrial use in jewellery applications.

The cobalt content in commercially available WC-Co machining grades ranges from 4-30 % by weight [6]. Carbide grain sizes in components composed of it ranges from 0.5-10 μm in the final fully sintered state. Titanium carbide (TiC), tantalum carbide (TaC) and niobium carbide (NbC) are usually added in varying proportions to the mixture to enhance the wear resistance of WC-Co [7]. Solubility of the transition metals from the afore mentioned transition metal carbides is low in both WC and Co. This results in the formation of a (M,W)C cubic carbide phase, the γ -phase where M is the transition metal. Incomplete dissolution of the transition metal carbide particles results in the γ -phase (rim) reprecipitating onto the undissolved transition metal carbide particles (core) to form the core-rim structure. The preserved transition metal carbide particles within the microstructure provide high wear resistance and hardness at high temperatures. The Co binder phase can either be alloyed with or replaced by chromium (Cr), iron (Fe), molybdenum (Mo), nickel (Ni) or alloys of these elements [7]. WC, Co and some combination of TiC, TaC and NbC form the primary phases in cemented carbides.

1.2 Tungsten Carbide Grades

An internationally accepted classification of cemented carbides does not exist. However, a cemented carbide classification based on composition or intended application will be discussed. First of these are the straight grades [8]. Straight grades are primarily composed of WC and Co with few trace elements.

Grades designed to improve corrosion resistance are termed the corrosion resistance grades [9]. Replacing the binder with a more corrosion resistant alloy or alloying the binder with elements such as nickel and chromium produces the corrosion resistance grades.

The functionally graded cemented carbides are another subset of WC-Co. These show a gradient in cobalt concentration (and/or WC grain size) resulting in a property gradient across the microstructure [10]. There are several variants of the functionally graded cemented carbides such as the WC-Co cutting tools made of cobalt rich surfaces (for higher toughness at the edges) and the mining tools made with a surface zone of lower cobalt content than the bulk (for high wear resistance at the surface). Processing of functionally graded cemented carbides is a challenge due to difficulty in limiting homogenisation of cobalt content during liquid phase sintering (LPS) via migration [10].

The final grades to be reviewed are the γ -phase grades. These consist of large quantities of other transitional metal carbides mentioned in the previous section in addition to WC and Co, forming three phases. γ -phase grades as explained earlier have modestly good wear resistance and toughness as well as a high resistance to oxidation and good thermal stability [11]. Hence, they are utilised in applications involving high pressure and temperature situations such as in the case of metal cutting.

1.3 WC-Co Processing

1.3.1 WC Powder Manufacture

The process of manufacturing WC-Co begins with the production of WC powder. Steps involved in the production process for WC powder are given as in the flow diagram in figure 1.1. Sheelite (CaWO_4) or Wolframite [$(\text{FeMn})\text{WO}_4$] are the main tungsten ores used for WC powder production [12]. Chemical extractive metallurgy of these ores produces ammonium paratungstate (APT). A chemical route is favoured over a pyrometallurgical route for extraction due to the high melting point of tungsten (3422 °C) [13]. The ore is subjected to a purification process before and after the chemical extraction to remove any impurities.

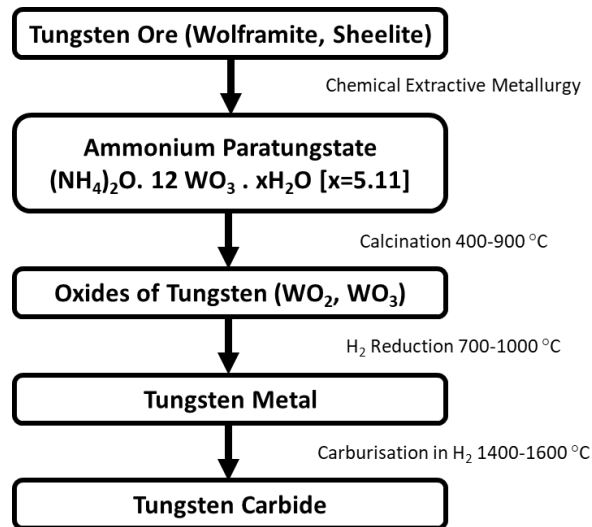
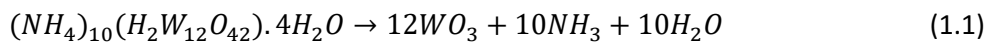
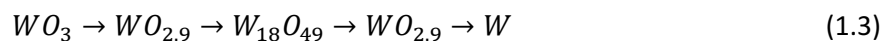


Figure 1.1: Production process for tungsten carbide powder [14].

This step is followed by calcination of APT; APT is heated to a high temperature in the range of 400-900 °C with the tungsten yellow oxide (WO_3) and the blue oxide (WO_{3-x}) being the key products in the presence and lack of excess air respectively [15]. Calcination of monoclinic ammonium paratungstate tetrahydrate, a variant of APT that is typically used as feedstock for manufacturing tungsten carbide powders occurs as per the reaction in equation 1.1 [16].



The oxides of tungsten are then reduced in hydrogen, forming tungsten metal powder [14]. This reduction reaction is given in equation 1.2. The actual process is a stepwise reduction forming intermediate products as shown in equation 1.3 [17].



The final step of the WC production process is the carburisation of the tungsten powder in a hydrogen atmosphere to produce WC. Carburisation directly from the ores or the oxides is also possible [18]. Carburising is a heat treatment process revolving around heating of tungsten and carbon bearing material such as carbon black. The carbon bearing material reacts with hydrogen, forming intermediate gaseous hydrocarbons. The hydrocarbons then react with the tungsten forming WC via the reaction shown in equation 1.4. The hydrogen atmosphere shields the WC from oxidation, protects the delicate parts of the carburising furnace, and carries away any impurities produced from the reaction.



The size of the resulting WC particles generally ranges between 0.15 to 12 μm [19]. There are two critical steps when forming WC powder: calcination of APT and reduction of tungsten oxides. The sizes of the tungsten oxide particles are influenced by these steps, which in turn affects the size of the

subsequent tungsten metal powder and the ensuing WC powder particles. This means the size of the tungsten carbide grains that control WC-Co properties depends upon these steps. Thus, the reason for nominating the steps to be vital.

1.3.2 Powder Metallurgy

1.3.2.1 Milling, Drying and Pressing

The WC powders are moulded using powder metallurgy processes into sintered WC-Co. The first stage involves milling of tungsten carbide along with cobalt powder. Cobalt ores unlike their tungsten counterpart are not readily available. So, cobalt is mainly produced as a by-product of other metal (copper or nickel) extraction processes [20]. Cobalt is also extracted via chemical means from cobalt oxides and cobalt hydroxides.

The powders are mixed and milled afterwards. In addition to the basic constituents making up the cemented carbides, a pressing aid (usually paraffin wax) and a milling aid (an organic liquid such as ethanol or acetone) are added to the mixture. The pressing aid is added to strengthen the green body while the milling aid is included to minimise the rise in temperature and prevent oxidation [12]. A rolling ball mill or an attritor mill is employed for milling the powder mixture.

The next step comprises drying and granulation of the milled powder slurry for compaction. The slurry is dried by the spray drying process [12]. The powders are later pressed to form a green body by extrusion, die pressing or powder injection moulding, with the choice of consolidation depending on the scale and complexity of the final part [21]. The shrinkage (~20%) that occurs during compaction must be accounted for during fabrication of a given part [19]. Granules in the green body are held together by the pressing aid.

1.3.2.2 Sintering

The green body is sintered via LPS. The driving force for the densification is the presence of porosity within the green body. Porosity introduces surfaces which contribute to excess interfacial energy: their removal reduces the total energy of the system. LPS is chosen over the sole use of solid state sintering (SSS) as one obtains higher densification rates attributed to material transport through the liquid, higher final densities and subsequent microstructure having superior mechanical properties [22]. It is beneficial to make use of sinter-HIP (hot isostatic pressing) or HIP (post sintering) rather than conventional sintering as it reduces or eliminates porosity resulting in a component with a density close to full theoretical density. Additionally, defects known as 'cobalt lakes' arise within the structure where cobalt is forced into macro voids during conventional sintering [23]. Sinter-HIP and HIP (post sintering) partially eliminates such defects promoting better homogeneity within the microstructure improving the mechanical properties of the final product. In recent years, additive manufacturing

(AM) routes have been proposed as alternative means for manufacturing WC-Co [24]. Steps for transforming WC powder to sintered WC-Co are provided in figure 1.2.

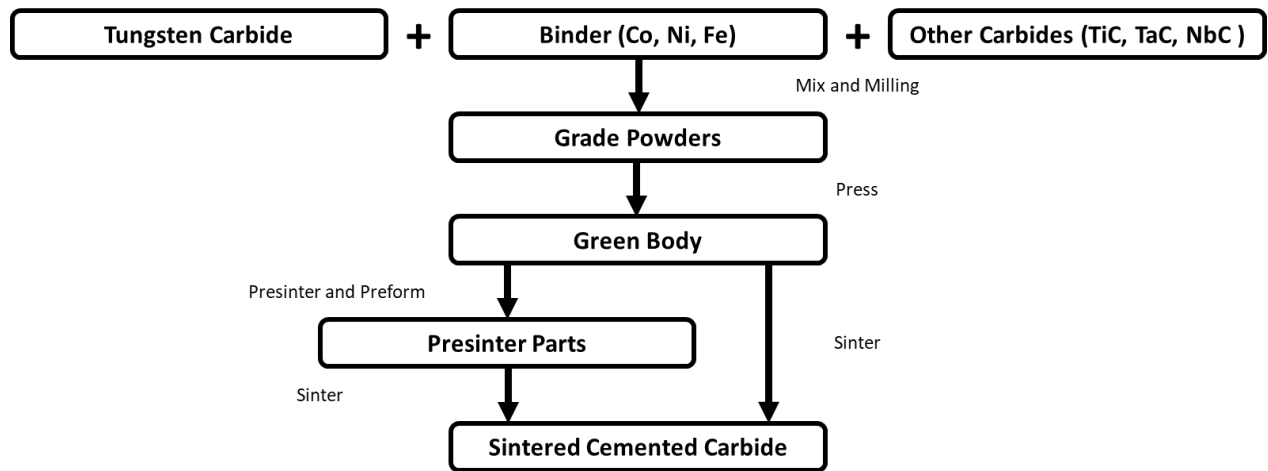


Figure 1.2: Powder metallurgy processes for manufacturing cemented carbide [14].

The progression of the sintering process is illustrated via the time-temperature cycle presented in figure 1.3. First, at a temperature range between 200-300 °C, organic binder used during milling is removed via vaporization, de-waxing [25]. This is done in a hydrogen atmosphere. The hydrogen atmosphere serves two purposes: it protects the powder compact from oxidation and actively participates in the decomposition of the organic binder [26]. At this stage, the pores within the green body are still open. So, as the temperature is raised to around 650-850 °C, surface oxides present on the exposed pores are reduced. Both de-waxing and reduction of oxides lead to shrinkage within the powder compact.

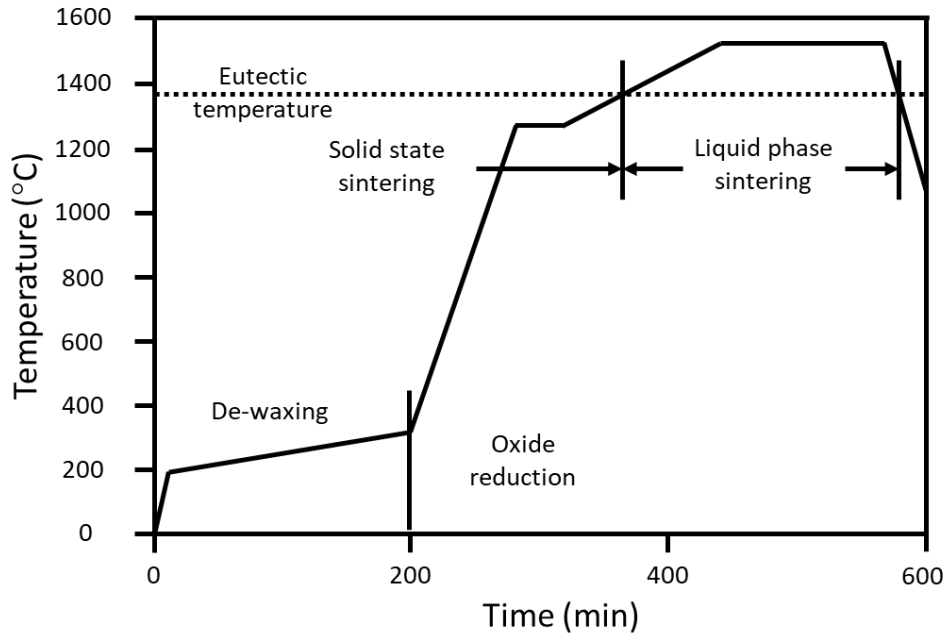


Figure 1.3: Time-temperature cycle for sintering of WC-Co. Redrawn after data from [25].

This is followed by SSS at around 1200 °C. It has been shown that almost total densification is attained during SSS [27]. It has been shown that SSS is driven by binder spreading assisted particle arrangement [28]. The shrinkage during this step is possible due to rapid spreading of metallic binder and rearrangement of WC grains under capillary forces. This is an interesting observation as SSS occurs below the eutectic and there would be no liquid binder to facilitate the rearrangement process. Furthermore, the particle rearrangement process is similar to the first stage of LPS. Theoretical approaches have shown that the creep of the binder during heating as the process that leads to shrinkage by rearrangement during heating [29]. However, Missiaen et al. have shown that the spreading of Co in solid state during heating is possible via bulk diffusion and material transport through surface that occurs as a result of curvature induced concentration gradients [30].

Once the melting temperature of cobalt is reached, LPS begins and occurs within a temperature range of 1400-1500 °C. At the onset of LPS, Co melts and the first liquid forms. The liquid binder is pulled into the pores via capillary forces which then rearrange the particles into a denser packing [5]. Afterwards, particle rearrangement becomes slower, and small thin liquid binder films separate the WC grains. At this stage densification and grain growth proceeds through the solution-precipitation process [6]. This occurs via two possible routes. Firstly, in regions where the capillary pressure is high such as in places where grains are in contact or where particles are close to each other, atoms preferentially go into solution and precipitate in locations where grains are not in contact or close. Secondly, atoms preferentially dissolve into binder solution at the solid-liquid interfaces with a high chemical potential as in the case of small particles and reprecipitate onto large particles that have

interfaces with a low chemical potential. The large grains grow at the expense of smaller grains in this process termed Ostwald ripening [31]. The growth of the grains at this stage is interface controlled. Carbide grains also grow through grain boundary migration [32]. Finally, as the temperature is reduced, cobalt solidifies. Some re-precipitation occurs at this stage leading to further coarsening of carbide grains.

Grain growth inhibitors such as chromium (Cr) or vanadium (V) can be introduced to limit carbide grain growth [33]. These are particularly useful when an application demands nanocrystalline carbide grained WC-Co.

1.3.2.3 Phase Constitution Control

Engineering desired phases constituting a sintered component is crucial, as the presence of unwanted phases undermines mechanical properties of said part. Small fluctuations in carbon content impact both the phase composition and microstructure which consequently dictates composite mechanical properties.

An additional carbide phase designated, η with a composition of $(W,Co)_6C$ forms if the carbon content is too low for a given cobalt content [34]. The complex carbides are detrimental to the mechanical properties owing to brittle behaviour. Provided that the carbon content is above a certain threshold, unbound carbon accumulates forming the graphite phase, which is also undesirable [34]. The threshold is dependent of the cobalt content in the WC-Co system. The graphite phase is not as deleterious to the mechanical properties as η -phase.

The formation of these two phases can be mitigated by working within the WC+Co two-phase region [35]. Figure 1.4 shows the phase diagram for a WC-10wt%Co system where the carbon content is varied. The following observation can be made from the phase diagram: the desired carbon content for forming cemented WC is in the range of 5.34-5.52 wt% – the two-phase region. The difficulty with regards to carbon content control arises simply due to the complexity of working within the narrow two-phase compositional window.

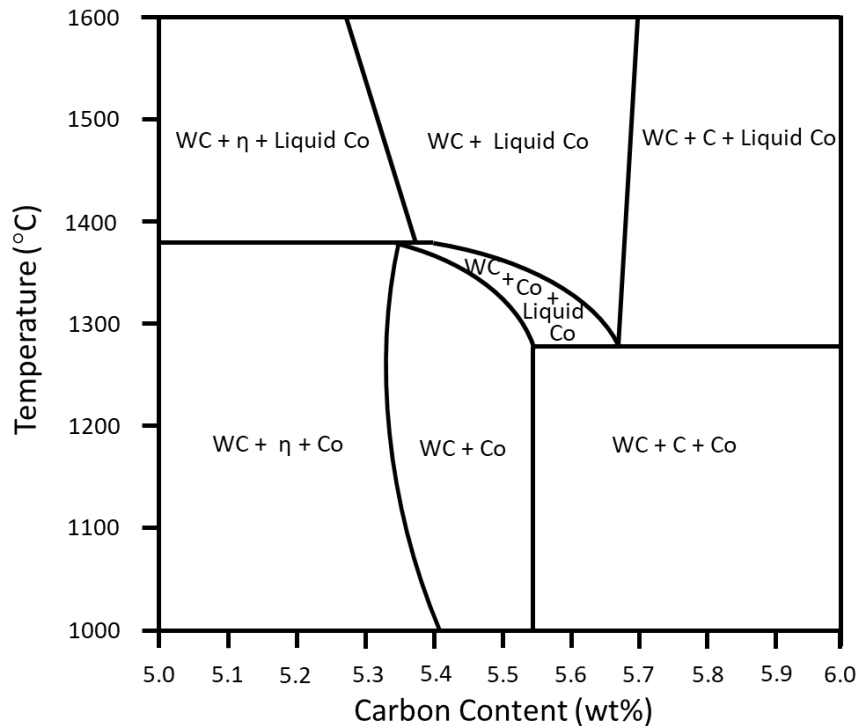


Figure 1.4: Phase diagram of the WC-10wt%Co system with varying carbon content within the range of 5.0-6.0 wt%. Redrawn after data from [14].

Even within the two-phase field region, variation in carbon content can affect mechanical properties through change in microstructure. The density and hardness of WC-Co tends to increase with accompanying reduction in carbon content within this region [36]. Choosing a low carbon content within the two-phase field region promotes more tungsten solution in the cobalt phase. This leads to a higher density for the cobalt phase and thus a high overall density for cemented carbide. It also retards solution re-precipitation, thereby inhibiting grain growth, producing smaller grains. So, the hardness of the final sintered cemented carbide increases.

The carbon content in the final sintered parts is governed by powder milling and sintering. Adjusting the quantity of raw materials used during milling will allow one to regulate the carbon content: adding graphite or tungsten carbide powder during milling increases or decreases the carbon level respectively. The carbon level during sintering can be affected through reduction of oxides, leaving behind carbon deficiency [37]. Organic binder composition and de-waxing steps will also affect the carbon content [37]. Therefore, these factors must be accounted to achieve accurate carbon control.

1.4 Microstructure

The microstructure of cemented carbides is vital as it regulates the mechanical properties of the material. WC-Co microstructure consists of hard phase grains embedded in a cobalt matrix. The brighter and darker regions in the SEM image in figure 1.5 are WC and Co respectively. Tungsten is

heavier than cobalt. Hence, the discrepancy in secondary electron yield and resulting compositional contrasts.



Figure 1.5: SEM micrograph of a WC-10wt%Co specimen in SE mode. Brighter and darker regions are WC grains and Co ligaments respectively.

Processing conditions have a significant effect on microstructure, affecting parameters such as carbide grain size, grain size distribution, grain morphology and binder ligament size [38]. The carbide grains in WC-Co are not completely isolated from each other by the binder. The grains instead form contacts with neighbouring grains forming a continuous skeleton: the binder also forms a skeleton of its own [39]. These skeletons are interpenetrating. A schematic of both the skeletons is presented in figure 1.6. The interpenetrating skeleton of the WC phase will be absent or possess minimal interconnectedness if its volume fraction is too small. Isolated carbide grains or cluster of carbide grains form in such a scenario.

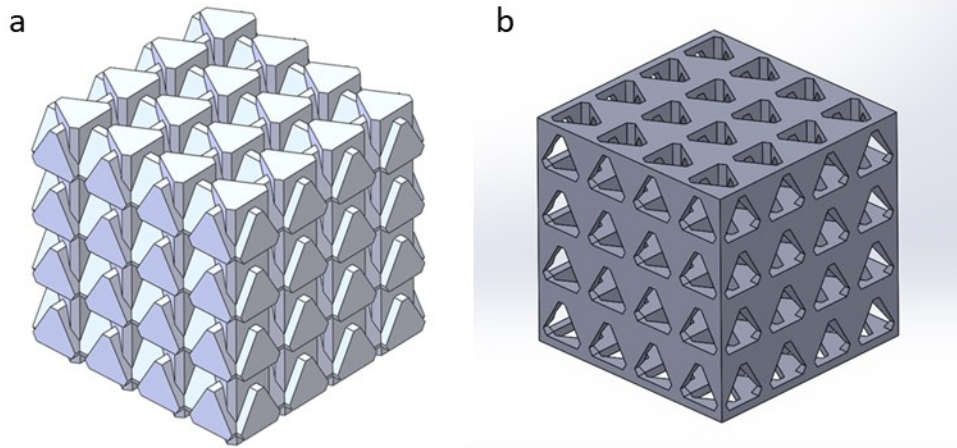


Figure 1.6: Pictorial depictions of the interpenetrating skeletons of (a) WC and (b) Co phases.

1.4.1 Tungsten Carbide

There are three carbides in the WC system: tungsten monocarbide (WC), tungsten semicarbide (W_2C) and γ - WC_{1-x} [40]. W_2C and γ - WC_{1-x} are thermodynamically stable above the temperature of 1250 °C and within the range of 2516-2785 °C respectively. Thus, WC is the most relevant carbide in the WC system for practical applications. WC has a simple hexagonal close packed (HCP) crystal structure with one carbon and one tungsten atom per primitive unit cell (see figure 1.7) [41]. The lattice parameters of the crystal are $a = 0.2906$ nm and $c = 0.2837$ nm, which means the c/a ratio is close to unity [42]. The importance of this will be explored when reviewing the WC grain boundaries. WC's space group is designated $P\bar{6}m2$, No. 187. A W atom is located at the (0,0,0) position while a carbon atom is present at either $(1/3, 2/3, 1/2)$ or $(2/3, 1/3, 1/2)$. WC crystal structure is composed of alternating layers of W and C planes stacked along the $\langle 10\bar{1}0 \rangle$ and $\langle 0001 \rangle$ directions.

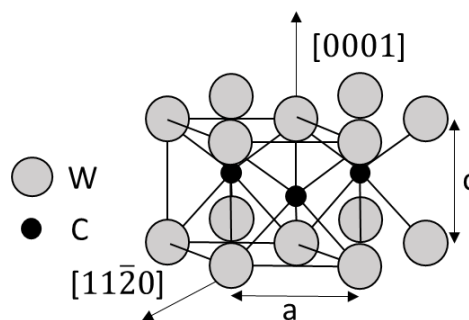


Figure 1.7: A drawing of the WC crystal structure with the primitive unit cell.

1.4.2 Tungsten Carbide Crystal Shape

The faceted growth of the WC grains into either the truncated trigonal prism or the equilibrium triangular prism was first observed in the work of Exner et al. [43]. These two grain shapes are presented in figure 1.8.

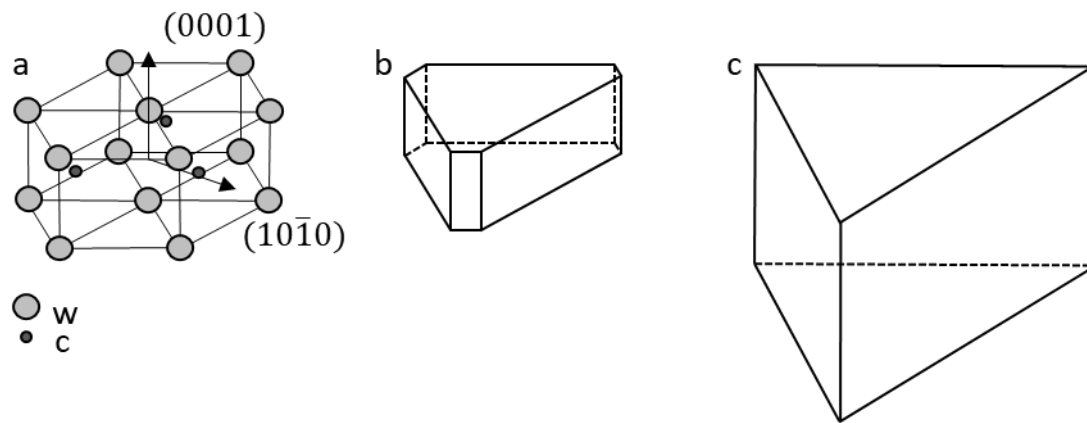


Figure 1.8: Diagrams showing (a) the HCP unit cell of WC as well as possible growth of the grains into either (b) the most likely truncated trigonal prism or (c) the eventual equilibrium triangular prism shape.

Crystal growth is governed by thermodynamics and kinetics. Thermodynamics is concerned with factors such as minimising surface energy. On the other hand, kinetics for example includes activation energies associated with processes related to diffusion such as dissolution/precipitation. Therefore, the resultant shape of the crystal is dependent on whether the growth is thermodynamics or kinetics controlled.

The morphology of crystals in a microstructure can be predicted via experimental and ab initio calculation routes. In terms of experimental means, Shatov et al. showed that WC crystal shapes in WC-Co are determined according to a balance between shape relaxation and carbide crystal growth processes [44]. Shape relaxation refers to thermodynamic aspect where the structure is influenced by surface energy of the crystal facets with the shape tending to an equilibrium form. In the case of carbide crystal growth processes, WC crystals form into growth determined structures depending on dissolution and growth kinetics of the crystal facets. However, it has been shown that WC grains exhibit a structure closer to a thermodynamic driven shape rather than a kinetic one in WC-Co [45]. Christensen et al. conducted the pioneering work in the field of applying ab initio calculations to examine the morphology of WC grains [46].

The faceted growth of the WC grains was explained as the result of the difference in the lattice spacings of the alternatingly stacked tungsten and carbon planes along the prismatic plane normal. The difference in spacing is illustrated in figure 1.9. The study by Christensen et al. however has proposed that the difference in interface energies of the phase boundaries shared with prismatic planes gives rise to the truncated trigonal prism shape [46]. The interface energies at the phase

boundaries are based on the capability of the interfacial atoms to form atomic coordination: that is their capability to form W-Co bonds. The interfaces mentioned previously formed along the $[10\bar{1}0]$ direction can be sub divided into type I and type II categories. The former allows for the formation of interfacial bonds that are more covalent in character between the low coordinated Co and W atoms compared to the latter. A type I surface consists of 4 dangling bonds per atom in contrast to the 2 dangling bonds on a type II surface.

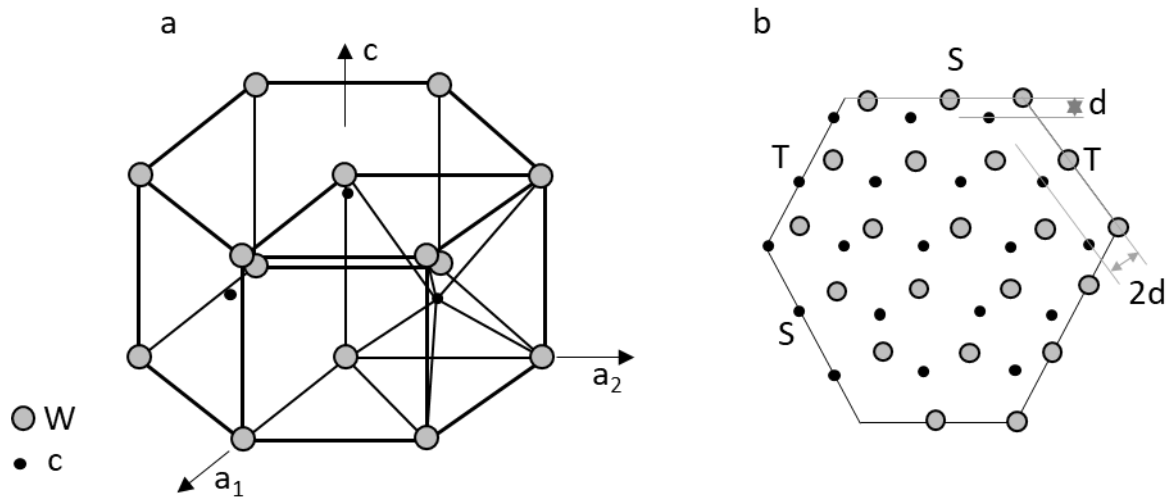


Figure 1.9: (a) Depiction of the HCP crystal structure of WC along with primitive cell. (b) Projection of the crystal lattice along the c axis showing the S and T prismatic facets. d and $2d$ are plane spacings with d being 0.084 nm. Redrawn from [47].

Lay et al. called the two sets of the prismatic plane facets, S (type II) and T (type I) based on the spacing between W and C planes as shown in figure 1.9 [47]. Lay et al. computed the WC plane energies and determined that the S (type II) prismatic facets tend to have the lowest energy [47]. Therefore, the preference for growth along S (type II) facets giving the characteristic shape of the WC grains.

At thermodynamic equilibrium, WC grains can grow into triangular prism shape. However, owing to presence of neighbouring grains in polycrystalline WC-Co, WC grain growth is hindered leading to a truncated trigonal prism shape [43]. WC grains are usually terminated with prismatic $\{10\bar{1}0\}$ and basal $\{0001\}$ planes. WC grain morphologies observed in a WC-Co sample are given in figure 1.10.

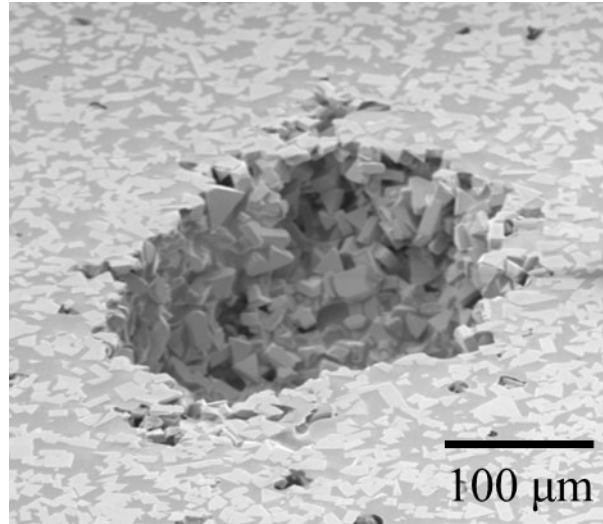


Figure 1.10: SEM image of a gas pore observed on the surface of a WC-10wt%Co sample showing typical WC grain morphologies.

Composition plays a key part in WC grain shape. It has been shown that WC grains grow into a more truncated shape in tungsten rich composites compared to carbon rich counterparts [46]. Yuan et al. found that WC grain shape varies with densification mechanisms [48]. This study showed that the WC grains had a more equal-axed grain shape when prepared by spark plasma sintering (SPS) rather than via sintering in hot isostatic press (sinter-HIP). Furthermore, addition of vanadium in the form of VC leads to sharp triangular prism grains [45]. This is because of the increased anisotropy between the type I and II. Finally, addition of chromium in the form of Cr_3C_2 during powder milling step leads to partially rounded grains in the final sintered WC-Co. The observed grain morphology in this instance is attributed to reduction in the anisotropy of the WC plane energies [49].

1.4.3 Cobalt Binder

Cobalt is the most widely used binder. Iron (Fe) and nickel (Ni) are possible alternatives [50]. Cobalt is typically the binder material of choice due to its ability to wet carbide particles thoroughly with a dihedral angle of zero during LPS [51]. The pseudobinary system formed between WC and the binder (Co, Fe, Ni) is shown in figure 1.11.

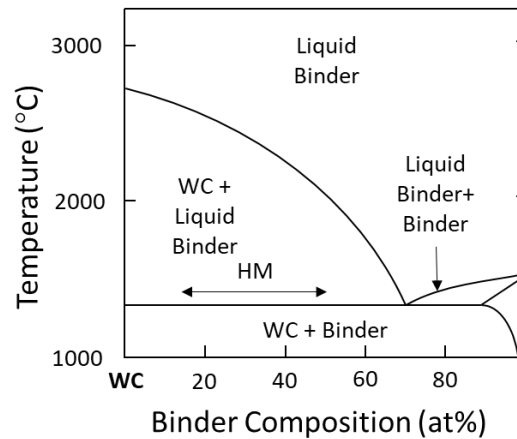


Figure 1.11: Phase diagram of the pseudobinary WC-(Co, Fe, Ni) system. Composition of the commercial hard metal is indicated as HM in the phase diagram. Redrawn after data from [52].

Pure cobalt exists in the HCP form until a temperature of 418 °C, when it transforms to a face centred cubic (FCC) crystal structure. However, given that the transformation of cobalt from HCP to FCC is slow, both phases are retained up to a temperature of 450 °C if the cooling rate is sufficiently low. After that cobalt remains in its FCC form until its melting point of 1495 °C [53]. Cobalt remains mostly as an FCC form in sintered cemented carbide with stacking faults while the rest are in the HCP form [38]. The FCC phase is stabilised by solute elements, W and C, dissolved in it, and the residual stresses generated by differential thermal contraction between the binder and the rigid carbide skeleton [12]. The transformation between the two allotropes of cobalt is martensitic in nature.

Binder ligaments can be mistaken for binder grains. Ligaments tend to be of a similar size to that of the carbide grains. However, binder grains have a dendritic morphology with a size in excess of several tens of μm due to the difficulties in nucleation [54]. The actual size of cobalt grains can be appreciated from the EBSD maps presented in figure 1.12. Cobalt tends to dissolve a large amount of W and C at high temperatures [38]. The solubility of the solute elements is dependent upon the amount of carbon and the temperature. Cooling of the sample in the final part of the sintering cycle leads to reduced solubility of the solute elements within the binder. These solute elements then reprecipitate onto carbide grains. Carbon has a faster diffusion rate compared to tungsten. Hence, almost no carbon is left behind in the binder. If cooling rate is high enough after LPS, tungsten gradients will be established across the binder in a fully sintered cemented carbide material.

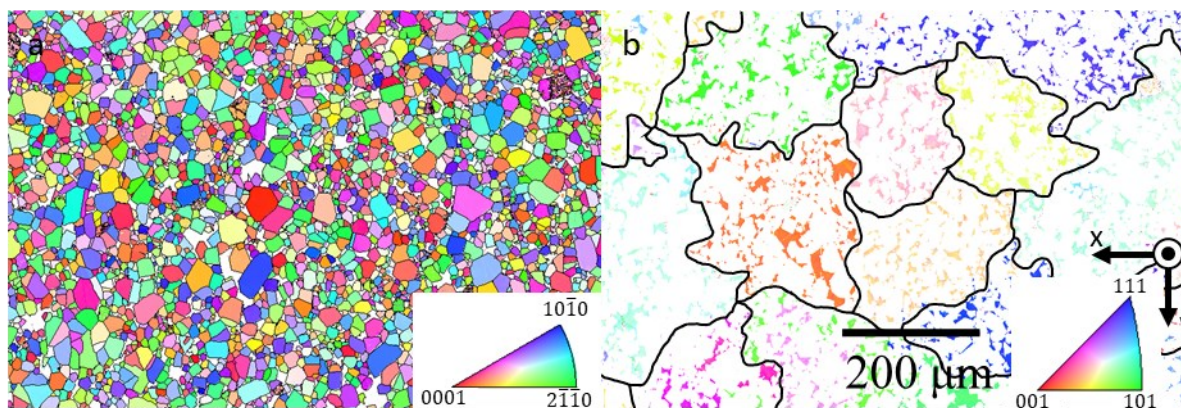


Figure 1.12: EBSD maps using IPF-Z colouring of (a) WC and (b) Co phases of a WC-10wt%Co specimen. The black lines in (b) are used to segment binder ligaments of the same orientation thereby showing the Co grains. Small regions of different misorientation to that of the majority misorientation for certain Co grains are possibly the result of misindexing.

1.4.4 Interfaces – Grain and Phase Boundaries

Understanding of interfaces is vital for engineering cemented carbide tools with superior mechanical properties and longer lifetimes. Interfaces along with other microstructural parameters such as WC grain size, cobalt content and cobalt binder mean free path do affect WC-Co fracture toughness [55]. Their effect on fracture toughness will be analysed in section 1.5, material properties.

WC-Co materials consist of three types of interfaces: WC/WC grain boundaries, Co/Co grain boundaries and WC/Co phase boundaries. Co/Co grain boundaries are not as important as other interfaces in WC-Co. This is because the larger cobalt grain size in comparison to carbide grains combined with them enveloping carbide grains means, the Co/Co grain boundaries have a negligible impact on fracture compared WC/WC and WC/Co interfaces.

1.4.4.1 Carbide Grain Boundary

Carbide contiguity gives a measure of the WC/WC grain boundaries compared to all the possible carbide interfaces within a given specimen [56]. In other words, carbide contiguity measures the degree of the interconnectedness of the continuous carbide skeleton. The contiguity is vital since most of the fracture path, as will be discussed later in this chapter is intergranular with respect to carbide grain boundaries [42].

Experimentally it has been found that some carbide grain boundaries contain approximately half a monolayer of Co-binder atoms [57, 58]. The atom probe tomography reconstruction of a carbide grain boundary from a WC-TiC-Co sample presented in figure 1.13 shows the presence of a cobalt layer at a WC/WC boundary.

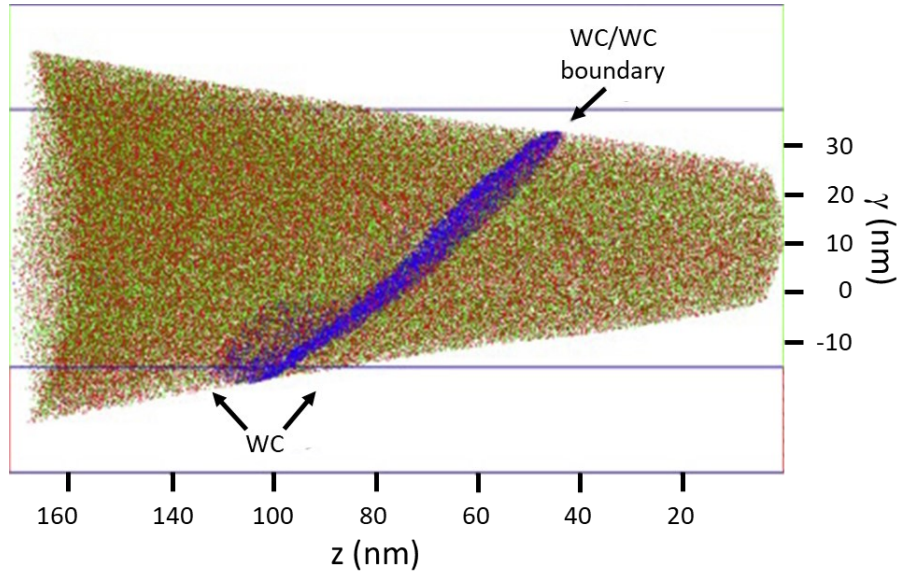


Figure 1.13: Atom probe tomography reconstruction of a WC/WC grain boundary showing the Co-layer in a WC-TiC-Co material. Green, red, blue and pink dots represent W, C, Co and Ti atoms respectively. The largest diameter and the length of boundary shown is 75 nm and 152 nm respectively. Adapted from [58].

Carbide grain boundaries are formed as grains grow and meet. Particular orientation relations between adjacent grains and in turn grain boundaries can be described by coincident site lattice (CSL) points [59]. Neighbouring grains at certain orientations will have overlapping lattice points, forming a super lattice structure at the boundary plane. Σ can be thought of as the degree to which the lattice points overlap: a ratio between number of lattice points in a unit cell of the CSL and that of the lattice of material [60]. So, grains of the same orientation would have a Σ of 1 while those of different orientations would have a higher value. WC has a hexagonal structure with a c/a ratio of 0.976, close to unity, giving rise to several potential low Σ boundaries with low energy that have special characteristics [42]. The low energies of the low Σ boundaries are due to the bulk like coordination across the interface while retaining no cobalt [61].

Figure 1.14 shows a carbide grain boundary misorientation angle chart for a WC-10wt%Co sample. It can be inferred from the chart that there are peaks at 90° and 30° with the former being the largest. The 90° peak corresponds to the $\Sigma 2$ boundary: the grain boundary with the $90^\circ/[10\bar{1}0]$ misorientation. The 30° peak on the other hand is due to the $\Sigma 13$ boundaries with the $30^\circ/[0001]$ misorientation. In accordance with this, the most studied grain boundary in the literature is the $\Sigma 2$ grain boundary. Illustrations of $\Sigma 2$ and $\Sigma 13$ boundaries are shown in figure 1.15.

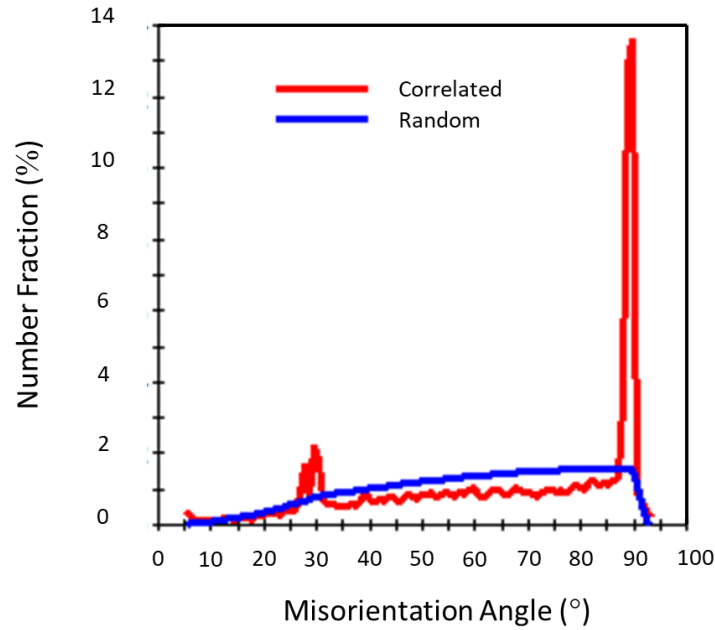


Figure 1.14: WC/WC grain boundary misorientation chart for a WC-10wt%Co sample. Grain boundary number fraction has been plotted as a function of the WC/WC grain boundary misorientation. 90° and 30° peaks can be observed from the misorientation chart. Correlated refers to the observed distribution while random refers to a misorientation in the case of the carbide grains being totally randomly distributed.

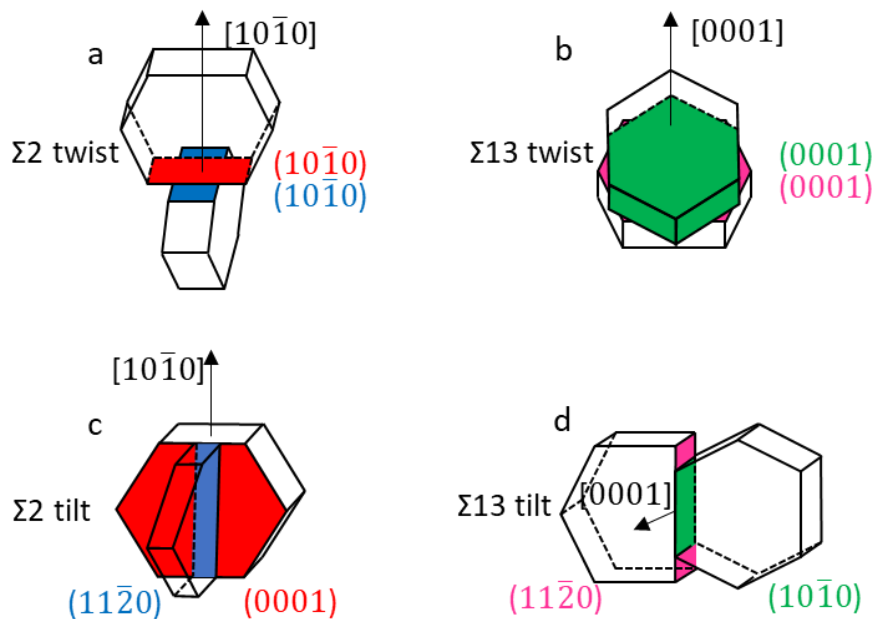


Figure 1.15: Schematics of the $\Sigma 2$ and $\Sigma 13$ boundaries showing the twist and tilt variants.

Mannesson et al.'s study of WC grain growth using EBSD analysis discovered that $\Sigma 2$ carbide boundaries in the starting WC powder are initially curved and rounded, having both tilt and twist characteristics [62]. These $\Sigma 2$ carbide boundaries then straighten as the temperature is increased in the sintering cycle into pure twist variants. Longer sintering times tend to also have a similar effect.

$\Sigma 2$ boundaries act as barriers to dislocation motion since grains sharing these lack a common slip plane [63]. $\Sigma 2$ boundaries accommodate plastic deformation that occur during the powder milling process via curving as observed by Mannesson et al. [62]. It has been found that the $\Sigma 2$ and $\Sigma 13$ grain boundaries make up about 11-14 % and 2-3 % of the entire population [64]. It was found that 60 % of the carbide grain boundaries contain either a prismatic or a basal plane [64].

It has been found that cobalt lamellae with a thickness of 10-50 nm infiltrates the WC grain boundaries during deformation [65]. Addition of substitute elements such as titanium, chromium, vanadium and manganese to the mixture while milling will negate this issue. Substitute elements segregate as a sub monolayer at the carbide grain boundaries increasing the work of separation and reducing the interfacial energy. The addition of these substitute elements improves resistance of these boundaries against cobalt infiltration and increases grain boundary cohesion.

1.4.4.2 Phase Boundaries

WC/Co phase boundaries are characterised as being planar and sharp in WC-Co [66]. However, for low carbon contents, carbide grain corners become rounded, and the phase boundaries adopt a stepped appearance as shown in figure 1.16. The strong adhesion at the phase boundaries is the result of the strong Co-C covalent bonds formed at this interface which are noticeably stronger than the W-C bonds [67]. The Co-C bonds also contribute to the high strength of the phase boundaries. The high work of separation combined with low interface energy is the reason for the excellent wetting properties of cobalt mentioned earlier.

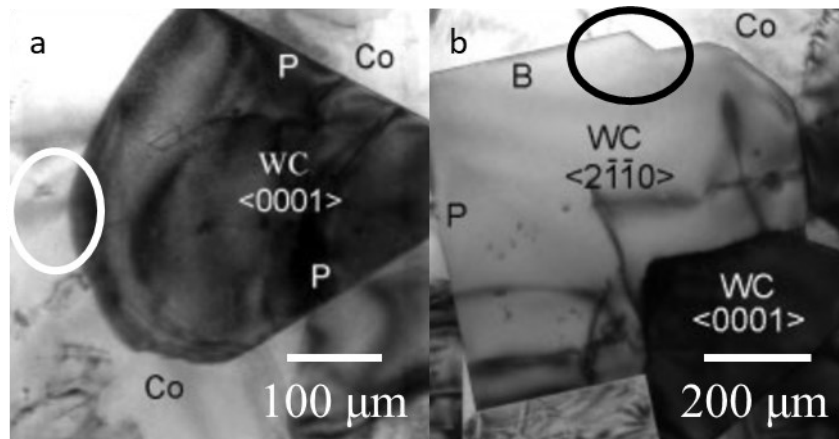


Figure 1.16: TEM images of the WC grains in a W rich cemented alloy, W-43at%C-13at%Co sintered at 1450 °C for (a) 0 hours and (b) 2 hours. (a) Projection of a grain along the $\langle 0001 \rangle$ direction showing the rounded corners as well as the planar edges. (b) Projection of two WC grain about the $\langle 2\bar{1}\bar{1}0 \rangle$ and $\langle 0001 \rangle$ directions showing rounded and faceted interfaces as well as a stepped interface at the phase boundary. Rounded and stepped interface have been highlighted with white and black ellipses. B and P are the basal $\{0001\}$ and prismatic $\{10\bar{1}0\}$ habit planes respectively. Adapted from [66].

Cobalt grains grow without any orientation relationship to carbide grains that they encompass during a sintering cycle [68]. Hence, there is no orientation relationship at the phase boundaries between the

carbide grains and the cobalt ligaments. But it was observed in the work of Kim et al. that 80 % of the WC boundary planes at the phase boundaries terminated with either a basal or a prismatic plane [64]. The study also interestingly found that phase boundaries contain few atomic layers thick WC_{1-x} . Chromium or vanadium can be added to WC-Co to limit grain growth: these are referred to as the grain growth inhibitors [33]. These function by continuous adsorption and desorption of grain growth inhibitor atoms at the phase boundaries forming grain growth inhibitor carbide rich thin layers [69]. Therefore, for carbide grains to grow, the adsorbed grain growth inhibitor atoms must be replaced by tungsten or carbon atoms. Given that grain growth is interface growth limited, this process is slow. Thus, the ability of the grain growth inhibitors to hinder grain growth.

1.5 Material Properties

Cemented carbide has desirable materials properties such as relatively high elastic modulus and high thermal conductivity with only materials such as diamond and cubic boron nitride being harder than it. Elastic modulus and hardness of pure WC is greater in comparison to WC-Co. This is attributed to the presence of the softer ductile cobalt phase in WC-Co. The trade-off of having the cobalt phase is the enhancement to fracture toughness. The higher thermal (and electrical) conductivity of WC-Co is impressive given that most ceramics are insulators. Additionally, the conductivity is also higher than most metals such as iron, nickel and cobalt. Therefore, it is understandable that an increase in binder content will reduce the overall thermal conductivity as was found by Frandsen and Williams [70]. The high thermal conductivity is the result of low frequency of point defects within the hexagonal crystal structure of WC leading to low phonon scattering.

The most relevant mechanical properties of WC-Co components for industrial applications are fracture toughness and creep as these determine the life of the components. It is very well established across the literature that hardness and toughness have an inverse relationship. This is illustrated in the plot in figure 1.17(a). These two properties are functions of cobalt content and WC grain size. Fracture toughness in WC-Co increases with cobalt content when the grain size is constant and that the fracture toughness also increases for a given cobalt content as the grains become coarser [71]. The opposite is true of hardness. The size of the cobalt pools, the mean free path (MFP) between grains increases as grain size and/or cobalt content increases. This is important as Sigl et al. found that when a crack propagated through WC-Co, most energy was expended due to the plastic deformation of the cobalt phase along the crack path [72]. This means that as the length of the crack path along the cobalt phase is increased, as is the case in a sample with larger cobalt pools, crack propagation is hindered and hence toughness is enhanced. The crack propagation is impeded via ductile tearing as well as crack bridging of cobalt.

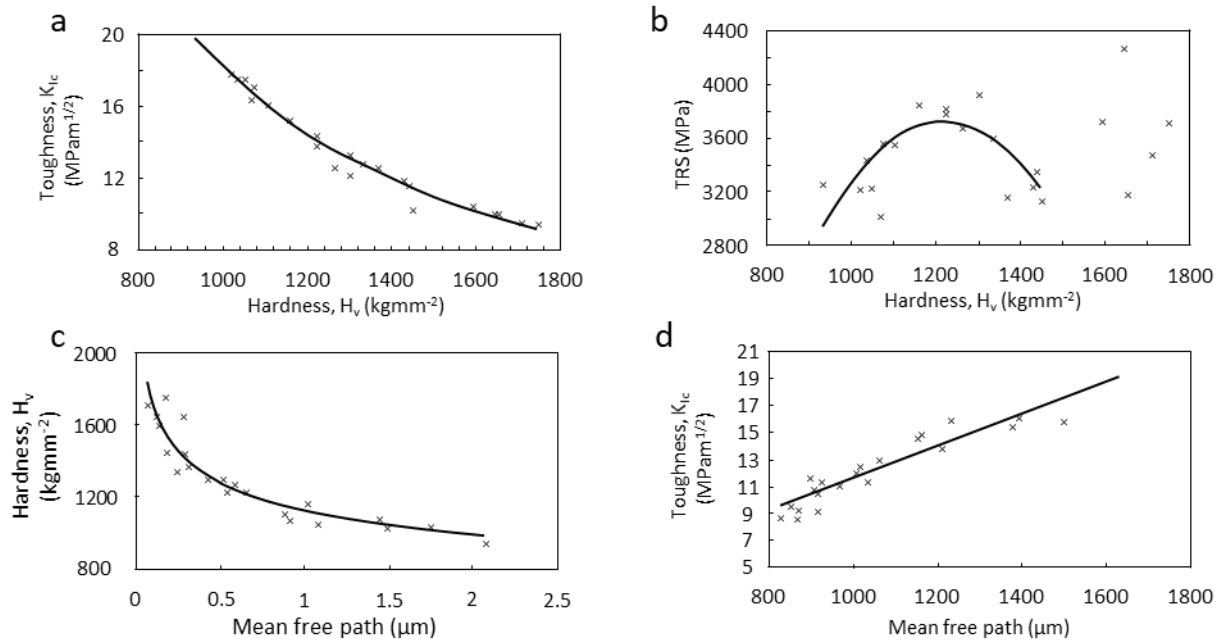


Figure 1.17: (a) A plot of hardness against fracture toughness for a range of WC-Co compositions showing the inverse relationship. (b) TRS versus hardness for WC-Co showing the bell-shaped curve. Finally, the mean free path plotted against (c) hardness and (d) fracture toughness of cemented carbide for a range of WC-Co compositions. Redrawn after data from [14].

Transverse rupture strength (TRS) is a measure of a specimen to resist bending, in essence an indicator of the material to bear an external load. It is the tensile stress at which a material fails in a three-point bending test. TRS can also be defined as the maximum flow stress during the plastic deformation, crack initiation and crack propagation before which a sample fails during a three-point bend test [73]. The maximum flow stress is the sum of initial yield strength of the material and the contributions of work hardening from the binder. Work hardening contributions arise from constrained Co within the material rapidly work hardening and exhibiting higher flow stress during testing. Yield strength and hardness of the material are proportional. Therefore, yield stress contributes to increase in flow stress as the hardness of the material increases. However, contributions to flow stress from work hardening reduce dramatically as the Co content drops as is the case when the hardness of WC-Co increases. This means initially the sum of the effect of increasing yield strength with increasing hardness increases the overall flow stress and TRS. But eventually the effect of reducing flow stress with increasing hardness causes a reduction in the net flow stress and the TRS. Peak values in TRS are obtained for cemented carbide samples with a cobalt content and grain sizes of 20 wt% and 3-4 μm respectively [74].

1.6 Room Temperature Deformation of WC-Co

1.6.1 Crack-Microstructure Interactions

Cemented carbides are an engineering material of choice in demanding applications that require high hardness and toughness. Lifetimes of components composed of these materials are determined by the resistance imposed by the WC and Co phases against fracture. Therefore, improving the understanding of crack propagation characteristic of WC-Co will enable one to engineer WC-Co microstructures with superior toughness and thereby prolonging the life of the components.

Deformation and fracture properties of WC-Co were studied initially by the Palmqvist method and bending tests. Fracture properties have been recently evaluated via other methods such as Hertzian indentation technique to characterise quasi-plastic deformation [75], rotating wheel abrasion and scratch tests to measure wear resistance [76] and turning operations of inserts made of WC-Co to simulate realistic machining conditions so as to analyse the deformation of the cutting edge [65]. Compression loading of large volumes of WC-Co has been used to study the deformation behaviour while tensile loading has been applied to evaluate the propagation of single cracks through the material and characterise fracture properties [77, 78].

Fracture process in WC-Co was extensively studied in the work of Sigl and Exner [77]. The study used WC-Co single edge notch bend (SENB) specimens with sharp pre-cracks. The specimens were subjected to tensile loading until failure. It was then found that there were four principal crack paths along the microstructure: Co phase, WC/Co interface, WC/WC grain boundary (intergranular) and WC grains (transgranular). Figure 1.18 is a SEM micrograph showing these crack paths. This work was followed up in a significant way by Mingard et al. where SEM and EBSD was combined to observe stable crack growth in WC-11wt%Co sample [79]. It was found that that most fracture paths are either through carbide grains or carbide grain boundaries. Another important finding was that the larger grains tended to undergo transgranular fracture while smaller grains had fractured in an intergranular manner.

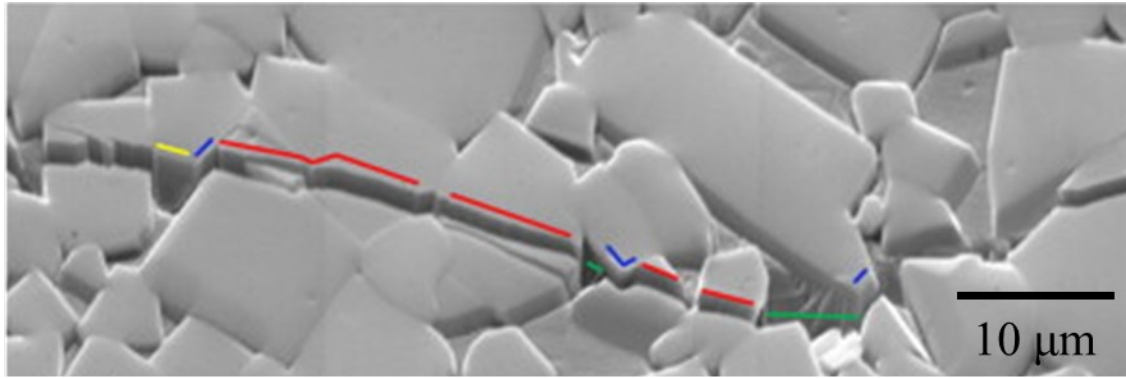


Figure 1.18: SEM image of a fracture path observed in a WC-11wt%Co sample from a double cantilever beam test. Crack paths highlighted in yellow, blue, red, and green are fracture paths along WC/Co, WC/WC, within WC grains and within Co ligaments respectively. Adapted from [79].

The process of crack-microstructure interaction in WC-Co as evaluated in the combined works of Sigl, Exner and Fischmeister, experimentally and through finite element modelling is as follows [72, 77, 80]. First, a continuous crack initiates in the carbide grains. The crack circumvents binder ligaments upon encountering them, leaving behind 2-4 binder pools on the crack face— the multiligament zone. The toughening and crack growth resistance behaviour in WC-Co has been attributed to the formation of the multiligament zone. Ligaments form isolated bridges across crack surfaces and are stretched as crack propagates. Later, voids nucleate and grow within the ligaments to uphold volume consistency. Finally, voids coalesce and lead to ligament failure. Formation of a multiligament zone has been illustrated in the figure 1.19. These observations were validated in a recent work by Tarrago et al. where focused ion beam (FIB) tomography was used to validate the conclusions derived from the works of Sigl, Exner and Fischmeister in regard to crack-microstructure interactions [81].

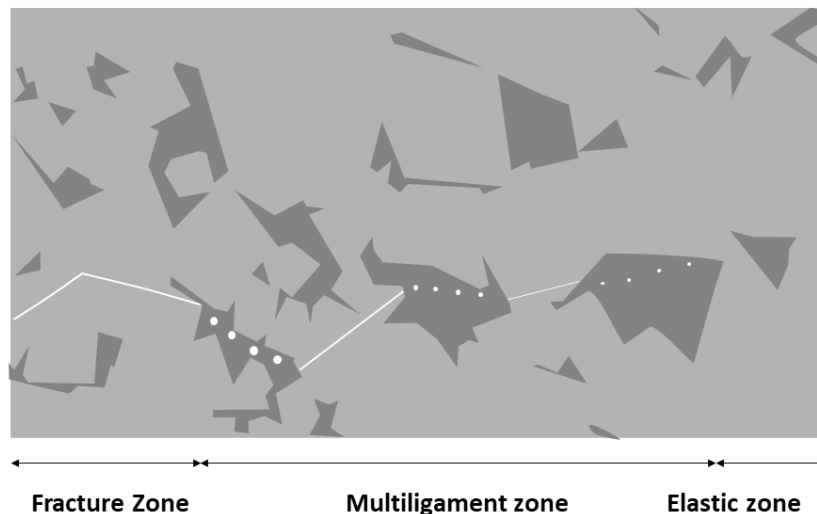


Figure 1.19: A schematic of the crack path through the binder phase producing the multiligament zone and eventual failure of the cobalt phase. The dark regions are binder ligaments, polygonal white regions are carbide grains, small circular white regions are pores and white lines are cracks.

There have been attempts to improve the toughness of cemented carbides other than by simply altering the grain sizes or the cobalt content. One approach is to produce carbide grains with platelet morphology [44]. The propensity of the carbide grains for gaining platelet morphologies has been explained via the presence of stacking faults which are 2-3 atomic layers thick and are parallel to the basal plane in carbide grains. These stacking faults allow for defect assisted carbide grain growth [82]. The stacking faults are proposed to have been introduced during powder synthesis [83].

Fracture surfaces of WC-Co samples are characterised by dimples and ridges. Ridges are the result of the cleavage fracture that the carbide grains undergo. Dimples are remnants of voids formed from void coalescence of the cobalt ligaments. Crack position within the fractured carbide grain relative to the adjacent ligament that the crack is going to enter determines the void path within the binder ligament. On the other hand, the path of the transgranular fracture is dependent on direction of the crack in the preceding grain and whether it could cross the binder. Deeper dimples are present within the bulk while shallow finer ones are observed near the WC/Co phase boundaries as shown in the illustrations in figure 1.20. The formation of the finer dimples was attributed to high triaxiality near the phase boundary interface as suggested by Fischmeister et al. [80]. Triaxiality is the ratio between hydrostatic stress and von Mises stress. A high or low triaxiality denotes a stress state dominated by hydrostatic stress (acting to change volume) or deviatoric stress (acting to change shape) respectively [84]. The constraint introduced by the carbide grains at the phase boundary leads to a high triaxiality which in turn promotes larger number dimples [84]. Hence, the finer dimple structure at the boundary. The reason for the formation of the voids near the phase boundary rather than on it is due to the strong Co-C bonding at this interface as discussed earlier.

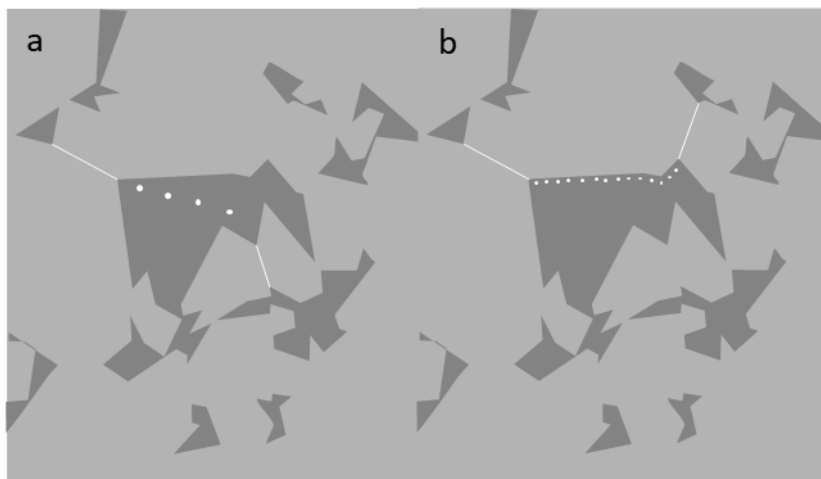


Figure 1.20: Schematic of the crack propagation across the binder through (a) a Co ligament and (b) a WC/Co phase boundary. The brightest and darkest region are WC grains and Co ligaments respectively. Small circular white regions are pores and white lines are cracks.

Mingard et al. investigated the relationship between the carbide boundary orientations and the intergranular crack path (both the WC/WC and WC/Co variants) [79]. This was possible due to the faceted nature of the carbide grains. The $\{10\bar{1}0\}$ and $\{11\bar{2}0\}$ family of planes were considered for the study. These planes are illustrated in figure 1.21 along with what it means for the fracture surface to be parallel to a plane trace. It was found that 60% of the total intergranular fracture occurred with at least one of the grains having a boundary parallel to the $\{10\bar{1}0\}$ trace. However, in the case of $\{11\bar{2}0\}$, grains that underwent intergranular fracture were evenly split in terms of the boundary being either aligned or not aligned to this plane trace. This work also evaluated the amount of plastic deformation in carbide grains that underwent transgranular fracture with the fracture plane being parallel to either $\{10\bar{1}0\}$ or $\{11\bar{2}0\}$ family of planes. Carbide grains in which the fracture surface was parallel to $\{10\bar{1}0\}$ planes had the largest amount of plastic deformation. Fracture surface being parallel to the $\{10\bar{1}0\}$ plane trace is illustrated in figure 1.21. The opposite was true for the $\{11\bar{2}0\}$, given that these lie in between the $\{10\bar{1}0\}$ planes. The $\{10\bar{1}0\}$ planes are the main slip planes in WC, with the dominant slip system being the $\{10\bar{1}0\} \langle 11\bar{2}3 \rangle$ [85].

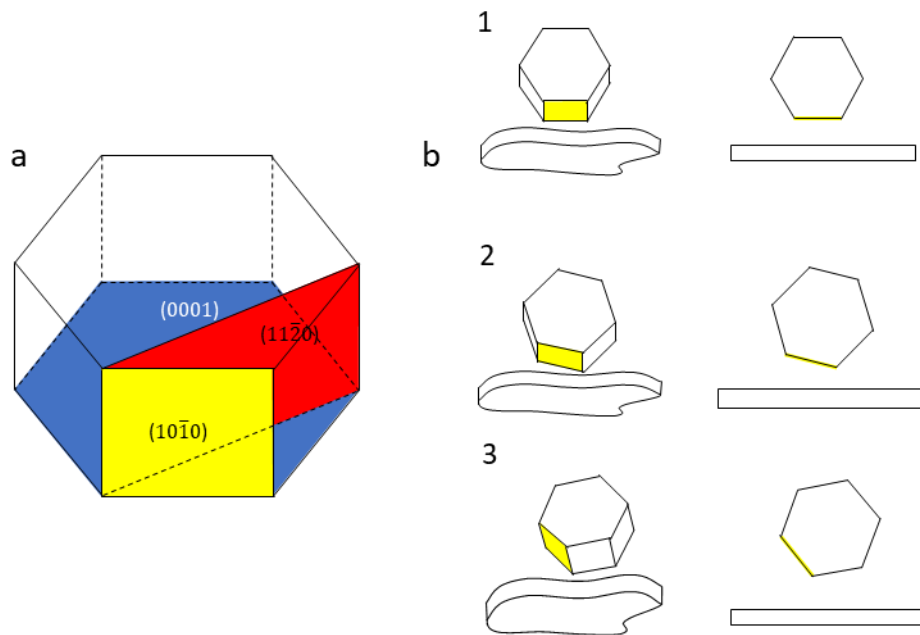


Figure 1.21: (a) Schematic of the elementary WC crystal showing the $\{10\bar{1}0\}$, $\{11\bar{2}0\}$ plane traces. (b) An illustration showing the $\{10\bar{1}0\}$ plane trace (1) being parallel to the crack face, (2) close ($\leq 15^\circ$) to crack path and (3) having no alignment to the crack path.

Macro hardness tests have been used to investigate the anisotropy in WC crystallographic plane hardness [86]. It was found that the hardness on the $\{10\bar{1}0\}$ planes is significantly lower than the (0001) planes. Recently, nanoindentation hardness tests were performed by Cuadrado et al. [87], Roebuck et al. [88] and Duszová et al. [89] to study the hardness as a function of the orientations of the carbide grains where upon similar conclusions were reached. Csanádi et al. fabricated micropillars

in grains of different orientations and loaded them to failure: the authors found that different slip systems and dislocation mechanisms present in differently oriented pillars were the cause of orientation dependence on hardness [90]. The predominant slip system ($\{10\bar{1}0\} \langle 11\bar{2}3 \rangle$) splits into partial dislocations as given by equation 1.5 [90]. The partial dislocations can then react together to form glissile or sessile dislocations depending on whether the prismatic or basal grains (pillars) are deformed respectively. Dislocations produced by such mechanisms when deforming prismatic and basal grains are given via the equations 1.6 and 1.7 respectively.

$$\frac{1}{3}[11\bar{2}3] \rightarrow \frac{1}{6}[11\bar{2}3] + \frac{1}{6}[11\bar{2}3] \quad (1.5)$$

$$\frac{1}{6}[11\bar{2}3](\bar{1}100) + \frac{1}{6}[2\bar{1}\bar{1}3](0\bar{1}10) \rightarrow \frac{1}{2}[10\bar{1}0] \quad (1.6)$$

$$\frac{1}{6}[\bar{1}2\bar{1}\bar{3}](10\bar{1}0) + \frac{1}{6}[\bar{1}\bar{1}23](\bar{1}100) \rightarrow \frac{1}{6}[\bar{2}110] \quad (1.7)$$

Figure 1.22 shows that micropillars which had the $\{10\bar{1}0\}$ orientation exhibiting slips in the structure while those loaded in the (0001) were crushed without any plastic deformation. This is shown in the micrographs presented in the figure 1.22. $\{10\bar{1}0\} \langle 11\bar{2}3 \rangle$ being the main slip system in WC, explains the observations from Mingard et al.'s work where carbide grains that had transgranular crack surface running parallel to the $\{10\bar{1}0\}$ direction exhibiting plastic deformation.

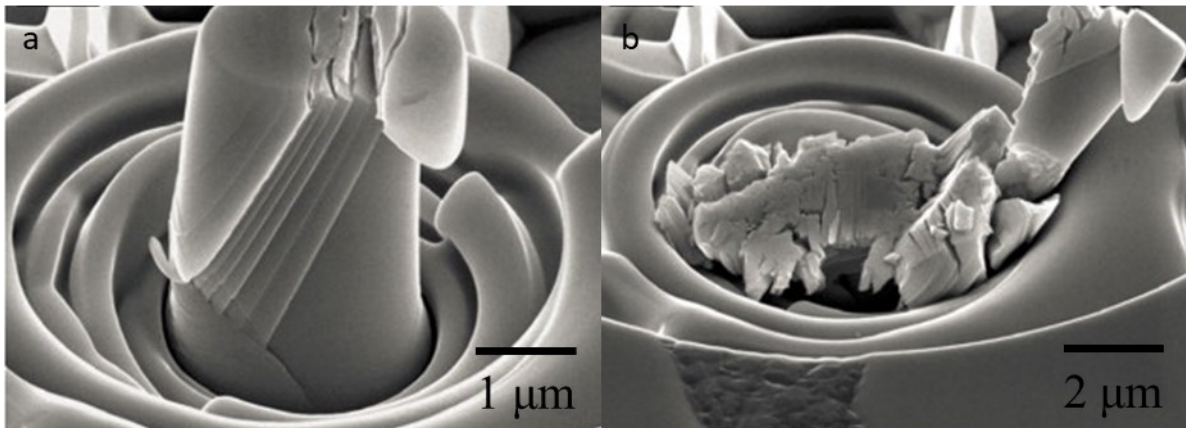


Figure 1.22: SEM images of a WC-9wt%Co sample where micropillar compression tests were performed on pillars oriented in the (a) prismatic direction loaded up to the elastic limit showing slips in the structure and (b) basal direction loaded beyond the elastic limit. Adapted from [90].

The crack path is dependent on microstructural features of WC-Co. Mingard et al. [79] found that when a WC-Co sample was loaded in a manner to have a controlled crack growth as described in the work of Gee et al. [76], an interesting phenomenon occurs. A new crack originates upon unloading and loading again. This crack does not nucleate from the tip of the older one and does not propagate through the plastically deformed binder region ahead of the older crack tip as shown in figure 1.23.

This is because the plastic deformation of the binder ahead of the crack arrests crack propagation via relaxation of stress at the crack tip. Further loading increases the energy stored at the crack tip until a certain energy threshold is met. Then a new crack nucleates and branches from the original crack, propagating around the plastically deformed binder region releasing stored energy.

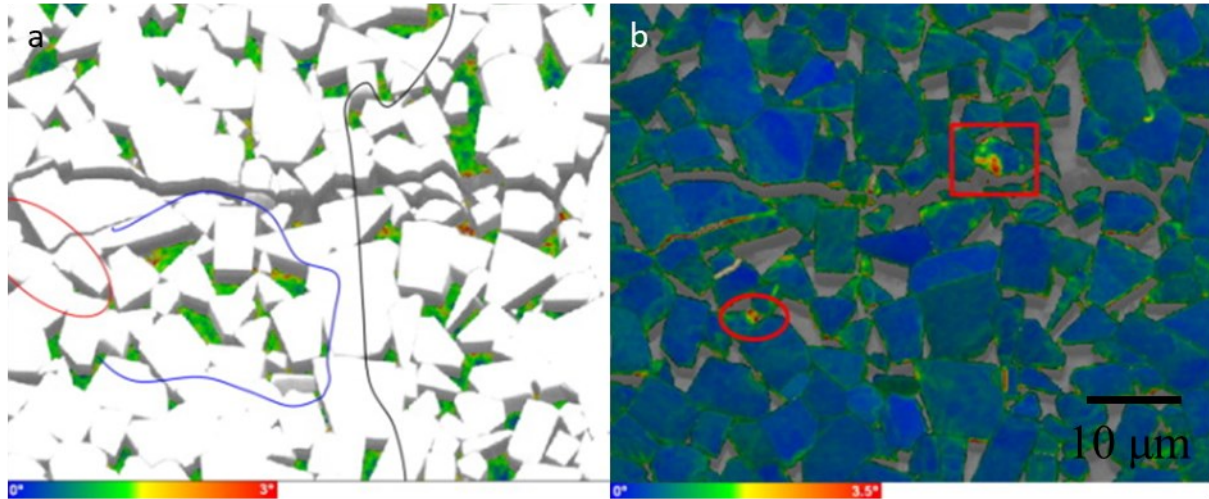


Figure 1.23: EBSD maps showing local misorientation of (a) Co and (b) WC phases in a WC-11wt%Co sample after a crack has propagated denoting the plastic deformation in the structure. Heavily deformed WC grains are highlighted with red ellipse and red square. Adapted from [79].

1.6.2 Small Scale Fracture

WC-Co fracture described so far is a process involving fracture of carbide grains and rupture of binder ligaments as was first described in the work of Sigl and Exner [77]. Advancements in experimental techniques in recent years have allowed scientists to shed light on the intricacies of this phenomenon [79]. The micromechanical modelling community on the other hand have developed models to study crack propagation in reference to binder deformation [91], orientation texture [92] as well as the carbide grain shape and grain size distribution [93]. The carbide contiguity is defined as the ratio of the WC/WC boundary area to the total area of the interfaces formed by the carbide interface [94]. The problem with these models is that they use bulk properties of the phases.

Micromechanical fracture tests have been used to overcome this limitation and further the understanding of the deformation and fracture aspects of WC-Co. Trueba et al.'s work was concerned with fabricating cantilever beams which were then bent using a nanoindenter [95]. It was found that a beam with carbide at the clamping end had a higher stiffness. This is assuming the material to be homogeneous. The stiffness was lower when the clamping end had binder. A higher work of fracture was also observed for beams in which the cracks propagated after significant deformation within the binder. The difference in work of fracture for crack through the binder and the carbide phase are presented in the load-displacement plots in figure 1.24.

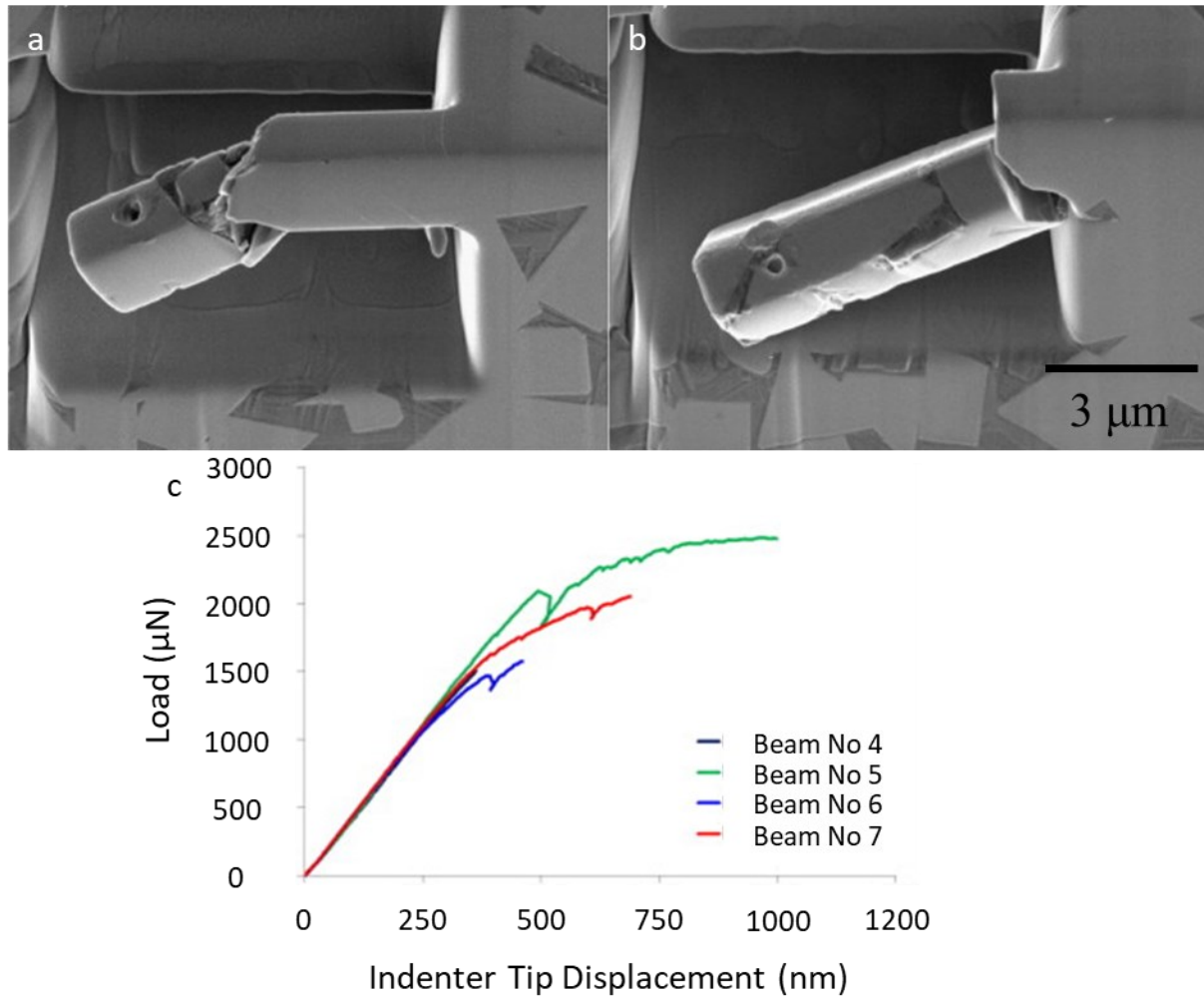


Figure 1.24: SEM images of the cantilever beams used for the study by Trueba et al. where fracture was along (a) binder (beam 5) and (b) carbide grain (beam 6) in cantilever beams. Additionally, fracture for beams 4 and 7 was also along a carbide grain. (c) The load-displacement plots for the tested beams. Beams 4-7 had a carbide grain at the clamping end. Adapted from [95].

A recent study by Sandoval et al. investigated the mechanical response of cemented carbides at micro scale [96]. The work involved fabrications of micro pillars with sizes closer to and larger than the carbide mean grain size. These pillars were then subjected to compression tests. It was found that pillars with a diameter closer to the carbide mean grain size fail catastrophically while exhibiting slip lines at 45° to the loading axis. These correspond to prismatic slip systems mentioned earlier. However, micropillars with sizes larger than the mean grain size tend to show additional deformations/failure mechanisms: glide within the WC/WC grain boundary, cracks within carbide interfaces, plastic deformation of the binder and infiltration of the carbide boundary via binder. This is shown in figure 1.25.

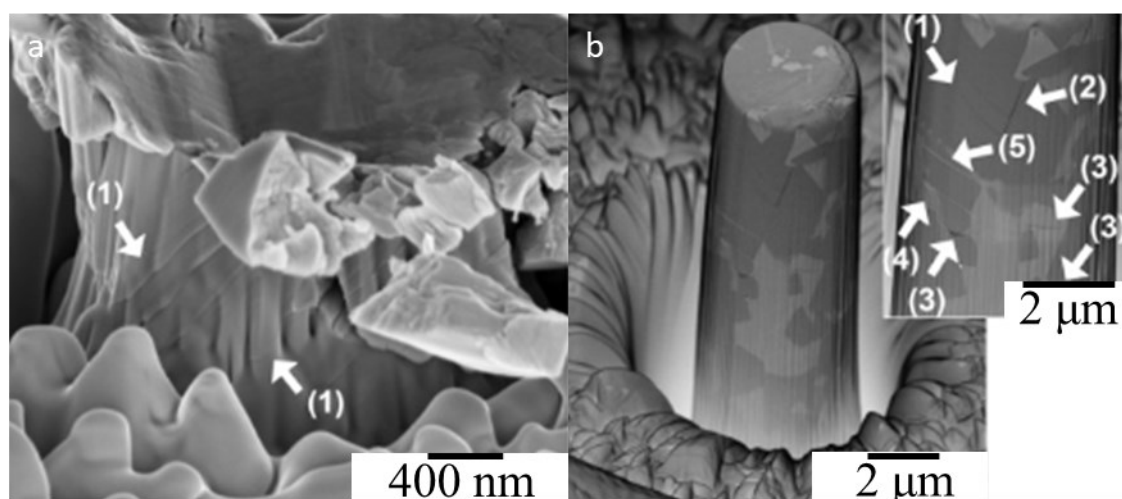


Figure 1.25: FEG SEM micrograph of (a) 1 μm and (b) 4 μm diameter pillars from a WC-11wt%Co sample subject to uniaxial compression test. The arrows point to the mechanisms observed in the structures: (1) slip lines in WC grains, (2) glide at the WC/WC grain boundaries, (3) crack initiation at the WC/WC grain boundaries and propagation through the binder at the phase boundary, (4) plastic deformation of the binder and (5) binder infiltration at the grain boundaries. Adapted from [96].

1.7 Cemented Carbide Literature Review Summary

A comprehensive guide to WC-Co has been provided in this chapter. The invention along with the applications of WC-Co has been discussed at the beginning of this chapter. This is followed by the detailed manufacturing process for WC-Co. This includes steps involved in WC powder production from tungsten ores such as wolframite or sheelite. Afterwards, powder metallurgy processes necessary for WC-Co manufacture have been discussed: milling, drying, pressing and sintering. This section of the chapter also explores the importance of carbon content control in producing desired phases in the finally sintered WC-Co material.

Then the WC-Co microstructure has been reviewed. The reason for the unique faceted morphology of WC grains has been discussed in detail. The difference between the WC and Co phases in the microstructure has also been considered. Finally, the interfaces in WC-Co, the WC/WC and WC/Co boundaries are discussed thoroughly. Attention is paid to the existence of WC/WC CSL boundaries in WC-Co and its relevance for mechanical properties especially in the case of the $\Sigma 2$ boundaries.

The materials properties of WC-Co including hardness, toughness and TRS have been considered subsequently. Furthermore, the effect of microstructural parameters such as WC grain size, cobalt content and MFP for the aforementioned properties have also been reviewed.

Finally, the room temperature deformation of WC-Co is discussed extensively. Crack microstructure interactions during indentation fracture and the main toughening mechanism in WC-Co during crack propagation are explored. This is followed by a review of micromechanical tests performed on WC-Co including pillar compression and single cantilever bending tests.

The literature review of WC-Co has shown that even though variables affecting bulk fracture toughness of WC-Co have been examined, the role of WC/WC boundaries in fracture has not been deciphered. Another aspect that is lacking is an understanding of the effect of dopants in the form of grain growth inhibitors (Cr and V) on the CSL grain boundary populations. These aspects are crucial as most of the fracture path in WC-Co is intergranular with respect to WC grains

1.8 Aims and Objectives

The main aim of this work is to study the WC grain boundary network in WC-Co. The first objective to be accomplished is the identification of interesting boundaries, i.e. due to particular orientation relationships or chemistry. The second task to be completed is performing micromechanical tests at identified boundaries. Finally, explore the effect of chromium doping on the boundary population of interesting boundaries in WC-Co.

2 Fracture in Ceramic Composites

2.1 Introduction to Fracture

The dominating property of brittle materials, especially ceramics such as cemented carbides is the fracture toughness or fracture energy. Fracture energy is defined as the energy per unit area of the crack plane necessary for a crack to grow in an infinitely large specimen [97]. Toughness of a material is dictated by the amount of energy expended during the fracture process. Hence, when one refers to a material as being brittle, the low energy absorption nature during fracture is being considered. Toughness depends on the crack path and the fracture micromechanisms. The crack path is simply the route taken by a crack during the fracture process. This path is usually along weaker segments of the microstructure for a given material. Cracks proceed through weaker planes in brittle materials leaving behind cleavage facets while tougher materials exhibit evidence of plasticity. The fracture micromechanisms are characterised based on the fundamental deformation and rupture processes leading to the formation of two new surfaces during fracture. These micromechanisms are categorised into five categories: microscopic cleavage of atomic planes, interface debonding as observed in composites, ductile shear, plastic flow and void coalescence [98].

2.2 Quantifying Fracture Toughness

Fracture toughness can be quantified via two routes: energy balance analysis (global) and crack tip elastic stress field analysis (local). These two routes consider fracture from a continuum approach point of view.

The continuum approach deals with material behaviour at distances greater than 10^{-4} m [99]. This approach uses classical thermodynamics and continuum mechanics. This means accounting for thermodynamic driving force and resistance as well as studying material as a body composed of continuous distribution of material points. Use of continuum mechanics approach requires two main assumptions. Firstly, microstructural dimensions are assumed to be smaller than the defects present within the material. Secondly, the material is assumed to be a homogeneous continuum.

Study of crack growth requires stress analysis and knowledge of predicting fracture. There are several approaches for specifying failure criteria. Each involves two quantities: one that measures the material's resistance to fracture and one regarding the material quantity. The two routes used for quantifying fracture, energy balance analysis and crack tip elastic stress field analysis are two such failure criteria.

2.2.1 Energy Balance Analysis

Griffith was the first to employ the energy balance approach [100]. Griffith's work was based on the elastic theory. Hence, it was designed for materials obeying the Hooke's law until crack propagation.

This approach considers a cracked elastic plate and its loading system which are assumed to be isolated from the working environment. This ensures that there is only exchange of work between the elastic plate and the loading system. The crack is elliptically shaped with a length of $2a$. The displacement between the two crack faces is $2b$. The crack is loaded perpendicular to the major axis of the ellipse. This is illustrated in figure 2.1. Energy balance means, the work done per unit time for crack propagation would be given as in equation 2.1 [99].

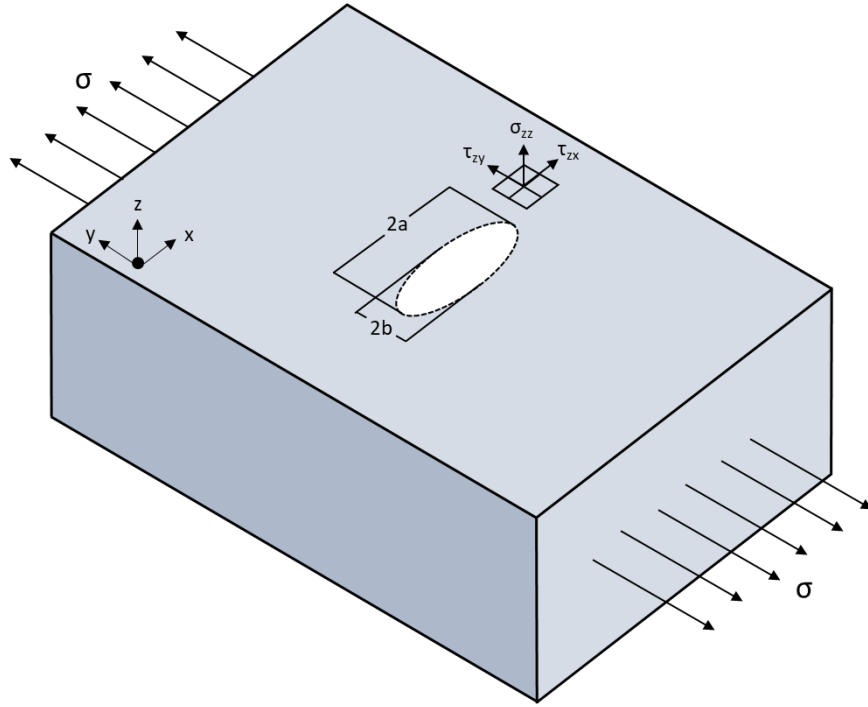


Figure 2.1: Illustration of a crack in a wide plate.

$$\frac{\partial W}{\partial t} = \frac{\partial E}{\partial t} + \frac{\partial K}{\partial t} - \frac{\partial U^s}{\partial t} \quad (2.1)$$

The terms W , E , K and U^s are work done by the load applied on the sample, internal energy of the body, kinetic energy and finally energy used to increase crack area respectively. These have been differentiated with respect to time, t . The internal energy component can be written as a sum of the elastic strain energy, U^e and the plastic work during crack growth, U^p as in equation 2.2.

$$E = U^e + U^p \quad (2.2)$$

The derivative with respect to time can be written as in equation 2.3, since all changes with respect to time are the result of change in crack length, a . Hence, the equation 2.1 can be rewritten into equation 2.4, with the kinetic energy component being neglected from the equation provided that the crack grows slowly, and application of load is time independent. Equation 2.4 can be further rewritten into

equation 2.5 assuming, the material in question is completely brittle and therefore lacks any plastic deformation.

$$\frac{\partial}{\partial t} = \frac{\partial a}{\partial t} \frac{\partial}{\partial a}, \text{ where } a \geq 0 \quad (2.3)$$

$$\frac{\partial W}{\partial a} = \left(\frac{\partial U^e}{\partial a} + \frac{\partial U^p}{\partial a} \right) - \frac{\partial U^s}{\partial a} \quad (2.4)$$

$$G = \frac{\partial W}{\partial a} - \frac{\partial U^e}{\partial a} = - \frac{\partial U^s}{\partial a} = 2\gamma \quad (2.5)$$

Equation 2.5 shows the energy required to produce two new surfaces of energy, γ each. γ is the surface energy per unit area. It represents the work required to break the atomic bonds per unit area for the formation of free surfaces. G represents the energy needed for crack growth– the elastic energy release rate. Equation 2.5 assumes that the energy is spent for the formation of fracture surfaces and no part of the energy is dissipated in any other way. The work done by the loads can be ignored to produce equation 2.6. The work performed by the applied loads can be ignored in the fixed-grips situation where the continuum upon which the loads are applied is assumed to remain stationary. The fixed-grips case is one where the sample is loaded at a constant displacement over time. For example, the bending force suffering no displacement in a wedge loaded double cantilever beam test loaded in direct displacement. In contrast, in a dead-load case, the work done by the external loads provides the energy required for crack growth. This is because according to Clapeyron's theory of linear elastics, the work done by the applied loads is two folds the increase in elastic strain energy ($\frac{\partial W}{\partial a} - \frac{\partial U^e}{\partial a} = \frac{\partial U^e}{\partial a}$). Hence, for the dead-load case, the sign ahead of $\frac{\partial U^e}{\partial a}$ will be positive signifying that work done by the external loads increases the elastic energy of the sample. In a dead-load case, the sample is loaded at a constant load over time (load controlled). The critical condition for crack growth will then be given by equation 2.7 [101].

$$G = - \frac{\partial U^e}{\partial a} = - \frac{\partial U^s}{\partial a} = 2\gamma \quad (2.6)$$

$$\frac{\partial}{\partial a} (U^e - U^s) = 0 \quad (2.7)$$

Based on Inglis' released solution of the stress and strain fields for an elliptical crack, Griffith deduced that the elastic energy per unit width along the crack front (U^e) can be written as in equation 2.8 [101]. Griffith also determined that the energy spent to increase the crack area per unit width of the crack front (U^s) can be written as in equation 2.9 [101].

$$U^e = \frac{\pi \sigma^2 a^2}{E} \quad (2.8)$$

$$U^s = 4a\gamma \quad (2.9)$$

Where σ is the applied stress and E is the elastic modulus. Substituting U^e and U^s from equations 2.10 and 11 into equation 2.7 produces equation 2.10. 2γ can be replaced with G in equation 2.10 and the equation itself can be rearranged to determine the stress required for unstable crack growth. The stress required for an unstable crack growth (σ) is given as in equations 2.11 and 2.12 for plane stress and plane strain conditions respectively.

$$\frac{\pi\sigma^2 a}{E} - 2\gamma = 0 \quad (2.10)$$

$$\sigma = \left(\frac{EG}{\pi a} \right)^{1/2} \quad (\text{Plane stress}) \quad (2.11)$$

$$\sigma = \left(\frac{EG}{\pi a(1 - \nu^2)} \right)^{1/2} \quad (\text{Plane strain}) \quad (2.12)$$

It should be noted that the Poisson's ratio values are typically in the range of 0.25-0.33 [102]. So, the difference between G in the plane stress and plane strain conditions are minimal. Since the surface energy per unit area (γ) of a truly brittle material is fixed, the critical energy release rate, G_c is constant.

2.2.2 Stress Field Analysis

Stress field analysis is the more sophisticated method to determine the toughness. The stress field around a crack tip is characterised via the stress intensity factor, K . Westergaard [103] and Irwin [104] were the first to publish solutions for crack tip stress distributions for the three main crack loading modes. The three modes of loading are shown in figure 2.2.

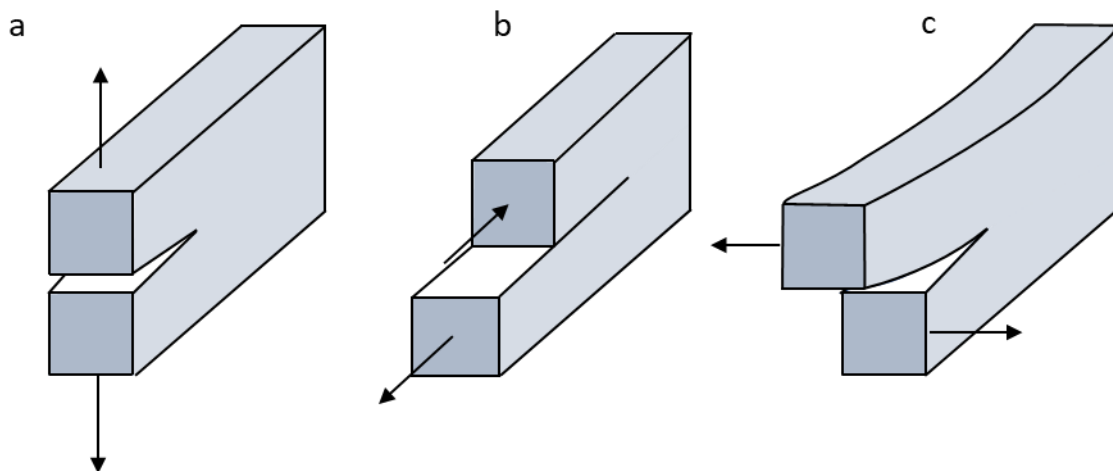


Figure 2.2: The crack loading modes, (a) mode-I opening, (b) mode-II in-plane shear (sliding) and (c) mode-III out-of-plane shear (tearing). Redrawn after [105].

Stress field around a given crack tip depends on the far field stress (σ), the crack length (a), the coordinates at which the stress components are to be measured (r, θ) and the sample geometry [106]. The stress state at a crack tip is given as in figure 2.3.

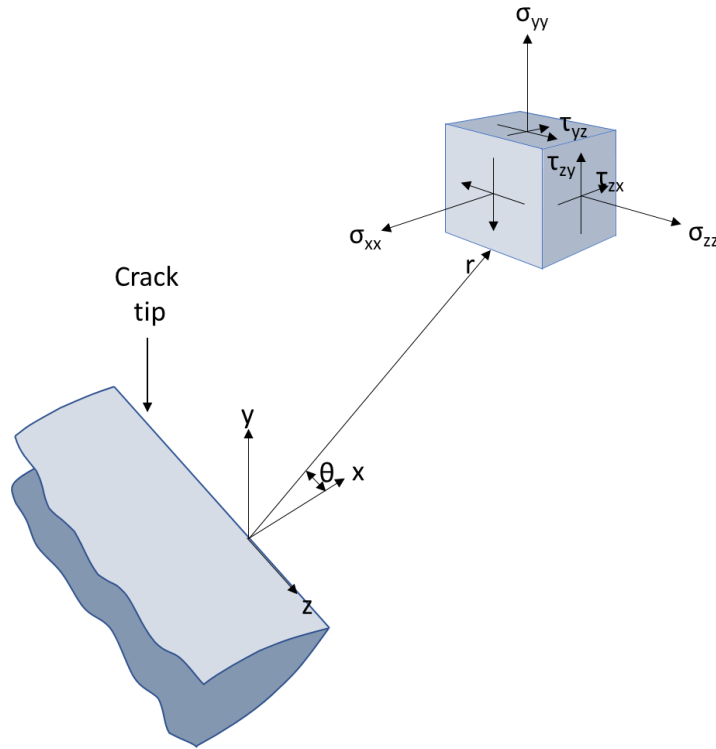


Figure 2.3: A drawing of the stress state at a crack tip.

The far field stress refers to stress at coordinates of the body where the high stress concentration at the crack tip is negligible. Polar coordinates are used for locating stress components. Finally, the specimen geometry refers to the position of a crack in relation to the body in question and the effect of the crack length with respect to the body. Thus, the stress component, σ_{ij} at the crack tip can be expressed as in equation 2.13.

$$\sigma_{ij} = f(\sigma, a, \theta, r, \text{Sample geometry}) \quad (2.13)$$

The universal form of the stress fields ahead of a crack tip independent of the applied loads are given below for mode I fracture [107].

$$\sigma_{xx} = \frac{K}{(2\pi r)^{1/2}} \cos \frac{1}{2} \theta (1 - \sin \frac{1}{2} \theta \sin \frac{1}{2} \theta) \quad (2.14)$$

$$\sigma_{yy} = \frac{K}{(2\pi r)^{1/2}} \cos \frac{1}{2} \theta (1 + \sin \frac{1}{2} \theta \sin \frac{3}{2} \theta) \quad (2.15)$$

$$\tau_{xy} = \frac{K}{(2\pi r)^{1/2}} \sin \frac{1}{2} \theta \cos \frac{1}{2} \theta \cos \frac{3}{2} \theta \quad (2.16)$$

K as mentioned before is the stress intensity factor: it denotes the stress state at a crack tip and is related to the crack growth rate. The θ term describes the distribution of the stresses. It is useful to know whether the maximum stress state at the crack tip is higher than critical stress intensity factor

(K_c) as it is a criterion for failure. So, critical stress intensity factor can be generalised and expressed in terms of applied stresses (σ) at the crack tip where $r \rightarrow 0$ and $\theta = 0$ into equation 2.17 for real crack geometries from an ideally sharp crack tip.

$$K = \sigma Y(\pi a)^{1/2} \quad (2.17)$$

Where Y is the geometric factor dependent on the crack geometry and a is the crack length. The critical value of the stress intensity factor (K_c) to be reached for crack propagation is termed the fracture toughness in the stress field analysis approach. This also provides a measure of the critical crack length that can be allowed before crack propagation. Fracture toughness is a measure of the material's ability to resist fracture. Irwin linked the elastic energy release rate (G) with stress intensity factor (K) to combine the relation between energy balance and stress field approaches [108]. The combined relation between the two approaches is given as in equations 2.18 and 2.19 for plane stress and plane strain conditions.

$$K = (EG)^{1/2}(\text{plane stress}) \quad (2.18)$$

$$K = \left(\frac{EG}{1-\nu^2} \right)^{1/2} (\text{plane strain}) \quad (2.19)$$

The stress field approach cannot easily be applied for any geometry and loading condition. So, the fracture toughness can instead be determined by evaluating the fracture energy and then obtained using equations 2.18 and 2.19.

Plane strain condition, fracture toughness (K_{Ic}) is measured for a mode-I crack loading. This provides the lower bound toughness of a material. For a plane stress condition, the three stress components (σ_{zz} , τ_{xz} and τ_{yz}) relating to the z direction are assumed to be zero. Therefore, the toughness calculated for the plane stress condition does not reduce with increasing specimen thickness (t). Plane stress condition is a good approximation for thin plates. The condition is completely true in the limit when the thickness approaches zero as is the case on the free surface of a body.

For plane strain condition, the strain components (ϵ_{zz} , γ_{xz} and γ_{yz}) in the z direction are zero. To put it another way, there is no displacement in the z direction during loading due to the body being constrained in the z direction by two rigid walls. So, stresses develop through the thickness of the material to counter contraction. The toughness does decrease with increasing specimen thickness for this condition. Hence, it provides the lower bound toughness. Plane strain condition is a good approximation for thick plates where the large amount of material through the thickness makes through thickness strain negligible. The criterion that needs to be satisfied for a plane strain condition is provided in equation 2.20.

$$t \geq 2.5 \left(\frac{K_I}{\sigma_y} \right) \quad (2.20)$$

2.3 Macroscale Fracture Testing

The Griffith energy balance criterion that needs to be fulfilled for a crack to grow is presented in equation 2.7. The change in the elastic energy release rate, as given by its second derivative, $\partial^2 U^e / \partial a^2$ determines the behaviour of the crack extension. Thus, conditions for crack stability are given as follows.

$$\left. \begin{aligned} \frac{\partial^2 U^e}{\partial a^2} < 0, & \quad (Unstable \text{ fracture}) \\ \frac{\partial^2 U^e}{\partial a^2} > 0, & \quad (Stable \text{ fracture}) \\ \frac{\partial^2 U^e}{\partial a^2} = 0, & \quad (Neutral \text{ equilibrium}) \end{aligned} \right\} \quad (2.21)$$

If $\partial(U^e)^2 / \partial a^2$ is negative, the crack growth will accelerate because the energy necessary to create two surfaces will be more than accommodated by the elastic energy released from crack propagation: unstable fracture. Additional energy must be provided for the system when this term is positive. This is the result of the elastic energy released not being sufficient for crack propagation: stable fracture. A stable crack growth is preferable as it allows the user to study the fracture properties of a material, e.g., the energy for crack growth [109]. This is achieved by reducing the elastic energy stored in the entire system (specimen and testing equipment) at the point of fracture initiation. This involves modifying the sample geometry so that a small amount of load is required for crack initiation and utilising a stiff testing machine [110]. Elastic energy stored in a body is proportional to the load applied upon it. Hence, the need to shape the sample, to have fracture at a smaller load. The reason for using a stiff machine is that the load is never applied directly onto the crack itself, instead using a medium. This results in the elastic energy being stored and then released spontaneously upon crack initiation leading to unstable fracture.

The test methods that can be used to study fracture are indentation fracture (IF) [111], chevron notch (CN) [112], single-edge notch beam (SENB) [113], single-edge pre-cracked beam (SEPB) [114], double torsion [115] and double cantilever beam (DCB) [116] tests. These will be described below.

2.3.1 Indentation Fracture

IF originates from the experimental procedure followed in hardness tests. It uses a standard micro hardness tester equipped with a sharp indenter i.e., Vickers indenter to produce an imprint on the sample surface. An ideal sample for IF testing has a flat stress-free surface and is void of cracks. Cracks emanate from the corners of the imprint for brittle materials such as ceramics upon indentation. Then, the length of the crack trace from the corners of the impression and peak applied load are used to

determine K_{Ic} . Simplicity of the test procedure combined with ease of sample preparation relative to other microscale fracture tests that will be explored subsequently makes IF an attractive prospect for determining fracture toughness.

Lawn et al. have reviewed the principles and application of IF [117]. They discussed the importance of the knowledge of stress field beneath the contact zone from indentation in forming a theory of IF. The boundary conditions for the stress field are dependent on the indent shape which in turn is dependent on the indenter shape. There are two types of indenters available for indentations: the Hertzian (spherical) indenter and the sharp (conical/pyramidal) indenter. Sharp indenters are typically favoured for IF as the geometry of the indenter and residual imprint are the same. This means the indent shape does not change with indent depth. So, the contact pressure /hardness (p_0) is independent of the indent size. Furthermore, hardness is solely a function of the applied load and the contact area as given in the equation 2.22 [117]. In contrast, cracks produced from a Hertzian indenter are not well defined [111].

$$p_0 = \frac{P}{\alpha \pi a^2} \quad (2.22)$$

Where P is the applied load, α is a dimensional quantity reflective of the indenter geometry and πa^2 is the contact area. $\alpha = 1$ for axially symmetric indenters as in the case of the Vickers indenter. Boussinesq first devised solutions for the stress field in a point loaded isotropic material [117]. The general form of these solutions is as follows when given in terms of the curvilinear coordinates as shown in figure 2.4. Curvilinear coordinates are the coordinate system where coordinate lines can be curved.

$$\sigma_{ij} = \left(\frac{P}{\pi R^2} \right) [f_{ij}(\phi)]_v \quad (2.23)$$

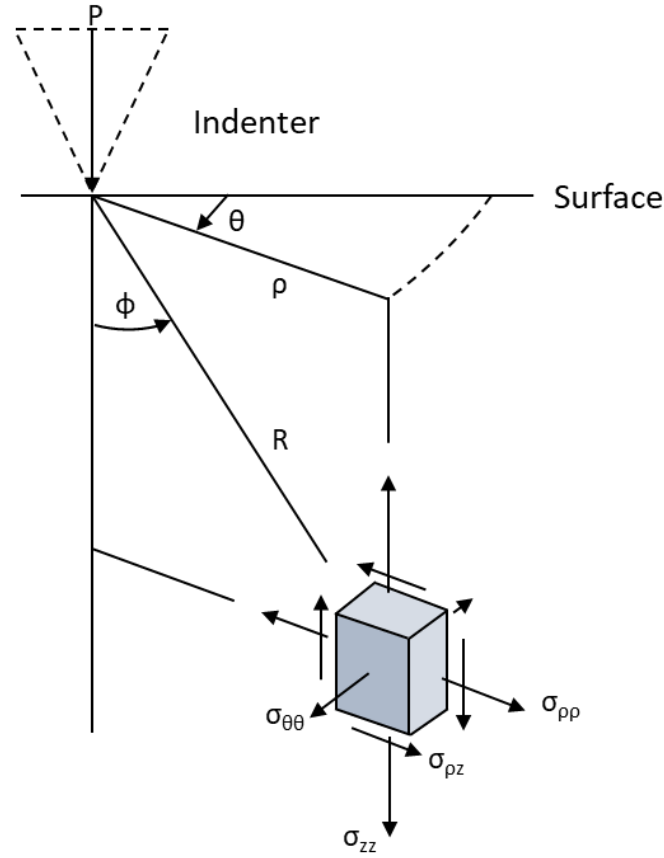


Figure 2.4: Coordinate system for the stress field generated beneath the indenter-sample contact point. Redrawn from [117].

Where σ_{ij} are the stresses, P is the applied load, R is the radial distance from the point of contact, $f_{ij}(\phi)$ is some angular function and ν is the Poisson's ratio. The main takeaway from equation 2.23 is that the magnitude of stresses in the stress field are directly and inversely proportional to the applied load and square of the radial distance from the point of contact. Hence, at the point of contact ($R = 0$), the equation has a singularity. This is a result of the assumption of point loading with a zero-contact area. However, in actuality, localised inelastic deformation relieves the singularity about the point of contact, distributing load over a non-zero contact area. Thus, the stress field is far more complex.

The driving force for the formation cracks of is the residual stress induced by material deformation upon the indenter impinging the sample surface [118]. Three types of crack systems can form during sample indentation: Palmqvist crack, median crack and lateral crack [119]. These are shown in the diagrammatic illustrations provided in figure 2.5.

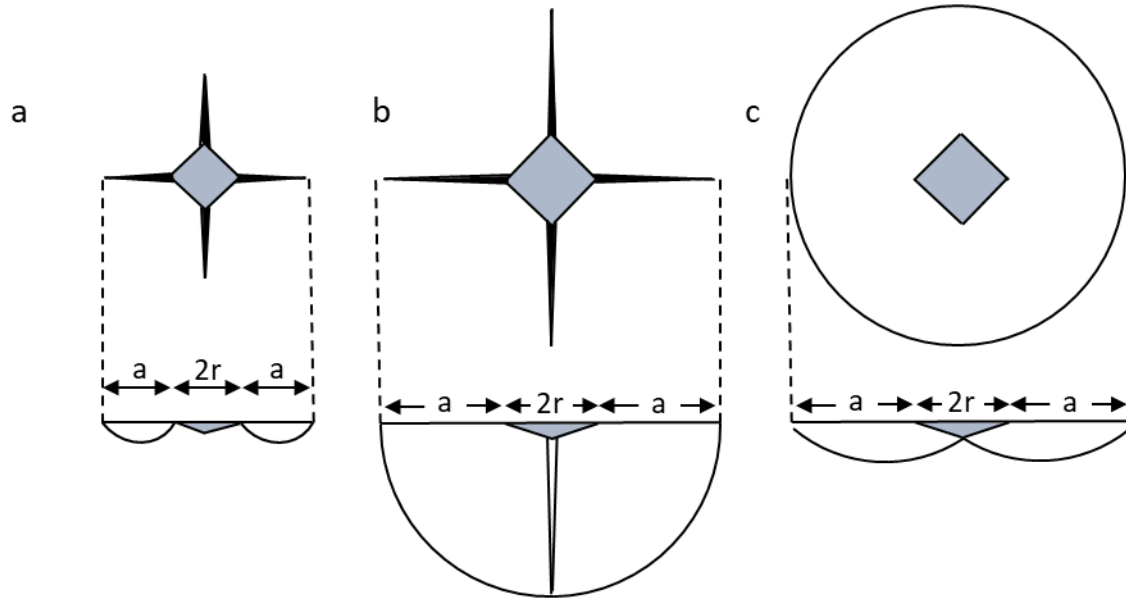


Figure 2.5: Illustrations of the (a) Palmqvist, (b) median and (c) lateral crack systems observed during indentation. Redrawn from [119].

The Palmqvist cracks are formed during initial loading, outside the plastic zone at the corners of the residual imprint. Upon further loading, median cracks form under the surface along the loading axis and are aligned about the direction of the diagonal of the residual imprint. The median crack systems are generated at the boundary between the elastic and plastic deformation region. These cracks might extend upwards and join with the Palmqvist cracks depending on the loading conditions. Lastly, lateral cracks are generated due to residual stresses from indentation. These might curve up and intersect the sample surface producing a surface ring. Since cemented carbide is brittle, rarely any plastic deformation occurs during crack propagation. Hence, the Palmqvist crack systems are usually observed in this material [120]. There are two means of discerning between the Palmqvist and the median crack. The ratio of crack length to half the diagonal length being less than 2.5 and cracks no longer remaining connected to the inverted pyramid of the indent after polishing will mean the presence of a Palmqvist crack system.

Another study by Lawn et al. has discussed the fracture mechanics analysis of the Palmqvist cracks [121]. The authors have shown that the fracture toughness is related to the crack length in accordance with the equation 2.24. This is called the Lawn-Evans-Marshall (LEM) model.

$$K_{Ic} = \xi \left(\frac{E}{H} \right)^{1/2} \left(\frac{P}{a^{3/2}} \right) \quad (2.24)$$

Where ξ is an empirical constant, E is the elastic modulus, H is the hardness, P is the applied load and a is the crack length. Shetty et al. have reduced equation 2.24 to show a simple relation between fracture toughness and crack length for cemented carbide as follows [122].

$$K_{Ic} = AH^{1/2} \left(\frac{P}{\sum a} \right) \quad (2.25)$$

Where A is an empirical constant and $\sum a$ is the sum of all crack lengths.

Several authors including Quinn et al. have explored the validity of using IF to determine fracture toughness [123, 124]. The study concluded that IF is different to standard toughness tests and does not measure fracture toughness. This is because the test produces a crack system with substantial deformation about the crack tip with a complex residual stress condition that is poorly understood. Additionally, the crack propagation proceeds via a complex crack arrest phenomenon. Finally, spalling of material occurs around an indent. Hence, IF has a bad reputation within the scientific community as it is considered to not be a reliable technique for measuring fracture toughness [124].

2.3.2 Flexural Testing

Standard macroscale fracture tests available to measure the toughness of ceramics at ambient temperature are given in the ASTM C1421-18 standard [125]. These techniques using LEFM approach usually have specimens with notches machined into them, where cracks initiate at notch tips upon loading in a three- or four-point bending setup. A schematic of the three-point bending setup shown in figure 2.6(a). Macroscale fracture tests specified in the ASTM C1421-18 standard are shown in figure 2.6. These will be explored in more detail in this section.

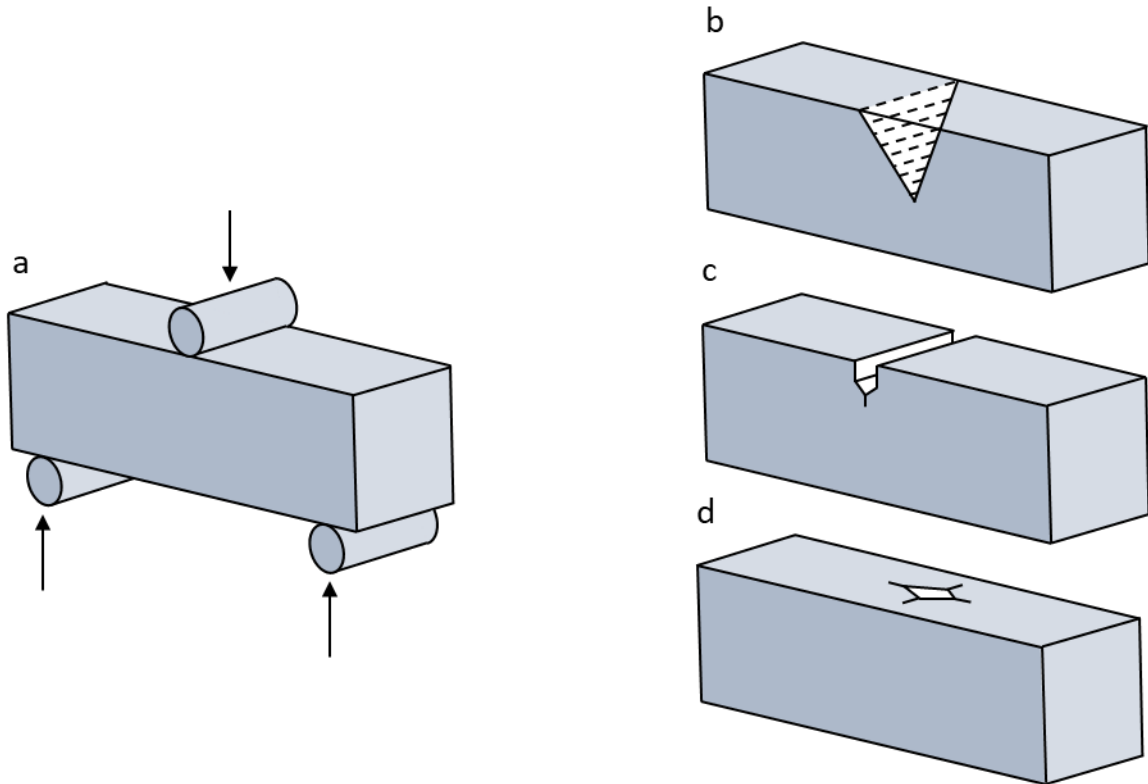


Figure 2.6: Schematic of (a) the three-point bending configuration and specimen geometries for (b) CNB, (c) SENB and (d) SEPB tests.

One of the first successful specimen configurations for stable crack growth, chevron notch (CNB) specimens were first used by Nakayama [126]. The method is as follows [112]. A triangular cross-section is carved into the central part of a square rod bend specimen. Then, upon loading in a three-point bending fixture, a crack is initiated at the apex of the triangle. Initiation of the crack is stable due to requiring less load than necessary for an unstable crack growth. This is due to the stress concentration at the apex of the triangle. The widening crack front acts as a means of improving the resistance for fracture, enabling a stable crack propagation. Tattersall and Tappin determined the work of fracture (fracture surface energy) by deducing the area under the load-displacement curve and dividing it by the fracture area [127]. Barker meanwhile used the maximum load to determine the fracture toughness [112]. Gross et al. provided a means of relating maximum load to the K_{Ic} via the specimen geometry parameters [128].

SENB is another prominent technique employed to study fracture [129]. The method makes use of a rectangular bend bar, pre-notched in the mid part of the body, which is then transversely loaded in a three-point loading fixture. The notches can either be a v notch or a sawn notch. The method assumes that a sharp crack nucleates at the notch upon loading. The relationship between the sample dimensions and load with K_{Ic} was established in the ASTM report of Brown and Strawley [113]. Bansal and Duckworth on the other hand examined the merits and limitations of the techniques [130]. The

authors concluded that SENB is a valid method for measuring fracture energy in ceramic materials. Simple sample geometry, loading fixture and test procedure were cited as advantages of the technique. Meanwhile the authors advised caution when inducing a crack as it can become unstable as well as difficulty associated with defining the depth of the crack.

Another method applied to examine fracture in brittle materials is the SEPB. The method was developed by Sadahiro et al. [131]. This was first used for measuring the fracture toughness of ceramics by Nose and Fuji [132]. The technique involves placing a Vickers indent on the centre of one of the surfaces of a bend beam specimen. Then a controlled bend load is applied to produce a median crack within the specimen via a pre-cracking fixture. The crack is then induced to develop inwards while extending sideways— crack pop-in. The crack is later arrested as a straight through pre-crack across the thickness of the specimen. The technique is also referred to as the bridge indentation method due to means by which the straight through crack is fabricated.

2.3.3 Double Torsion

Double torsion is another technique used for measuring the fracture toughness at the macroscale. The technique was first used by Outwater et al. to determine the fracture energy of cast epoxy resin [115]. The test specimen for a double torsion test is a rectangular plate with a notch or a crack on one of the ends. The test configuration involves symmetric four-point loading about the crack. This results in torsional deformation in the two plate halves. Maximum load at failure is then used to determine the fracture toughness using the equations 2.26-2.27 for plane stress and plane strain conditions respectively [133].

$$K_{Ic} = P_c S_m \left(\frac{3(1 + \nu)}{S t^4 \psi} \right)^{1/2} \quad (\text{Plane Stress}) \quad (2.26)$$

$$K_{Ic} = P_c S_m \left(\frac{3}{S t^4 (1 - \nu) \psi} \right)^{1/2} \quad (\text{Plane Strain}) \quad (2.27)$$

Where P_c is the maximum load at failure, S_m is the size of the moment arm (distance between two points of contact in a half plate), S is the sample width, t is the sample thickness, ψ is the finite beam thickness correction factor and ν is the Poisson's ratio. Schematic of the double torsion test setup is shown in figure 2.7.

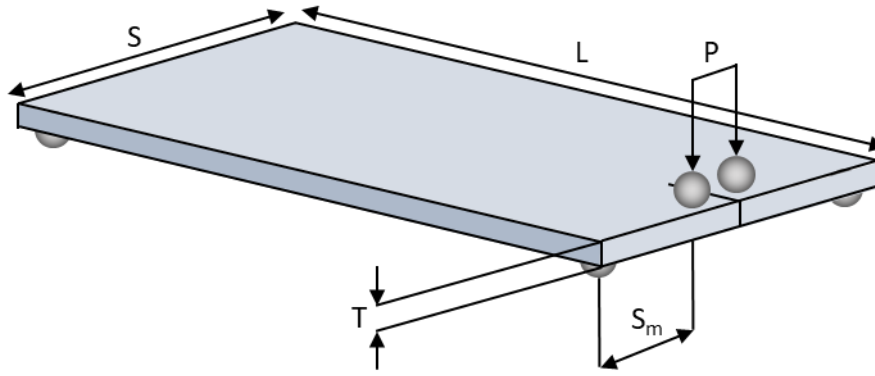


Figure 2.7: An illustration of the double torsion test specimen and loading configuration. Redrawn after [133].

Reviews of double torsion tests that have delved into the analytical, experimental and practical aspects emphasize the importance of interpreting double torsion test data [133]. This is due to the test method not having been standardised. The main advantage of this technique is that a stable fracture can be obtained during this test procedure. This allows for several values of fracture energy to be measured as the crack propagates along the body of the test specimen.

2.3.4 Double Cantilever Beam

Double cantilever beam (DCB) tests are another possible avenue for studying the fracture behaviour of materials. This is an evolution of the Obreimoff experimental setup [134]. There have been several investigations since Obreimoff using the DCB geometry [135]. The method uses a sample configuration where a rectangular beam is symmetrically pre-cracked producing two cantilever arms fixed at the crack tip. These are then pulled apart via an opening load applied using piano hinges, end blocks with clevis holes or by driving a wedge between the arms.

Evaluation of the mechanics behind DCB tests specimen was first performed by Berry [109] and later Gillis et al. [136]. Berry modified the specimen configuration by suggesting to a machine groove onto the DCB as a means of directing the crack during crack propagation. The reasoning for the alteration is as follows. The stress acting along the body of the DCB is typically lower than the bending stress when applying the opening load to the DCB. Therefore, the crack will veer off from propagating in the midplane of the sample and break one of the cantilever arms; the opening mode-I crack necessitates the principal stress be perpendicular to the direction of propagation.

The loading can be either in constant wedging displacement (using a wedge), constant point force load (pulling apart the arms) and finally in constant moment [105]. These are illustrated in figure 2.8. The strain energy release rate, G in these scenarios is given as in the equations 2.28 [105]. The variables E , h , d , c , w , P and M are elastic modulus, wedging displacement, half thickness of the beam, crack length, width of the specimen, point force load and momentum respectively. It can be seen for constant displacement, constant load and constant momentum cases, G is a decreasing, increasing,

and invariant function of crack length respectively allowing to study a stable, unstable and neutral crack growth.

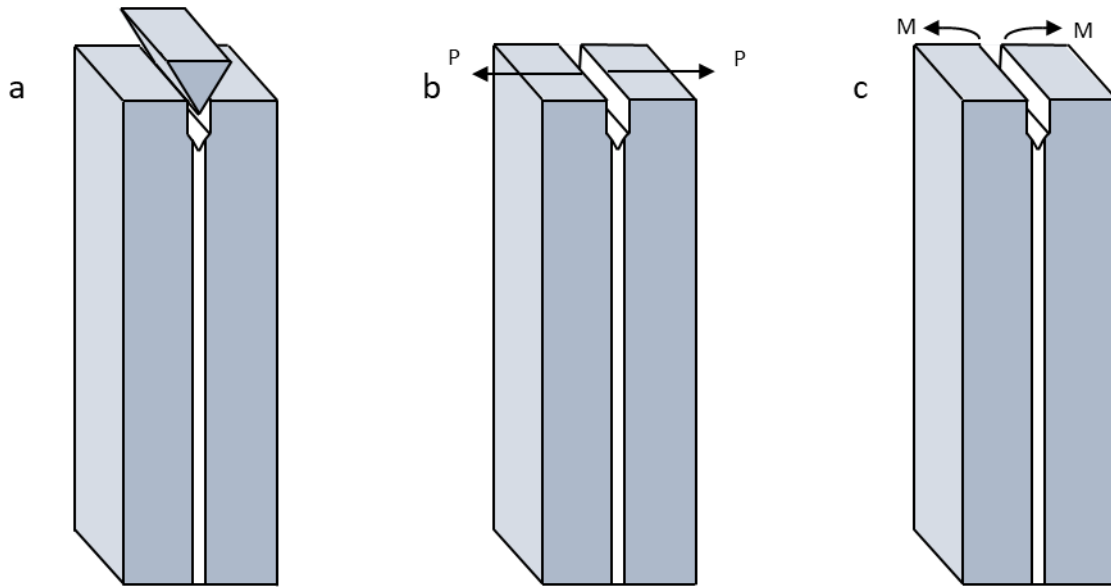


Figure 2.8: Double cantilever beam tests in (a) constant wedge displacement, (b) constant point force load and (c) constant moment. Redrawn after [105].

$$\left. \begin{aligned} G &= \frac{3Eh^2d^3}{4c^4}, & (h \text{ const}) \\ G &= \frac{12P^2c^2}{Ew^2d^3}, & (P \text{ const}) \\ G &= \frac{12M^2}{Ew^2d^3}, & (M \text{ const}) \end{aligned} \right\} \quad (2.28)$$

2.3.5 Summary of Macroscale Fracture Testing

The choice of the suitable method for a given test depends on a number of variables. IF is generally used if small amounts of samples are available. The technique is still popular due to its relative ease in terms of testing and data evaluation. However, large uncertainties surrounding measurement of crack lengths, the cracks systems ranging from Palmqvist, median to lateral cracks and dependence of the residual stresses driving the cracks on a variety of factors means, it is not a preferred technique to study fracture.

CN is usually the preferred method due to producing consistent results if the notches are made properly. But the saw cutting process used to produce the CN geometry is time consuming and the loading fixture is usually expensive [137].

The most commonly used technique for studying fracture is the SENB technique. Yet, producing a sharp crack in a given specimen is challenging [138]. SEPB overcomes this issue. Conversely, it suffers from difficulties associated with controlling crack depth and reliable generation of a pre-crack [114, 139].

Double torsion tests are suitable for samples where tracking the crack tip is challenging. This is because the fracture toughness is independent of the crack length. Both double torsion and DCB tests allow for stable crack growths. So, multiple values of fracture toughness can be determined from each test. DCB tests do not suffer from the shortcomings of the afore mentioned techniques. However, there are some difficulties in determining K_{Ic} due to the interaction of the cracks with the grooves machined to guide them.

2.4 Microscale Fracture Testing

There are several standard micromechanical tests that are available for measuring the bulk fracture toughness of ceramics as discussed in the 2.3 Macroscale Fracture Testing section. Tests that measure bulk fracture toughness enable the user to understand component performance, act as a useful metric for gauging the merits of different processing techniques and as a means for quality control. However, deciphering the contributions of microstructural features to material performance requires targeted experiments at these features. Micromechanical tests allow the user to accomplish this task.

Micromechanical testing of microstructural features has significantly advanced in the last decade with Nanoindentation being the progenitor in the field. Availability of novel micro machining techniques like micro-electrical discharge machining (EDM) [140], laser machining [141], focused ion beam (FIB) machining [142], deep reactive ion etching (DRIE) [143] and lithography [144] has aided in the progress of micromechanical testing.

Most micromechanical fracture tests employ a nanoindentation test frame to load specimens with a variety of indenter tip shapes. Fracture toughness values are determined from crack initiation and fracture load as identified from load-displacement data. Four test geometries are typically used for microscale fracture tests: pillar splitting [145], single cantilever bending [146, 147], clamped beam bending [148, 149], DCB compression [150].

2.4.1 Nanoindentation

This was a technique initially designed to understand the mechanical behaviour of thin films and small volume materials. Mechanical properties such as hardness and elastic modulus [151], strain rate sensitivity [152] and residual stress [153] have been measured with nanoindentation. The nanoindentation process is illustrated in figure 2.9.

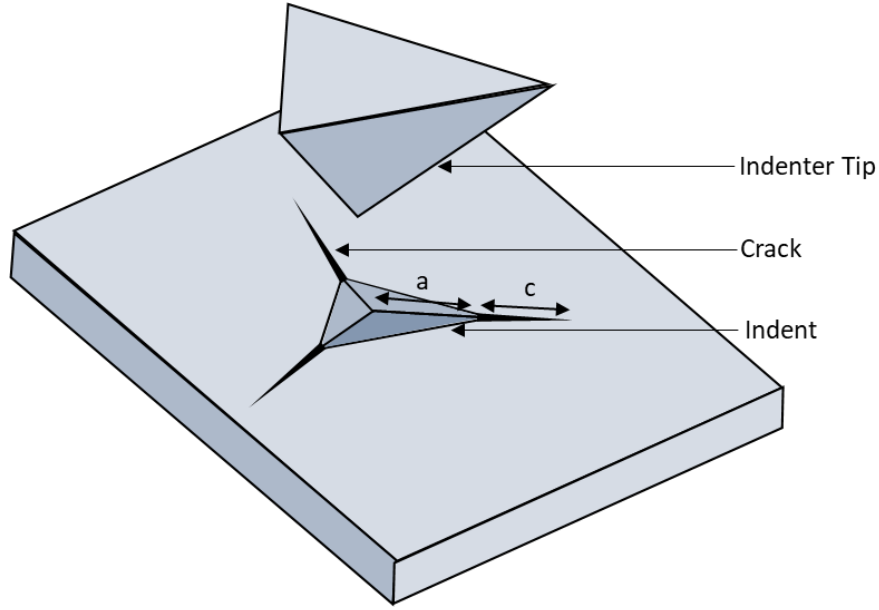


Figure 2.9: Depiction of the nanoindentation procedure with an indent made using a sharp pyramidal indenter.

Nanoindentation in essence is a microscale variation of IF. The technique uses a sharp pyramidal indenter to indent. Fracture toughness is again deduced by measuring the length of the cracks emanating from residual imprint at a given load. Geometry of the pyramidal indenter and type of crack system generated upon indentation governs the model chosen for determining fracture toughness. Equations used for determining fracture toughness from nanoindentation have the following form [154].

$$K_{IC} = \frac{P_{max}}{c^{3/2}} \prod \left(\frac{E}{H}, \nu, \psi, \frac{c}{a} \right) \quad (2.29)$$

Where P_{max} is the maximum indentation load, c is the crack size, E is the elastic modulus, H is the hardness, ν is the Poisson's ratio, ψ is the axis to face angle of the indenter and a is half the diagonal length of the residual imprint. To use equation 2.29 in calculating fracture toughness from nanoindentation tests, one needs to know the indenter geometry, length of the cracks and sample materials properties.

The simplified LEM model analysis can be performed as shown in equation 2.24 for longer cracks ($c/a \ll 1$). Finite element calculations have shown that LEM coefficient ξ depends on the E/H ratio [154]. This is because Palmqvist cracks dominate at high E/H ratio while median cracks are more prevalent at low ratios. The type of crack system therefore dictates how the fracture toughness is related to crack length. Hence, the choice of the most appropriate model for determining fracture toughness is complex. Microstructural features further compound the problem by affecting the types of crack systems generated. Finally, there can be difficulty in measuring the crack length at small length scales.

Further problems are encountered when using this technique on thin films [155]. Measurements of fracture toughness are made more complex by the presence of a substrate. This is because the substrate can affect the formation of the plastic zone and the crack development as the size of the indent gets closer to the thickness of the film. Additionally, residual stresses present in thin films can influence crack growth. Therefore, residual stresses present in the thin film will have to be known precisely to determine fracture toughness.

2.4.2 Pillar Splitting

This technique was developed by Sebastiani et al. and is based on the nanoindentation fracture testing [145]. In pillar splitting, cylindrical micropillars are loaded to fracture by a sharp pyramidal indenter, usually a Berkovich indenter. Pillar splitting is depicted in figure 2.10.

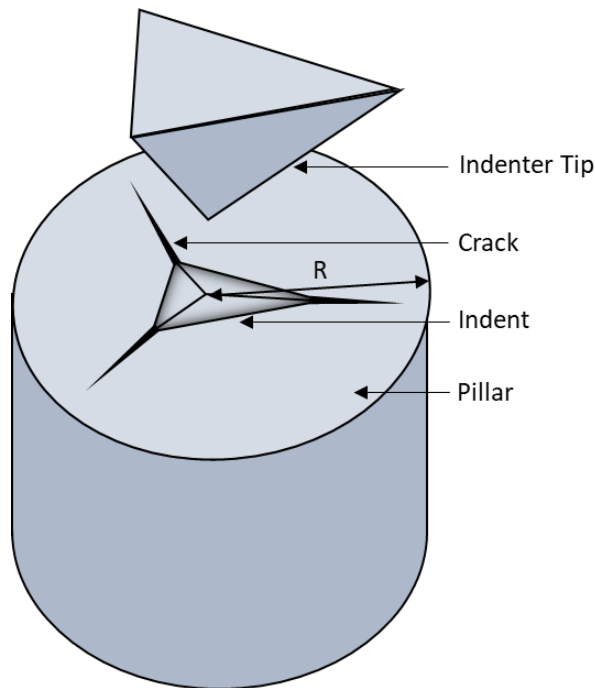


Figure 2.10: Schematic of pillar splitting test procedure with the indentation performed using a sharp pyramidal indenter.

Ghidelli et al. made two major findings with regards to pillar splitting [156]. The authors found that for a given material, the critical load for failure reduced with indenter angle. They also discovered that the fracture toughness is not influenced by pillar diameter as long as the pillar diameter is far greater than the grain size in a polycrystalline material. The toughness is measured from the critical load at failure (P_{Ic}) and the radius of the pillar (R) according to the following equation [145].

$$K_{Ic} = \gamma \frac{P_{Ic}}{R^{3/2}} \quad (2.30)$$

Where γ is a dimensionless coefficient. P_{Ic} is determined by recording the load at which a displacement burst is detected on the load-displacement curve. γ is not the same as the LEM coefficient, ξ . γ is affected by the elastic and plastic properties of the material. Thus, it is material

specific. Hence, the main drawback of using pillar splitting is that γ needs to be calibrated for a given material using finite element modelling.

However, there are several advantages for using indentation fracture. First, the pillar splitting retains most of the positive aspects of indentation fracture with regards to ease of application. Secondly measurement of crack length is not required for deduction of fracture toughness. Moreover, the effect of FIB ion beam damage resulting from pillar fabrication is negligible as crack nucleation and growth occur within the core of the pillar.

With regards to thin films, residual stresses are relieved from the top of the pillars when aspect ratio, (height/diameter)>1 [157]. Hence, the effect of residual stresses in the measurement of fracture toughness is negligible. The influence of the substrate is also muted as pillar splitting can be performed at shallow specimen depths.

2.4.3 Single Cantilever Beam

Single cantilever beam testing was a technique first described and used by Di Maio et al. to determine the fracture toughness of brittle coatings [146]. The technique uses a beam that has been fabricated and is supported at one of the ends. The beam is pre-notched with the notch being closer to the clamped end as shown in figure 2.11. An indenter is used to deform the beam in bending until crack initiation and propagation.

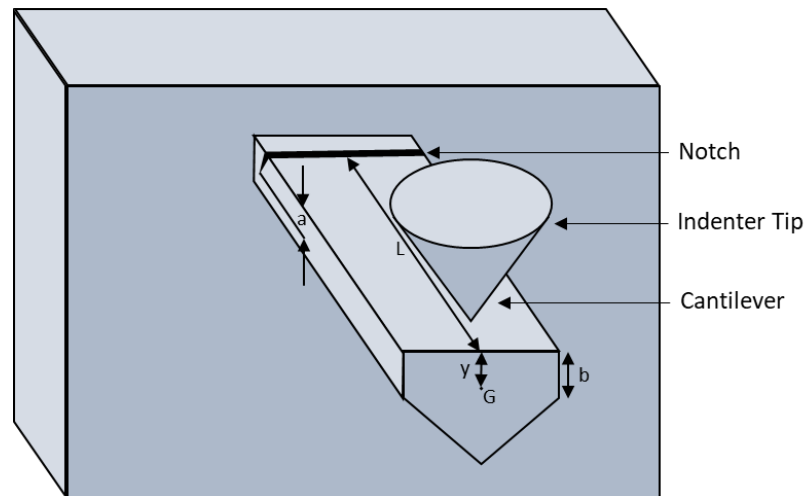


Figure 2.11: Schematic representation of the single cantilever beam geometry. G is the gravity centre. Redrawn after [146].

Fracture toughness is determined from single cantilever beam testing using equation 2.31 for a plane stress condition [146].

$$K_{Ic} = \sigma_c (\pi a)^{1/2} F \left(\frac{a}{b} \right) \quad (2.31)$$

Where σ_c is the fracture stress, a is the crack length and $F(a/b)$ is a dimensionless shape factor dependent on the beam geometry. σ can be determined assuming that only a small deformation occurs as follows

$$\sigma = \frac{PLy}{I} \quad (2.32)$$

Where P is the applied bending force, L is the distance between the location of loading and the crack, y is the vertical distance between the upper surface and the neutral plane, and I is the moment of inertia of the beam. This technique has the drawback of the dimensionless shape factor having to be calculated from finite element simulations.

2.4.4 Double Cantilever Beam

DCB in compression was first proposed by Liu et al. [150]. It involves loading a double cantilever beam (DCB) geometry (see figure 2.12) in compression using a flat punch. Fracture toughness is then determined from the fracture toughness at crack extension.

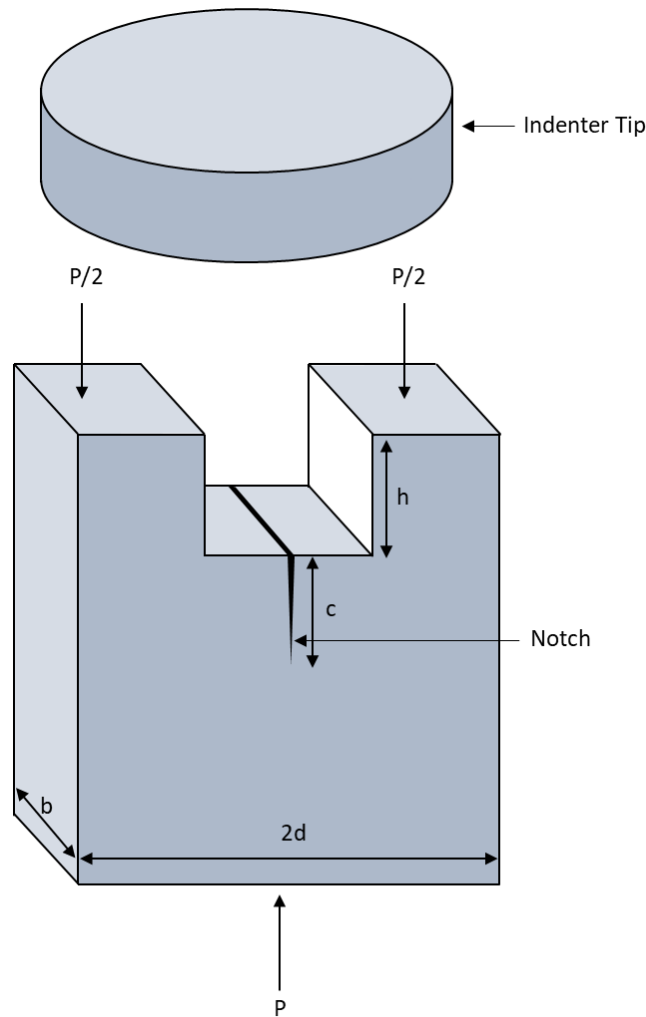


Figure 2.12: Depiction of the DCB geometry loaded with a flat punch. Redrawn after [150].

Applying a compressive load (P) gives rise to a moment (M_B) on each beam. Friction between the indenter and the DCB generates another moment (M_f). These moments are given as in equations 2.33-2.34 [150].

$$M_B = \frac{Pe}{2} \quad (2.33)$$

$$M_f = \frac{-P\mu h}{2} \quad (2.34)$$

Where e is the distance between the line of action of the compressive load and the neutral axis of the beam, μ is the coefficient of friction between the flat punch and the DCB, and h is the height of the DCB trough. Hence, the total moment is

$$M = \frac{P}{2}(e - \mu h) \quad (2.35)$$

The second moment of area (I_x) and strain energy release rate (G) are given as [150]

$$I_x = \frac{bd^3}{12} \quad (2.36)$$

$$G = \frac{M^2}{EI_x b} \quad (2.37)$$

Where b and $2d$ are thickness and width of the DCB respectively and E is the elastic modulus. Substituting equations 2.35 and 2.36 into 2.37 produces [150]

$$G = 3P^2 \frac{(e - \mu h)^2}{Eb^2 d^3} \quad (2.38)$$

Using the relation in equation 2.18 between G and K , K_{Ic} can be written as in equation 2.39.

$$K_{Ic} = 3^{1/2} P_c \frac{(e - \mu h)}{bd^{3/2}} \quad (2.39)$$

The main downside for using a DCB geometry loaded in compression is the calibration process involved in determining μ .

2.4.5 Limitations of Micromechanical Tests

There are several key limitations for conducting micromechanical tests. High crack propagation velocities due to unstable fracture is problematic in ceramics as the fracture energy values are likely to be erroneous. Compliance within the test fixture can lead to undesirable unstable fracture. Compliance within the test fixture is primarily introduced via the compliance of nanoindentation frames ($\sim 10^{-7} \text{ mN}^{-1}$) and the samples [158]. Additional compliance to the test fixture is introduced through indenter tip compliance, surface roughness effect and free movement of parts within the frame [159]. These contribute to a large fraction of the total energy stored in the system before crack nucleation.

In the afore mentioned micromechanical tests, test specimens are loaded via an indenter using a load-controlled ramp. In such cases, displacement control is achieved by a feedback loop with the aid of a

displacement sensor. However, the frequency of the feedback loop is too slow to keep pace with crack propagation velocities in ceramics. Thus, change in displacement is fast upon crack initiation and is difficult to control [160].

In summary, the energy stored owing to compliance of the system and the load-controlled loading leads to an increasing energy release rate with crack growth, an unstable crack growth. An unstable crack means, only a single value of fracture toughness can be determined from each test.

Since FIB machining is the predominant technique for producing microscopic samples, effect of ion implantation must be considered. Best et al. have shown that ion implantation at the notch root tip leads to either toughening because of residual stress or embrittlement, based on the material of choice [161]. This results in erroneous measurements of fracture toughness. The effect of friction between the sample and the indenter tip further compounds the measurement of fracture toughness.

3 Microscale DCB Tests

3.1 Reason for the DCB Geometry

Sernicola et al. discussed a DCB geometry loaded by a wedge tip to overcome the limitations of the micromechanical tests detailed in the previous chapter [162]. The inception of wedge loaded DCB test fixture can be traced back to Obreimoff's work in mica [134].

A DCB structure is fabricated by milling an upright single cantilever beam protruding out of the sample surface. A trough is then milled along the beam through the top middle surface for the placement of a wedge. A notch is then milled at the centre of the trough. This means a DCB geometry is composed of two cantilever arms being clamped at the location of the crack tip. The cantilever arms are point loaded at the arm-wedge contact point when a wedge tip is driven through the DCB trough. Elastic strain energy is stored in the cantilever arms during point loading of the arms. The elastic strain energy is then used for crack initiation and propagation.

The wedge loaded geometry is illustrated in figure 3.1. The technique involves loading a DCB in direct displacement control in situ inside a scanning electron microscope (SEM). Use of a displacement head piezo (DHP) actuator makes direct displacement control possible. A direct displacement control will mean strain energy release rate (G) in a DCB decreases as a function of crack length: in other words, a stable crack propagation [105]. Hence, a crack will only grow if there is sufficient energy stored from driving the wedge further into the DCB and bending the arms. A wedge loaded DCB geometry also allows for multiple toughness measurements during crack growth. Since fracture energy measurements are obtained as the crack evolves, erroneous measurements near the notch with FIB milled damage can be discarded. Finally, this set up negates the need to know the effect of indenter-sample contact friction.

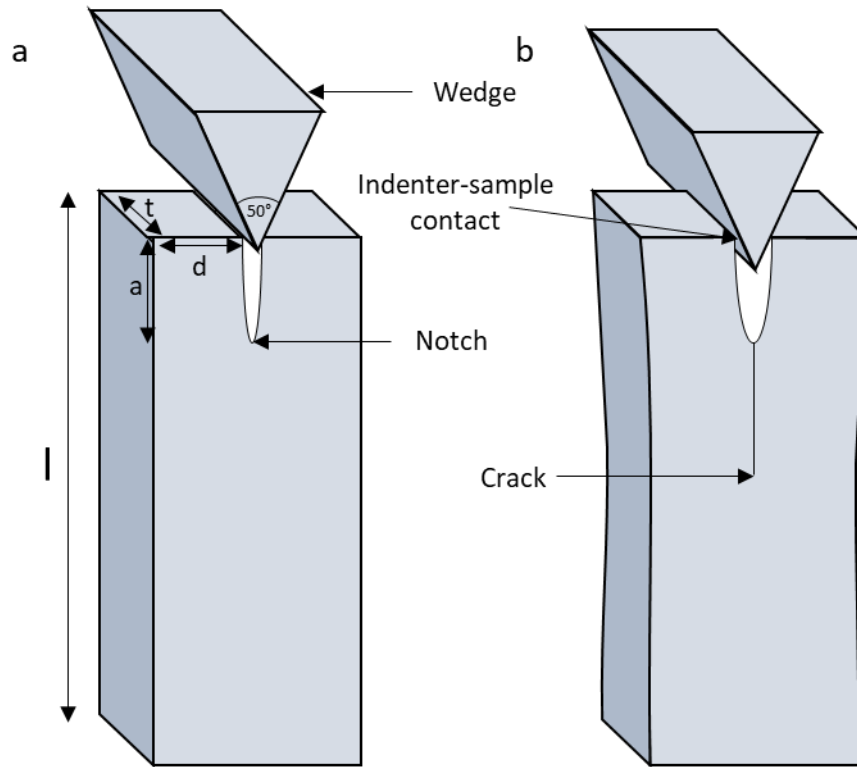


Figure 3.1: Depiction of the wedge loaded DCB geometry (a) before and (b) during loading.

3.2 Beam Theory

DCBs can be thought of as two cantilever beams clamped at one of their ends. The crack tip or notch will be the location of the clamped end with the arms being point loaded at the contact points of the wedge and the cantilever arms.

A beam is a structural member with the axial dimensions being significantly greater than the transverse dimensions [163]. The beam axis is along the longest dimension, with the cross section varying smoothly along it. This rough definition applies to the beam-like cantilever arms composing DCBs.

Beam theories originating from solid mechanics are vital for structural analysis of beams, with the energy spent in bending of the beams being of interest. Several beam theories have been proposed with different assumptions, offering varying degrees of accuracy. The simplest of the theories is the Euler-Bernoulli beam theory (EBT) with Timoshenko and Reddy and Bickford being the more complex variants [164]. The later counterparts account for the shear deformation neglected by Euler-Bernoulli beam theory [165]. Timoshenko (TBT), and Reddy and Bickford beam theories are first and third order shear deformation theories respectively. The Euler-Bernoulli beam theory and Timoshenko beam theory will be extensively discussed in this section.

3.2.1 Euler-Bernoulli Beam Theory

The most basic assumption of the Euler-Bernoulli beam theory as with other beam theories is that the beam is elastic and isotropic. The kinematic assumptions of the theory are, the beam's cross section being infinitely rigid in its own plane, remaining planar after deformation and being normal to the beam axis [166]. This can also be thought of as the straight-line transverse to the beam axis staying straight, inextensible and perpendicular to the midplane after deformation respectively. These amount to ignoring shear, transverse and normal strains as well as the Poisson effect. An illustration of a beam clamped at one end and point loaded at the other end are shown in figure 3.2.

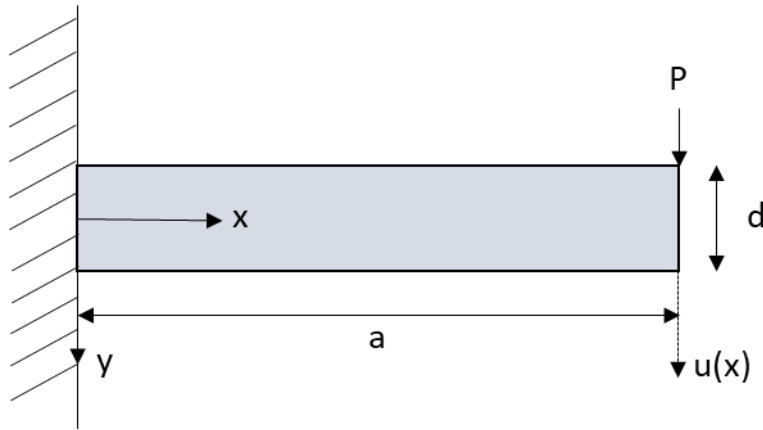


Figure 3.2: Schematic of a point loaded cantilever arm clamped at the crack tip end with a crack length a .

Loading a clamped beam results in the neutral axis deforming into a curve. The assumption of the beam being elastic and isotropic means the bending moment can be expressed as a function of the curvature as shown in equation 3.1 [167].

$$M = EI\kappa \quad (3.1)$$

Where M is the bending moment, E is the elastic modulus, I is second moment of inertia (also called the second moment of area or the area moment of inertia) and κ is the curvature of the bending. The moment of inertia is the measure of the efficiency of a cross sectional shape in resisting bending resulting from loading. The curvature is given by equation 3.2.

$$\kappa = \frac{\frac{\partial^2 u}{\partial x^2}}{\left[1 + \left(\frac{\partial u}{\partial x}\right)^2\right]^{3/2}} \quad (3.2)$$

Where u is the deflection of the beam given as a function of the distance (x) along the beam from the free end– the deflection at any location x . The deflection is measured as the distance between the original position to deflection position of the neutral axis at any point x . $\partial u / \partial x$ is the slope of the deformed beam at point x . If the kinematic assumption holds true, then $\partial u / \partial x \ll 1$. To put it another way, small deflections will mean that the slope, $\partial u / \partial x$ will also be small. Hence, the value of $(\partial u / \partial x)^2$ is negligible compared to unity. Thus, the bending moment can be rewritten as,

$$M = EI \frac{\partial^2 u}{\partial x^2} \quad (3.3)$$

The elastic strain energy, U stored in a volume of body, V in terms of the applied stress (σ) and the elastic modulus (E) is in the form of equation 3.4 [168]. Here the cantilever arm is considered to be composed of small cubic elements of volume, dV . Integrating the incremental strain energy for each cubic element over the entire volume of the beam gives the total strain energy as shown in equation 3.4.

$$U = \int \frac{\sigma^2}{2E} dV \quad (3.4)$$

Stress across the beam thickness is given by equation 3.5, where y is the distance from the neutral axis to any other radius on the cross section during bending [169]. This means at the neutral axis, $y = 0$. The second moment of area is written as in equation 3.6 [170]. Moment acting at the point of loading on the cantilever is simply given as in equation 3.7, where P is the point load.

$$\sigma = \frac{My}{I} \quad (3.5)$$

$$I = \int_A y^2 dA \quad (3.6)$$

$$M = P(a - x) \quad (3.7)$$

Hence, by substituting σ , I and M from equations 3.5, 3.6 and 3.7 respectively into equation 3.4, the equation 3.4 reduces to equation 3.8 where a is the length of the clamped beam. In a DCB, a is the crack length and therefore the length of the cantilever arms.

$$U = \int \frac{M^2 y^2}{2EI^2} dV = \int_0^a \frac{M^2}{2EI} dx = \int_0^a \frac{P^2 (a - x)^2}{2EI} dx = \frac{P^2 a^3}{6EI} \quad (3.8)$$

Deflection, δ according to the Euler-Bernouli beam theory is given as in equation 3.9. This can be rearranged with the point load as the subject as shown in equation 3.10. In the clamped beam, the beam width is considered to be unitary. The second moment of inertia of the beam is given as in equation 3.10 where d is the beam thickness [171].

$$\delta = \frac{Pa^3}{3EI} \quad (3.9)$$

$$P = \frac{3EI\delta}{a^3} \quad (3.10)$$

$$I = \frac{d^3}{12} \quad (3.11)$$

Equations 3.10 and 3.11 can be substituted back into the equation 3.8 producing equation 3.12 for U . Finally, the elastic energy release rate in accordance with the Griffith criterion for this scenario is given by equation 3.13, provided that the energy expended in bending the beams is the same as that of the energy stored in the beams. This allows the user to determine the fracture energy from a DCB test.

This is because the energy spent causing the cantilever arms to deflect when they are point loaded by a wedge tip will be the same as that used for crack propagation along the body of the DCB.

$$U = \frac{Ed^3\delta^2}{8a^3} \quad (3.12)$$

$$G = -\frac{dU}{da} = \frac{3Ed^3\delta^2}{8a^4} \quad (3.13)$$

3.2.2 Timoshenko Beam Theory

TBT is the beam model that takes into consideration of the effects of rotational inertia/axial deformation and first order transverse shear deformation [172]. TBT overcomes the drawbacks of EBT producing solutions closer to the exact one. It is suitable for analysing the behaviour of a short thick beams where $a \ll d$ condition applies [173]. This will be the case initially during the DCB tests.

Timoshenko and Goodier showed that the integration of the differential equation presented in equation 3.14 with regards to specific boundary condition allows to generate solutions for 2D problems when the forces acting upon a body are either constant or absent [174].

$$\frac{\partial^4 \varphi}{\partial x^4} + 2 \frac{\partial^4 \varphi}{\partial x^2 \partial y^2} + \frac{\partial^4 \varphi}{\partial y^4} = 0 \quad (3.14)$$

The differential equation must satisfy the boundary condition that the external forces exist as a continuation of the internal stress distribution. Stress components are given as below.

$$\sigma_x = \frac{\partial^2 \varphi}{\partial y^2}, \quad \sigma_y = \frac{\partial^2 \varphi}{\partial x^2}, \quad \tau_{xy} = -\frac{\partial^2 \varphi}{\partial x \partial y} \quad (3.15)$$

For rectangular bodies, solutions for 3.14 take the form of polynomials. By taking polynomials of different degrees called the stress functions and adjusting their coefficients accordingly, solutions to different loading conditions on rectangular bodies can be attained. The second-degree polynomial in equation 3.16 is used for a beam where all the stress components are constant throughout the body. This means the beam is under uniform compressions and tensions normal to it in addition to a uniform shear.

$$\varphi_2 = \frac{a_2}{2} x^2 + b_2 xy + \frac{c_2}{2} y^2 \quad (3.16)$$

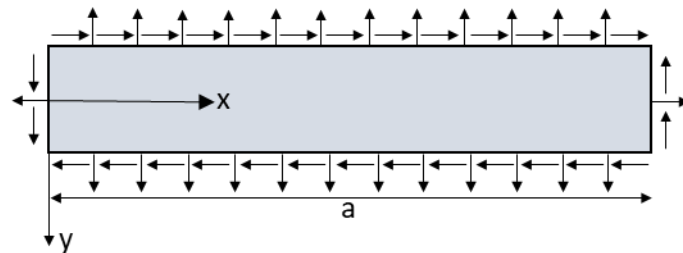


Figure 3.3: Schematic of a beam under the loading condition described by the second-degree polynomial.

A condition of pure shear is given by setting the coefficients c_2 and a_2 to zero. The stress components for such a case are given as follows.

$$\sigma_x = \frac{\partial^2 \varphi_2}{\partial y^2} = c_2 = 0, \quad \sigma_y = \frac{\partial^2 \varphi_2}{\partial x^2} = a_2 = 0, \quad \tau_{xy} = -\frac{\partial^2 \varphi_2}{\partial x \partial y} = -b_2 \quad (3.17)$$

Point loading the end of a beam is the same as the resultant of parabolically distributed shear stress acting at the loaded end. By taking all the coefficients of the fourth-degree polynomial provided in equation 3.18 apart from d_4 to be zero, the condition of a beam with the longitudinal sides under pure shear and one of the ends subject to parabolically distributed shear stress is obtained. Superimposing the second-degree polynomial for a pure shear condition with a fourth-degree polynomial described creates the condition for point loading seen in DCB tests. This is because the uniform shear stress along the longitudinal sides is cancelled while parabolically distributed shearing forces along the edge of the beam are retained.

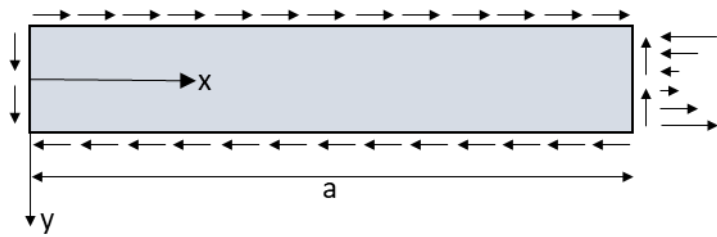
$$\varphi_4 = \frac{a_4}{4.3}x^4 + \frac{b_4}{3.2}x^3y + \frac{c_4}{2}x^2y^2 + \frac{d_4}{3.2}xy^3 + \frac{e_4}{4.3}y^4 \quad (3.18)$$


Figure 3.4: Schematic of a beam under the loading condition given by the fourth-degree polynomial.

Where a_4 , b_4 , c_4 , d_4 and e_4 are the coefficients of the fourth-degree polynomial. Magnitude of the coefficients making up the second-degree polynomials can be freely chosen, since equation 3.14 can be satisfied regardless. However, the stress function in the fourth-degree polynomial requires certain relation between coefficients to be met. Substitution of equation 3.18 into 3.14 reveals, that equation 3.14 is only solved if the following condition is fulfilled.

$$e_4 = -(2c_4 + a_4) \quad (3.19)$$

Stress components for the fourth-degree polynomial are shown as,

$$\begin{aligned} \sigma_x &= \frac{\partial^2 \varphi_4}{\partial y^2} = c_4x^2 + d_4xy - (2c_4 + a_4)y^2 \\ \sigma_y &= \frac{\partial^2 \varphi_4}{\partial x^2} = a_4x^2 + b_4xy + c_4y^2 \\ \tau_{xy} &= \frac{\partial^2 \varphi_4}{\partial x \partial y} = -\frac{b_4}{2}x^2 - c_4xy - \frac{d_4}{2}y^2 \end{aligned} \quad (3.20)$$

The condition for the point loading of a cantilever beam requires all coefficients other than d_4 to be zero as mentioned earlier. This reduces the stress components to

$$\sigma_x = d_4 xy, \quad \sigma_y = 0, \quad \tau_{xy} = -\frac{d_4}{2} y^2 \quad (3.21)$$

Addition of the stress components of second- and fourth-degree polynomial results in

$$\sigma_x = d_4 xy, \quad \sigma_y = 0, \quad \tau_{xy} = -b_2 - \frac{d_4}{2} y^2 \quad (3.22)$$

Beam sides which are $y = \pm \frac{d}{2}$ from the neutral axis must be free from forces. Therefore,

$$\begin{aligned} \tau_{xy} = -b_2 - \frac{d_4}{2} \frac{d^2}{4} &= 0 \\ d_4 &= -\frac{8b_2}{d^2} \end{aligned} \quad (3.23)$$

Given that the resultant of the parabolically distributed shear stress at the loaded end must equal the point load, P , the value of coefficient b_2 is as shown below.

$$\begin{aligned} \int_{-\frac{d}{2}}^{\frac{d}{2}} -\tau_{xy} dy &= \int_{-\frac{d}{2}}^{\frac{d}{2}} (b_2 - \frac{4b_2}{d^2} y^2) dy = P \\ b_2 &= \frac{3P}{2d} \end{aligned} \quad (3.24)$$

Substituting d_4 and b_2 back into the stress components presented in equation 3.22 gives

$$\sigma_x = -\frac{12P}{d^3} xy, \quad \sigma_y = 0, \quad \tau_{xy} = -\frac{3P}{2d} (1 - \frac{4}{d^2} y^2) \quad (3.25)$$

The second moment of inertia, for the cross section of the cantilever arm is given as in equation 3.13.

So, $d^3/12$ is substituted with I into the stress components in equation 3.25 to produce 3.26.

$$\sigma_x = -\frac{P}{I} xy, \quad \sigma_y = 0, \quad \tau_{xy} = -\frac{P}{2I} (\frac{d^2}{4} - y^2) \quad (3.26)$$

Hence, the strains would be given in accordance with the Hooke's law as follows.

$$\varepsilon_x = \frac{\sigma_x}{E} = -\frac{P}{IE} xy, \quad \varepsilon_y = -\frac{\nu \sigma_x}{E} = \frac{\nu P}{IE} xy, \quad \gamma_{xy} = \frac{\tau_{xy}}{G} = -\frac{P}{2IG} (\frac{d^2}{4} - y^2) \quad (3.27)$$

Where ν and G are Poisson's ratio and shear modulus respectively. The stored elastic energy, U in the body is then expressed as in equation 3.28. Then, substituting P from equations 3.10 and 3.11 into 3.28 results in equation 3.29. Finally, differentiation of the strain energy with respect to crack/beam length gives energy release rate for the Timoshenko scenario shown in equation 3.30. Equation 3.30 reduces to equation 3.12 when $a \gg d$ as is the case when the crack grows during a DCB test.

$$U = \frac{1}{2} \int_V (\sigma_x \varepsilon_x + 2\tau_{xy} \gamma_{xy}) dV = \frac{P^2 a^3 d^3}{24EI^2} \left(\frac{1}{3} + \frac{1}{5} (1 + \nu) \left(\frac{d}{a} \right)^2 \right) \quad (3.28)$$

$$U = \frac{3Ed^3 \delta^2}{8a^3} \left(\frac{1}{3} + \frac{1}{5} (1 + \nu) \left(\frac{d}{a} \right)^2 \right) \quad (3.29)$$

$$G = -\frac{dU}{da} = \frac{3Ed^3 \delta^2}{8a^4} \left(1 + (1 + \nu) \left(\frac{d}{a} \right)^2 \right) \quad (3.30)$$

3.2.3 Correction for Rotation at the Clamped End

There is some rotation of the cantilever arms at the crack tip when a DCB is wedge loaded. This results in the measured strain energy release rate being erroneous if the actual crack length were to be used. Hence, Williams developed a solution to account for the rotation at the crack tip [175]. The correction involves increasing the real cantilever arm length/effective crack length by χd . Thus, the crack length (a) is replaced by $a + \chi d$ in equations 3.13 or 3.31. χ and Γ are given as in equations 3.31 and 3.32 respectively.

$$\chi = \sqrt{\frac{2(1+\nu)}{11}} \left[3 - 2 \left(\frac{\Gamma}{1+\Gamma} \right)^2 \right]^{1/2} \quad (3.31)$$

$$\Gamma = 2.36 (1 + \nu) \quad (3.32)$$

Williams approximated the value of χ to be 0.67. This value was calculated with the assumption of the arm being isotropic as required for the application in beam theory. This study also showed that χ was not influenced by the Poisson's ratio (ν). This was validated with a finite element analysis (FEA) approach. Aldegaither et al. substantiated the use of employing Williams' correction when determining fracture energy values from DCB tests [176].

4 Grain Boundary Statistical Analysis

4.1 Introduction

It has been shown in the literature that the most common grain boundary habit planes are the same planes that govern the equilibrium crystal shape of a given material [177, 178]. In other words, grain boundary habit planes are usually the lowest surface energy crystallographic planes. This implies that a correlation exists between crystallographic plane surface energies and the grain boundary energies. The reason for such observation is that both energies are caused by disruption of bonding in comparison to bonding in the perfect crystal structure.

Furthermore, it has been demonstrated that grain boundary populations and their respective energies are inversely correlated [179]. This is a reasonable result as grain boundaries with a lower grain boundary energy are likely to be more frequent in the microstructure than those with higher energy, at least in the annealed microstructure. Hence, the relative population of grain boundaries are indicative of their grain boundary energies.

Finally, studies examining the effect of solutes/dopants in grain boundaries have revealed that change in grain boundary chemistry affects grain boundary distributions [179, 180]. Addition of dopants alter boundary composition. Therefore, a change in the fraction of grain boundary types with dopant addition will denote a change in the grain boundary energy of grain boundaries.

4.2 Theory of Grain Boundary Statistical Analysis

4.2.1 Grain Boundary Plane and Character Distribution

Polycrystalline materials such as WC-Co consist of WC and Co grains connecting at interfaces to form an interfacial network. Knowledge of internal interface distributions and 3D structure of grain boundary networks allows for the sound understanding of material microstructure. This is because grain/phase boundaries have a significant effect on material properties.

Yet, direct access to grain boundary network is difficult to obtain. Grain boundaries are usually revealed as line traces within the planar sections of the microstructure. Techniques for analysing grain boundary distributions require determination of grain shape and grain boundary plane normals. Techniques such as the computer integrated polarization microscopy (CIP) [181], three dimensional x-ray diffraction microscopy (3DXRD) [182], differential aperture x-ray microscopy (DAXM) [183] and serial sectioning combined with EBSD have been employed in direct study of grain boundary network analysis.

Grain boundaries are specified via five independent parameters. Three parameters define the misorientation (Δg) between grains adjoining the boundary. The latter two define the orientation of the boundary plane normal ($\mathbf{n}$). Lattice misorientation is easily determined via 2D EBSD. However,

direct measurement of boundary plane orientation is more difficult. Studies have been carried out for grain boundary distribution using serial sectioning in tandem with EBSD [184, 185] and x-ray diffraction tomography [186]. The five grain boundary parameters can instead be statistically evaluated with the use of EBSD.

4.2.2 Grain Boundary Plane Distribution

Distribution of grain boundary planes (GBPD), $\lambda(\mathbf{n})$ is given as a function of the grain boundary plane normal, $\mathbf{n}$. A grain can be modelled as a volume covered with surfaces that are either faceted or curved. These surfaces can be approximated to be made of triangular tangent planes each of distinct orientation. This is shown in figure 4.1. Therefore, a grain can be estimated to be a polyhedral volume covered in faceted planes. The boundary plane normal $\mathbf{n}'_{ij}$ is then described in terms of the triangular tangent edge vectors $\mathbf{r}$, other than the boundary trace vector $\mathbf{l}'_{ij}$ as in equation 4.1 for an i^{th} grain and j^{th} facet.

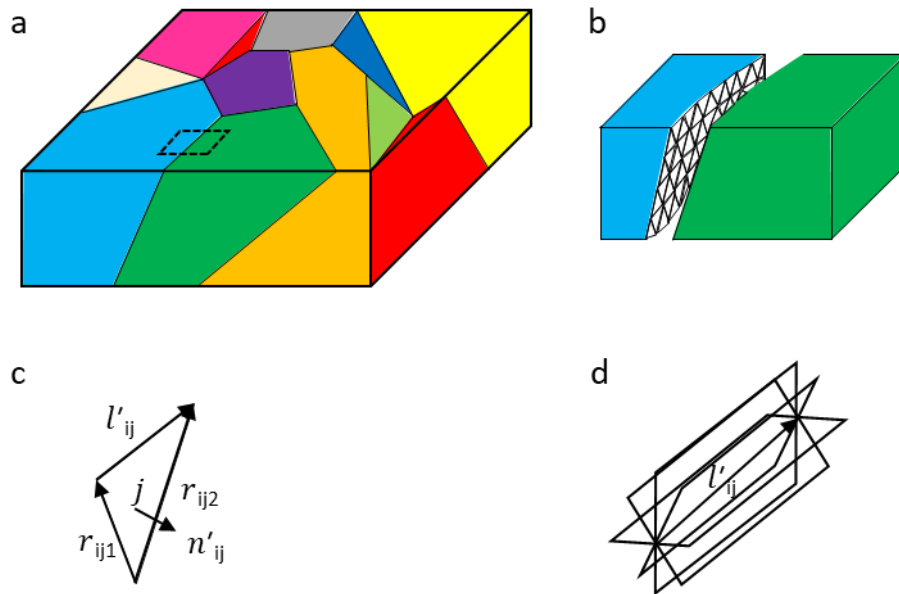


Figure 4.1: Schematic of (a) a polycrystalline sample, (b) selected boundary from the polycrystalline sample showing internal grain interfaces approximated as triangular facets (c) a triangular tangential facet at a grain boundary and (d) potential habit planes about a boundary trace $\mathbf{l}'_{ij}$ [1].

$$\mathbf{n}'_{ij} = \frac{\mathbf{r}_{ij1} * \mathbf{r}_{ij2}}{|\mathbf{r}_{ij1} * \mathbf{r}_{ij2}|} \quad (4.1)$$

Euler angles, φ_1 , Φ and φ_2 specify grain orientations. These describe a series of rotations required to transform from the sample reference frame to the crystal reference frame. The transformation is facilitated via the rotational matrix, $g(\varphi_1, \Phi, \varphi_2)$. So, the triangular tangent normal, $\mathbf{n}_{ij}$ in the sample reference frame is given as,

$$\mathbf{n}_{ij} = g\mathbf{n}'_{ij} \quad (4.2)$$

The number of symmetry operators in the crystal system of the material being studied is important for grain boundary statistical analysis. For reference, WC has a HCP crystal structure with six symmetry operators. If the crystal system has M symmetry operators, there will be M indistinguishable vectors for each triangular tangent normal, $\mathbf{n}_{ij}$ in the crystal reference frame. These equivalent vectors are given as,

$$\mathbf{n}_{ij} = C_m g \mathbf{n}'_{ij} \quad (4.3)$$

Where C_m are the symmetry operators of the crystal system.

2D EBSD does not provide direct access to the boundary planes as mentioned earlier. It instead gives information about the boundary trace. However, one can determine a set of possible habit planes (triangular tangential facets) for a given boundary trace from the following criterion.

$$\mathbf{l}'_{ij} \cdot \mathbf{n}_{ij} = 0 \quad (4.4)$$

This is to say the plane normal of the real boundary plane must be perpendicular to the boundary trace. This gives a set of possible boundary habit planes about the boundary trace that fulfil the above criterion. An example of a set of planes that satisfy the above criterion for a given boundary trace are illustrated in figure 4.1(d).

All possible $\mathbf{n}$ can be separated into discrete cells based on the two spherical angles θ and φ that define them onto the surface of a unit sphere. In other words, possible grain boundary plane normals for all boundary traces can be mapped onto a unit sphere. This is illustrated in figure 4.2(a). Out of the planes that satisfy the criterion presented in equation 4.3 for a given boundary trace, the probability of sampling planes perpendicular to the sample planar section is greater than those parallel to the surface when producing a GBPD. Spherical angles, θ and φ are in the range of 0 to $\pi/2$ and 2π respectively. The spherical angles are parameterised by $\cos(\theta)$ and φ so that each cell on the surface of a unit sphere will have the same area. This is convenient since each cell has an equal area, each cell has the same probability of being populated by a random grain boundary plane.

GBPD is determined by first adding the area of potential triangular tangential boundary planes for each boundary traces into a cell on a unit sphere depending on the orientation of the plane. Each area is included $M/2$ times: M times due to the number of crystal symmetries and a factor of $1/2$ as GBPD is plotted as a stereographic projection of the upper hemisphere of the unit sphere. Finally, the area in each cell is divided by the average area for a cell.

The units of the normalised area are given in multiples of random distribution (MRD) [187]. A value of MRD equal to unity will mean a random plane distribution. A high or low likelihood of grain boundary plane occurrence is implied if the MRD is less than or greater than unity respectively.

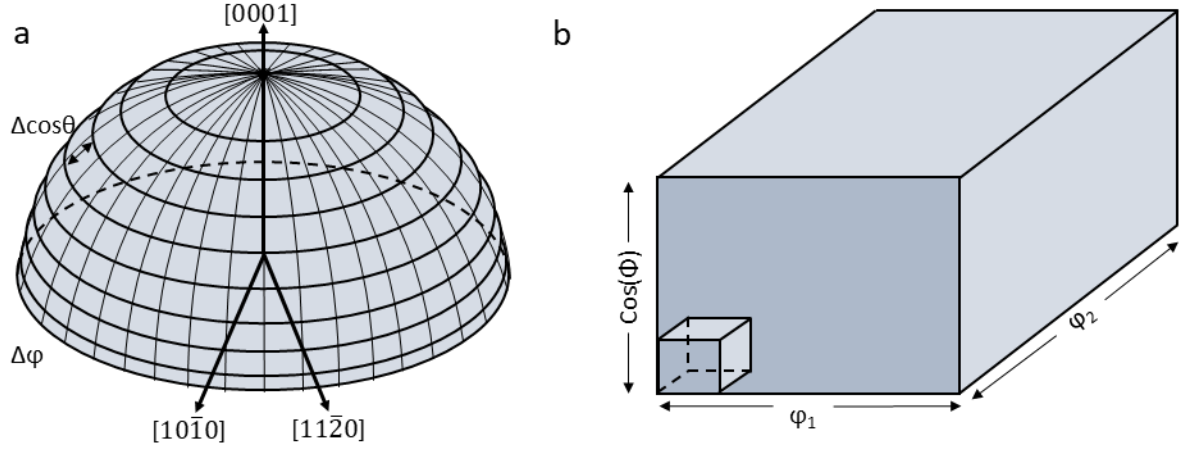


Figure 4.2: (a) An illustration of all possible $\mathbf{n}$ parameterised by spherical angles (θ and ϕ) into cells of equal area onto a hemisphere. (b) Depiction of misorientation parameterised by Euler angles (ϕ_1 , Φ and ϕ_2) into cells of equal volume rectangular parallelepiped [1].

4.2.3 Grain Boundary Character Distribution

Grain boundary character distribution (GBCD), $\lambda(\Delta g, \mathbf{n})$ is a five-parameter distribution that is defined as the area of the boundary planes with orientation $\mathbf{n}$ normalised with respect to average area per orientation [1]. GBCD allows for representation of relative proportions of boundaries of unique character as a function of grain boundary misorientation (Δg) and boundary plane normal orientation [177]. Δg is given as in equation 4.5 where g_1 and g_2 are orientations of the grains on either side of the boundary. Then, misorientations with respect to each grain will be given as in equations 4.6 and 4.7.

$$\Delta g = g_1 g_2^T \quad (4.5)$$

$$\Delta g = C_{P1} g_1 (C_{P2} g_2)^T \quad (4.6)$$

$$\Delta g = C_{P2} g_2 (C_{P1} g_1)^T \quad (4.7)$$

Where $P=M/2$ (number of symmetry operators). This leads to $2.P^2$ equivalent misorientations for both crystals. Therefore, for each indistinguishable Δg , a new equivalent boundary plane normal will be produced as shown in equation 4.8 and 4.9 for each grain.

$$\mathbf{n}_{ij} = C_{p1} g_1 \mathbf{n}'_{ij} \quad (4.8)$$

$$\mathbf{n}_{ij} = C_{p2} g_2 \mathbf{n}'_{ij} \quad (4.9)$$

Finally, arbitrary choice of the direction of the plane normal into one of the grains will increase the number of equivalent boundary planes by a factor of two. Hence, a triangular boundary facet produces $2.2.P^2$ symmetrically equivalent boundaries.

GBCD is represented by discrete sets of grain boundaries like representing GBPD as distinguished sets of plane normals. Spherical angles θ and ϕ producing all possible values of $\mathbf{n}$ are again parameterised in accordance with the convention mentioned in the GBPD section. Misorientation as with orientation is specified by the Euler angles, ϕ_1 , Φ and ϕ_2 in the range of $0-2\pi$, $0-\pi$ and $0-2\pi$ respectively. These are parameterised by ϕ_1 , $\cos(\Phi)$ and ϕ_2 . The misorientation parameter range and in turn domain size depends on the crystal symmetry. A misorientation sub-domain with reduced parameter ranges will remove some degeneracy associated with symmetrically associated boundaries.

Cells containing parameterised plane normals can be visualised as polygonal structures on the surface of a unit sphere as detailed in the previous section. In contrast, cells of Δg can be pictured to be rectangular parallelepiped volumes within a larger parent rectangular parallelepiped as shown in figure 4.2(b). The total volume of the rectangular parallelepiped has dimensions of the earlier specified misorientation parameter ranges. These cells are of equal volume when the orientation parameters are equally divided.

Reducing the size of discrete cells in the misorientation space increases the number of distinguishable boundary types. In other words, increase in the angular resolution of the Euler angles and spherical angles for specification of misorientation and boundary plane normal increases the number of unique boundary types identified. The total number of distinguishable boundaries is approximately given by equation 4.10.

$$N = \frac{8\pi^5}{4P^2\Delta^5} \quad (4.10)$$

Where the total volume ($8\pi^5$) is divided by volume of a single resolved boundary (Δ^5). Δ is the resolution of the five angular parameters. Grain boundary properties have been shown to vary over intervals smaller than 10° [177]. However, measuring the five parameters with an accuracy greater than 10° requires large number of measurements. The distribution of grain boundary planes (GBPD) can be plotted for specific misorientations to represent the GBCD. Misorientations are typically represented as an axis-angle pair [188].

5 Materials and Methods

5.1 Manufacture of WC and WC-Co Samples

This chapter describes the production routes used for production of samples examined in the study as well as the material characterisation techniques that were employed.

In brief, WC single crystals and cemented carbide polycrystalline samples used in this study were provided by the National Physical Laboratory (NPL) and Sandvik Hardmaterials respectively. Liquid phase sintering was used to produce these samples. Later samples were metallographically prepared for electron microscopy analysis and micromechanical testing to collect data which focussed on understanding: grain boundary character and double cantilever beam-based micromechanical fracture analysis.

5.1.1 Production of WC Single Crystals

Larger WC single crystals were used to enable fabrication of several micro-scale DCBs from each crystal to enable measurement of the surface energy of type II $\{10\bar{1}0\}$ planes. The large crystals were prepared with a polished surface with the $[0001]$ pointing outwards in the sample reference frame, thereby enabling fracture of the type II $\{10\bar{1}0\}$ planes.

Gary Sweetman from Sandvik Hardmaterials (Coventry, UK) and Helen Jones from the NPL prepared the WC single crystals used in this study. The WC single crystals were grown on the walls of a sintering furnace at Sandvik Hardmaterials (Coventry, UK). WC crystal growth was unintentionally uninhibited leading to large crystal formation.

5.1.2 Production of WC-Co Polycrystalline Samples

WC-Co polycrystalline samples were produced for grain boundary character analysis and determination of $\Sigma 2$ twist boundary energy. Co was used as the metal binder of choice in the production of the cemented carbide samples.

Susanne Norgren from Sandvik Hardmaterials (Stockholm, Sweden) and Lund Technical University manufactured the WC-Co polycrystalline samples used for this project. The polycrystalline samples were prepared using conventional powder metallurgy routes. Initially, pure WC and Co powders were mixed by milling in ethanol-10% H_2O (milling aid). An extra coarse WC powder of 15 μm Fisher Sub Sieve grain size (FSSS) from Wolfram Bergbau und Hütten AG, Co from Freeport Cobalt and polyethylene glycol as pressing agent were used in the milling stage. The powder mixture was milled for 4 h in a WC-lined 0.25 l rotating mill. The coarse WC powder and relatively short milling time ensured the formation of large WC grains. Thereafter, the powder mixture was dried at 40 °C in a N_2 atmosphere. This was followed with powder mixture being uniaxially pressed into a rectiliner (SNUN) geometry. The green bodies were then subject to de-waxing in a H_2 atmosphere at 450 °C to remove

the polyethylene glycol. Finally, the resulting green bodies were sintered at 1500 °C in controlled vacuum. A second set of samples were manufactured in a similar fashion with 1wt% Cr doping. Details of the samples manufactured for this work are provided in table 5-1.

Table 5-1: Details of the WC-Co polycrystalline samples manufactured for study in the project.

Sample	Carbon (wt%)	Cobalt (wt%)	Chromium (wt%)	Phases
Designation				
Standard	5.41	10	0	WC+Co
Chromium doped	5.41	10	1	WC+Co+ Cr ₇ C ₃

5.2 Sample Mechanical Polishing

5.2.1 Introduction to Polishing

Polishing is essential for preparing samples with surfaces ideal for electron backscatter diffraction (EBSD) data acquisition. This is because EBSD is highly surface sensitive: the quality of data acquired is directly related to the level of surface finish. EBSD is typically performed at high sample tilt and accelerating voltages of 15-30 kV. For these experimental conditions, the electron backscatter pattern (EBSP) is generated from an information depth of around 10-50 nm based on the material and the accelerating voltage [189, 190]. Hence, it is critical to minimise the surface damage caused by sample preparation and can reduce the quality of the EBSPs (e.g., due to rotation gradients within the interaction volume from the presence of dislocations within a layer of sample preparation induced cold work). Degraded EBSPs are challenging to routinely index and the orientation precision is reduced.

Therefore, the main aim of the polishing step is to produce a clean surface with minimal deformation and contamination. There are several polishing techniques available for sample preparation: mechanical polishing, electro-polishing, chemical polishing, fracturing and ion beam techniques. Choice of polishing technique is critical as different materials respond differently. In addition, composite materials polishing has further complexities owing to distinct phases wearing off at different rates during polishing.

The WC-Co polycrystal material is challenging to polish as the two phases have different hardness values, which can lead to preferential removal of one phase over the other; and the Co can phase transform. Following prior experience in the research group and my own experiments, I have used a combination of mechanical polishing followed by ion beam polishing.

5.2.2 Theory of Mechanical Grinding and Polishing

The original cut section of a sample is typically chosen for grinding and polishing. The surface is then ground to remove the effects of sectioning. Grinding is an abrasive process like cutting that involves

the use of a grinding wheel made of abrasives and a bonding material. Grinding is carried out wet like cutting. Wet grinding serves two purposes: keep the heating of the sample to a minimum and remove debris resulting from grinding. Grinding wheels used for successive grinding steps have finer abrasive grit. This means damage produced in each of the grinding steps is removed via subsequent steps. Additionally, depth of damage reduces with decreasing abrasive grit size. Depth of damage introduced corresponds to the hardness of the material. Hence, as mentioned earlier in a ceramic composite such as WC-Co, the two phases will be unevenly ground.

Polishing is similar to grinding with the main difference being that the medium holding the abrasives is capable of higher shock absorbency. In other words, grinding uses fixed abrasives while polishing uses free abrasives. Shock absorbency refers to the ability of the medium to allow abrasives to move and follow the sample surface morphology. Free abrasives are suspended in a lubricant on a cloth during polishing that allows them to slide between sample-specimen surfaces. As in grinding, polishing steps start with the coarser abrasives and end with of finer abrasives.

The choice of the polishing cloth is just as vital as the abrasives themselves. A soft polishing cloth allows for greater shock absorbency which results in minimal surface damage. Yet, the minimal damage is at the cost different areas being abraded at different rates leading to surface relief. In contrast, hard cloths produce flatter surface with the drawback of leaving behind polishing damage such as scratches. Nylon cloths and oil-based polycrystalline diamond suspensions were employed during the polishing stage in this work.

5.2.3 Sample Polishing Procedure

The polycrystalline WC-Co samples were prepared in the following manner. First, polycrystalline samples were cut into 10x5x5 mm³ cuboid pieces using a Buehler Isomet 5000 Linear Precision Saw. A low concentration diamond bonded cut-off wheel was used for cutting samples. Then, the samples were embedded onto an epoxy cold-mounting resin system.

On the other hand, WC single crystals were mounted with the aid of a resin onto a Gatan disc grinder, as the WC crystals were too small for embedding in cold mounting.

Samples were ground and polished using a Beuhler EcoMet™ 250 grinder-polisher. Hardness of an abrasive needs to be multiple times higher than that of the material to be polished in accordance with Rabinowicz' criterion [191]. Given that WC has a high hardness of 2800-3500 HV, conventional abrasives such as silicon carbide (2400-2800 HV) are not suitable for polishing. Thus, diamond was used for polishing.

In this work, resin-bonded diamond grinding discs were used for grinding. To remove damage produced in each of the grinding steps, the size of the grinding media was gradually reduced from 500 to 4000 grit (see table 5-2). Polishing was performed with a nylon cloth and a diamond suspension,

starting with a 3 μm diamond slurry and finishing with 0.25 μm diamond slurry in an oil-based suspension (see table 5-2).

Table 5-2: Recipe used for grinding and polishing of WC-Co samples.

Grinding wheel/Polishing Cloth	Grit Size	Diamond Particle Size (μm)	Time (min)
Resin-bonded	500	30.2	20-30
diamond grinding discs	1200	15.3	4
	2000	10.3	4
	4000	5	4
Nylon cloth		3	4
		1	4
		0.25	4

Since carbide grains are brittle, significant plastic deformation does not occur within carbide grains during polishing. Scratches are the only polishing artifacts that are typically observed on carbide grains. In comparison, cobalt ligaments tend to sustain significant surface damage. Additionally, mechanical grinding and polishing leaves behind a ~ 100 nm amorphous layer, the Beilby layer [192]. These artifacts lead to diffuse EBSPs. Different material removal rates of the two phases also gives rise to strong surface topography. SEM image of a WC-Co sample surface depicting these issues is shown in figure 5.1.

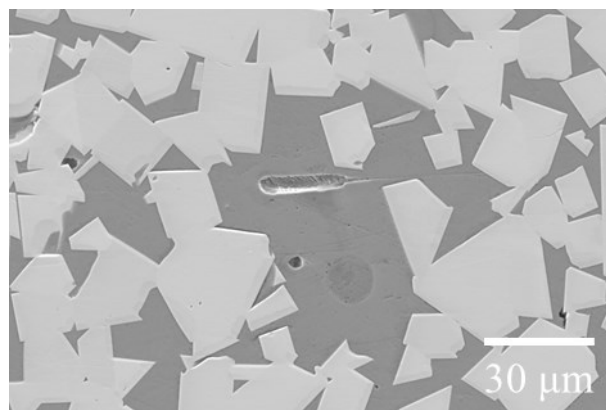


Figure 5.1: SEM image of a mechanically polished WC-10wt%Co sample depicting damaged cobalt ligaments.

5.3 Ion Beam Polishing

5.3.1 Introduction to Ion Beam Polishing

To overcome residual artifacts introduced from mechanical grinding and polishing, ion beam polishing was used. The process involves material sputtering of atoms from sample surface via ion

bombardment. Incident ions transfer energy to target atoms during collision. Target atoms escape the surface provided that they receive sufficient energy. Hence, material removal rate, i.e., sputter yield is dependent on the binding energy of target atoms and the energy density afforded by the ion beam [193]. Energy density in turn is a function of mass and energy of the ion beam as well the angle of the beam with respect to the sample. Material removal rate is dictated by voltage, ion gun current and sample material. For WC-Co polycrystals, it was found that the best EBSD quality is obtained at small ion gun tilt angles, low voltages and low currents for longer durations.

Two types of ion beam polishing techniques are possible. First is the use of inert gases such as Ar^+ or Xe^+ in glancing/ near parallel beam formation- broad ion beam (BIB) milling [194]. Second is the use of focused ion beam (FIB) liquid metal ion source setup, typically with Ga^+ [195]. Additionally, either of these techniques can be operated at low (0.1-2 keV) or high energies (2-20 keV). Higher beam energies impart more energy to the surface causing more damage to the surface. Therefore, initially higher energies are used for removing artifacts from mechanical polishing finishing off with lower energies for superior surface quality.

The main limitation of FIB milling (30 kV Ga^+ ion) is the damage imparted on the sample's crystalline structure. The damage can be in the form of Ga^+ ion implantation [196]. Ion implantation is the capture of Ga^+ ions within the crystal lattice. This leads to crystal defects such as vacancies and dislocation loops [197]. Amorphization can also occur within the sample crystal structure due to ion implantation [198]. Broad ion beam milling overcomes these issues and as the name suggests is applicable over a wider surface area compared to FIB milling.

5.3.2 Sample Preparation of WC-Co with Ion Beam Polishing

This work made use of Gatan PECS II, an automated Ar^+ ion polishing system for the final polishing step [199]. The ion polisher employs two miniature Penning ion guns (PIGs) that use an Ar gas source. The two PIGs can traverse independently within an operating angle range of 0° - 18° . The sample stage can rotate at a rate of 0.5-6 rpm. PECS II can deliver a beam energy of up to 8 keV. The PIGs were set to operate at 2° delivering a beam energy of 6 keV for 1.5 h and then 2 keV for 30 min. The sample stage was set to rotate at 6 rpm.

Figure 5.2 illustrates the difference between mechanically and ion polished surfaces from two different WC-10wt%Co sample surfaces. The two surfaces look similar in secondary electron imaging (Figure 5.2(a) and (b)) but more subtle variations can be seen in forescatter (Figure 5.2(c) and (d)) imaging and EBSD measurements (figures 5.2(e)- 4.2(h)). Forescatter electron images reveal subtle variations in surface topography, Z-number and crystalline defects [200]. Therefore, forescatter electron images highlight residual scratches and preferential milling of the two phases for the mechanical polishing in Figure 5.2(c), which is improved after BIB polishing as seen in Figure 5.2(d).

This improvement is reflected also in the EBSD mapping, where the BIB polishing shows greater indexing success (specifically of the Co binder) as well as a reduction in the number of residual scratches in the WC grains.

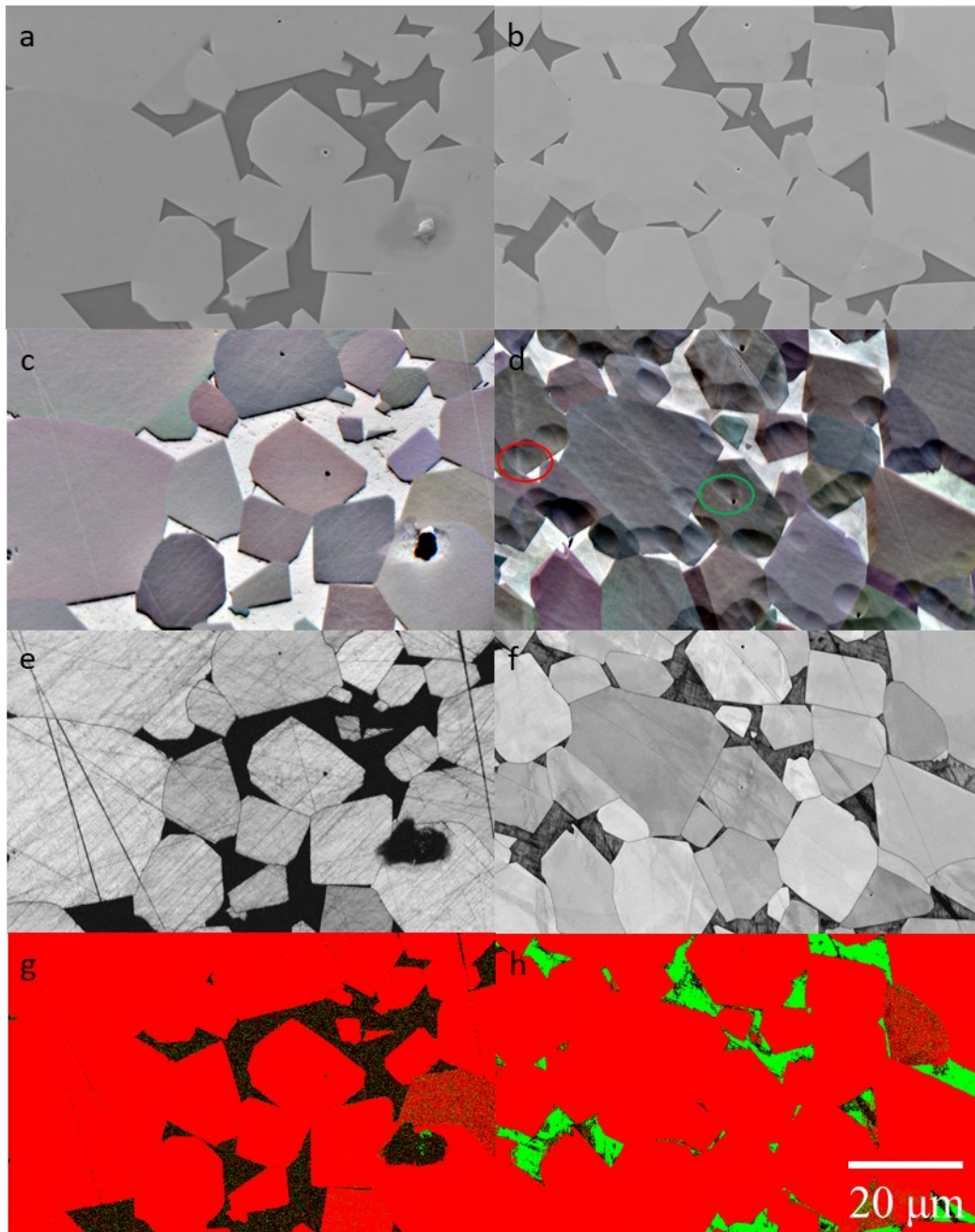


Figure 5.2: SEM, backscatter, IQ and phase maps of (a), (c), (e), (g) mechanically polished and (b), (d), (f), (h) ion polished surfaces of a WC-10wt%Co sample. Ripple effect arising from BIB at a phase boundary and a pore are highlighted with red and green ellipses respectively.

The curtaining effect observed on the surface of carbide grains in figure 5.2(d) is a consequence of the pre-existing artefacts from mechanical polishing. Mechanical polishing leaves behind a surface with protruding carbide grains and sunk-in Co pools. The ion beam glances the sample surface at a shallow

angle of 2° . As the beam impinges on the Co pools near the phase boundaries, reflected and backscattered ions strike the protruding carbide grains. So, material is sputtered away from carbide grains at all phase boundaries given that the sample also rotates. This leads to ripple like structures observed near the phase boundaries. Ripples are also observed at the location of pores. This is due to the ion beam sputtering material away from the walls of the pores. These processes are illustrated in figure 5.3.

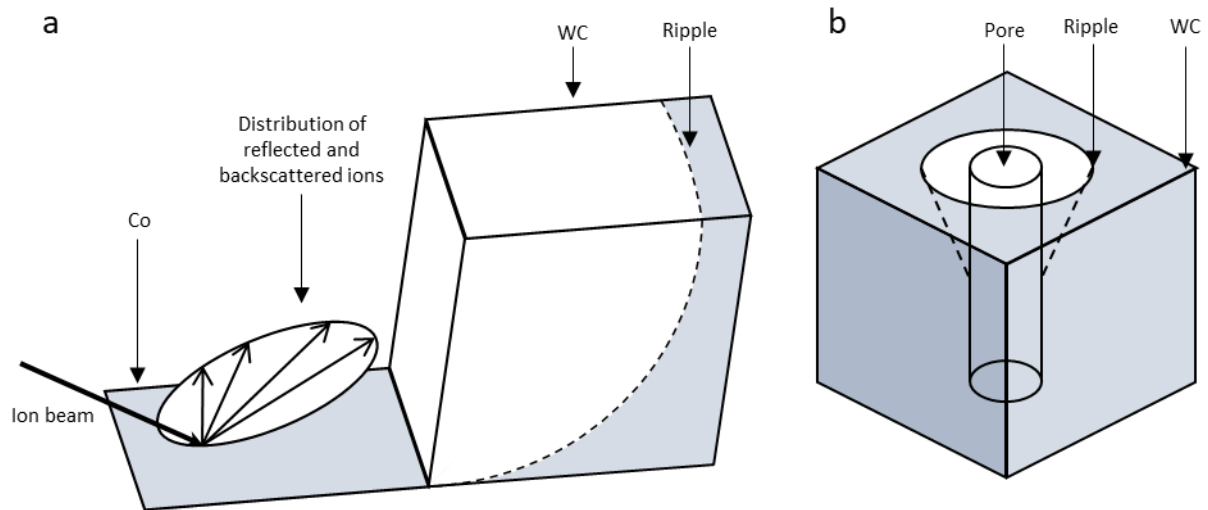


Figure 5.3: Illustration of the ripple effect observed (a) at the edge of a phase boundary and (b) one observed near a pore.

Image quality (IQ) maps of the mechanically and ion polished samples in figures 5.2e and 5.2f show further differences. An IQ map reveals information regarding the image quality or sharpness of the acquired EBSP at each point on the sample surface [201]. In essence, each point contains information regarding measure of the contrast between Kikuchi pattern and the background noise—band contrast. This information is used to plot a map of the scanned area as a grayscale image. The sharper the EBSP from a point, the higher the grey scale of the pixel corresponding to the point [202]. Contrast in IQ maps arises from features such as phase, topography, and strain that affect EBSP quality. Thus, IQ maps can show microstructural features invisible to optical and SEM images such as grain boundaries and surface damage. The IQ map of the mechanically polished sample shows that there are several scratch marks on the carbide grains, and Co pools have extremely poor band contrast owing to heavy deformation. In contrast, carbide grains on the BIB polished sample surface are scratch free and Co pools have a relatively low surface damage as indicated via higher grey scale.

These observations are further backed by phase maps presented in figures 5.2(g) and 5.2(h). Cobalt pools and the scratch marks on the carbide grains are revealed as non-indexed EBSD data points in the mechanically polished surface. On the other hand, most points are indexed on the BIB polished sample. Finally, EBSPs from carbide grains and cobalt pools in figure 5.4 illustrate the benefits of using BIB polishing as the final sample preparation step. EBSP from the carbide grain of the BIB polished

sample is sharper than that observed for the mechanically polished one. The difference is even more pronounced in the case of the Co where the EBSD is completely absent for the mechanically polished sample.

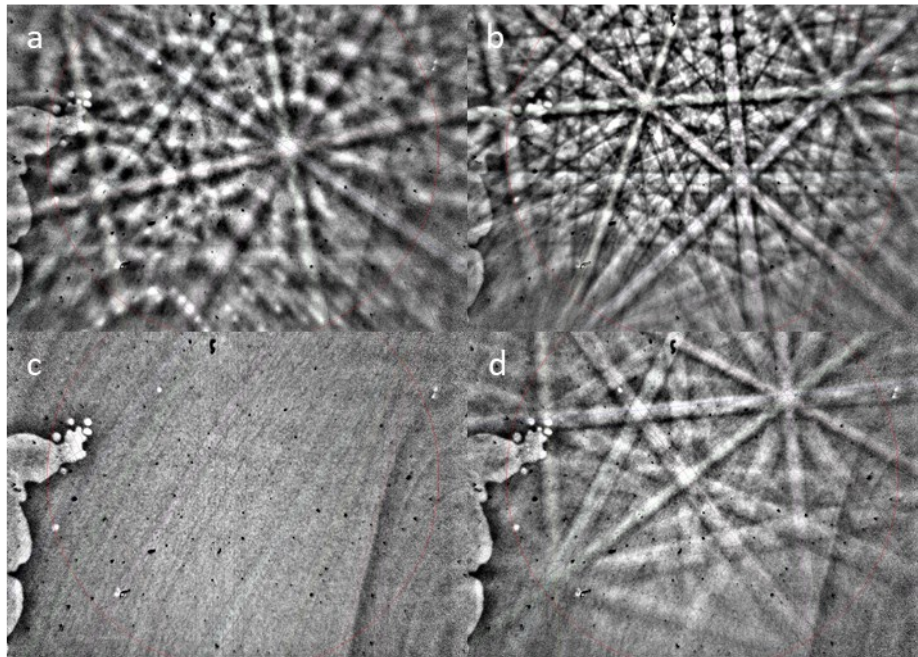


Figure 5.4: EBSD of a WC grain from (a) a mechanically and (b) a ion polished sample. EBSD of Co pool from (c) a mechanically and (d) a BIB polished sample. The artifact observed on the left edge of all EBSDs presented here is believed to be the result of potentially dirt on the phosphor screen of the EBSD detector during data collection.

5.4 EBSD Characterisation of WC-Co

5.4.1 Introduction to EBSD

EBSD is a technique employed in SEM to investigate crystallographic information of a given material. It allows one to relate the crystallographic texture, spatial distribution of crystallographic orientation, with the microstructure to obtain valuable information. EBSD also provides nearest neighbour misorientation called the microtexture. Both the texture and the microtexture affect the mechanical properties of polycrystalline materials. Thus, EBSD being capable of measuring such properties makes it a highly useful technique in the characterisation toolbox.

The schematic for the process for forming EBSDs is shown in figure 5.5. An electron beam probe (~ 20 kV) is scanned across a highly tilted sample (60° - 80°) [203]. Backscattered electrons from the sample are captured by a detector comprising of a planar scintillator screen (phosphor) attached to either a charge coupled device (CCD) detector [204] or complementary metal oxide semiconductor detector. The projection on the scintillator screen is gnomonic in nature [205]. Thus, the image is highly distorted near the edges and the corners. Typically, for EBSD analysis, the chamber is configured to enable analysis at a working distance of ~ 15 mm with a similar sample-detector distance.

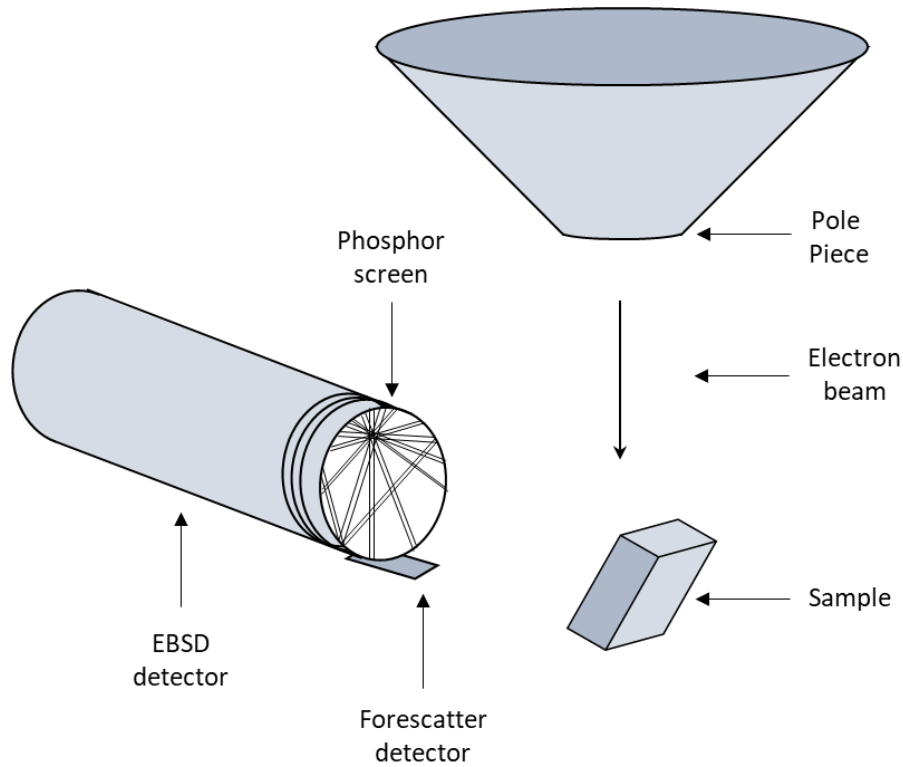


Figure 5.5: Schematic of the setup used for EBSD data collection inside the SEM sample chamber.

5.4.2 Theory of EBSD

EBSD requires a double scattering event within the sample for EBSD to be produced [206]. Formation of a coherent and divergent virtual source within the sample through a quasi-elastic scattering is the first scattering event. The second scattering event is when the electrons re-scatter at the atomic planes and are reflected out of the sample.

Sample tilt during EBSD data acquisition is crucial. This is because sample tilt increases the interaction volume of the primary electron beam with the sample during the first scattering event, reduces the path length of the electrons escaping from the sample after diffraction and improves the backscattered yield during the second scattering event: enhancing the signal to noise ratio (SNR) [207]. Even though increasing the tilt angle improves the SNR, the lateral resolution diminishes as a result. So, sample tilt angles in the range of 60° - 80° are used.

The EBSDs consist of bands of varying intensity—Kikuchi bands. The Kikuchi diffraction of electrons occurs in a similar manner to the Kossel diffraction of x-ray. Incoming primary electrons are (near) elastically scattered out of the sample and appear to come from a virtual source due to the double scattering event as explained earlier. Figure 5.6 shows the geometry of Kikuchi band formation. These are in the form of Kossel diffraction cones that intersect with the plane of the detector. Electrons that arrive to the reflecting planes at angles of θ_{hkl} are reflected into two Kossel cones separated by $2\theta_{hkl}$ which then cut the plane of the observation producing the Kikuchi lines separated by an angle of $2\theta_{hkl}$.

[208]. The lines despite appearing to be straight are truly curved and are hyperbolae due to the nature of the Kossel cones. The lattice plane spacing d_{hkl} is the sole factor that determines the width of the Kikuchi bands for a given energy of diffracting electrons.

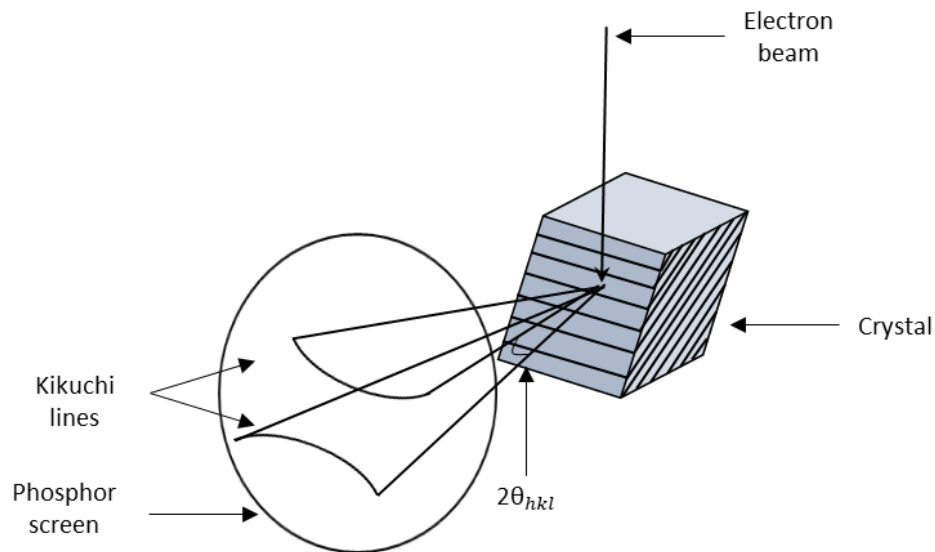


Figure 5.6: Illustration showing the primary electron beam interacting with a lattice plane producing Kossel cones which when intersecting the phosphor screen forming the Kikuchi lines found in the EBSP.

First order Kikuchi lines found in EBSPs are from low index planes (e.g. (0001) and $(10\bar{1}0)$) and these tend to appear diffuse and broad [209]. The maximum of these lines lies outside the exact Bragg position. The first order lines may appear brighter or darker depending on the specimen thickness: these are referred to as excess or deficit Kikuchi bands [210]. The Kikuchi bands appear darker than the background beyond a certain thickness and show broad intensity peaks outside the first order lines. In contrast, Kikuchi lines of high order index reflections are sharp and lie near their Bragg's position. Typical EBSPs contain Kikuchi lines from low order planes superimposed with high order ones. A Kikuchi line pair is symmetrical with the same intensity if the incident beam is directed parallel towards the corresponding reflecting plane [211]. Complementary excess and deficit line pairs are produced when the incident beam is not parallel to the specimen. EBSPs tend to be non-uniformly illuminated. This is due to three main contributing factors: inverse square distance effect, lens vignetting/light fall-off (darkening of the corners of the image compared to the centre) and finally variation in the backscattered electron signal with Bragg's angle [205].

5.4.3 Indexing of EBSPs

Once EBSPs are acquired from a sample region of interest, EBSPs are indexed. Kikuchi pattern geometry in a EBSP is unique to a crystal structure (phase) and lattice orientation. As phases constituting a sample are known prior to EBSD data acquisition, the correct phase out of the known phases and the orientation must be attributed for a given EBSP and thus the corresponding data point.

Unlike a human eye, pattern recognition routines in commercial image analysis software cannot easily distinguish lines in a diffuse or noisy images. This is even more problematic for detecting Kikuchi lines in a EBSD where lines can be diffuse with non-uniform intensity distributions in a noisy background. So, a Hough transform is typically applied to EBSDs to circumvent the issue in indexing patterns.

Hough transform converts lines (Kikuchi bands) from image space into points in Hough space. Relationship between coordinates in the image space (x, y) and coordinates in the Hough space (ρ, θ) are given as in equation 5.1.

$$\rho = x \cos \theta + y \sin \theta \quad (5.1)$$

Straight line in the image space can be characterised by ρ , the perpendicular distance from the line to the origin, and θ , the angle made by the line corresponding to this distance, and the x axis in image space. This Hough transform procedure is illustrated in figure 5.7.

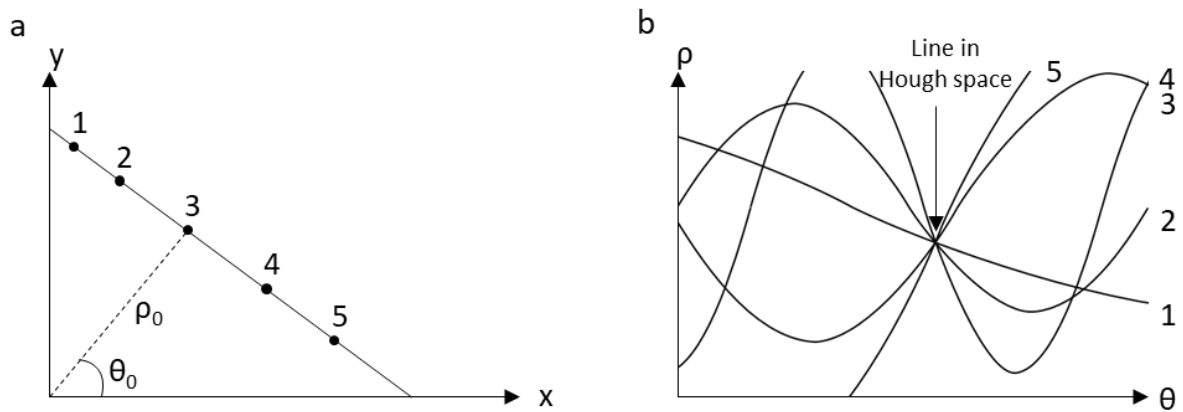


Figure 5.7: An illustration showing the use of the Hough transform to convert (a) a line image space into (b) a point in Hough space. Five points along the line in the image space have been converted to sinusoidal curves in the Hough space. The point where the sinusoidal curves converge in the Hough space correspond to the line in the image space.

In essence, individual pixels from each EBSD in image space are transformed into sinusoidal curves in Hough space. The intensity of pixels that constitute a sinusoidal curve in Hough space are augmented based on the intensity of the corresponding pixel in image space. For pixels from a single line (co-linear pixels), corresponding sinusoidal curves intersect to form a spot (such as in the case of pixels from a Kikuchi band). The EBSD software detects these spots in the Hough space owing to their higher intensities compared to the background. The intensities at these spots are higher due to two interlinked reasons. Firstly, the sinusoidal curves corresponding to pixels from Kikuchi bands have a higher intensity than pixels from other areas in an EBSD. Furthermore, the intensities of the sinusoidal curves are added at the location of intersections.

The high intensity spots detected in Hough space by the EBSD software are used to generate a list of detected band positions. The Kikuchi band positions are then used to reproduce EBSDs from which angles between detected bands are calculated. Subsequently, by comparing the calculated angles to

interplanar angles from a look-up table, the automated commercial EBSD analysis software assigns an orientation and a phase for each data point in an EBSD map.

5.4.4 Orientation

Orientation is the passive set of rotations required to bring a crystal in the sample reference frame into coincidence with the crystal reference frame. Most commercial EBSD systems including the Bruker system employed in this work utilise the Euler angle convention to define the orientations. In the Euler angle convention, rotations are performed about the z axis followed by a rotation about the rotated x axis (x') and then finally a rotation about the rotated z axis (z''). The Euler angles used for the rotations are φ_1 , Φ and φ_2 with the limits of $0 \leq \varphi_1 < 2\pi$, $0 \leq \Phi < \pi$ and $0 \leq \varphi_2 < 2\pi$. The Euler angle convention is visualised in figure 5.8.

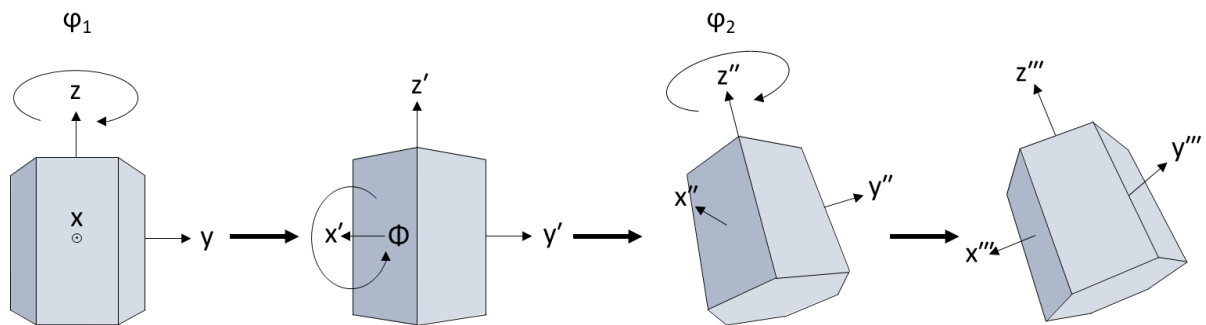


Figure 5.8: A schematic of the Euler angle convention used to transform a crystal from a sample reference frame to a crystal reference frame. Rotations are performed about z , x' and z'' axes consecutively. Crystal orientation has been represented with a hexagonal prism.

5.4.5 Representing Orientation

To visualise orientation for an EBSD mapped region from a sample, one common approach is to assign colour to each orientation. Simplest approach is to assign the Euler angles the RGB values of colour. This produces the so-called Euler coloured maps. Euler coloured maps represent grains in a map of crystallographically equivalent orientations to have the same colour and those of different orientations to have dissimilar colours. But the approach to representing orientation suffers from one major downside: small changes in orientation are not necessarily represented via small changes in colour scale. The alternative and conventional approach is to map orientation to colours based on inverse pole figures (IPF) to overcome this limitation. Colours are assigned to each of the directions in the fundamental zone of the inverse pole figure, to represent orientation in the IPF maps.

5.4.6 EBSD Data Acquisition

In this project, EBSD data were acquired using a Bruker High Resolution e-FlashHR detector attached to a FEI Quanta 650 FEG-ESEM or a ZEISS Sigma 300 FE-SEM microscope. An acceleration voltage of 20 kV was used for data acquisition. Samples were tilted by 70° with respect to SEM stage with a

working distance and sample-detector distance of ~ 15 mm. An EBSD detector tilt of 9° was used in this work. EBSPs were acquired at a 320×240 pixel resolution with an exposure time of ~ 10 ms. Step size was typically about ~ 0.4 μm .

5.5 Focussed Ion Beam Sample Fabrication

FIB milling is used for precise fabrication of 3D micro-/nano-structures. The technique is analogous to SEM with the use of high mass ions such as Ga^+ in place of electrons. FIB is an inherently destructive process as ion bombardment of the surface results in the atomic sputtering of surface atoms. Sputtered atoms are projected towards the FIB column or normal to the sample surface and towards the FIB column depending on the ion beam source being at normal or oblique incidence [212].

Sputtering in essence is an energy and momentum transfer process. The incident Ga^+ ions capture electrons from the target material and reach the surface as neutrals. Hence, charge of the ions is irrelevant. Three possible sputtering events can occur upon incident ion/neutral-sample interactions as outlined by Sigmund [193]. These are shown in figure 5.9. First of these is the single-knock-on regime. In this event, once the incident ion transfers energy to the target atoms, the target atoms undergo few further collisions. These target recoil atoms escape the sample surface if they have sufficient energy to overcome the binding energy. However, they do not have energy required to generate recoil cascades. The second and third type of events are the linear cascade and the spike regimes. In both, recoil atoms have sufficient energy to generate recoil cascades producing secondary and high-generation recoil atoms that can escape from the surface of the target material. The difference between linear cascade and spike regimes is in the density of recoil atoms within the interaction volume. In the case of linear cascade regime, the density of recoil atoms is low such that the collision between moving atoms is rare. Hence, knock-on regime is the dominant sputtering process. In comparison, most of the atoms within the so-called spike volume are in motion owing to the high density of recoil atoms.

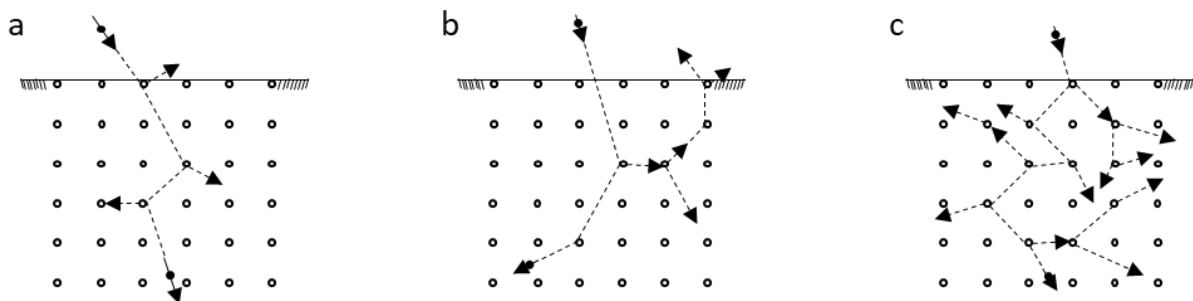


Figure 5.9: An illustration of the three types of sputtering events that can occur on ion-sample interaction: (a) single-knock-on, (b) linear cascade and (c) spike regimes. Redrawn after [213].

Several factors need to be accounted for when designing the milling steps required for DCB fabrication: acceleration voltage and beam current are the major ones. In FIB microscope, the liquid

metal flows from a heated metal source and wets a tungsten needle where an extraction voltage applied between this tungsten needle and the extraction aperture which allows the metal ions to be extracted from the needle tip via field emission [214]. A high accelerating voltage means the ions are travelling down the ion column at higher speeds which in turn leads to a greater amount of energy being imparted on the sample surface. 30 kV acceleration voltage is typically used for milling as it provides high sputtering yield and high lateral resolution [215]. Sputter yield as mentioned in the sample polishing section is a measure of the efficiency of matter removal from FIB milling. At first, sputter yield increases as the accelerating voltage is increased. However, eventually the sputter yield drops as the ions penetrate deep at higher accelerating voltages into the material: their energies are expended, and the ions are trapped within the material resulting in ion implantation [216]. Additionally, sputter yield also has an angular dependence with regards to ion beam owing to two competing effects: energy deposited on the surface and the distance travelled into the material by the incident ions and sputtered atoms respectively.

Beam current defines the beam spot size which in turn determines the resolution [217]. In other words, at lower current, matter is removed at a slower rate, imaging is possible at a higher resolution and milling at a finer quality. Higher currents are chosen if the opposite is desired. Hence, in general, initially higher currents are used to mill large amount of matter from the material with lower currents being employed near the end to produce trenches or features with finer quality.

Redeposition is an undesirable consequence of FIB milling. It occurs because of some of the sputtered material not being evacuated by the vacuum system from the SEM sample chamber and instead reattaching to the sample surface [218]. This occurs as the sputtered atoms condense back into solid phase upon collision with a nearby surface. The driving force in this case is the fact that the sputtered atoms are not in their thermodynamic equilibrium state. Sputtered matter atoms redeposit onto the edges of a trench with the amount of redeposited pile-up decreasing with distance to a given trench [219]. Height/depth ratio (aspect ratio) is crucial when considering deposition. For a 3D structure with a small aspect ratio (<1), sputtered material tends to accumulate at the bottom resulting in variation in milled depth. In contrast, sputtered material adheres to the side walls for a structure with an aspect ratio (>1). Furthermore, redeposited pileups are amorphous in nature leading to diffuse EBSPs, providing poor quality EBSD data around a FIB milled trench.

In this work, DCBs were fabricated via FIB milling using a FEI Helios Nanolab 600 DualBeam microscope. The technique established by Sernicola was referenced in this work to manufacture the DCBs [220]. Samples were tilted by 52° with respect to the SEM stage inside the Helios for the samples to be normal to the FIB column. The milling process was automated with the aid of a custom script written in Nano-builder software. The software enabled graphic drawing of the different sections of

the DCBs to be milled as different layers. Ion beam parameters necessary for milling individual layers were set separately.

Milling condition for DCB fabrication is as follows. Ion beam was operated at 30 kV. First, a fiducial cross was cut next to the region chosen for DCB milling, at a current of 1 nA. The fiducial cross was to provide a means for the Nano-builder to identify and ensure that milling is done at the intended location despite beam drift issues. A trench was cut into WC at currents of 9.7 nA, 6.5 nA and 2.8 nA respectively leaving behind a pillar. The sidewalls of the pillar were then cleaned with a 1 nA ion current. A groove for placing a wedge indenter tip was made by milling a trough at 0.46 nA onto the pillar's top surface. Finally, a notch that acts as a stress concentrator was milled at 10 pA into the groove. The resulting pillar is of the DCB geometry with dimensions of 2 μm thickness, 2 μm width and 10 μm length. The resultant surface from milling the individual steps in succession is presented in figure 5.10.

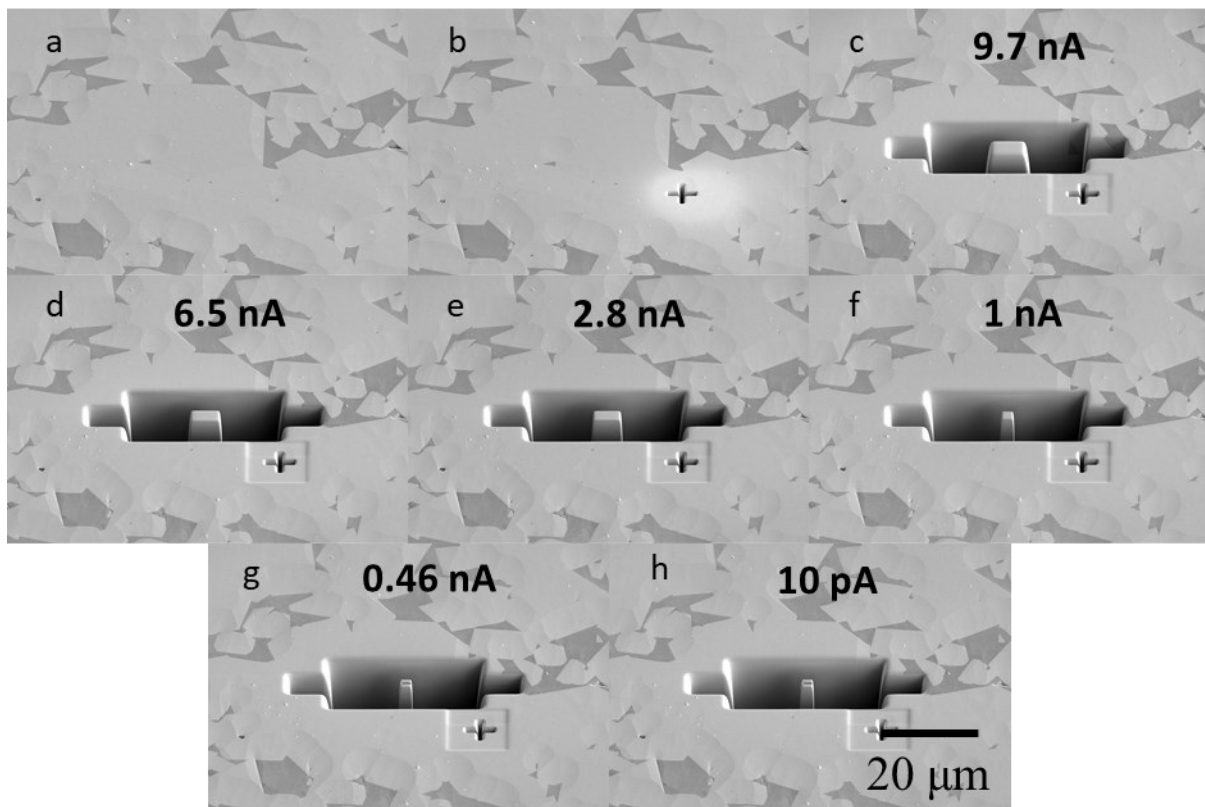


Figure 5.10: SEM images showing the evolution of the sample surface during DCB milling. (a) Image of the sample surface before FIB milling. (b) Sample surface after milling the fiducial cross in the location of interest. DCB resulting from rough milling of the trenches around the pillar at (c) 9.7 nA, (d) 6.5 nA, (e) 2.8 nA and (f) 1 nA currents. Finally, the appearance of the DCB after milling (g) a trough and (h) a notch.

5.6 Micromechanical Testing

The micromechanical fracture testing was performed using an Alemnis nanoindenter. An image of the Alemnis indenter is provided in figure 5.11. The indenter is fitted with two motors enabling the sample

movement about the plane of the sample surface and a third motor for the movement of the indenter tip. Tests were conducted with a $50^\circ/60^\circ$ cone angle $10\text{ }\mu\text{m}$ diamond wedge tip. The indenter tip was attached to the front end of the piezo stack which can move using piezo actuation enabling the wedge tip to load DCBs in direct displacement mode. Samples were attached to a rotation stage mounted onto the load cell of the indenter. The rotation stage was critical as it allowed for rotation of the sample to align the trough of a given DCB with the wedge tip.

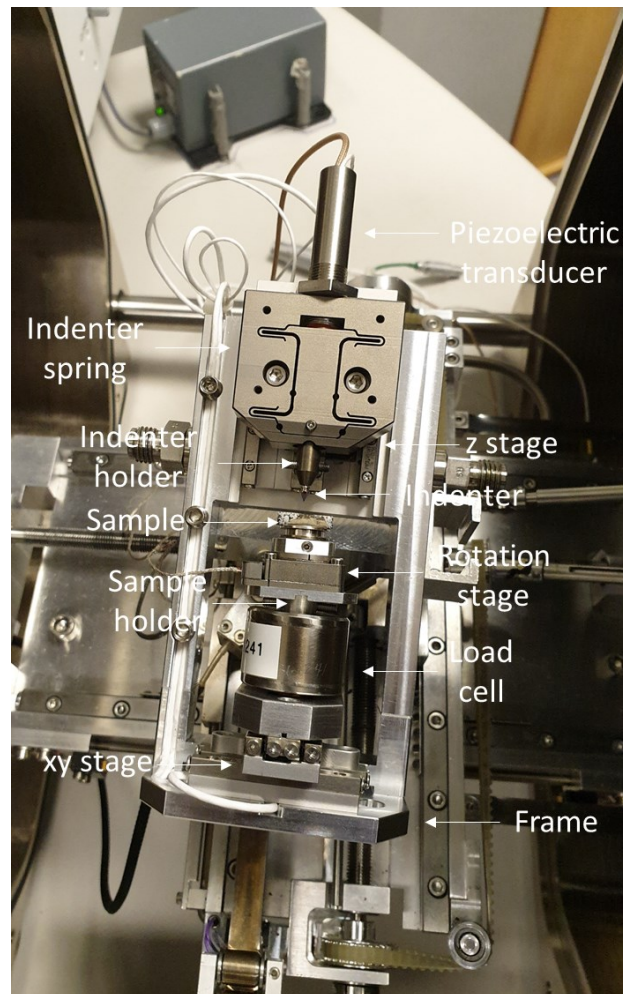


Figure 5.11: Image of the Alemnis indenter rig used in this study inside an open SEM sample chamber.

Testing was conducted in situ inside a FEI Quanta 650 FEG-ESEM microscope. This allowed for continuous high spatial resolution imaging of the tests. This includes alignment of the DCB trough and wedge tip as well as tracking crack growth. The SEM operating conditions for image capture were an accelerating voltage of 5 kV and a working distance of $\sim 10\text{ mm}$.

6 Technique Development

The faceted nature WC grains means WC-Co is likely to contain faceted grain boundaries as necessary for DCB fracture testing. Given that the $\Sigma 2$ twist boundaries were the most abundant boundary type in WC-Co as described in the literature review, these were chosen for analysis. This chapter deals with the process associated with identification of $\Sigma 2$ twist boundaries suitable for fracture testing and the challenges with regards to performing DCB tests on WC-Co.

6.1 Identification and Verification of $\Sigma 2$ Twist Boundaries

6.1.1 Identifying $\Sigma 2$ Twist Boundaries

To determine the toughness of $\Sigma 2$ twist boundaries, three goals must be realised. First, these preferred boundaries must be identified. Then, a subset of $\Sigma 2$ twist boundaries perpendicular to the surface must be extracted. Finally, the ideal subset of WC boundaries must be subject to fracture testing (DCB tests) and toughness values calculated.

The $\Sigma 2$ boundaries were identified in MTEX based on the following criteria: grains sharing a $\Sigma 2$ boundary will have $\{10\bar{1}0\}||\{10\bar{1}0\}$ and $\{0001\}||\{11\bar{2}0\}$ relationships. One of the main differentiating features between $\Sigma 2$ twist and tilt is in the habit plane. The former has two $\{10\bar{1}0\}$ planes while the latter has a $\{0001\}$ and a $\{11\bar{2}0\}$. Since, $\Sigma 2$ twist is of interest, the tilt variant will not be considered. Given that the boundary habit planes are prismatic, they were transformed from the sample reference frame to the crystal reference frame. This was done by performing a matrix multiplication between the rotation matrix of the respective grains and the prismatic planes as shown in equations 6.1 and 6.2.

$$g_A * \{10\bar{1}0\} = 6 * v_A \quad (6.1)$$

$$g_B * \{10\bar{1}0\} = 6 * v_B \quad (6.2)$$

Where g is the rotation matrix, while A and B refer to adjacent grains sharing a boundary. Six vectors are produced for each grain as there are six prismatic planes. Then, the dot product of the vectors from each of the grains is taken to test if the boundary planes are parallel. If parallel, this dot product is one. Finally, the dot products between vectors that satisfies the above condition and $[0001]$ is calculated to check if the subset of boundary planes are perpendicular to the sample surface. The dot product is zero if the boundary is perpendicular to the sample surface. Equations 6.3 and 6.4 checks for these criteria.

$$v_A \cdot v_B = 1 \quad (6.3)$$

$$v_A \cdot [0001] = 0 \quad (6.4)$$

All the criteria so far were to verify the following. The boundaries chosen to test were $\Sigma 2$ boundaries. The grains adjacent to these boundaries had $\{10\bar{1}0\}||\{10\bar{1}0\}$. Finally, the $\{10\bar{1}0\}$ planes were perpendicular to the surface. However, these specifications do not distinguish between tilt and twist variants. Hence, for each boundary, pole figures must be plotted for the grains about the boundary examining the $\{10\bar{1}0\}$ poles. If the poles are shared, located at the edge of the pole figure, and are split by the boundary trace, the boundary is $\Sigma 2$ twist (figure 6.1(b)). The boundary will be a tilt variant if the same criteria are true for (0001) and $\{11\bar{2}0\}$ as these are the habit planes for a $\Sigma 2$ tilt boundary (figure 6.1(d)).

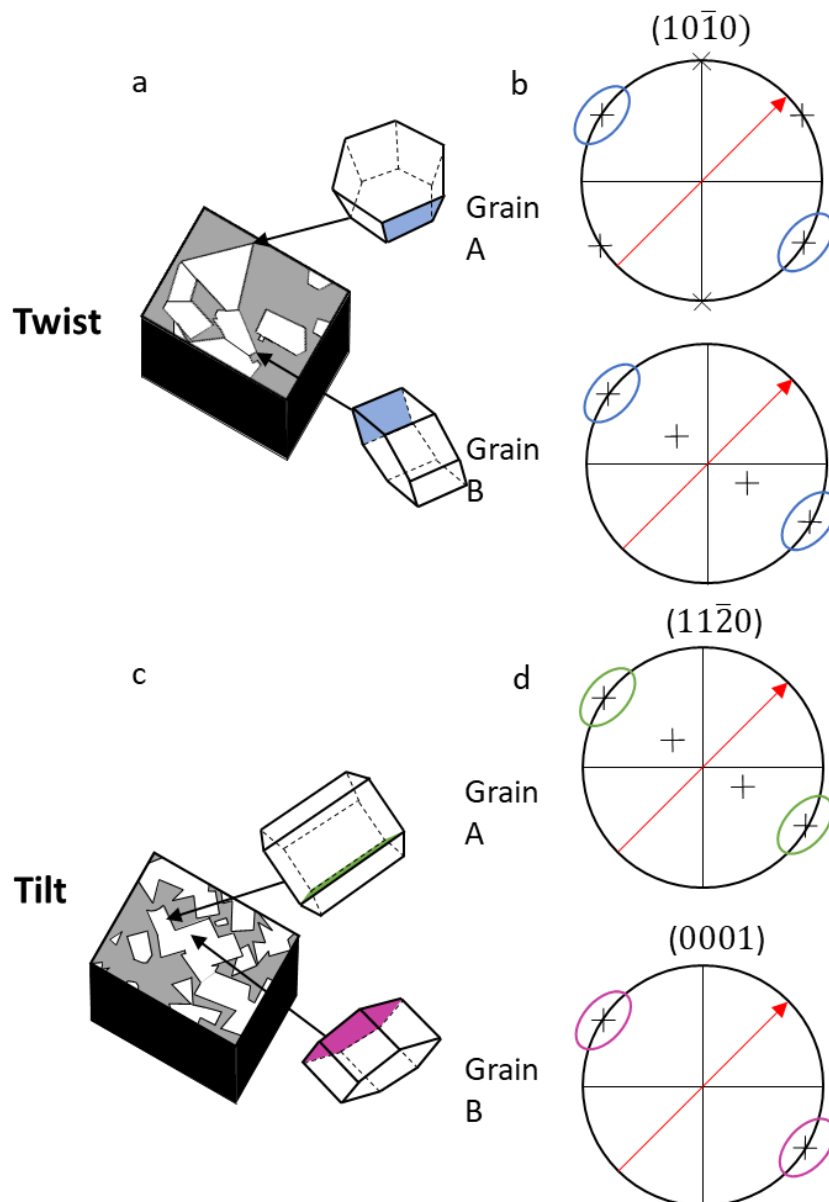


Figure 6.1: Procedure for identifying the subset of $\Sigma 2$ twist boundaries. (a) and (c) are illustrations of the WC-Co microstructure. (b) and (d) are poles figures plotted for each grain looking for the habit planes. The cross marks the locations of the poles while the red arrow represents the boundary trace from the microstructure. The boundary habit planes shared between the grains are highlighted with distinct colours and corresponding poles are highlighted in the pole figures.

6.1.2 EBSD Analysis of WC-Co Sample

EBSD was used to acquire orientation data essential for identifying $\Sigma 2$ boundaries of interest. EBSD data was acquired from a WC-10wt%Co sample with a $\sim 700 \times 500 \mu\text{m}^2$ area being scanned for analysis. A region of interest on the sample surface was first marked by four fiducial crosses using FIB milling before EBSD analysis. The acceleration voltage, spot size and aperture size used for data acquisition were 20 kV, 5.5 and 50/40 μm respectively. The working distance and the sample-detector distances were both $\sim 15 \text{ mm}$. EBSD maps were recorded at a low resolution of 200×150 pixels. The step sizes of the EBSD maps were $0.4 \mu\text{m}$. Figure 6.2 shows the SEM, forescatter and IPF images of a region chosen for EBSD data acquisition.

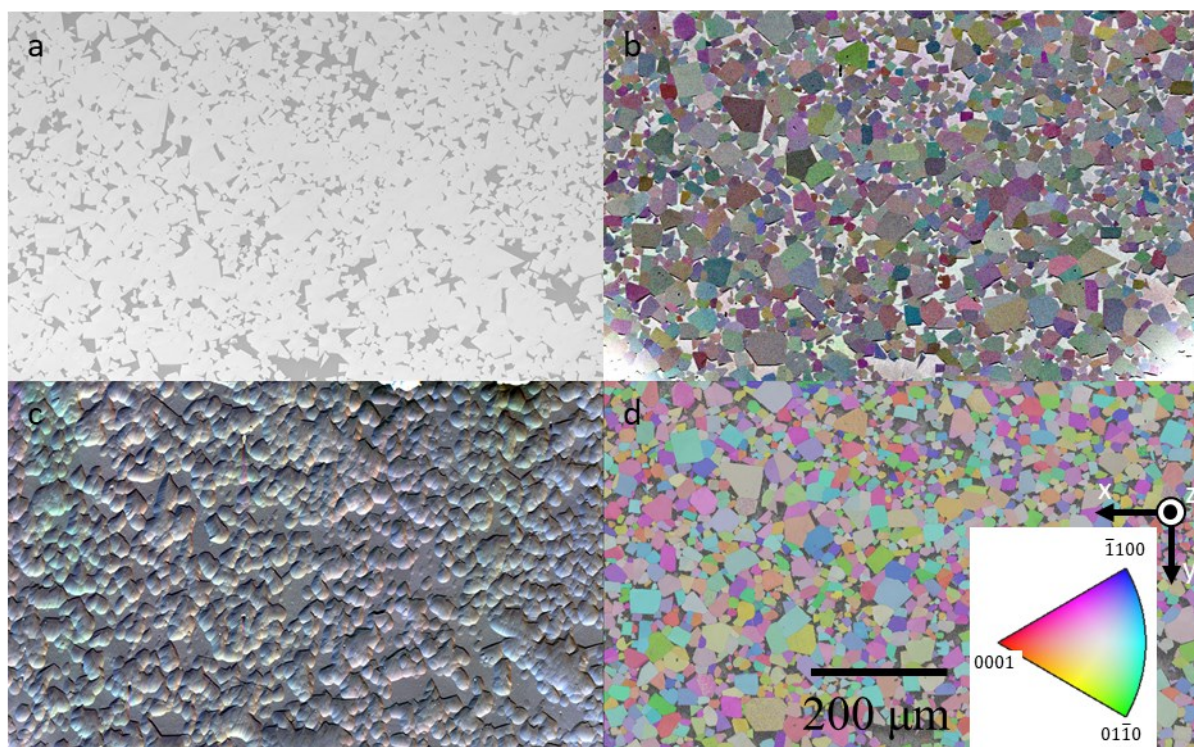


Figure 6.2: Overview of a region chosen for EBSD data acquisition from a WC-10wt% Co sample. (a) SEM image of the region chosen for EBSD acquisition. Forescatter images of the same region imaged with the forescatter detector at sample-detector distances of (b) 50 mm and (c) 15 mm. (d) IPF map of the same region.

Once the EBSD data was obtained, it was analysed according to the criteria specified in the 'Identifying $\Sigma 2$ twist boundaries' section. In practice, the collected EBSD data was converted from .bcf to .hdf5 and imported into MTEX for analysis. Analysis was performed using a custom script that included the following steps: (1) established the coordinate system of the sample, with x and z directions set as west and out of plane respectively; (2) clean-up was performed (3) WC grains were identified; (3) $\Sigma 2$ grain boundaries were selected from the grain boundary map, and then the trace tested to see if it was consistent with a vertical grain boundary criteria as per previous section.

6.1.3 EBSD Data Clean-up

After the EBSD data was loaded into MTEX, a clean-up procedure was applied to the EBSD data. Initially, non-indexed data were removed from the data set. Non-indexed refers to EBSD data points without a phase assignment. This occurs due to poor EBSD data points which in turn are difficult to index and assign a phase for. Afterwards, the function, `calcGrains` was applied to the data set to segment the EBSD data into grains. `calcGrains` reconstructs grains from the 2D EBSD data set by taking the EBSD data set as the input and returning a list of grains.

Three main modelling assumptions are made by the algorithm (`calcGrains`) used for grain reconstruction [221]. The first assumption is that the surface is composed of grains that are separated by boundaries. The presence of non-indexed data arising from an amorphous phase or a highly distorted crystalline phase as in the case of a grain boundary or a damaged region will violate the first assumption. So, these are assigned to a null phase to stay within the model used for grain reconstruction. Secondly, grain boundaries are taken to exist between two adjacent data points if the points are from different phases or if the misorientation angle between the data points is greater than a user defined threshold. The misorientation angle threshold depends on what constitutes as the low and high angle grain boundaries. Traditionally low angle grain boundaries refer to interfaces between grains with slight misorientation ($<15^\circ$). But sub-grain boundaries, the dislocation walls that form within grains are also a subset of low angle boundaries. In contrast, high angle boundaries refer to boundaries that exist between grains with a misorientation greater than 15° . In this work, a 5° misorientation tolerance was used. The final assumption is that the grain boundary is taken as the perpendicular bisector of two EBSD data points if the misorientation angle between them surpasses the misorientation angle threshold.

At first, the algorithm for grain reconstruction performs a Voronoi decomposition of the mapped surface. This results in a list of Voronoi cells with each cell corresponding to a EBSD data point. Voronoi cells that share the same phase as well as having a misorientation lower than the user defined threshold are joined together. These combined Voronoi cells form the reconstructed grains.

The argument, '`unitCell`' was also passed onto `calcGrains` in addition to EBSD data to ensure that grain boundaries are at the intended location. This is because the Voronoi cell decomposition tends to distort the grain boundaries of interest when non-indexed phases or undesirable phases are removed from the microstructure. Removing non-indexed phases or undesirable phases results in the phase of interest essentially expanding into the void left behind by the undesirable phases. Thus, the resulting grains and boundaries are distorted. The '`unitCell`' argument omits Voronoi decomposition and treats the grain as originating from a unit cell lattice. The resulting grain boundary network from both approaches are shown in figure 6.3.

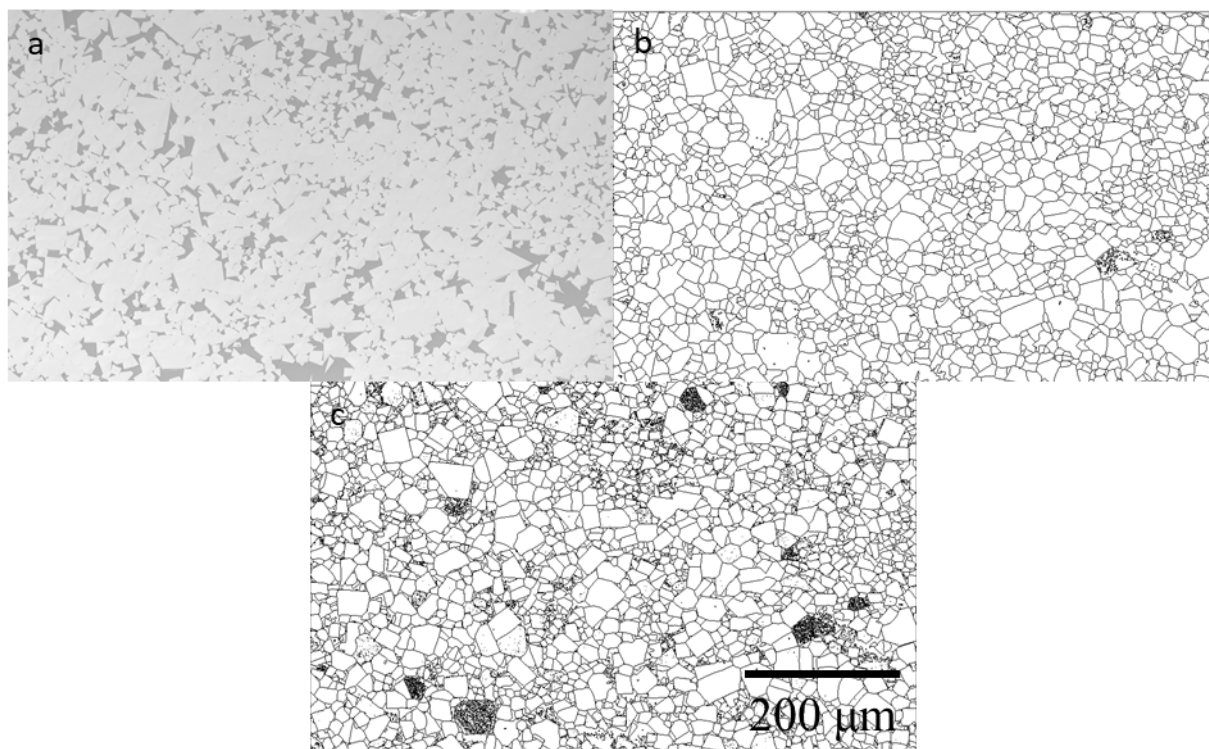


Figure 6.3: Images depicting the two possible grain reconstruction algorithms. (a) SEM image of the region chosen for analysis. Schematic of the WC grain boundary network as obtained from recalculating grains with (b) the Voronoi decomposition and (c) using the 'unitCell' argument in the calcGrains function.

Afterwards, grains smaller than 5 pixels were eliminated from the data set and the grains were recomputed. Then a smoothing function, smooth was applied to the data set. A smoothing function is not necessary for determining $\Sigma 2$ twist boundaries. It is useful for a more accurate schematic representation of the grain boundaries.

EBSD data was obtained in a grid. In this work, data was acquired over a square grid. Hence, the grain boundaries of all possible directions cannot be truly represented. The smoothing function allows one to overcome the inherent limitation of the acquired EBSD data. As the name implies, the function allows the user to smooth over the jagged grain boundaries into a smooth line by interpolating grain boundaries. Caution must be taken with the degree of smoothing as it affects microstructural features such as boundary length and boundary curvature. A high degree of smoothing will distort grain dimensions providing a false image of the microstructural features. So, a small degree of smoothing was applied via a smoothing parameter of 5. The smoothing parameter refers to the number of iterations of smoothing applied to the boundaries.

6.1.4 Identification of Ideal $\Sigma 2$ Boundaries for DCB Testing

After EBSD data clean-up, the data was restricted to the WC phase. Later, $\Sigma 2$ twist boundaries were identified according to the procedure detailed earlier in this chapter. First, the $90^\circ/[10\bar{1}0]$

misorientation for the $\Sigma 2$ boundaries was specified. This was defined by the condition of $\{10\bar{1}0\} \parallel \{10\bar{1}0\}$ and $\{0001\} \parallel \{11\bar{2}0\}$. Subsequently, all possible grain boundaries were extracted. Then a subset of WC/WC grain boundaries was extracted from all possible boundaries. $\Sigma 2$ boundaries were then determined as those WC/WC boundaries that have the intended misorientation within a threshold of 5° .

The following steps were carried out to determine the $\Sigma 2$ boundaries perpendicular to the surface. First, grains sharing $\Sigma 2$ boundaries were separated into two subsets. Each subset was assigned to a variable with the function, grains. The input argument for the function is the grainID of the grains that satisfied the criteria of having a $\Sigma 2$ boundary. This was followed by defining the Euler angles in Bunge notation for rotating each set of grains from the crystal reference frame to the sample reference frame. Then the rotation matrix for each grain was set by passing Euler angle through the matrix function. After this, matrix multiplication was done between the six possible $\{10\bar{1}0\}$ prismatic planes and the rotation matrix of each grain as was explained in the previous section. This gave rise to six vectors for each grain in each of the subsets. Then a dot product was performed between the six vectors of every pair of grains that share a $\Sigma 2$ boundary. This produced thirty-six values for each pair of grains that share a boundary. Then, the script checked if any of the thirty-six values are between 0.9-1. This is to ensure that the $\{10\bar{1}0\}$ planes in either grain are parallel to each other. 0.9-1 limit is chosen to account for any variability in data.

$\Sigma 2$ boundaries that fulfil this criterion are selected for further analysis. This is followed by performing a dot product between the six vectors corresponding to the one set of grains from the aforementioned subset of boundaries and [001]. Here the [001] refers to the direction in the sample reference frame that corresponds to z direction out of the sample. This dot product produces six values for each grain. Afterwards, boundaries for which at least one of the 6 values are between 0-0.1 were selected. This is to verify the $\{10\bar{1}0\}$ planes are perpendicular. In this section, it is also made certain that the same set of $\{10\bar{1}0\}$ planes that are parallel are perpendicular as well. Then, boundaries that fulfil these criteria are chosen and overlaid with a red highlight over a schematic of all possible WC grain boundaries of a region of interest. Given that $\Sigma 2$ twist boundaries are far more numerous than their tilt counterpart, the highlighted boundaries are likely to be twist variants. But, as a crude way of checking this, grain shapes were plotted over grains from an IPF-Z map and potential perpendicular $\Sigma 2$ twist boundaries were examined. This is shown in figure 6.4.

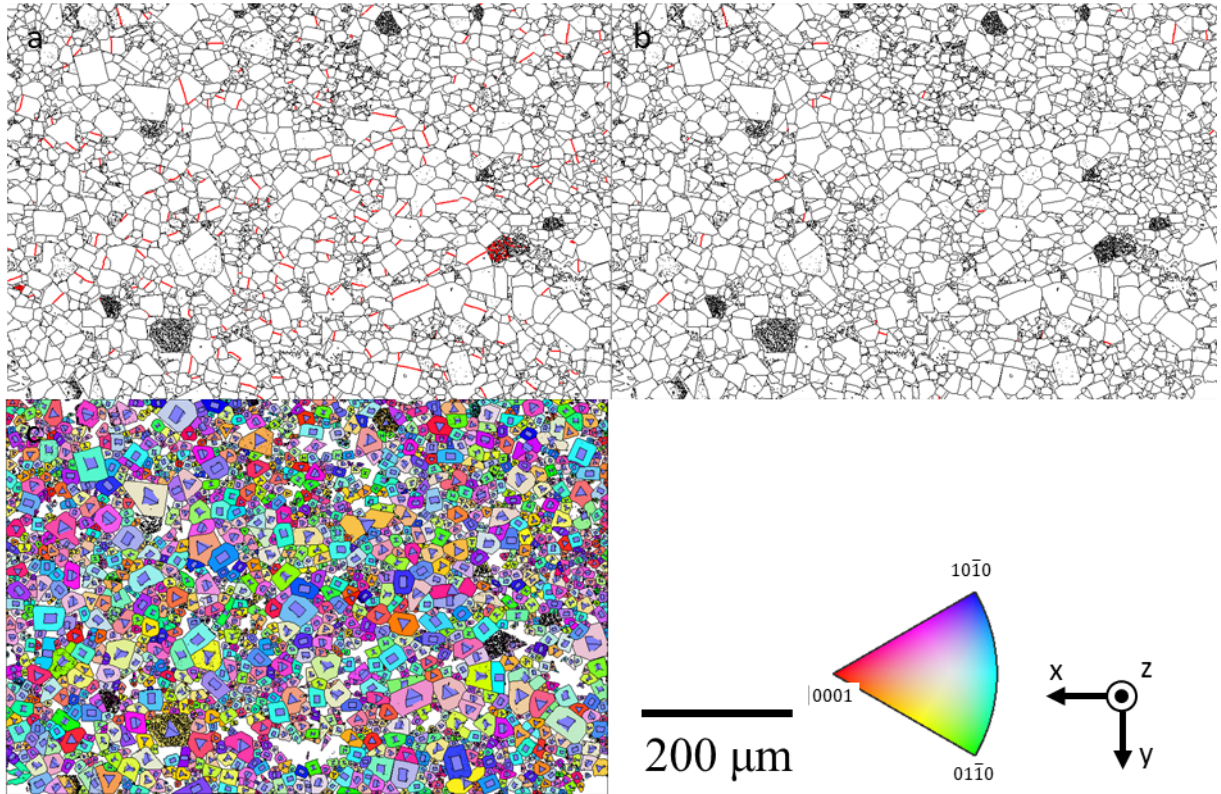


Figure 6.4: Illustrations of the grain boundary network in the region of interest with (a) all possible $\Sigma 2$ boundaries and (b) perpendicular $\Sigma 2$ boundaries highlighted in red. Depiction of grain orientations in the region of interest plotted as an IPF-Z map with equilibrium WC shapes plotted at the centre of the grains.

6.1.5 Verification of Perpendicular Boundary Character

Once potentially perpendicular $\Sigma 2$ twist boundaries ideal for testing were identified, the validity of the method used for detection had to be verified. Initially, attempts were made to mill trenches perpendicular to the boundary traces of ideal $\Sigma 2$ twist boundaries. Trenches had the dimensions of $25 \times 10 \times 10 \mu\text{m}^3$. The trenches were milled with a high current of 10 nA and the trench walls were then cleaned at a lower current of 24 pA. SEM images taken from one such boundary before and after milling are shown in figure 6.5.

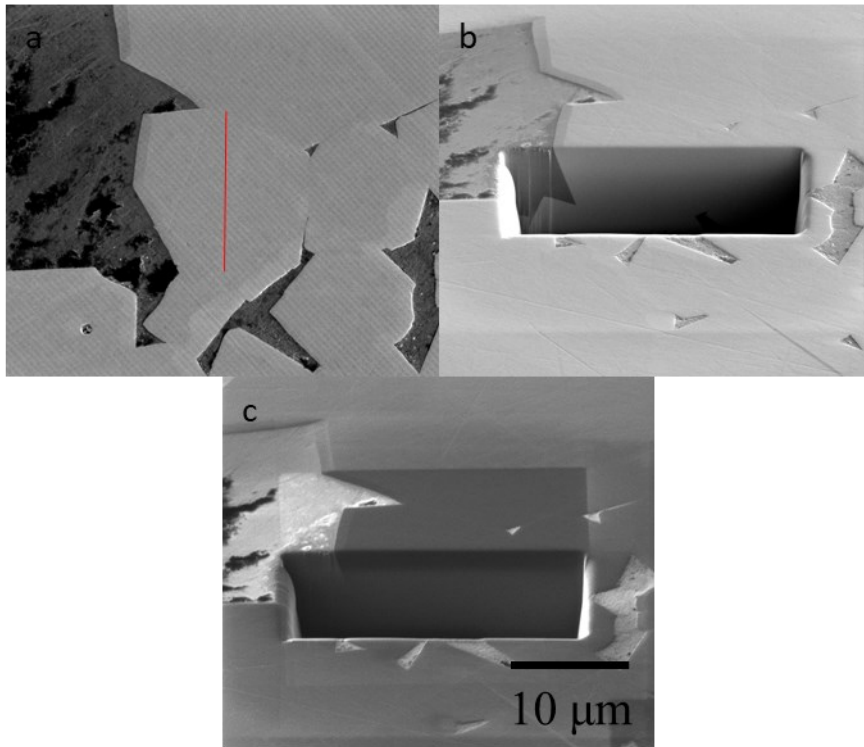


Figure 6.5: Attempt to verify perpendicular character of an identified $\Sigma 2$ twist boundary using ion channelling contrast. (a) SEM image of a region on a WC-10wt% Co sample with a perpendicular $\Sigma 2$ twist boundary highlighted with a red line. (b) SEM image of the same region after milling a trench as viewed from the (b) electron and (b) ion beams.

As the sub-surface trace was not clearly visible in ion-channeling imaging, TEM lamellae were extracted from the ideal boundaries and viewed in TEM to verify the perpendicular boundary character. This was performed by Oriol Gavalda Diaz in the following manner. Firstly, the location of the ideal $\Sigma 2$ twist boundary was marked with a $10 \times 2 \times 1 \mu\text{m}^3$ platinum layer deposited under electron beam. The electron beam was operated with an accelerating voltage and beam current of 5 kV and 0.69 nA respectively. The platinum layer was deposited about the middle of the boundary perpendicular to it. Then the sample stage was tilted by 52° . Afterwards, another platinum layer of $17 \times 2.5 \times 2 \mu\text{m}^3$ dimensions was placed using ion beam on the same location as the previous platinum layer. The ion beam was operated with an accelerating voltage and beam current of 30 kV and 0.46 nA for this step. The platinum layer deposition under ion beam is done to protect the lamella during the thinning process. Two trenches were then cut above and below the platinum layer at 21 nA current. The trenches were $25 \times 10 \times 10 \mu\text{m}^3$ and were cut in parallel milling. Then the stage was tilted $52^\circ \pm 3^\circ$ to clean the walls of the lamella. 6.5 nA beam current was used for this step. The stage was then tilted back to 7° . The sides of the lamella attaching the lamella to the sample were milled away at 2.8 nA. After this, the lamella was attached to an OmniProbe micromanipulator with platinum. The OmniProbe micromanipulator is a tungsten needle that is actuated via piezoelectric motors operating

in closed loop feedback. Then, the bottom end of the lamella was cut off to detach the lamella completely off the sample.

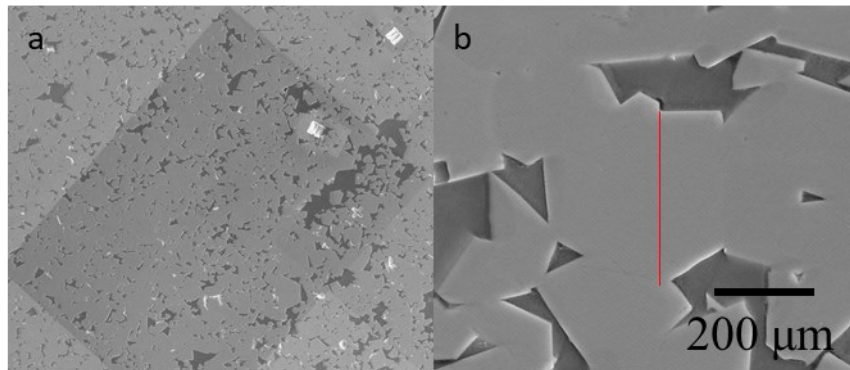


Figure 6.6: SEM images showing region and $\Sigma 2$ twist boundary chosen for TEM lamella extraction. (a) SEM image of the surface of a WC-10wt% Co sample chosen for lamella extraction to verify perpendicular character of $\Sigma 2$ boundaries. (b) SEM image of a region the same sample with the ideal $\Sigma 2$ twist boundary marked in red.

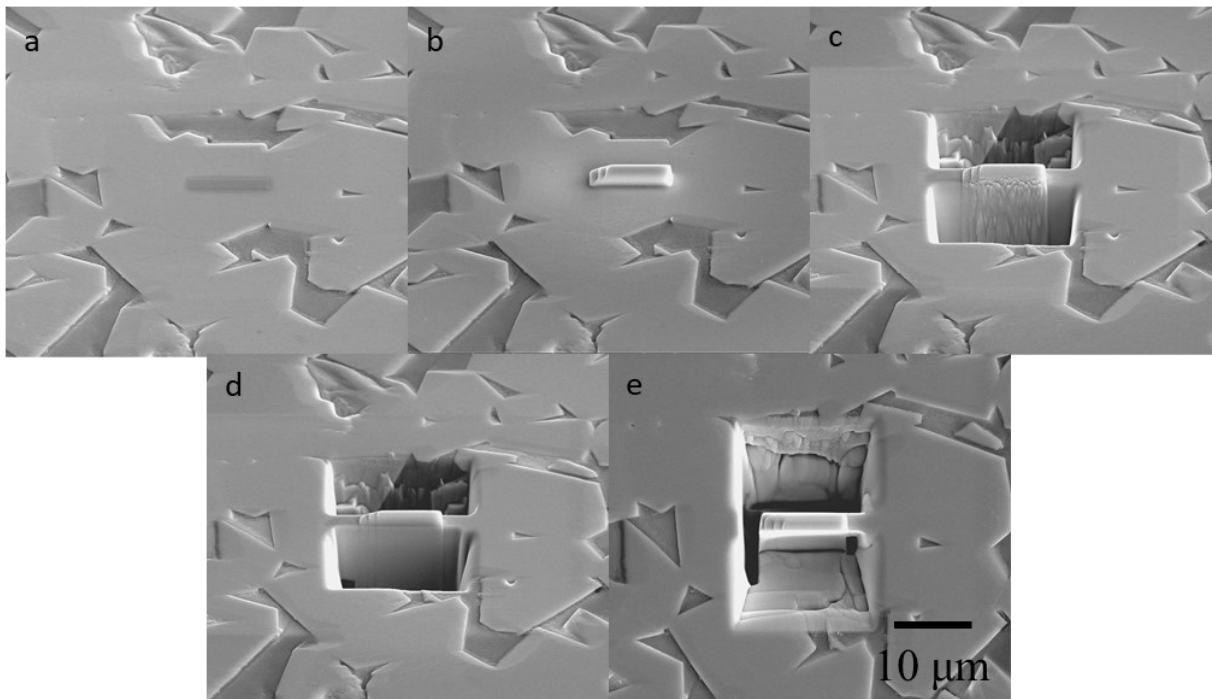


Figure 6.7: SEM image depicting the steps involved in TEM sample preparation. Platinum deposition under (a) electron and (b) ion beams. (c) Trenches milled with a current of 21 nA. (d) Lamella walls cleaned with a 6.5 nA beam current. (e) Lamella being cut off from the sample surface with a 2.8 nA beam current.

The lamella was later attached to a protrusion of a TEM grid with platinum using the OmniProbe micromanipulator. It was then thinned with acceleration voltages and ion beam currents starting with 30 kV and 0.92 nA, 30 kV and 0.46 nA, 30 kV and 0.28 nA, 5 kV and 93 pA and finally 5 kV and 47 pA. The stage was tilted $52^\circ \sim \pm 5^\circ$ during the thinning process to mill the front and back faces of the

lamella. The lamella was thinned until reasonable electron transparency as necessary for TEM imaging as shown in figure 6.8. The lamella was then viewed in a JEOL JEM-2100F TEM to verify the boundary character. TEM image of one such lamella is given in figure 6.9.

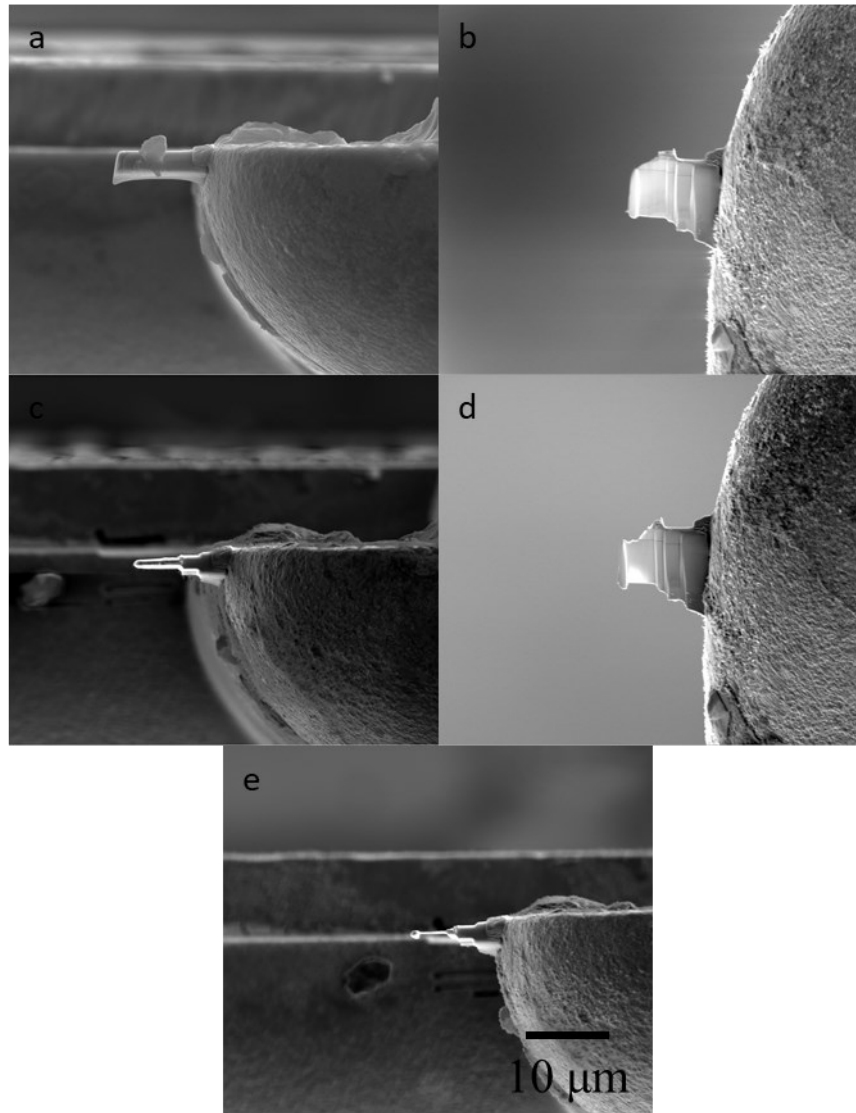


Figure 6.8: Series of SEM images showing the result of thinning a lamella attached on a TEM grid using FIB to electron transparency. (a) Top view of lamella as obtained from the sample before thinning. Lamella as viewed from the side after milling with currents of (b) 0.92 nA, 0.46 nA and 0.28 nA and (d) 93 pA and 47 pA. (b) and (d) are top view of the same lamella after thinning with the afore mentioned currents.

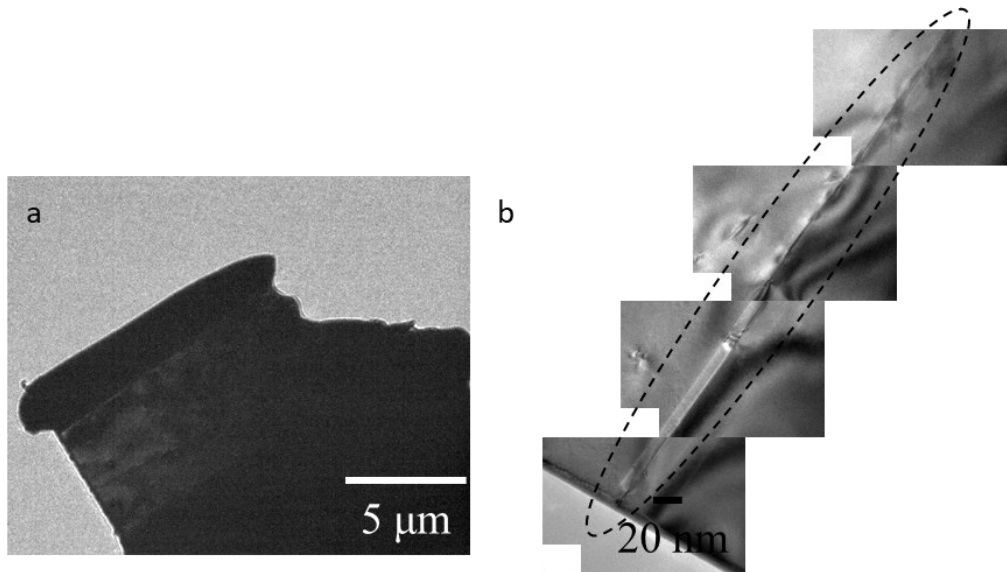


Figure 6.9: (a) TEM image of the lamella extracted from the $\Sigma 2$ boundary. (b) High magnification TEM images of the boundary depicting the perpendicular nature of the $\Sigma 2$ twist boundary of interest. The boundary has been highlighted with an ellipse.

6.2 DCB Milling

6.2.1 Milling DCBs on A WC Single Crystal

The objective of this work was to study the interface properties of WC/WC boundaries using DCB tests. However, to validate the use of DCB tests in WC-Co, preliminary tests were performed on WC single crystals. Type II $\{10\bar{1}0\}$ planes in WC crystals were chosen as the candidate crystallographic planes to be cleaved in the preliminary DCB tests. This was done as type II $\{10\bar{1}0\}$ planes have the lowest cleavage energy as will be shown in the next chapter. Cleavage of type II prismatic planes requires DCBs to be milled on WC crystals oriented with $[0001]$ direction pointing out of the sample surface. Image of one such single crystal is given in figure 6.10. This ensures crack propagation along $[0001]$ cleaving type II $\{10\bar{1}0\}$ planes during DCB tests.

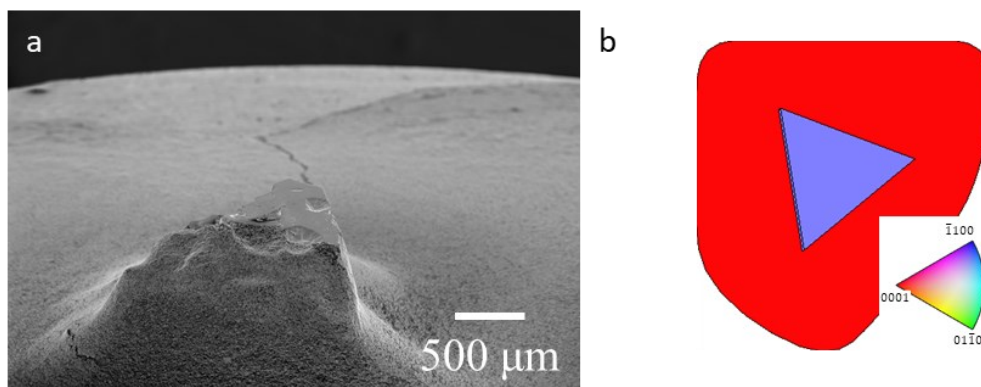


Figure 6.10: SEM image and orientation of the single crystal chosen for EBSD testing. (a) SEM image of the WC single crystal after polishing and (b) IPF map of a single point acquired from the surface of the WC single crystal. The orientation of the point on the surface is represented by an equilibrium triangular prism. The single crystal was manually reoriented with the $[0001]$ being perpendicular to the sample surface.

The WC single crystals were roughly polished and subject to EBSD characterisation to determine their orientations. The single crystals were then reorientated to have the $[0001]$ direction parallel to the sample surface normal before being polished thoroughly. Afterwards, the crystals were characterised via EBSD. The acquired EBSD data along with the orientation of the crystal within the SEM chamber during EBSD acquisition was used to aid in the alignment of the DCB milling. Once the very first DCB was milled, a matrix of additional DCBs were milled relatively easily as necessary using the very first DCB for alignment. Image of a matrix of DCBs milled on the surface of a WC single crystal is presented in figure 6.11.

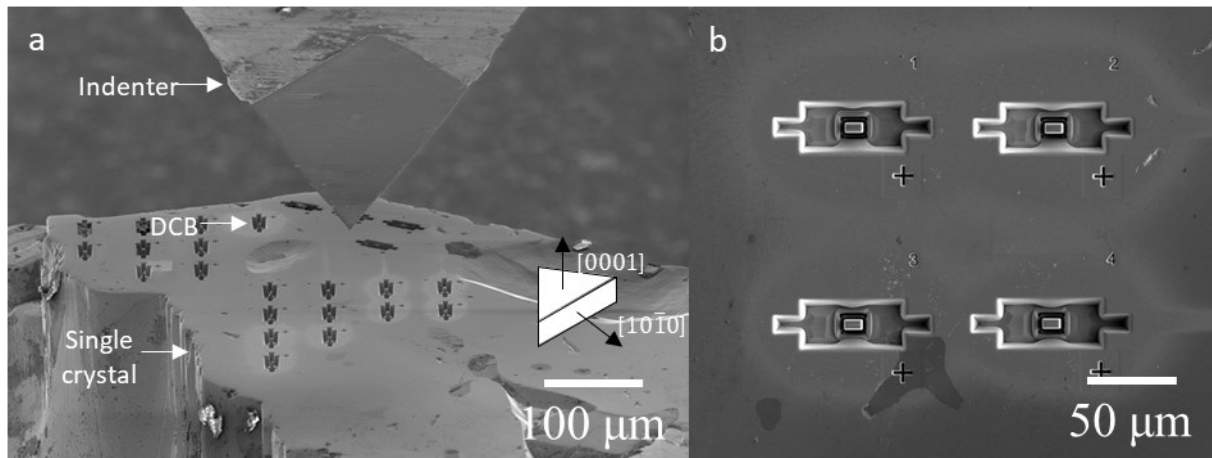


Figure 6.11: SEM images of a matrix of DCBs milled on the surface of a WC single crystal to cleave type II $\{10\bar{1}0\}$ planes.

DCBs were milled with a spacing of $60\ \mu\text{m}$ between the centre of any two given DCBs to prevent any issues during the automated milling procedure. The reason for this is that during the alignment procedure for the currents used for milling, a cross-correlation function scans a horizontal field width of $50\ \mu\text{m}$ centred about the region for the fabrication of a new DCB. If features from an older DCB were to overlap into the field of view assigned for alignment procedure of currents of a new DCB, the functionality of the cross-correlation function might become impeded. Hence, the need for a spacing of $60\ \mu\text{m}$ between any two DCBs.

6.2.2 Milling DCBs on WC-Co

Once the DCB tests were successfully conducted on the WC crystal, focus was shifted to testing on polycrystalline WC-Co. This started with identification of $\Sigma 2$ twist boundaries ideal for fracture testing by analysing the EBSD data from a WC-10wt%Co sample as explained earlier in this chapter.

However, tests could not be readily performed. This is because the WC/WC boundaries are not visibly apparent on a FIB SEM and therefore manufacture of DCBs is not as straightforward. So, high spatial resolution SEM images and EBSD maps of ideal $\Sigma 2$ twist boundaries were captured to aid in the identification of the said boundaries during milling in FIB SEM. The DCBs were milled in such a manner

that the $\Sigma 2$ twist boundaries were aligned to run along the middle of the DCB. A SEM image of such DCBs at $\Sigma 2$ twist boundaries are given in figure 6.12. This means, during DCB testing, the residual grains along the arms of the DCBs will be point loaded allowing for crack propagation along the $\Sigma 2$ twist boundaries.

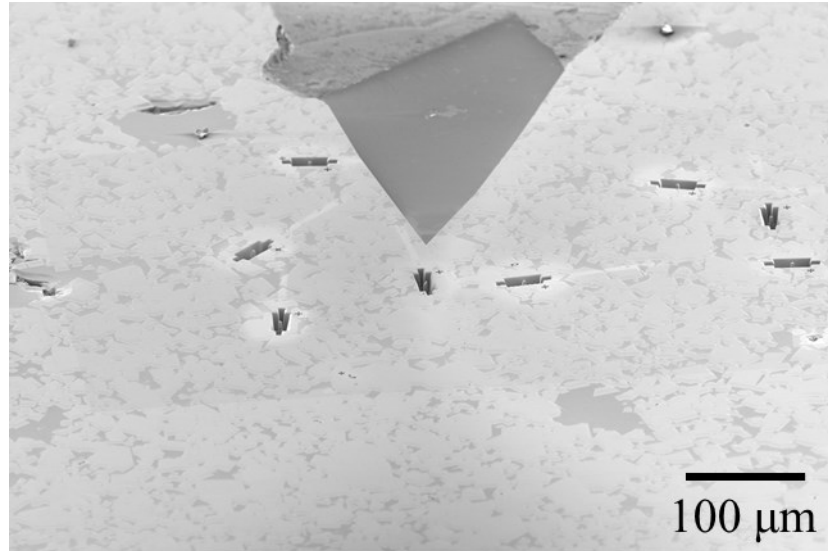


Figure 6.12: SEM image showing DCBs milled at $\Sigma 2$ twist boundary sites on a WC-10wt%Co sample surface.

6.3 Issues and Lessons from DCB Tests

6.3.1 Single Crystal DCB Tests

There were several issues when implementing the use of DCB tests to measure the fracture energy of type II $\{10\bar{1}0\}$ planes in WC crystals. Initially tests were to be conducted on a WC-60wt%Co sample with a typical WC grain size of 5-10 μm . However, it was soon realised that the grain size was too small for the intended DCB geometry. DCB pillars on this sample were partly composed of cobalt. Hence, the WC-60wt%Co sample was abandoned for a WC-75wt%Co sample with a grain size of 10-100 μm . The WC-75wt%Co sample had few abnormal grains that were large with a grain size far in excess of 100 μm diameter. Examples of DCBs milled on the surface of WC-60wt%Co and WC-75wt%Co samples is shown in figure 6.13.

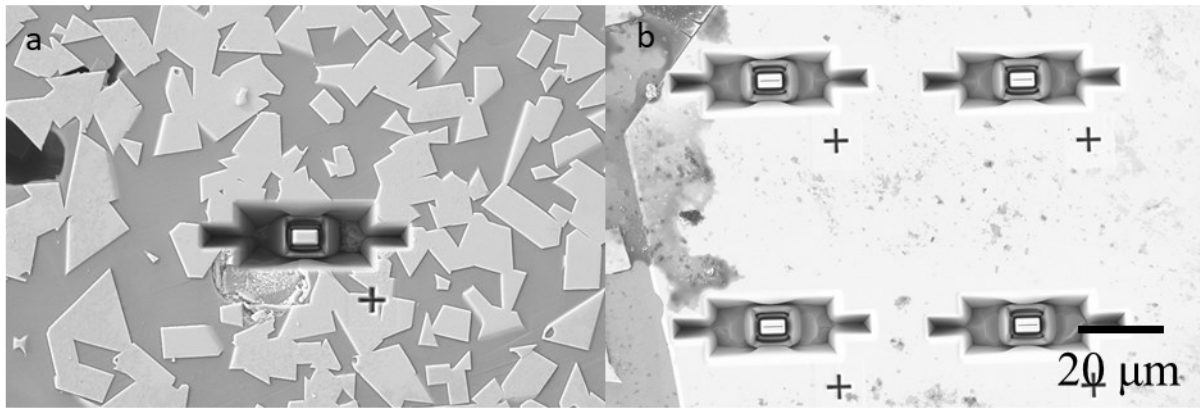


Figure 6.13: SEM image of DCBs milled on (a) WC-60wt% Co and (b) WC-75wt% Co samples.

DCBs were milled on the WC-75wt% Co sample on WC grains with the [0001] direction being parallel to the sample normal. Tests failed in this attempt usually with (1) one of the DCB arms being typically cleaved from the notch section and (2) without the crack propagating vertically down the body of the DCB.

It was identified that the conductive carbon adhesive tape used to mount the sample onto the SEM stub might have introduced additional compliance to the test fixture. SEM image of a WC-Co sample mounted on the carbon tape is shown in figure 6.14. The whole sample was observed to sink in during loading in the Alemnis indenter onto the carbon tape before the DCB arms were actually point loaded. Thus, a large amount of elastic strain energy will be stored before the actual loading, leading to unstable fracture. Additionally, since the actual loading occurs sometime after initiating the test, there might be some drift between the load cell and the piezo stack. This means the indenter and the DCB will be slightly misaligned during the actual loading.

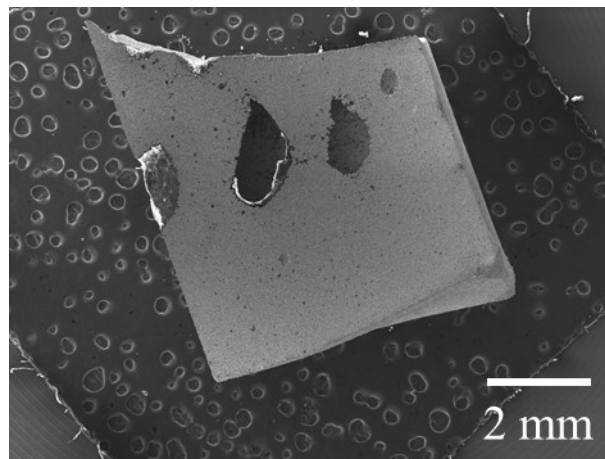


Figure 6.14: SEM image of a WC-60wt%Co sample mounted on carbon tape.

So, the samples were instead mounted with the aid of silver adhesive conductive paint to minimise the compliance introduced to the test fixture. However, the DCBs still failed in a similar manner in

subsequent attempts. It was then hypothesised that the cantilever arms of the DCB geometry was too short and thus a large amount of elastic strain energy was being stored before crack initiation. Therefore, upon crack initiation, cracks did not necessarily have to propagate vertically down the DCB along the lowest energy type II $\{10\bar{1}0\}$ planes. So, the DCB geometry was modified to have longer notches and in turn have longer cantilever arm lengths. DCB arm lengths were altered from $1.4\text{ }\mu\text{m}$ to $2\text{ }\mu\text{m}$. Yet, successive DCB tests failed in the same fashion as before with the cantilever arms being completely cleaved upon crack nucleation as presented in figure 6.15.

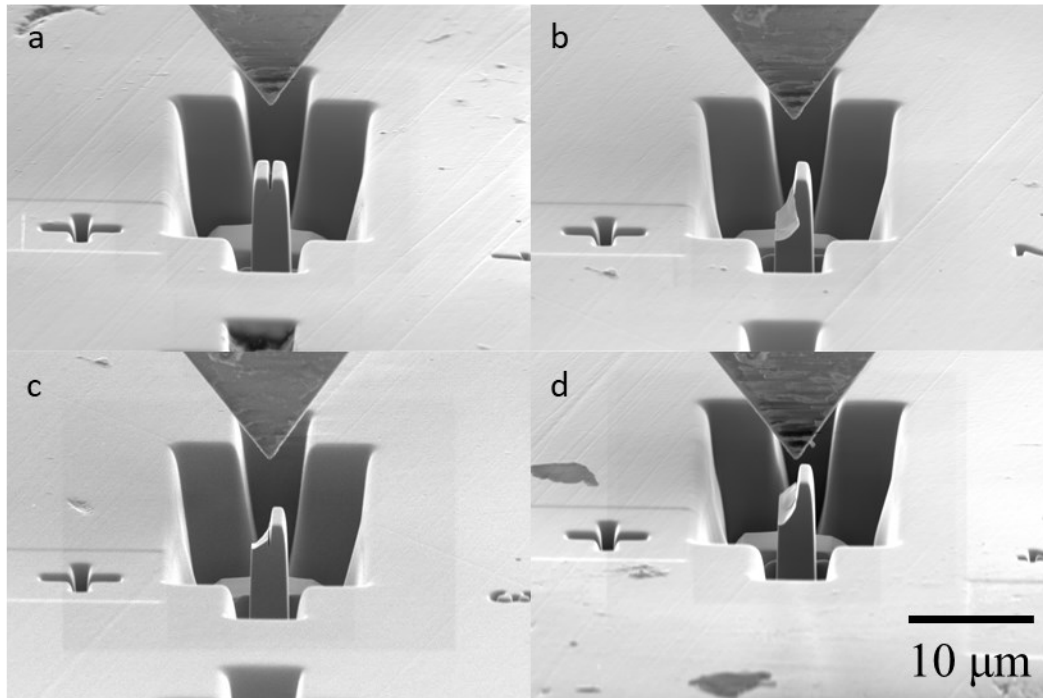


Figure 6.15: SEM images depicting the various ways that the cantilever arms were cleaved in unsuccessful WC single crystal DCB tests.

It was then proposed that the failed tests can be attributed to individual or combination of three possible reasons. Firstly, x, y or z motors in the Alemnis rig being possibly damaged. This means the indenter and sample were not aligned properly prior to each test, leading to complete cleavage of DCB arms during tests. Secondly, significant independent drifts between the load cell and the piezo stack. This will suggest that even if the indenter and the sample were well aligned with the wedge sitting within the trough, misalignment was introduced over time. This led to the DCB arms being unevenly loaded producing the failed tests that were recorded. Finally, the piezo stack being bent/damaged. A bent piezo stack will mean that the indenter was not being driven perpendicular to the sample surface during loading of the DCBs in direct displacement control. So, the DCB arms will be unevenly loaded leading to complete cleavage of a DCB arm.

The reason behind the failed tests was checked in the following manner in a SEM. The setup used to investigate this issue is shown in figure 6.16. The sharp front end of a Omniprobe tungsten needle was

mounted on the load cell and a conical indenter tip was attached to the piezo stack in the Alemnis rig. To check the damage to the x and z motors, each motor was moved independently while the other was inactive. The movement of the tungsten needle and indenter tip was used to check if the x and z motors were indeed moving these parts along the intended directions. Given that the tungsten needle is essentially a one-dimensional line during imaging, the damage to the y motor could not be verified. The drift between the load cell and the piezo stack were verified by switching off the motors and imaging the tungsten needle and the indenter over period of an hour. Finally, the damage to the piezo stack was verified by moving the indenter tip via piezo actuation and checking that the tip moved along the intended direction. It was determined that the reason behind the failed tests was the damaged piezo stack as well as the large drift between the piezo stack and the load cell. Hence, further DCB tests were performed on a new Alemnis rig thereafter.

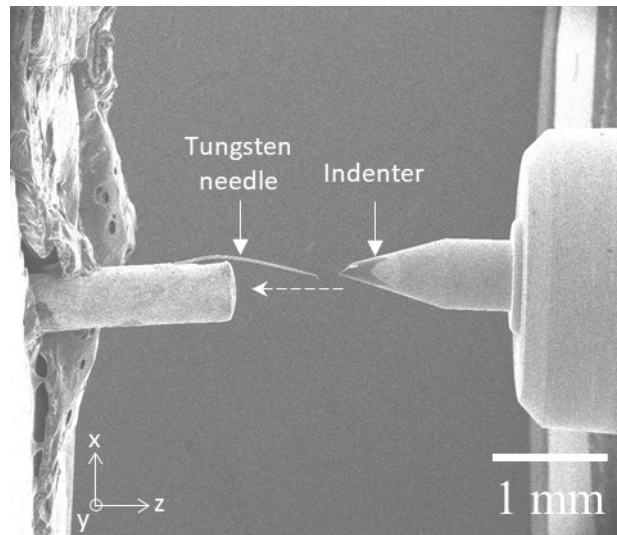


Figure 6.16: Image of the test setup used to check for problems arising from the Alemnis rig. Directions that the x, y and z motors move are shown via the axes given on the left-hand side of the image. The intended direction that the indenter tip is to move when approaching a sample surface is highlighted with a dashed arrow.

There was a major drawback for performing single crystal DCB tests on WC-75wt%Co samples. This was the difficulty associated with identifying sufficiently large number of WC grains with the preferred orientation and sufficiently large diameter for intended DCB geometry. Hence DCB tests were performed on large WC single crystals with diameter in the range of 1-2 mm from that point.

6.3.2 WC-Co DCB Tests

Once DCB tests were successfully conducted on the $\Sigma 2$ twist boundaries on the WC-10wt%Co sample, additional tests were to be performed on $\Sigma 2$ tilt boundaries. However, there were difficulties encountered when identifying $\Sigma 2$ tilt boundaries suitable for testing. The first problem was that $\Sigma 2$ tilt boundaries are rarer than their twist boundary counterparts. This was because the grain boundary energy of tilt boundaries ($2\text{--}4\text{ Jm}^{-2}$) is two orders of magnitude higher than the twist boundaries (0.02

Jm^{-2}) [63]. This means the tilt boundaries are less favourable to form during sintering and are hence present sparsely within the WC-Co microstructure. Furthermore, one or both the grains sharing a twist boundary can be smaller than ideal for the intended geometry for DCB tests. Figure 6.17 shows that out of the four $700 \times 500 \mu\text{m}^2$ regions from a WC-10wt%Co from which EBSD data was acquired, only three tilt boundaries were ideal candidates for DCB testing. Consequently, due to the afore mentioned reasons, the DCB tests at $\Sigma 2$ tilt boundaries were abandoned.

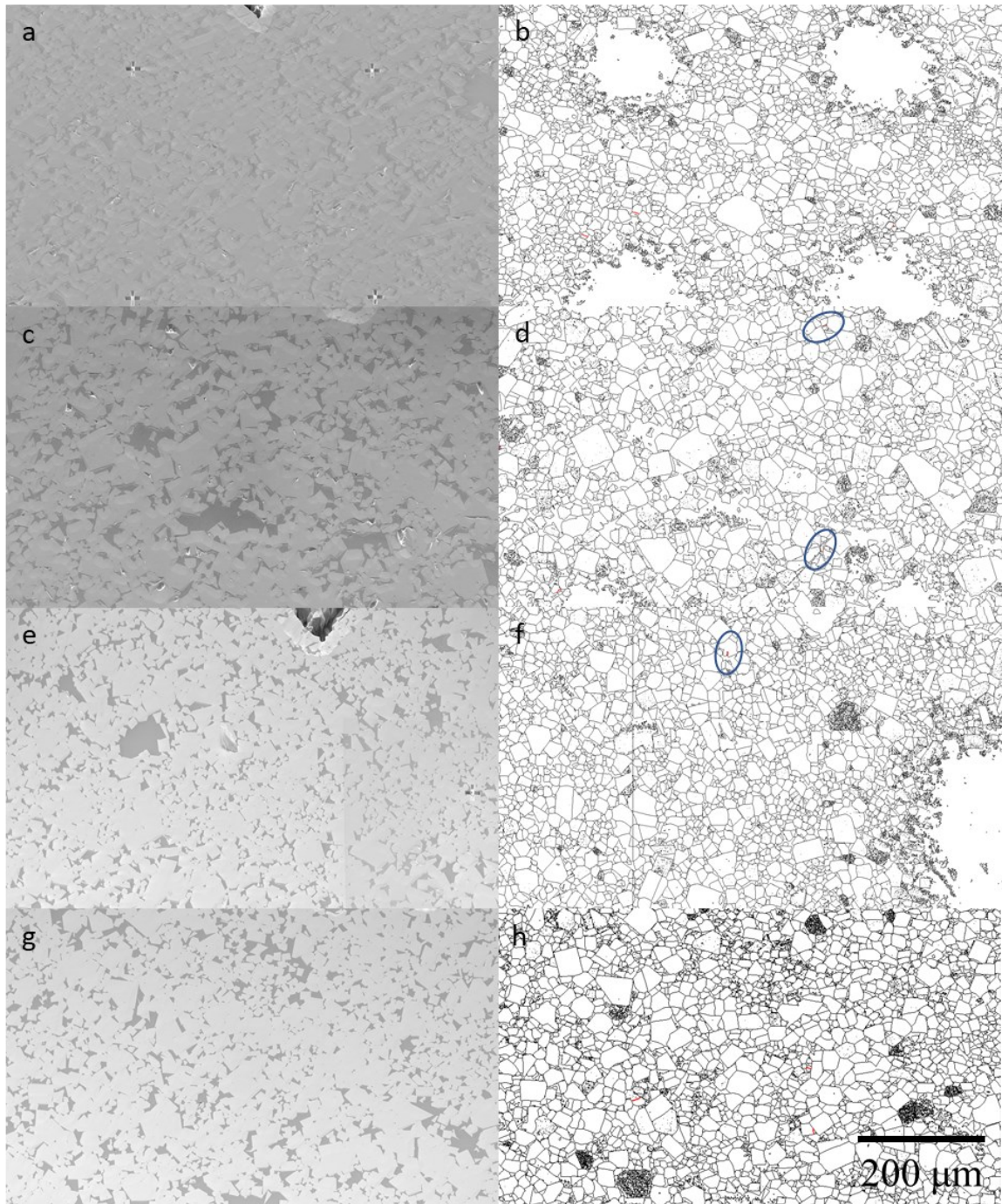


Figure 6.17: An Illustration showing the issue of low count of $\Sigma 2$ tilt boundaries present in a given scanned region in a WC-Co sample. SEM images and corresponding WC boundary schematic for four regions scanned from a WC-10wt%Co sample. Idle $\Sigma 2$ tilt boundaries suitable for DCB testing are marked with blue ellipses.

7 DCB Fracture Work

7.1 In Situ Fracture Testing

The DCB tests were performed using an Alemnis nanoindenter as mentioned in the materials and methods chapter. Tests were conducted in situ within a FEI Quanta 650 FEG SEM to record crack propagation. It was made certain that the thermal drift was sufficiently low inside the SEM sample chamber before initiating DCB testing. The thermal drift is a result of the contraction/expansion of the load cell/frame over time. The nanoindenter was operated in direct displacement mode during tests. The DCBs were loaded with a 50°/60° diamond wedge tip. Low displacement rates (1-2 nms⁻¹) were used for loading to ensure a stable crack growth. The indenter tip was set to be driven up to a target displacement of 5 µm into the DCBs. However, the indenter tip was retracted if the crack deviated from the intended path (straight down the DCB) before complete failure or if the crack tip can no longer be observed. The tip was retracted at a rate of 200 nms⁻¹ at the end of the tests.

7.2 Fracture Energy Measurement

7.2.1 Determination of Fracture Energy

Determination of cleavage energy (G) necessitates variables from equation 7.1 to be known. These variables include the elastic modulus (E) of the WC crystal, cantilever arm width (d), cantilever arm deflection (δ) and crack length (a). The orientation dependence of elastic modulus needs to be accounted for when determining its magnitude for a WC crystal along a particular direction. Equation is 7.1 used to determine the elastic strain energy release rate for a single arm. This is derived from the Euler-Bernoulli beam theory with the application of the rotation correction given that the arm is sufficiently long ($a \gg d$). The cleavage energy is then obtained by summing the elastic energy release rate for both arms of a DCB.

$$G = \frac{3Ed^3\delta^2}{8(a + \chi d)^4} \quad (7.1)$$

7.2.2 Elastic Modulus

The elastic modulus was determined using elastic constants obtained from Landolt-Börnstein [222] in conformity with Hearmon's work [223]. For the [0001] oriented WC crystal, an elastic modulus of 825.6 GPa was calculated and used in the deduction of cleavage energy of the type II {10 $\bar{1}$ 0} planes. The elastic moduli calculated for the WC grains sharing a Σ 2 twist boundaries where a successful DCB test was conducted are provided in table 7-1.

Table 7-1: WC grain orientations at $\Sigma 2$ boundaries and their respective elastic moduli. Grain orientations are provided as Euler angles in the Bunge convention and as Miller indices of the direction out of the sample. Euler angles are given in degrees. Miller indices have been rounded off to the nearest whole number.

Boundary	Euler Angle ($^{\circ}$)			Direction [UVTW]	Elastic Modulus (GPa)
	ϕ_1	Φ	ϕ_2		
$\Sigma 2B1$	159.2	23.0	195.0	$[1\ \bar{4}\ 3\ 10]$	821.55
	55.9	83.8	278.5	$[\bar{1}\bar{2}\ 2\ 10\ 1]$	600.21
$\Sigma 2B2$	52.4	41.0	308.3	$[\bar{8}\ 5\ 3\ 9]$	776.20
	243.0	51.9	113.5	$[12\ \bar{5}\ \bar{7}\ 9]$	724.07
$\Sigma 2B3$	2.7	79.1	356.1	$[\bar{6}\ 11\ \bar{5}\ 2]$	608.53
	147.3	8.4	217.6	$[0\ \bar{1}\ 1\ 8]$	826.00

7.2.3 Processing of DCB Test Videos

The other three variables were determined from the SEM images acquired within the duration of the tests. The resolution of the images was chosen such that images were captured reasonably frequently while retaining an appreciable resolution ideal for analysis. The SEM was operated with an acceleration voltage, spot size and aperture size of 5 kV, 5.5 and 100 μm respectively. The SEM images were captured at a resolution 1024x884 every 500 ms (2 FPS). The stacks of images were converted into videos in the .avi format through ImageJ. These videos were then processed via custom MATLAB scripts as required for cleavage energy calculations. A parent script was structured as a main body to call nested functions to accomplish various tasks necessary for cleavage energy calculations.

The first custom function called from the main script extracted the resolution, frame rate, number of frames and video length of the test videos. This function also deconstructed the videos back into individual frames while converting from RGB to greyscale and saved the data in .mat format for further processing. Subsequently, a second custom function was called from the parent script to crop the subregion of interest within the first frame to register a subregion. This is done by picking two diagonally opposite corners from the very first frame by mouse clicking. The cropped frame ideally includes the DCB and a section of the surface ahead of it. After this, two boxes are selected within the subregion for the registration of the shifts in the video. This is done by choosing two points within the subregion where the surface meets the milled area. These boxes are chosen as the contrast between pixel edges is high and remain consistent. The boxes contain features that are not affected by loading such as the sample surface ahead of a DCB.

Then a pixel wise cross correlation function, `normxcorr2`, was used where the previously chosen subregion from the first frame was cross correlated to all frames from the test by tracking the shift in the chosen features. `normxcorr2` calculates a matrix of correlation coefficients between the first frame and all the frames within the stack including the first frame. Then the maximum value of cross correlation coefficient is found for each matrix. An offset for each frame is calculated by determining the difference between the matrix index of the maximum correlation coefficient of the current and the first frame. A registration threshold is set as the maximum movement possible between any two frames. If the difference between the matrix index position of the correlation coefficient is less than the registration threshold, the offset for each frame is calculated as mentioned earlier. However, if the offset is greater than the registration threshold, the offset is taken to be the same as that of the previous frame. The offsets are then added to each frame as appropriate to correct for the shifts in the video.

The frames are cropped with the intent of improving the computation time. Meanwhile, cross correlation allows for a stable tracking of the DCB inside the window of interest across all frames. This is vital as the SEM image drift is typically observed during testing. The image drift mainly arises from sample or Alemnis rig compliance. This manifests as the entire test fixture appearing to drift downwards within the SEM image window during loading. Yet, sample charging under electron beam or switching the electron beam on and off can also cause image drifting.

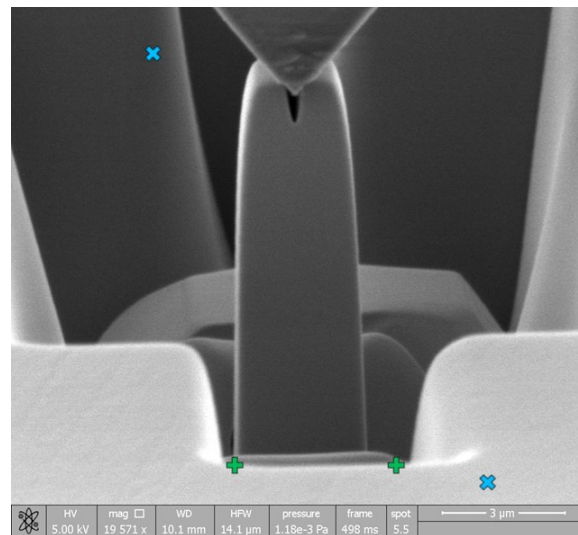


Figure 7.1: A SEM image of a DCB showing points selected for cropping as well as stabilised tracking of the DCB within the window of interest. Points selected for cropping the frame and tracking the image are coloured green and blue respectively.

7.2.4 Extraction of Data from DCB Test Videos

This was followed by measurement of the cantilever arm deflection with a cross correlation function as before. The cross-correlation function was then used to track the right and left cantilever arms independently. Firstly, two points were selected along the horizontal line where the wedge tip is in

contact with a DCB about the two edges of the DCB with the mouse cursor. This was done on the very first frame of the video. A horizontal line was extracted centred about each of the chosen points for all subsequent frames. The length of the line was set to be 60 pixels. Pixel intensities were recorded for all extracted lines in greyscale giving an intensity distribution for each line. The mean values in each case were subtracted to determine the zero mean distribution and then divided by the standard deviation to normalise the intensity distributions. Afterwards, the distributions were windowed to make them pseudo periodic. Subsequently, the distributions were fast Fourier transformed (FFT). This transforms the intensity signals into the frequency domain. Later the FFT signals from the first frame and subsequent frames were compared to determine the cantilever arm deflections. It was assumed that if the measured arm deflection was greater than 25% of the cropped SEM subregion, the measurement will not be accurate. This is a reasonable assumption as the cropped window is likely to have a width of $\sim 4\text{--}6\text{ }\mu\text{m}$ while maximum arm deflections are likely to be a few hundred nanometres. The crack length was determined from another function by clicking the crack tip position with a mouse. This function also allows for the adjustment of both contrast and brightness to make choosing crack tip position easier. The measured crack lengths were corrected for the foreshortening of the sample features as seen in the SEM. The foreshortening was the result of the Alemnis rig being inclined at 20° with respect to the horizontal and hence the mounted sample being 70° with respect to the horizontal. Finally, the individual beam widths were determined from the last frame used for analysis with the maximum crack length. Three measurements were taken for each beam along the height of the beam with an average being calculated from the three. Any given one of the three measurements for a beam is determined by selecting two points across the width of an arm with one at the outer edge and one at the crack location along the same horizontal line.

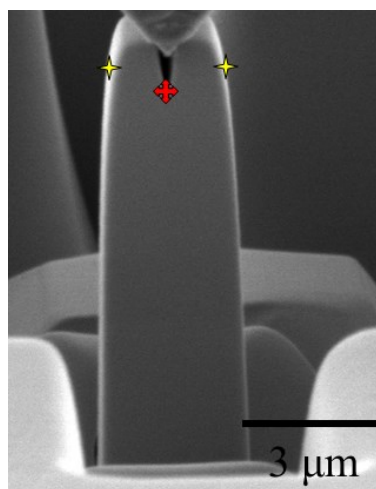


Figure 7.2: SEM image of a cropped frame depicting the points selected for lateral arm displacement tracking and identifying the crack tip coloured yellow and red respectively.

7.3 Error Analysis

An error analysis is important to quantify and record the errors contributing to the scatter of measurements in an experiment. Errors in measurements are inevitable owing to experimental uncertainties. Measured values $\pm$ error provides the limits within which the actual value is likely to exist. In this work, a Monte Carlo based error propagation analysis has been used to gauge limits of the measured fracture energy [224]. Error propagation refers to when uncertainties from measured quantities are merged in a series of calculations and are transferred onto the end product.

In the Monte Carlo analysis, inputs for chosen variables are varied independently within their respective uncertainty limits each time a value is calculated. Each input is changed by random selection from the error distribution with the measured value being given by the mean values of the input data. This will provide a distribution of all possible results from the combination of all the variables.

The variables varied for the error analysis are given in table 7-2. The error distributions of the input were generated as Gaussian distributions with known standard deviations. For each input, 1000 random numbers were generated for every fracture energy measurement within their respective uncertainty limits. This was accomplished via a custom MATLAB script using the normrnd function. Gaussian distributions produced for each input are provided in figure 7.3.

Table 7-2: Variables accounted for in the Monte Carlo based error analysis. SD is used to denote the standard deviation.

Variable	Description	Uncertainty
Viewing Angle	Angle for correcting foreshortened perspective of the sample surface in the SEM due to the tilt of the Alemnis.	3° SD
Pixel to micron	Pixel to micron conversion applied when measuring distances in the test video	1 pixel SD
Disp L and Disp R	Correction factor applied for measured cantilever arm deflection to disregard movement resulting without pure bending and any erroneous frame registration.	0.5 pixels SD
Cantilever width L and cantilever width R	Right and left cantilever arm widths (d) used in equation 6.1.	1 % error

Pre-notch length	Location of wedge-DCB contact used to determine pre-notch and crack lengths. This reference point can be moved by applying a correction factor.	10 pixels SD
Elastic modulus	Elastic modulus (E) used for equation 7.1.	10 GPa SD

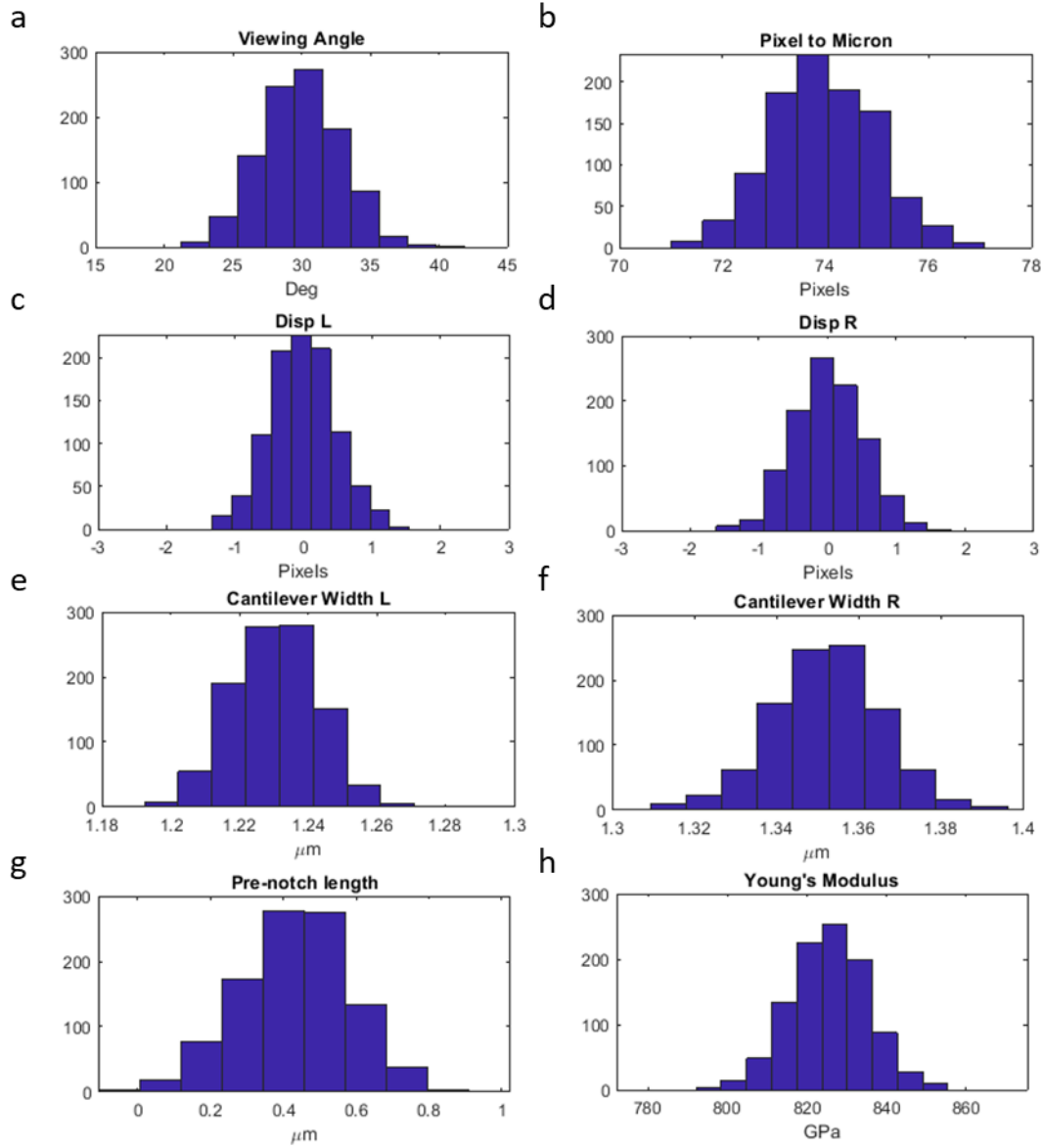


Figure 7.3: Gaussian distributions of the random numbers generated from the SC1 single crystal test used for the Monte Carlo analysis.

The mean fracture energy (μ_{DCB}) for splitting each DCB was calculated as the mean of the totality of mean fracture energy values determined for crack increment as given in equation 7.2. The error (SD_{DCB}) for the fracture energy determined for each DCB was calculated from the standard deviation

for each crack increment shown in equation 7.3. Here the crack increment is synonymously used as a stand in for a frame in the DCB test video. This has been previously detailed in a work by Sernicola [220].

$$\mu_{DCB} = \frac{1}{N} \sum_N \mu_{crack,n} \quad (7.2)$$

$$SD_{DCB} = \sqrt{\frac{1}{N} \sum_N (SD_{crack,n})^2} \quad (7.3)$$

Where $\mu_{crack,n}$ is the mean fracture energy value and $SD_{crack,n}$ is the standard deviation calculated at the n^{th} crack increment from the Monte Carlo error propagation analysis. Two error analyses, one for a single crystal (SC1) and one for a $\Sigma 2$ twist boundary DCB test ($\Sigma 2B3$) are shown in figure 7.4.

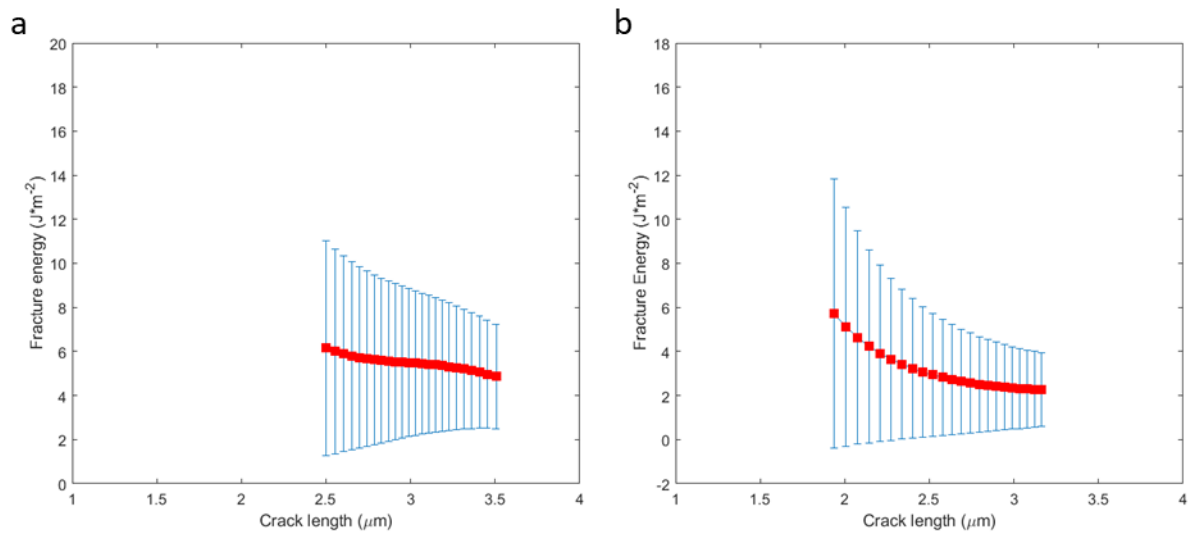


Figure 7.4: Crack length plotted as a function of fracture energy from the Monte Carlo error propagation analysis. The red data points are mean fracture energy values and blue bars are the corresponding standard deviations for various crack increments.

7.4 Discussion

7.4.1 Measured Prismatic and $\Sigma 2$ Twist Boundary Cleavage Energy

Figure 7.5 shows an example of data analysed from a DCB test (SC1). The first plot shows the displacement of the left and right cantilever arms during wedge loading. The displacement of each arm is shown as increasing in opposite directions to reinforce the notion of the opening of the cantilever arms with loading.

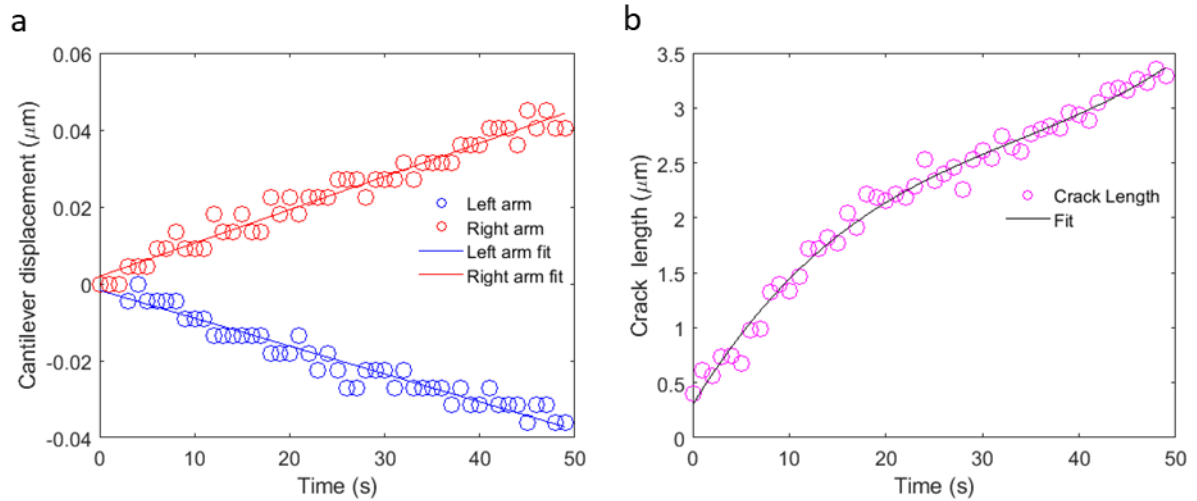


Figure 7.5: Plots showing analysis of the SC1 DCB test conducted on the WC single crystal. (a) Plot of cumulative right and left cantilever displacements plotted as a function of time along with a fit for each data set. (b) Cumulative crack length measured against time.

Crack length vs time plot from figure 7.5(b) indicates that the crack propagation velocities ($40 - 100 \text{ nms}^{-1}$) reduced with time. This is explained by the fact that the elastic energy required for crack propagation reduces with crack length. Linear and third-degree polynomial fits were used for cantilever displacement against time and crack length against time data sets respectively. A fitting was applied in both cases to reduce the scatter during fracture energy calculations.

Cracks were usually observed to initiate at the centre of the troughs and then propagate along the body of the DCB until deviation to one side. A sharp notch acts as a stress concentrator. Since notches are milled at the centre of a trough, cracks tend to initiate at these locations. Large bursts in crack lengths were observed upon crack initiation. This is due to the vast amount of elastic energy being stored in the cantilever arms and the load frame from the wedge loading. Once cracks initiated, they propagated in a stable manner. This is because the elastic energy necessary for crack propagation reduced as the crack length increased. However, eventually the cracks deviated from the intended path to the side of the DCB. Series of SEM images from a successful test are presented in the figure 7.6 illustrating the crack path along the DCB.

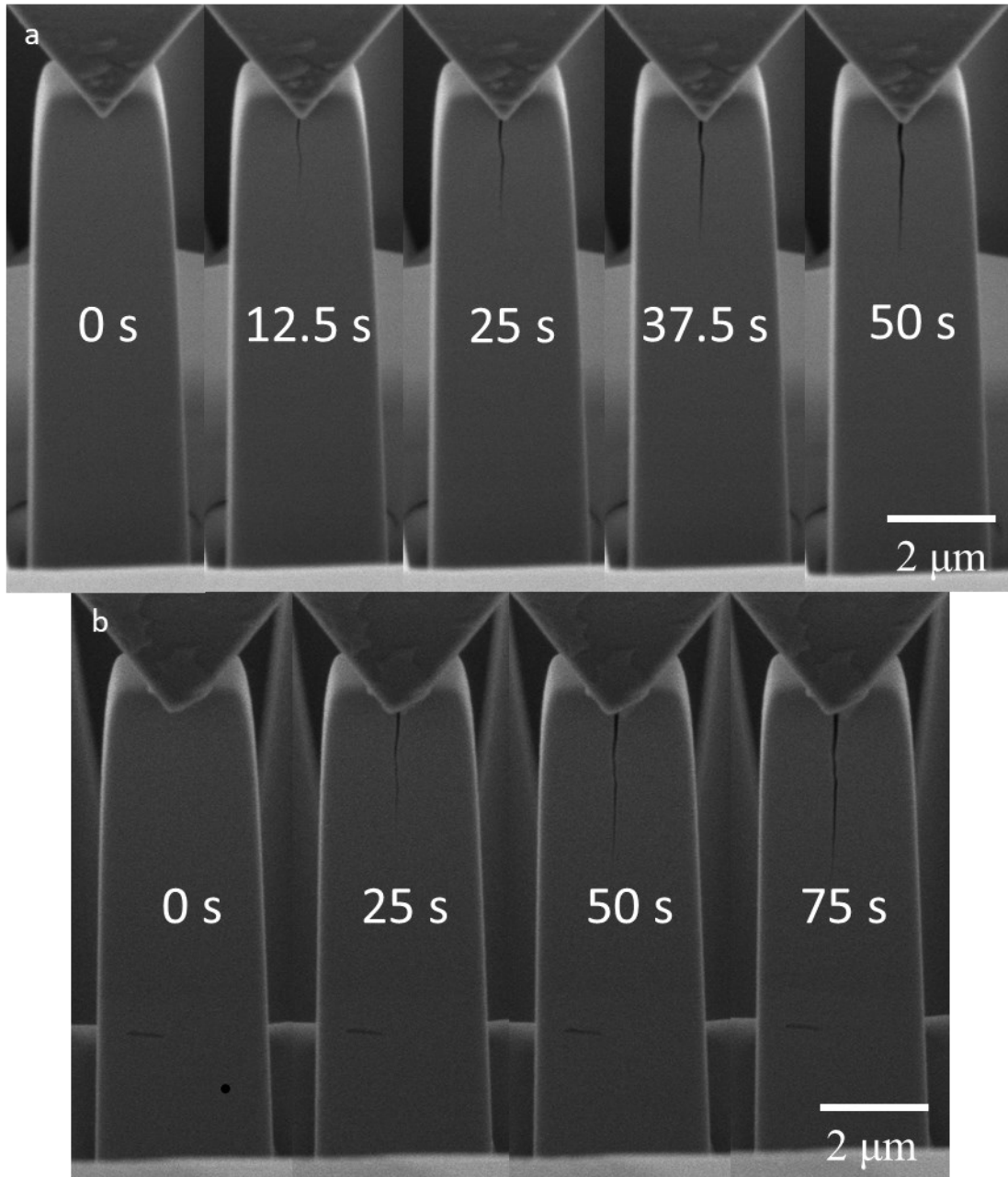


Figure 7.6: Series of SEM images depicting initiation and propagation of a crack at various time intervals across (a) a single crystal DCB (SC1) and (b) a $\Sigma 2$ twist boundary DCB ($\Sigma 2B3$).

Cleavage energies were calculated once crack lengths exceeded 1 μm . This ensured that the crack length was greater than the beam width. Crack lengths for WC single crystal DCB tests were typically shorter ($\sim 1.5 \mu\text{m}$) as is the case for SC2 and SC3. But SC1 is an exception with a maximum straight crack length of $\sim 3.5 \mu\text{m}$. In contrast, maximum crack lengths in boundaries were in excess of 2 μm . The reason for shorter cracks in WC single crystal DCBs could be due to some WC planes having similar energies as in the case of type II $\{10\bar{1}0\}$ and $\{0001\}$ planes. Hence, cracks deviated from the intended path. Presence of small variability in fracture energy measurements can be seen from the figure 7.7

for all cases. This alludes to the possibility of crack branching or even the crack jumping between multiple planes.

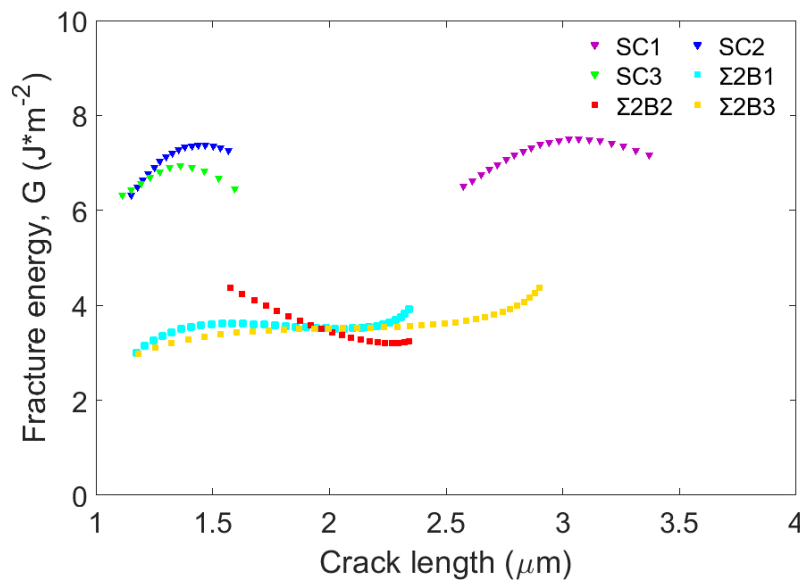


Figure 7.7: Fracture energy plotted against crack length for three successful tests on the WC single crystal (SC1, SC2 and SC3) and WC/WC $\Sigma 2$ twist boundaries ($\Sigma 2B1$, $\Sigma 2B2$ and $\Sigma 2B3$).

Figure 7.7 shows that the fracture energies for $\Sigma 2B1$ and $\Sigma 2B3$ boundaries increase close to their respective maximum crack lengths. The increase in energy is related to the cracks deviating from a straight path and onto DCB edges near the end of their respective straight crack paths. Bending of a crack means the thickness of the cantilever arms are no longer well defined. Since the cantilever arm thickness is assumed to be constant during crack propagation, the equation for calculating fracture energy is no longer valid. This gives rise to the increase in fracture energy calculated for $\Sigma 2B1$ and $\Sigma 2B3$ boundaries close to maximum crack lengths.

As discussed in the previous chapter, it must be noted that milling a DCB with a boundary sitting exactly in the middle of the DCB geometry is difficult. This is understandable as a boundary is typically a few atomic layers thick while the precision afforded (~ 100 nm) when selecting the location for milling is not sufficient to mill a DCB notch at the exact location of a boundary. Therefore, it is highly likely that the crack initiates away from the boundary location. Nevertheless, it will in due course shift onto the boundary due to it being a low energy crack path.

7.4.2 WC Crystallographic Plane Energies from Literature

WC is non-centrosymmetric. This results in corresponding pairs of prismatic planes (e.g. $(10\bar{1}0)$ and $(\bar{1}010)$) exhibiting polar character and not being equivalent. This results in the growth of one set of prismatic planes being promoted by the presence of cobalt during LPS. French and Thomas investigated the polar nature of the two sets of prismatic planes using Knoop microhardness tests and

wetting experiments [225]. Specifically, the $(10\bar{1}0)$ and $(\bar{1}010)$ planes were experimentally studied. The authors used four different liquids for the wetting experiments: mercury, mineral oil, water and phosphate ester. They measured different sessile drop contact angles for the two types of prismatic planes when using polar liquids while no appreciable difference was found with non-polar liquids. The contact angles were greater on $(\bar{1}010)$ planes than $(10\bar{1}0)$ planes. Finally, the study also found that the hardness on $(10\bar{1}0)$ planes was higher than $(\bar{1}010)$ planes.

The two types of prismatic planes are called type I and II as was discussed in the first chapter. The two plane types are illustrated in figure 7.8. The difference between the prismatic plane types can be inferred from the number of bonds between the atoms of the terminating and penultimate layers. If each of the terminating W or C atoms are bonded to two C or W atoms respectively, the prismatic plane is type I. In other words, if the terminating atom has 4 dangling bonds, the prismatic plane is type 1. On the other hand, the prismatic plane is type II if the opposite is true. The two non-equivalent prismatic planes are depicted with W and C carbide terminations.

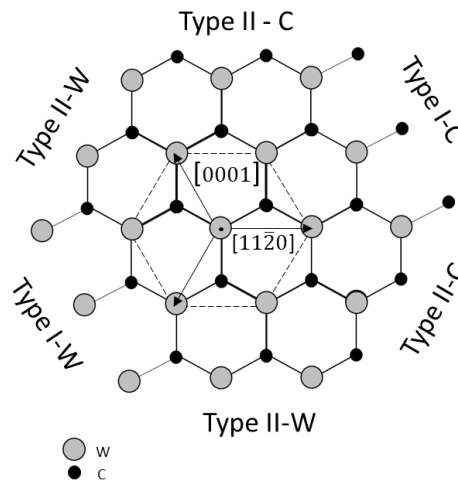


Figure 7.8: Schematic of the type I and type II prismatic planes as seen from the $[0001]$ direction.

Another way to distinguish between the two sets of the prismatic planes is in the sequence of atomic planes parallel to the normal of the prismatic plane [47]. The interlayer distance between the atomic planes arranged from the centre of the grain to the surface varies in two sequences. These sequences for type I and type II surfaces are given below.

$$\text{Type I: Core} \rightarrow W (d) C (2d) W (d) C (2d) \rightarrow \text{Surface}$$

$$\text{Type II: Core} \rightarrow W (2d) C (d) W (2d) C (d) \rightarrow \text{Surface}$$

Where W and C are the tungsten and carbon atomic layers while d is the interlayer spacing between the atomic planes. The interlayer spacing, d is given in terms of the lattice constant as $d = a\sqrt{3}/2$ (0.084 nm). The interlayer spacing is also different between the two types of prismatic planes. Interplanar spacing between type II, W and C planes is twice the size of that for the type I counterpart

[47]. DFT studies have been conducted to determine surface energies of WC crystallographic planes.

A summary of such DFT data is given in table 7-3.

Table 7-3: Surface energies of WC (0001) and (10 $\bar{1}0$) planes determined via DFT calculations for η limit (carbon deficient) and graphite limit (carbon rich) conditions.

Crystal Plane	Termination Layer	Number of Dangling Bonds	Surface Energy (Jm ⁻²)					
			η Limit			Graphite Limit		
			Ref. [226]	Ref. [227]	Ref. [228]	Ref. [226]	Ref. [227]	Ref. [228]
(0001)	W	3	3.45	2.9941	-	3.77	3.5933	-
(0001)	C	3	6.07	6.3984	-	5.75	5.7977	-
Type I (10 $\bar{1}0$)	W	4	5.07	4.4712	5.09	5.44	5.1841	5.39
Type I (10 $\bar{1}0$)	C	4	9.02	9.6008	8.76	8.64	8.7277	8.47
Type II (10 $\bar{1}0$)	W	2	3.77	3.4971	3.74	3.96	3.8528	3.88
Type II (10 $\bar{1}0$)	C	2	3.56	3.7503	3.51	3.37	3.3946	3.37

The minor difference between energies calculated by the three studies is due to two main factors. Firstly, variation in lattice constants used for surface energy calculations lead to minor discrepancies. Difference in the definition of the carbon chemical potential is another cause of surface energy deviation. For example, carbon deficient conditions being set by the W₂C phase instead of the η phase.

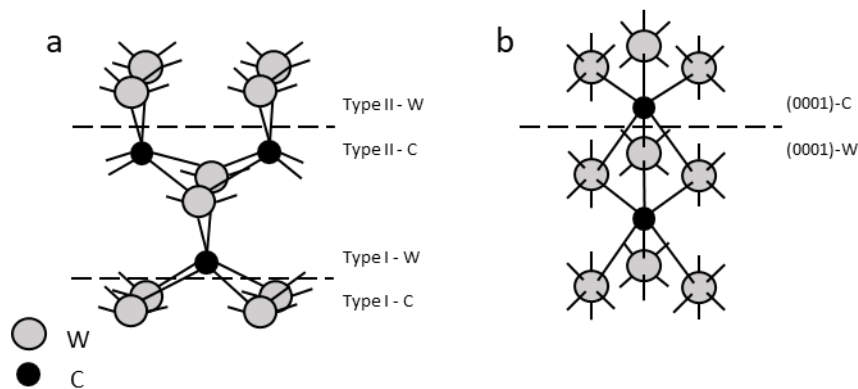


Figure 7.9: A sketch showing the bonds broken for each carbon and tungsten atom when cleaving (a) type I and II {10 $\bar{1}0$ } as well as (b) {0001} surfaces.

W-C bonds in WC is strong polar covalent and metallic in character. These bonds are broken when a WC crystal is cleaved. Two free surfaces are created during cleavage, one with W and one with C termination. The cleavage energy for a given plane is the sum of the surface energies of said plane with C and W termination. Cleavage of {0001} basal planes is rather simple with a cleavage energy of

9.39-9.52 Jm⁻². Three bonds are broken per unit surface area ($a^2\sqrt{3}/2$). In contrast, prismatic planes can be split in two ways as illustrated in figure 7.9. A WC crystal can be split between a W and C terminated type I or type II planes. The cleavage energies in each of the cases will be 13.85-14.09 Jm⁻² and 7.25-7.33 Jm⁻² respectively [226-228]. Four and two W-C bonds are broken per unit surface area for type I and II surfaces respectively. This results in the cleavage energy of type I planes being twice the magnitude of that determined for type II planes. The {0001} and type II {10 $\bar{1}$ 0} planes grow preferentially during LPS owing to the lower surface energy.

7.4.3 Discussion of the Fracture Work

7.04 ± 0.36 Jm⁻² fracture energy was measured for cleaving type II {10 $\bar{1}$ 0} planes. The errors presented here are based on the dispersion of the data rather than determined via the Monte Carlo error analysis. Measured fracture energy values agrees well with those (~7.3 Jm⁻²) determined from ab initio calculations as taken from the literature. This shows that the DCB fracture test method to be a valid technique for measuring the cleavage energy in WC. A fracture energy of 3.57 ± 0.28 Jm⁻² was measured for Σ 2 twist boundaries. This measurement is half the value measured for type II {10 $\bar{1}$ 0} planes. This observation implies that the type II {10 $\bar{1}$ 0} planes (the weakest planes in WC) have a higher resistance to crack propagation than the Σ 2 twist boundaries (the most abundant boundary). This is reflected in macroscopic nanoindentation scale fracture tests where cracks have been observed to propagate mostly in an intergranular fashion in WC-Co relative to the fraction of transgranular fracture with respect to carbide grains [79].

Further DCB tests were performed at Σ 2 twist boundaries on a chromium doped sample (WC-10wt%Co-1wt%Cr) similar to that reported here. ~30 DCB tests were carried out at ideal (perpendicular to the surface) Σ 2 twist boundaries on the chromium doped sample. All of the tests had either unstable crack growth or deviation of the crack path from the intended path after a short crack propagation followed by cleavage of the cantilever arms. In comparison, 1-2 out of 5 DCB tests at Σ 2 twist boundaries on a standard sample (WC-10wt%Co) yielded stable crack growth ideal for fracture energy measurements. Thus, it was concluded that the Σ 2 twist boundaries in the chromium doped sample were tougher than their standard sample counterpart. This is because the increased difficulty in getting a stable crack growth in a DCB test is consistent with the notion of increased fracture toughness.

7.5 DCB Crack Path in TEM

7.5.1 TEM Lamella Preparation

TEM lamellae were extracted from successful DCB tests for TEM inspection. TEM sample preparation and imaging was again done by Oriol Gavalda Diaz. Lamella extraction procedure is like that detailed in the Technique Development chapter. This was done to achieve the following goals: to confirm the

crack had propagated along intended WC planes or boundary, inspect crack deflection, look into possible presence of crack branching or plastic deformation around crack path and finally examine the boundary chemistry.

Thinning of DCB lamellae was fairly challenging. This was due to the propensity of the region around the crack on the DCB to undergo excessive milling. This meant that either the region around the crack might be lost or one of the DCB arms would break off.

Lamellae were extracted from a WC single crystal and $\Sigma 2$ twist boundary DCB after fracture. Images of two such DCBs are given in figure 7.10. In the case of the WC single crystal DCB, the crack was visible after test unlike the boundary counterpart. The same observation was also made after thinning lamellae extracted from these DCBs to electron transparency as shown in figure 7.11 and 7.12.

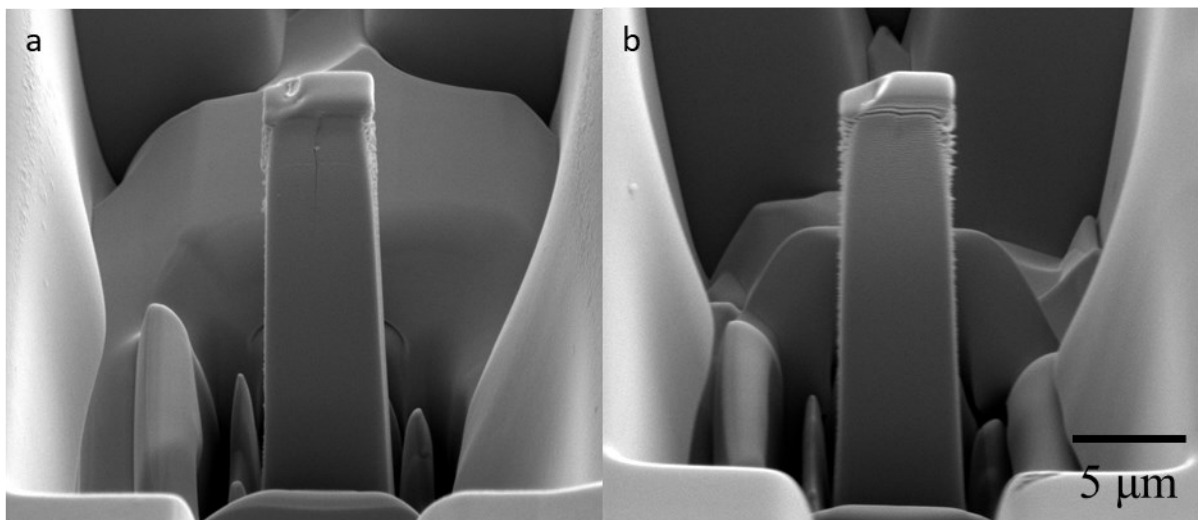


Figure 7.10: SEM images of the (a) single crystal and (b) $\Sigma 2$ twist boundary DCB chosen for TEM lamella preparation with platinum deposition.

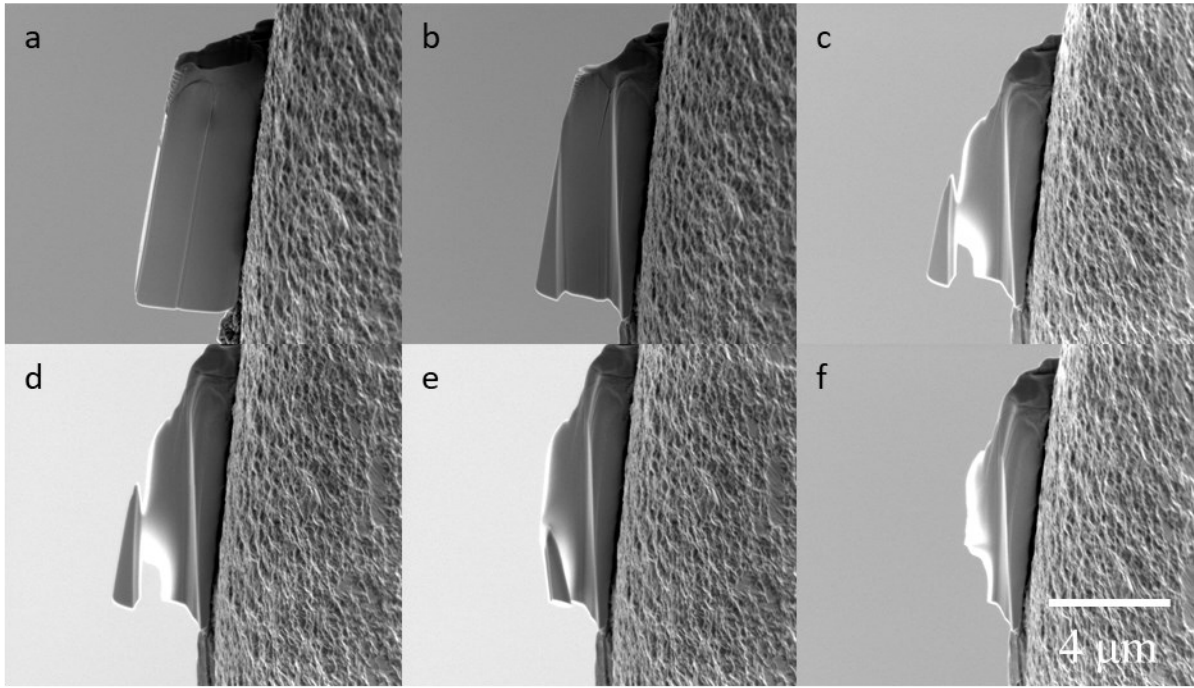


Figure 7.11: SEM images depicting the thinning process of a TEM lamella extracted from the WC single crystal.

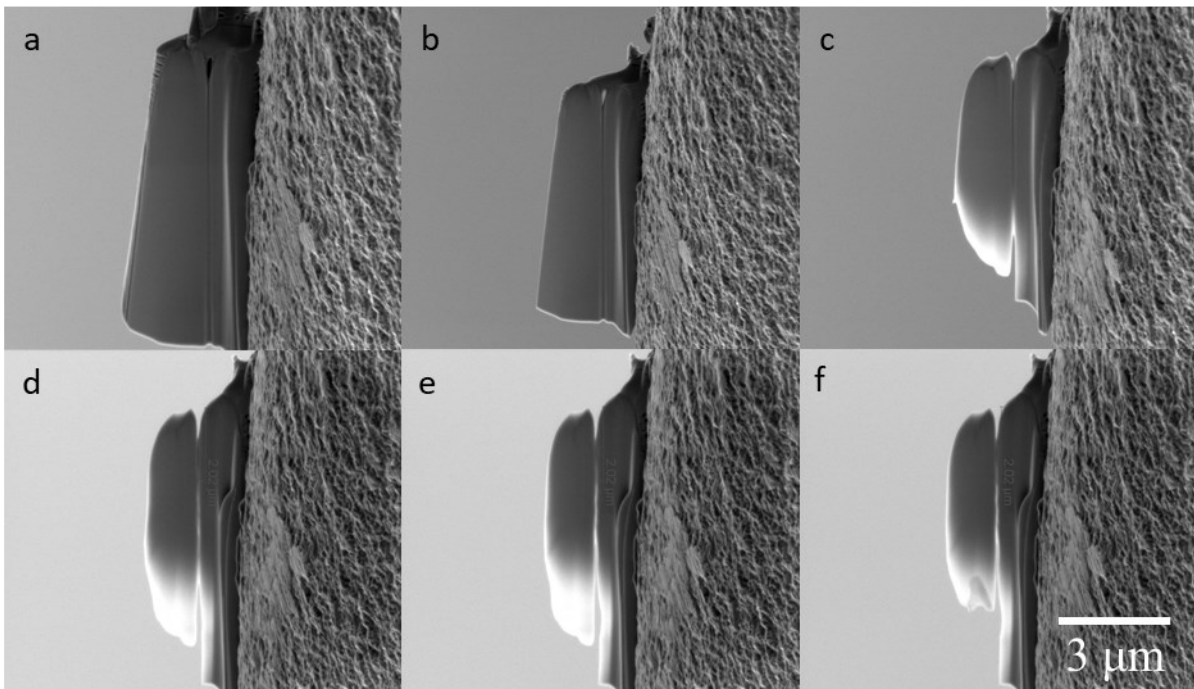


Figure 7.12: SEM images showing the thinning process of the lamella extracted from the $\Sigma 2$ twist boundary.

7.5.2 TEM Imaging of DCBs

Figure 7.13 shows a series TEM images from the WC single crystal DCB. The crack path can be traced in these images. It can be seen that the crack propagated up to 2 μm straight down the middle of the DCB. The true crack length is greater than 2 μm as the top part of the DCB arms were lost during lamella thinning. The crack had then shifted and propagated to the left edge of the cantilever arm. It

can be noted from the high resolution TEM images of the crack path in figure 7.14 that the crack ran parallel to the $\{10\bar{1}0\}$ planes during the straight section.

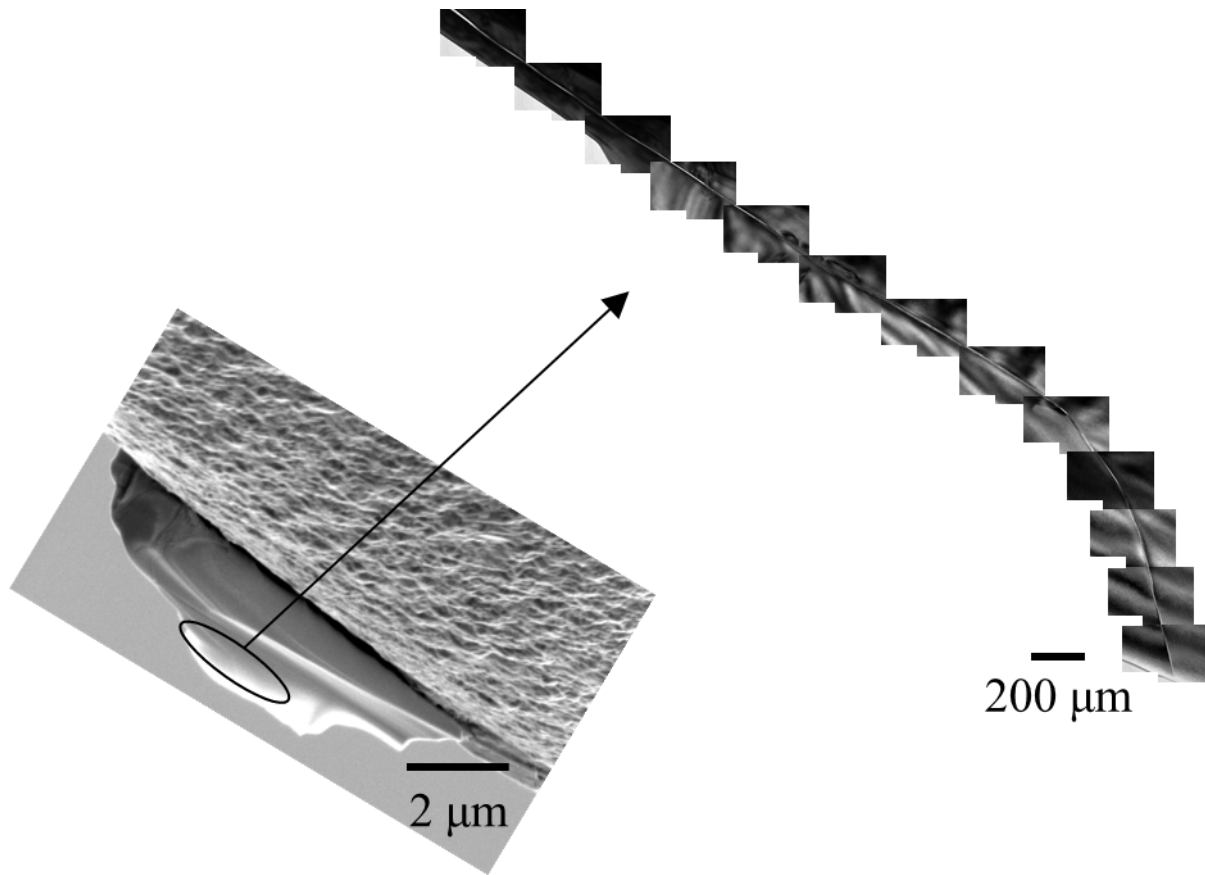


Figure 7.13: Examination of crack path in a single crystal DCB (SC1). (a) SEM image of a lamella prepared for crack path investigation. (b) TEM images of the crack path in the same lamella.

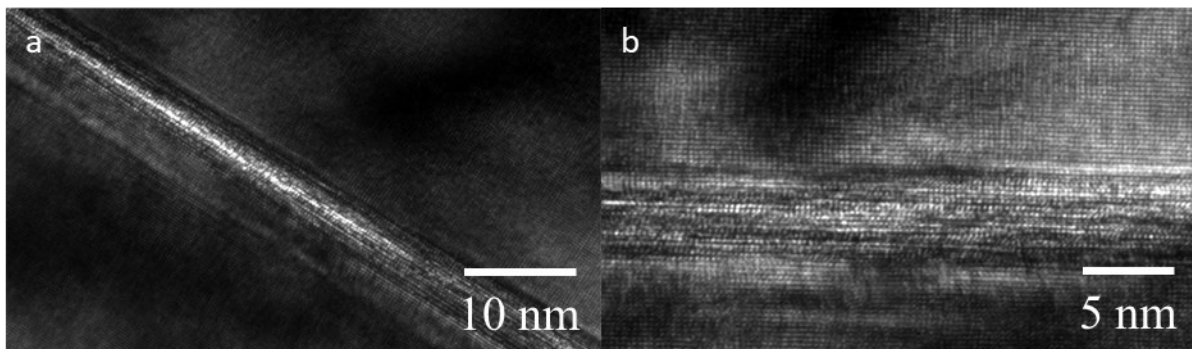


Figure 7.14: TEM images showing the crack path being parallel to the prismatic planes before deviation to the side of the DCB.

Series of TEM images from figure 7.15 show what appears to be a plastically deformed region around the location of the cracks. The plastically deformed region has a width of ~ 6 nm. There are two possible causes that can give rise to this plastically deformed region. Firstly, a large plastic zone around the crack tip during fracture. High compressive stresses acting on the fracture surfaces during crack closure as the wedge indenter tip is retracted is another possibility. Crack branching was also observed

within the plastic region. It should be noted that the region that tends to appear as a plastically deformed region around the crack could actually be an imaging artefact resulting from not looking exactly perpendicular to the intended surface or even an overlap of the two crystals from each of the DCB arms.

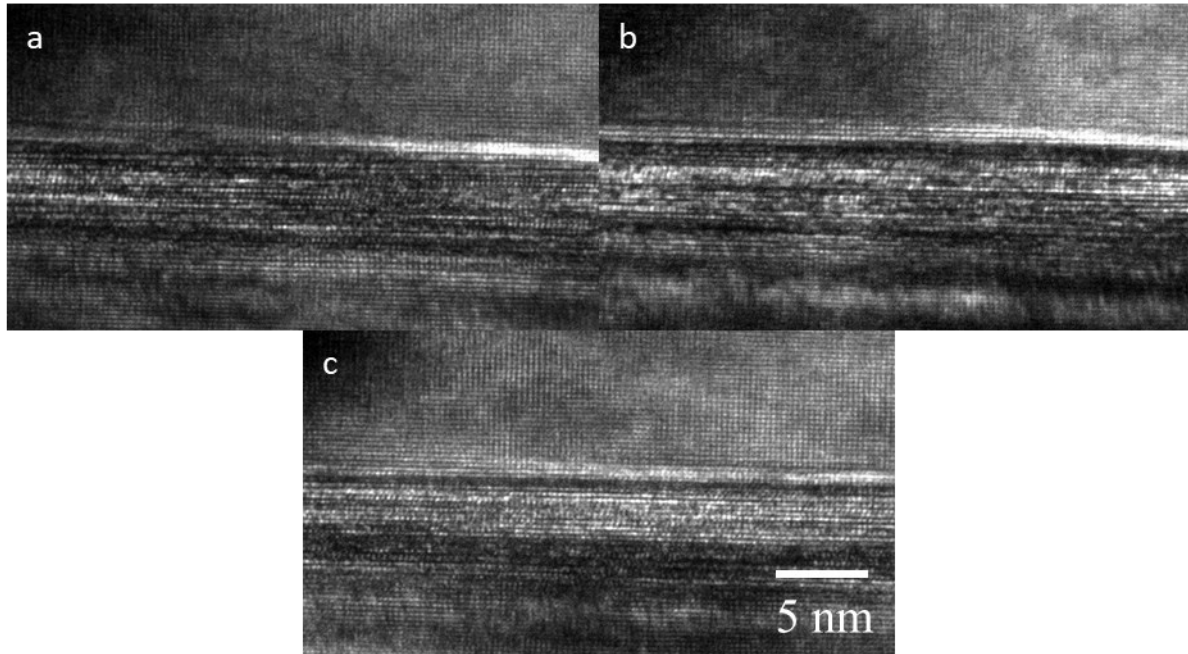


Figure 7.15: TEM images showing a deformed plastic region around the crack path along with crack branching.

TEM images of the crack path in a $\Sigma 2$ twist boundary DCB are shown in figure 7.16. This shows that the crack initiated on the left WC grain sharing the boundary, ~ 20 nm to the left of the notch. It can be visually deduced that the crack eventually propagated towards and then through the $\Sigma 2$ twist boundary. Finally, the STEM EDX evaluation of the boundary revealed that there was no cobalt infiltration.

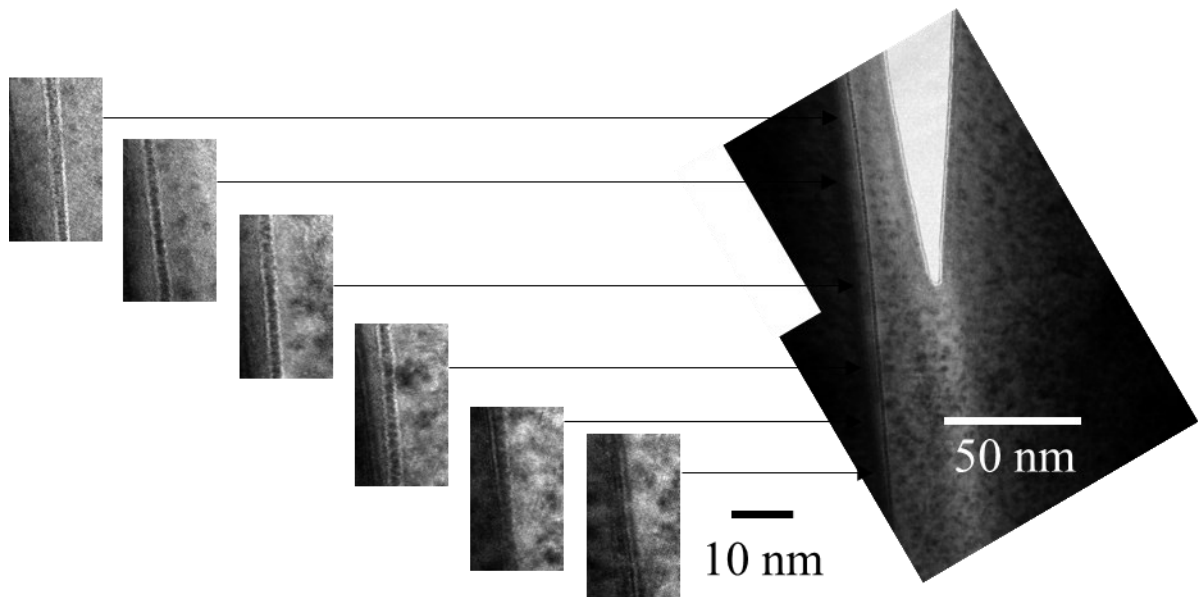


Figure 7.16: TEM images showing crack path through a $\Sigma 2$ twist boundary DCB.

7.6 Summary

Fracture energies of the type II $\{10\bar{1}0\}$ planes ($7.04 \pm 0.36 \text{ Jm}^{-2}$) in a WC single crystal and $\Sigma 2$ twist boundaries ($3.57 \pm 0.28 \text{ Jm}^{-2}$) in polycrystalline WC-Co samples were measured via DCB tests. Measured fracture energy values for type II $\{10\bar{1}0\}$ planes were like the cleavage energies ($\sim 7.3 \text{ Jm}^{-2}$) determined from DFT calculations in the literature.

Crack paths from successful DCB tests were examined in a TEM to verify if the cracks propagated along the intended planes or boundaries. In the case of the WC single crystal DCB tests, cracks were observed to run parallel to the $\{10\bar{1}0\}$ planes as expected. Similarly, cracks were observed to propagate along the $\Sigma 2$ twist boundaries for the tests on the WC-Co samples. Though, cracks were observed to initiate to the side of the boundaries as anticipated. This was attributed to the inherent difficulty in milling a DCB with the boundary running precisely down the middle of it. Plastically deformed regions were observed around the crack paths in the single crystal DCB tests. But it was theorised that imaging artifacts could also explain such observations.

8 EBSD Boundary Analysis of WC-Co

In this chapter, the effect of chromium doping on the grain boundary plane distribution and populations of the most abundant WC boundary types ($\Sigma 2$ and $\Sigma 13$ boundaries) have been investigated against a standard WC-Co material. Additionally, grain size and texture analyses of the two samples were also carried out.

The grain boundary statistical analysis was performed with the intent of examining how frequent are the most abundant WC boundaries. Higher population for a given grain boundary type will suggest a lower grain boundary energy. This means better atomic coordination at the grain boundaries. Therefore, a higher fracture toughness for that specific grain boundary type. It is preferable to have such favourable boundaries in the microstructure to improve the bulk fracture toughness of WC-Co. Addition of chromium to WC-Co is likely to alter the grain boundary distributions as a direct result of alterations to the WC boundary chemistry. Thus, by comparing the grain boundary distributions between a standard and a chromium doped WC-Co sample, one can identify if the favourable boundary populations are altered. This knowledge can then be utilised to tailor WC-Co microstructure via GBE to produce WC-Co components with superior fracture properties and increase component lifetimes.

8.1 EBSD Data Processing

EBSD data necessary for the grain boundary statistical analysis was acquired as described in the Materials and Methods chapter. Data was obtained from nine $700 \times 500 \mu\text{m}^2$ regions from each of the WC-10wt%Co and WC-10wt%Co-1wt%Cr samples. These were the same large WC grained samples specially tailored for the DCB tests. Once the EBSD data was acquired, it was then processed with the EDAX OIM Analysis™ v8 software. The EBSD data was captured in a .bcf format and was then converted to a .ctf format before export from the Bruker Esprit 2.2 software. This was done to ensure file compatibility with the OIM Analysis™ software.

The .ctf file was then imported into the OIM software. Some of the .ctf parameters were then mapped onto OIM parameters. These include the number of Kikuchi bands detected, assigned as the confidence index (CI). CI is a measure of the degree of credence for an orientation being the solution to a data point. CI of -1 is for non-indexed patterns. Band contrast was mapped onto the image quality (IQ) parameter. Band contrast is a measure of the EBSD quality by determining the sharpness between the Kikuchi bands and the background. Other parameters imported from the .ctf file include the phase, coordinates, Bunge Euler angles, mean angular deviation (MAD) and band slope (BS). Misfit between the measured and the computed angles between the Kikuchi bands is specified as MAD. BS is a gauge of the gradient of intensity at the edge of the Kikuchi bands. It is another index of pattern quality

similar to BC. Finally, the basis was rotated by 30° for the hexagonal crystal per the EDAX convention during import.

Once the EBSD data had been imported, a clean-up step was deployed to minimise or eliminate any potential artefacts. Artefacts included mis-indexed data points due to pseudosymmetry issues and non-indexed data points. First grains and inclusions smaller than 200 and 100 pixels were removed from the data set. It was also ensured during this step that the grains and inclusions be composed of multiple rows. Afterwards, a grain dilation routine was applied where the procedure stops after the data changes $> 1\%$. An angle of 5° for the grain tolerance and a confidence index of 0.2 were used during the clean-up step.

Cleaned data was converted from a square grid to a hexagonal grid. EBSD data is acquired in a square grid in the Bruker EBSD system. This is a consequence of the way in which the SEM electron beam probe is scanned across the sample. The electron beam is raster scanned across the sample in a grid like fashion starting from the top left corner of the region of interest in a SEM.

The cleaned data was converted into a hexagonal grid due to the following merits. A hexagonal grid more efficiently samples axisymmetric structures than a square grid. In other words, a hexagonal grid more accurately renders microstructural features. Another advantage is that in a hexagonal grid there is less ambiguity when trying to define a neighbourhood. In a square grid a data point can have four or eight neighbours depending on if the diagonals are considered as a part of neighbours. Four neighbours mean the neighbours are not contiguous. Eight neighbours mean point to point distances are no longer constant. In contrast each data point has six equidistant neighbours except for those at the edges of the grid in a hexagonal grid. This ensures a contiguous series of neighbours for almost all data points. This is crucial as equidistant and contiguous neighbours allows for higher simplicity and accuracy in neighbour connectivity calculations employed across grain grouping algorithms in the OIM Analysis™ software. Difference between neighbour grains in a square grid and a hexagonal grid are shown in the figure 8.1.

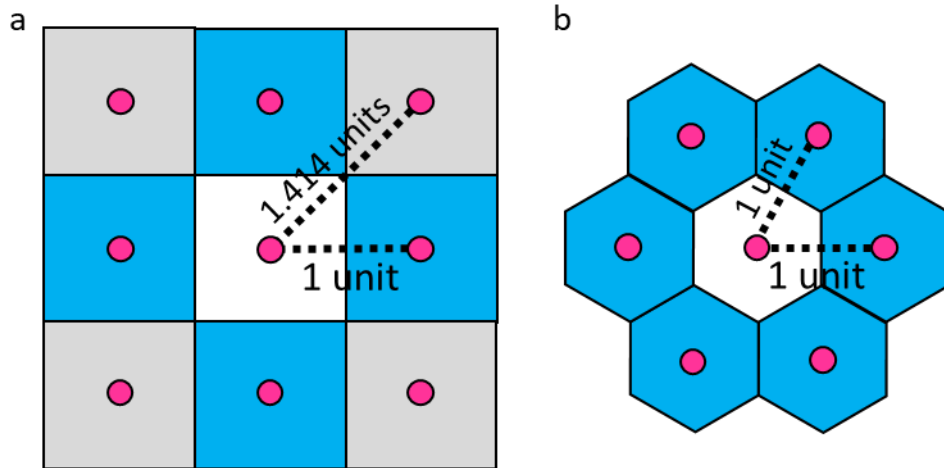


Figure 8.1: A sketch depicting the ambiguity in defining neighbouring grains in a square grid unlike a hexagonal grid. Neighbouring EBSD data points in (a) a square and (b) a hexagonal grid. Distance between two points is measured in units. Centre of data points are represented as red circle. Data point of interest is coloured in white. The closest neighbours to data of interest are coloured in blue. Diagonal neighbours in the square grid are shown as grey squares.

In the OIM Analysis™ software, if the misorientation between two points exceeds a user defined threshold (5°), a boundary line segment is drawn. Allowable angles for any such line segment are limited to 0° , 60° and 120° in a hexagonal grid compared to 0° and 90° . This means the hexagonal grid provides a truer representation of the boundary angle and length. Yet, the limitation of the data points being spaced out due to the inherent nature of EBSD data collection means errors associated with the boundary angle and length persist.

To overcome this limitation, boundary segments between any two triple points are linked to create the so-called reconstructed boundaries. This was done by first drawing a reconstructed boundary segment between two triple junctions. The triple junctions can be thought of as nodes connecting a reconstructed boundary segment. If the maximum deviation between the reconstructed boundary and the corresponding boundary segments is smaller than twice the step size, further nodes are added until this threshold is met. Difference between the boundaries in a square grid, hexagonal grid and reconstructed boundaries are shown in figure 8.2.

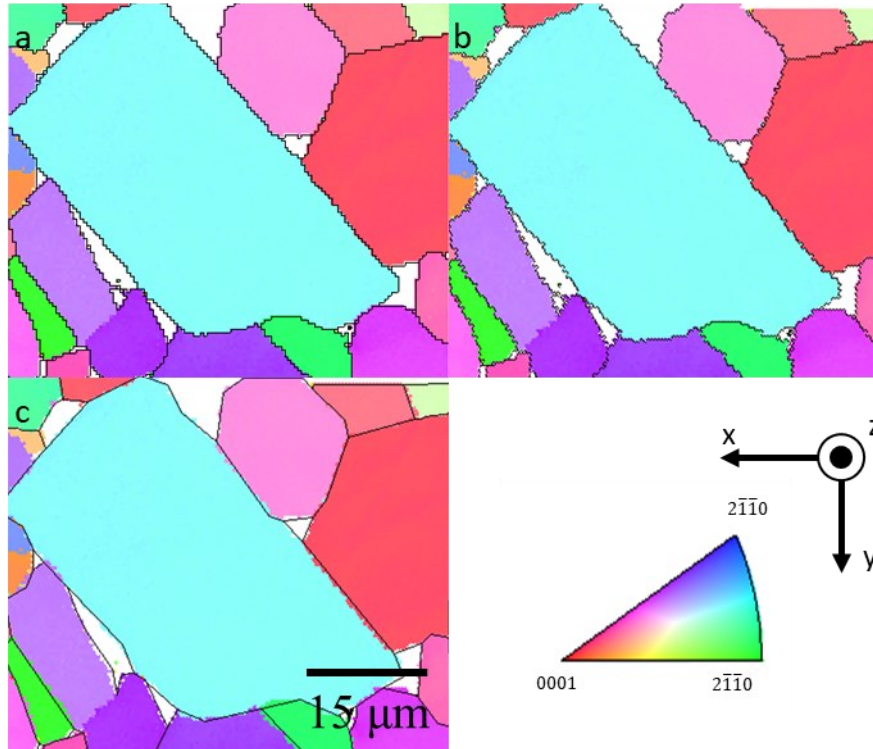


Figure 8.2: IPF-Z maps of a region from the standard sample plotted with (a) a square grid, (b) a hexagonal grid and (c) a hexagonal grid with reconstructed boundaries.

Afterwards, the cleaned data was rotated by 90° counter-clockwise about the axis 3 in the sample reference frame. Axis 3 in the sample reference frame is given as in figure 8.3. This was to account for the difference in data conventions between the Bruker and EDAX software. Then, WC reconstructed boundary segments were extracted from each of the 9 data sets for each sample as .txt files. These files contained information such as IDs, Bunge Euler angles and misorientation axis for grains on either side of a boundary, misorientation angle, boundary length, boundary trace angle and coordinates of boundary end points. After this, segment files were imported into MATLAB and with the help of the GBCD stereology toolbox (developed at CMU, Pittsburgh), segments files for the samples were combined independently to form two segment files. $4.5 \cdot 10^5$ WC boundary segments were extracted for each of the samples.

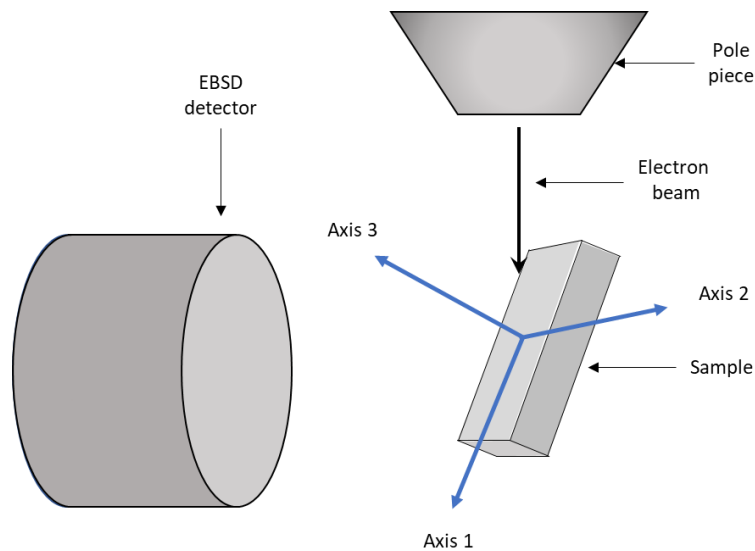


Figure 8.3: Diagram illustrating the sample reference frame of a sample as when located within a SEM sample chamber during EBSD data collection.

Later WC/WC boundary segments from each of these files were extracted. This was done by omitting grain boundary segments that had one of the grains with all three Bunge Euler angles being zero. All three Euler angles being zero implies that the data belongs to the cobalt phase or is from a non-indexed data point. At the end, there were two segment files per sample: one with all carbide boundary segments and another with WC/WC boundary segments.

8.2 Grain Size

8.2.1 Importance of Grain Size in Microstructure

WC grain size in WC-Co is an important parameter. This is because the grain size affects physical properties especially hardness of WC-Co which in turn is linked to material behaviour during processes such as wear and creep. An inverse correlation exists between hardness and grain size which is modelled by a Hall-Petch like relationship [56]. Moreover, commercial WC-Co grades are partly defined by the grain size. Since grain growth of WC powder occurs during sintering, grain size is measured from the final sintered product.

8.2.2 Grain Size Distribution

WC grain size in WC-Co is not homogeneous. So, it is given as a distribution. Berbenni et al. have shown that the degree of grain size dispersion influences physical properties such as yield stress for polycrystalline iron (Fe- α) [229]. This effect is most pronounced for small mean grain sizes. Work was carried out to determine grain size distribution, mean grain size and grain size dispersion for the WC-10wt%Co and WC-10wt%Co-1wt%Cr samples. Difference in mean grain size and grain size dispersion will possibly contribute to difference in material performance.

One approach for calculating grain size is to determine WC grain areas from an image of the microstructure and then convert them to equivalent geometrical shapes, traditionally a circle [230]. The grain size is then reported as the equivalent circle diameter (ECD) with the same cross-sectional area as the real grain. The ECD approach was used in this work to evaluate the WC grain size of the WC-10wt%Co and WC-10wt%Co-1wt%Cr samples via the EDAX OIM Analysis™ v8 software. The idea of ECD has been illustrated via figure 8.4. Grain sizes were characterised per the following equation:

$$D = \frac{4A}{P} = 2 \sqrt{\frac{A}{\pi}} \quad (8.1)$$

Where D is the WC grain size, A is the grain area and P is the equivalent circle perimeter.

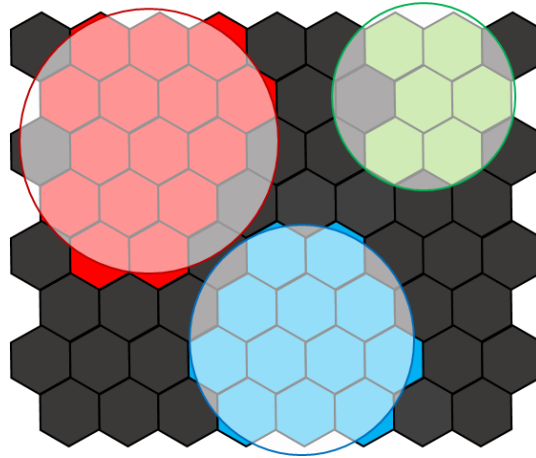


Figure 8.4: Schematic of the ECD procedure used to determine grain size. Equivalent circles overlaid on top of grains. Data points are represented as equilateral hexagons. Grains are illustrated as collection of same-coloured hexagons. Data points assigned to a phase that is not of interest are coloured in black.

SEM images, phase maps, IPF-Z map overlaid over image quality and IPF-Z map with reconstructed boundaries are given in figure 8.5 for the regions from which grain size analysis was performed for the standard and chromium doped samples.

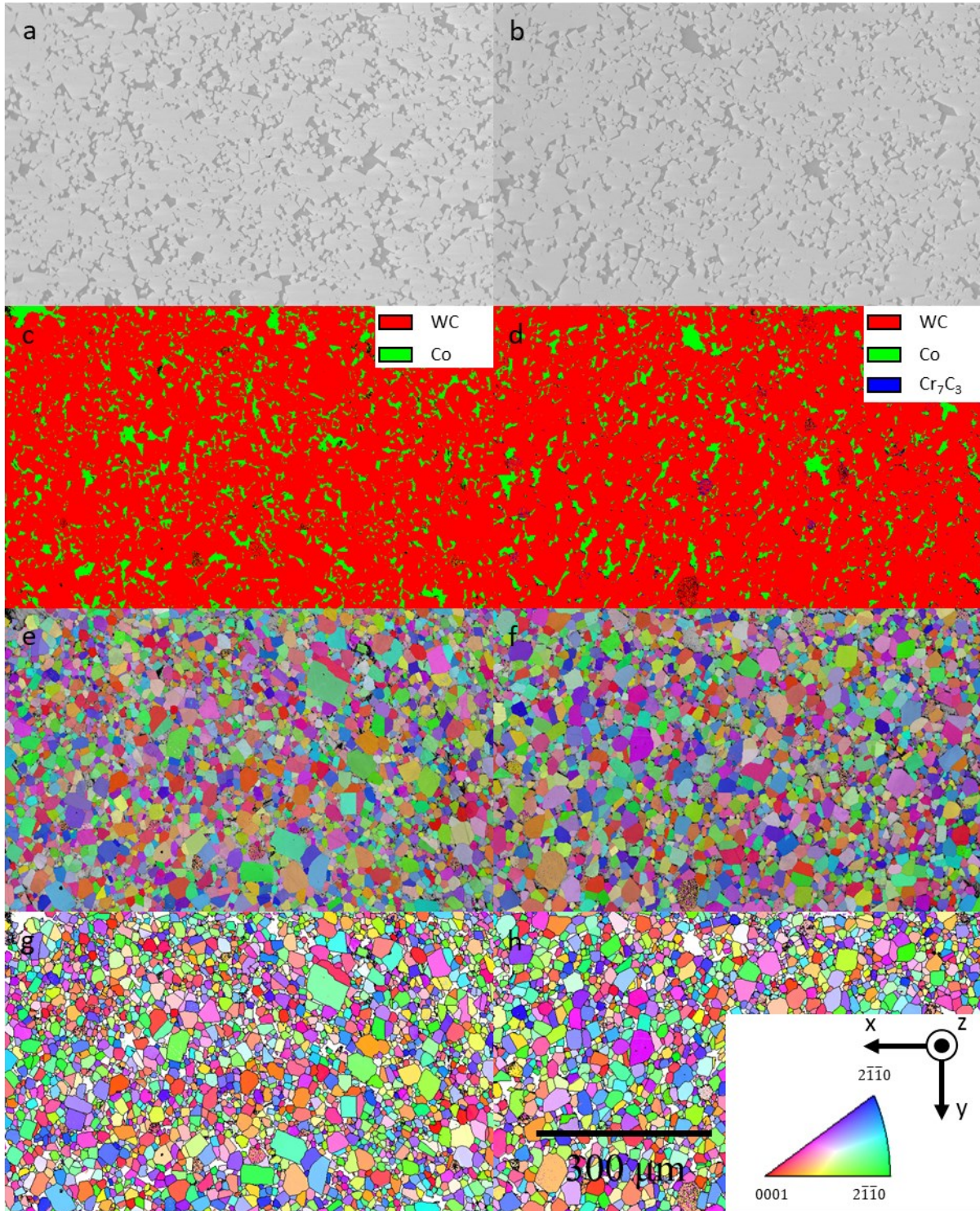


Figure 8.5: SEM images of regions from (a) the WC-10wt%Co and (b) the WC-10wt%Co-1wt%Cr samples. Depictions showing image quality, IPF-Z map overlaid over image quality and IPF-Z map with reconstructed boundaries for the same respective regions.

Grain size distributions determined for the standard and chromium doped WC-Co samples are given in figure 8.6. The mean grain size of the data from the standard and chromium doped samples were determined to be 13.6 μm and 13.8 μm respectively. The grain size dispersion was calculated to be

43.6 μm and 51.7 μm for the standard and chromium doped samples. The difference in grain size dispersion between the two samples can lead to difference in material performance.

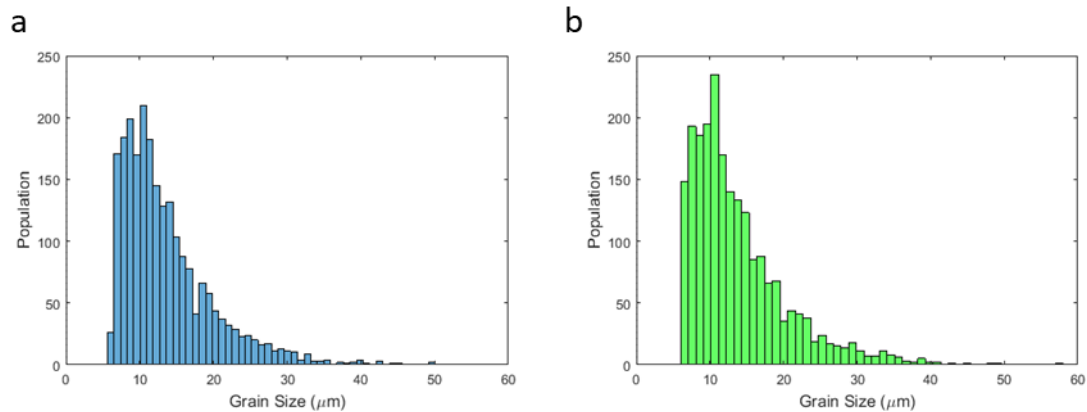


Figure 8.6: Grain size plotted as function of population for (a) the standard and (b) the chromium doped WC-Co sample. Grain sizes were determined according to the ECD approach. Histograms in (a) and (b) were plotted with 50 bins of uniform width.

8.2.3 Extremities in Grain Size Distribution

Grain size distribution evolves towards a lognormal distribution as the grains grow during sintering. Kim et al. have shown that the width of the lognormal grain size distributions is the same for a variety of WC-Co samples with different binder volume fractions and mean grain sizes [64]. The lognormal grain size distributions do not reveal the existence of any significant deviations in the tail of the distributions.

Cumulative distribution function of a lognormal distribution plotted as a probability plot will reveal extreme tails in the lognormal distributions [231]. The rare extreme grain sizes that do not fit the lognormal distribution can cause substantial changes within the microstructure. This is deleterious to material performance and is life limiting. For example, it was found in the study investigating the effect of grain sizes in fatigue crack initiation of nickel based super alloys that the cracks initiated about the crystallographic grain facets of large grains [232]. Therefore, knowledge of extreme grain sizes in material microstructure is vital and can be examined via analysis of lognormal distribution of grain sizes.

Figures 8.7(a) and 8.7(b) show that the grain sizes in both samples have a lognormal distribution. However, the fit applied to both data sets don't seem to be exact. This is due to the removal of grains smaller than 200 pixels ($\sim 5.7 \mu\text{m}$) during the EBSD data clean up procedure. The probability plots for both cases in figures 8.7(c) and 8.7(d) depict that the lognormal distribution is accurate for data within two standard deviations from the mean. Yet, there are outliers, especially smaller grains than predicted by the lognormal distribution as evident by the lower tail. These smaller grains are likely to

improve the hardness of the WC-Co. However, they might also affect the physical properties of these materials but this is not well understood.

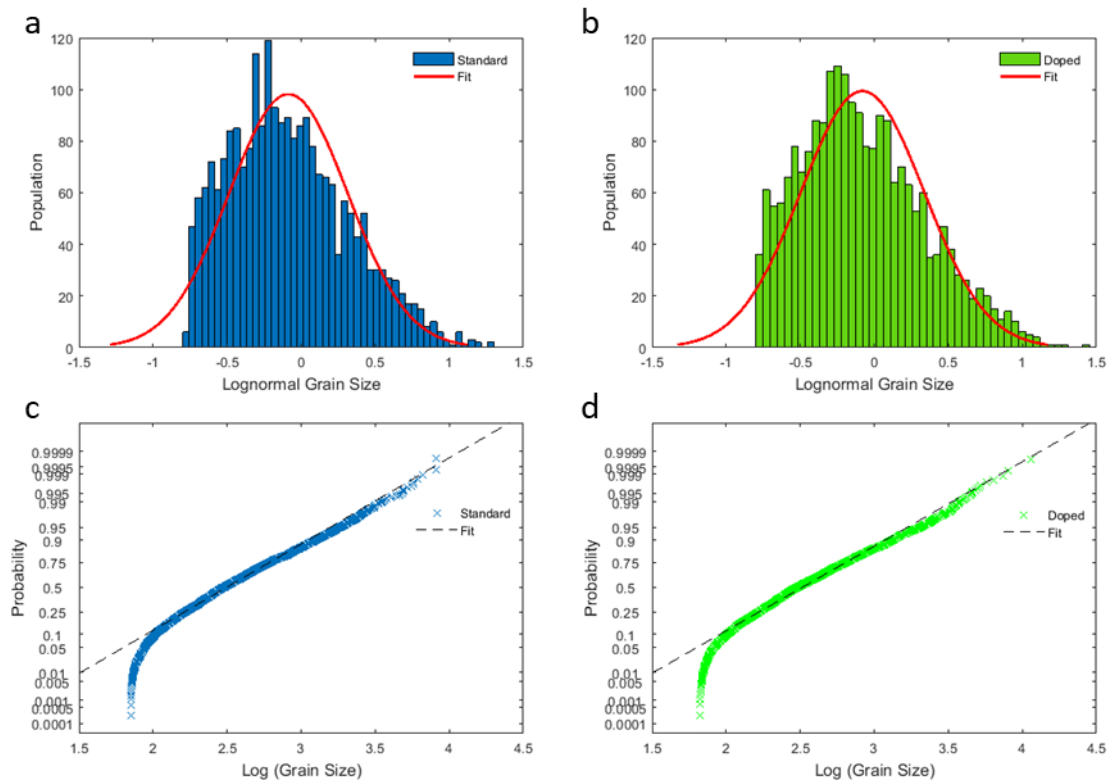


Figure 8.7: Lognormal carbide grain distributions of (a) the standard and (b) the chromium doped samples. A normal fit was applied for both the distributions. Lognormal grain size is given as a ratio of actual grain size to mean grain size. Probability plot of the measured data for (c) the standard and (d) the chromium samples with lognormal distribution fits. 2308 and 2164 grains were examined from standard and chromium doped samples. Histograms in (a) and (b) were plotted with 50 bins of uniform width.

8.3 Texture of WC-Co

Texture defines the distribution of grain orientations within a polycrystalline material. EBSD data from the standard and chromium doped WC-Co samples were examined to check if a crystallographic texture existed with regards to the carbide grains. Crystallographic texture also called the preferred orientation means a fraction of grains within the material are crystallographically aligned along a narrow orientation range. Texture was examined to verify that it will not be a factor that affects GBPD and GBCD in this work.

Pole figure is the most conventional method of representing texture. Orientations of specific crystallographic planes rather than individual grains are plotted in a pole figure. Orientation of crystallographic planes are projected onto a sphere as points which are then projected onto a flat surface by a stereographic projection. A complete description of all poles pertaining to a certain plane are depicted by plotting one point per crystal. The process of producing a pole figure is illustrated in figure 8.8.

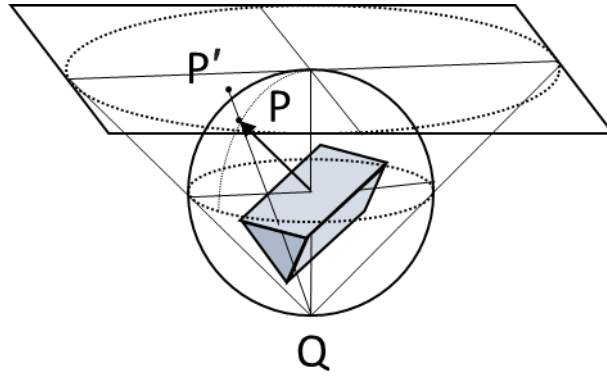


Figure 8.8: Schematic showing the way a plane on a pole figure is depicted. Crystallographic plane orientation projected onto the surface of a sphere at point P which then through stereographic projection is projected from Q onto a plane at point P'.

In figure 8.9, pole figures have been given as intensity plots with a resolution of 5° and a maximum polar angle of 90° . Pole figures have been plotted for the $(10\bar{1}0)$, (0001) and $(11\bar{2}0)$ planes in WC for the standard and chromium doped samples. These pole figures show data from the positive hemisphere. The maximum intensity for the standard and chromium doped sample is around ~ 18.9 and ~ 29.8 respectively. Reconstructed pole figures for the standard and chromium doped samples show the presence of very little texture. This agrees well with the IPF-Z maps in which WC grains were observed to be randomly oriented.

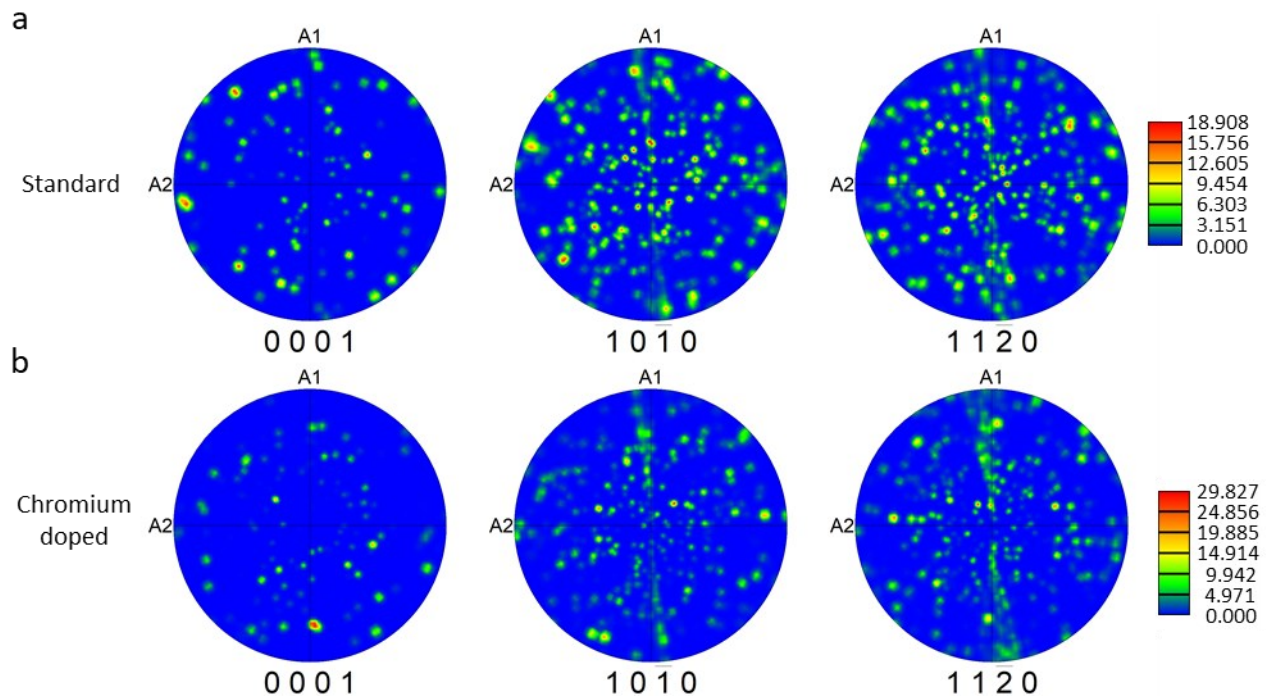


Figure 8.9: Pole figure plotted for the $(10\bar{1}0)$, (0001) and while $(11\bar{2}0)$ planes in the (a) standard and (b) chromium doped samples.

8.4 GBPD and GBCD of WC-Co

Full Domain stereology codes written by Gregory S. Rohrer (CMU, Pittsburgh) in Fortran were used to plot the GBPD and GBCD for WC/WC and all WC boundary segments extracted from standard and chromium doped samples. The location of $\{0001\}$, $\{10\bar{1}0\}$ and $\{11\bar{2}0\}$ planes in GBPD and GBCD plots and $\langle 0001 \rangle$, $\langle 10\bar{1}0 \rangle$ and $\langle 11\bar{2}0 \rangle$ directions in the axis-angle plots are given as illustrated via the stereonet presented in figure 8.10.

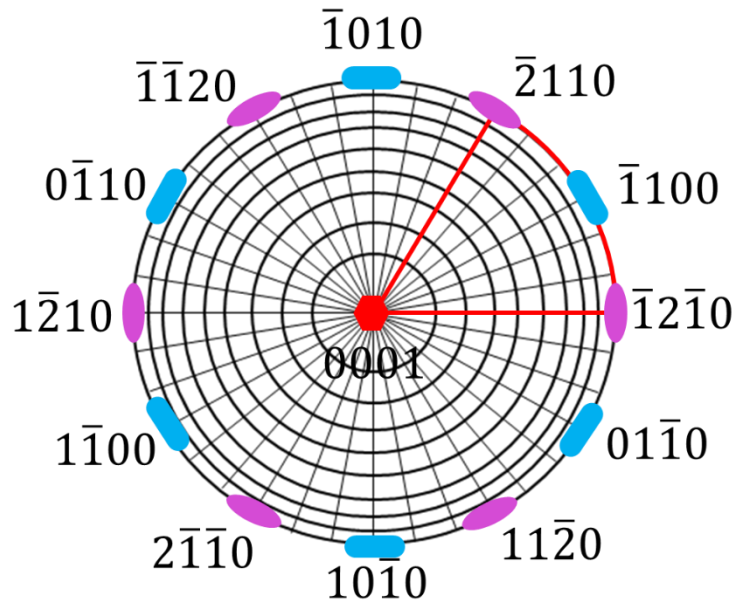


Figure 8.10: A stereonet depicting $\{0001\}$, $\{10\bar{1}0\}$ and $\{11\bar{2}0\}$ plane locations in GBPD and GBCD plots.

8.4.1 GBPD of WC-Co

The GBPD plots as given in figure 8.11 showed that the $\{10\bar{1}0\}$ and $\{0001\}$ planes were the most abundant boundary habit planes while $\{11\bar{2}0\}$ planes were lower than the normal distribution when examining all four boundary segment files. This implies that the WC grains are most frequently terminated with $\{10\bar{1}0\}$ and $\{0001\}$ planes. This was expected as the type II $\{10\bar{1}0\}$ and $\{0001\}$ planes have the lowest surface energy in WC.

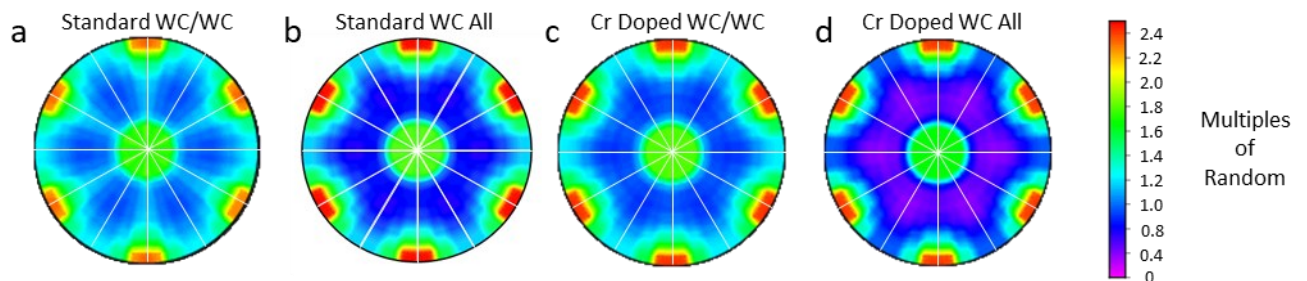


Figure 8.11: GBPD plotted for (a) WC/WC and (b) all WC boundary segments for the standard sample as well as (c) WC/WC and (d) all WC boundary segments from the chromium doped sample.

The area fraction of the $\{10\bar{1}0\}$ and the $\{0001\}$ boundary planes were determined as follows. First, a stereonet was placed over the GBPD plot. Since the data was discretised into 10° intervals, the stereonet has 324 bins with 81 bins per quarter of the stereographic projection. This includes 54 bins per fundamental zone owing to the six-fold symmetry originating from the HCP crystal structure of WC. Then a fundamental zone in each GBPD was selected and the number of bins attributed to the $\{10\bar{1}0\}$ and the $\{0001\}$ planes were counted and multiplied by the MRD corresponding to the respective planes. Afterwards, equation 8.2 was used to determine the area fraction of each of the planes.

$$\text{Area fraction} = \frac{MRD}{\text{No of Bins in a Fundamental Zone}} \quad (8.2)$$

Table 8-1: Area fractions calculated for the $\{10\bar{1}0\}$ and the $\{0001\}$ planes determined from WC/WC and all WC boundary segments files from the standard and chromium doped samples.

Segment File	Area Fraction of Boundary Planes (%)	
	$\{0001\}$	$\{10\bar{1}0\}$
Standard WC/WC	15.6	17.8
Standard WC All	16.7	17.8
Cr Doped WC/WC	15.6	18.5
Cr Doped WC All	16.7	18.5

The data presented in table 8-1 shows that the area fraction of the $\{0001\}$ boundary habit planes do not change with chromium doping. However, the area fraction of $\{0001\}$ planes do seem to be greater in all possible WC grain boundaries (16.7 %) than WC/WC boundaries (15.6 %). Additionally, it can be inferred from table 8-1 that the area fraction of $\{10\bar{1}0\}$ planes increase with doping from 17.8 % to 18.5 %. Furthermore, the area fraction $\{10\bar{1}0\}$ stays the same regardless of looking at all WC boundaries or WC/WC boundaries for a given sample.

8.4.2 GBCD of WC-Co

As mentioned earlier, the GBCD is just the GBPD plotted for a specific misorientation. So, to plot sensible GBCD data, most abundant misorientations must be identified. This was done by plotting a misorientation angle chart to identify the most recurring disorientation angles. A disorientation angle is the smallest misorientation angle out of all symmetrically equivalent misorientation angles that are within the fundamental zone. The misorientation angle chart determined for the four segment files is shown in figure 8.12.

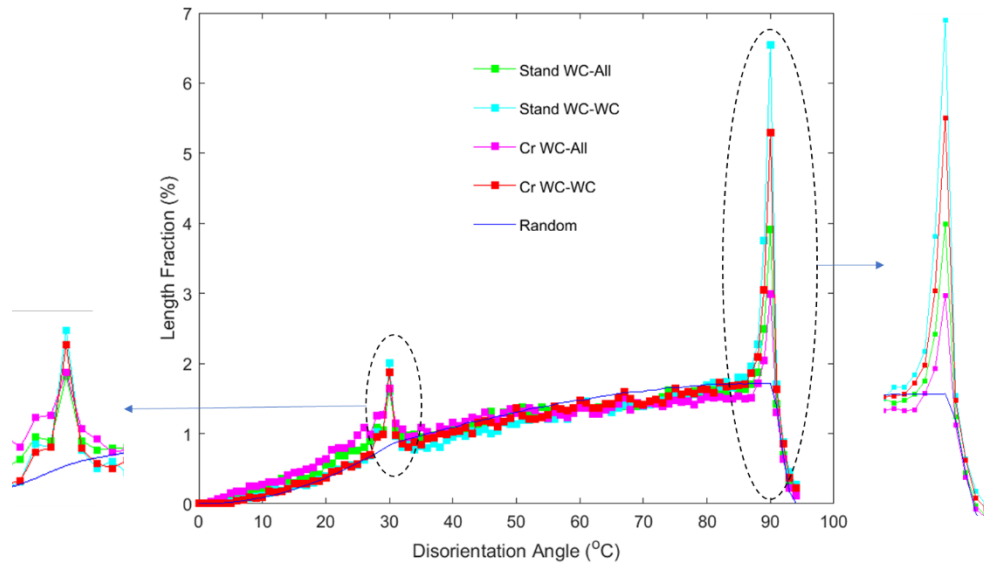


Figure 8.12: Disorientation distributions for the standard (Stand WC-All and Stand WC-WC) and chromium doped (Cr WC-All and Cr WC-WC) samples for all WC and WC/WC boundary segments files.

Figure 8.12 shows that 90° and 30° are the most common disorientation angles for WC boundaries regardless of chromium doping. This was anticipated from reviewing the literature as was discussed in the Cemented Carbide chapter. It can also be observed that the length fraction of the WC boundaries attributed to the 90° and 30° disorientation angles is greater ($\sim 3\%$ and $\sim 0.5\%$ respectively) within WC/WC boundaries compared to all possible WC boundaries. Finally, chromium doping seems to reduce the length fraction of WC boundaries attributed to the 90° and 30° disorientation angles.

Once the disorientation angles were determined, axis-angle distributions were plotted for each of the segment files. Axis-angle distributions for all WC segment files from the standard and the chromium doped samples are given in figure 8.13. The axes with the highest MRD were determined for the 90° and 30° disorientation angles to determine the most often found misorientations in WC-Co. The most abundant misorientations were determined to be $90^\circ/[10\bar{1}0]$ and $30^\circ/[0001]$ respectively. These are the $\Sigma 2$ and $\Sigma 13$ boundaries respectively. This observation is again as expected from the literature review. Additionally, the 30° axis-angle plot showed a low MRD close to one for the $[0001]$ axis. Furthermore, the intensity to be attributed to the $[0001]$ axis was somewhat spread. This meant the area fraction of the $\Sigma 13$ boundaries could not be reliably determined.

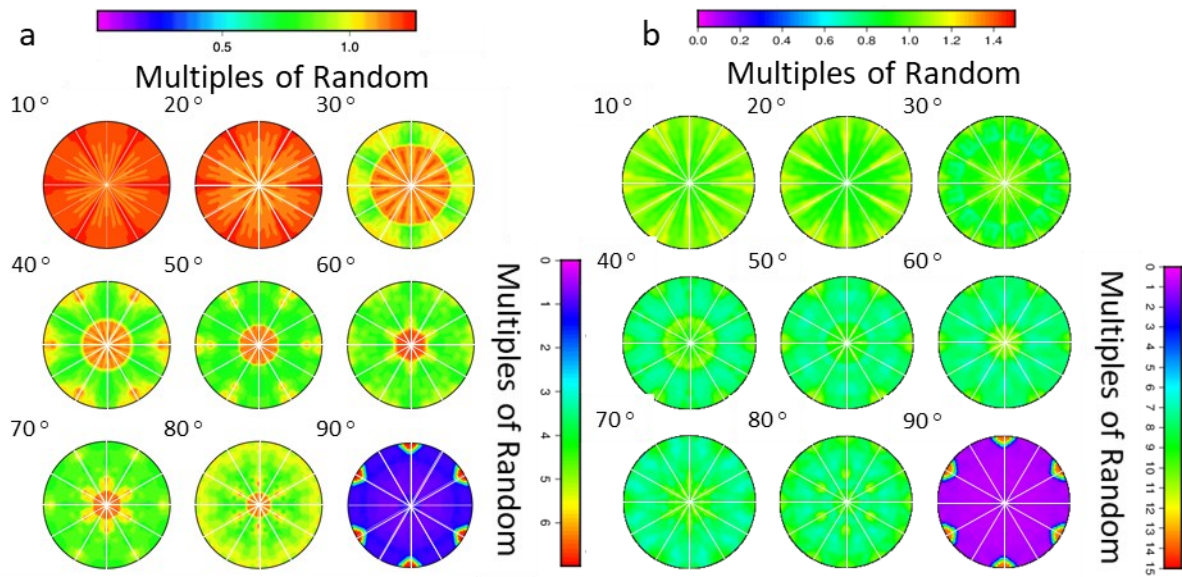


Figure 8.13: Axis-angle charts plotted for the all WC boundary segments file from the (a) standard and (b) chromium doped WC-Co samples. The axis-angle distributions are plotted in increments of 10° between 0°-90°. The vertical colour keys in both axis-angle distributions are attributed to the 90° misorientation. This is because the range of the horizontal keys will not be able to sufficiently represent the distribution for the 90° misorientation.

Afterwards, GBCD were plotted for the aforementioned misorientations from the four boundary segment files as presented in figures 8.14 and 8.15. 90°/[10 $\bar{1}$ 0] misorientation GBCD plots revealed that the {10 $\bar{1}$ 0} planes (Σ 2 twist boundary planes) were the most abundant boundary habit planes for this particular misorientation. MRD of {0001} and {11 $\bar{2}$ 0} planes (Σ 2 tilt boundary planes) were very small and thus close to a random distribution. This implies that the Σ 2 twist boundaries are far more abundant than the tilt variants as anticipated. GBCD of the 30°/[0001] misorientation showed that the {10 $\bar{1}$ 0} and {11 $\bar{2}$ 0} boundary habit planes occur more frequently compared to the {0001} planes. Therefore, the Σ 13 tilt boundaries occur more frequently than the twist counterpart. This is because the boundary habit planes of a Σ 13 tilt boundary are the {10 $\bar{1}$ 0} and {11 $\bar{2}$ 0} planes while two {0001} planes are the habit planes for a Σ 13 twist boundary.

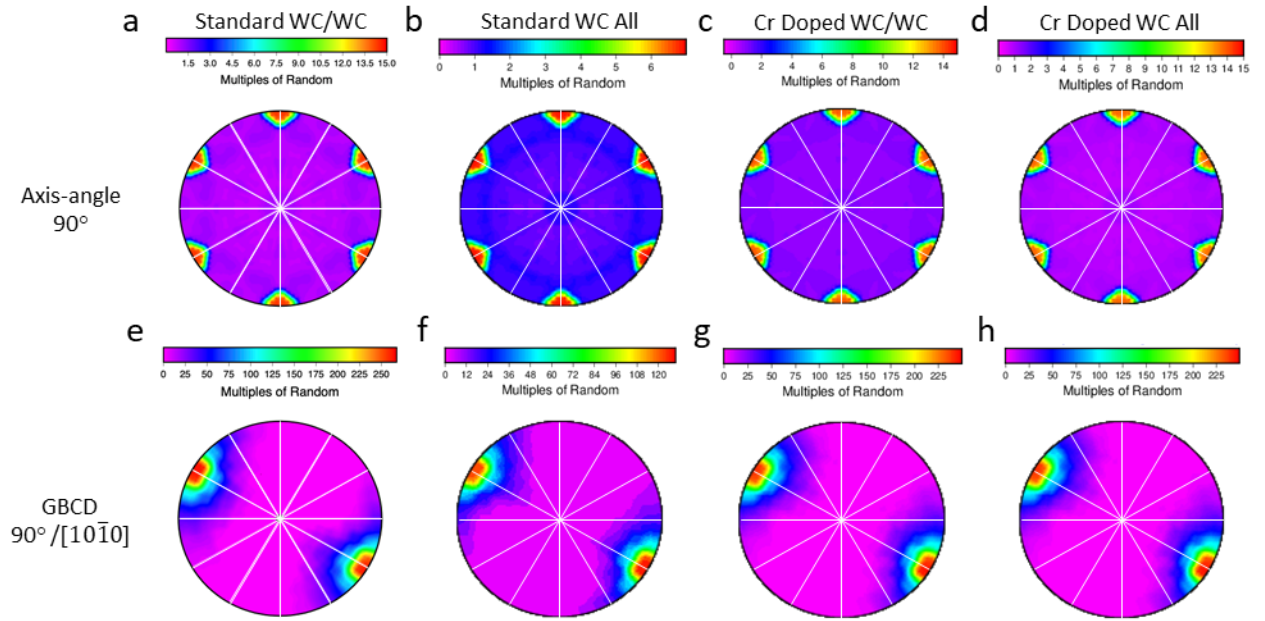


Figure 8.14: 90° axis-angle distribution and GBCD for the 90°/[10 $\bar{1}$ 0] misorientation plotted for the (a), (e) WC/WC boundaries and (b), (f) all WC boundaries from the standard sample as well as (c), (g) WC/WC boundaries and (d), (h) all WC boundaries from the chromium doped sample. The scale bars are different between each of the data sets.

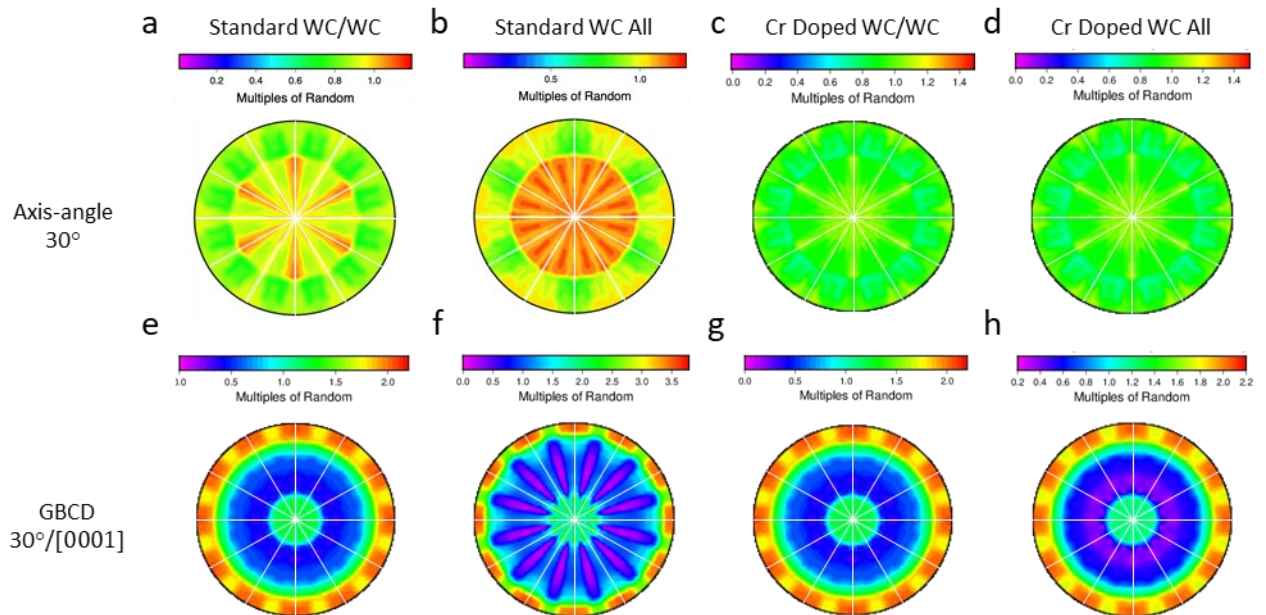


Figure 8.15: 30° axis-angle distribution and GBCD for the 30°/[0001] misorientation plotted for the (a), (e) WC/WC boundaries and (b), (f) all WC boundaries from the standard sample as well as (c), (g) WC/WC boundaries and (d), (h) all WC boundaries from the chromium doped sample. The scale bars are different between each of the data sets.

The area fractions for the $\Sigma 2$ twist boundaries were determined from all four segment files in the following manner. First, the length fraction attributed to the 90° disorientation was recorded from the corresponding misorientation angle chart. This was followed by counting the MRD attributed to the [10 $\bar{1}$ 0] axis in the axis-angle distribution within a fundamental zone. Later, the MRD for the {10 $\bar{1}$ 0}

planes were recorded within a fundamental zone. All three of these values were multiplied and then divided by the square of the number of bins per fundamental zone (54) in the axis-angle distribution and GBCD. Area fractions obtained for the four segment files are presented in the table 8-2.

Table 8-2: Area fraction of $\Sigma 2$ twist boundaries determined for WC/WC and all WC segment files of the standard and chromium doped WC-Co sample.

Segment File	Area Fraction of the $\Sigma 2$ twist boundary (%)	Grain Boundary Segments
Standard WC/WC	39.6	2.07×10^5
Standard WC All	5.1	4.50×10^5
Cr Doped WC/WC	28.3	2.35×10^5
Cr Doped WC All	15.4	5.41×10^5

Data from table 8-2 shows that the area fraction of $\Sigma 2$ twist boundaries increases by three-fold with chromium doping from 5.1 % to 15.4 % within all possible WC boundaries. However, in contrast, the area fraction of $\Sigma 2$ twist boundaries is slightly lower within WC/WC boundaries within the standard sample in comparison to the chromium doped variant. So, it would be reasonable to expect that the increase in the area fraction of $\Sigma 2$ twist boundaries out of all possible WC boundaries from standard to the doped sample is the result of higher fraction of WC/WC boundaries within the doped sample. However, it is interesting to note that the fraction of WC/WC boundaries segments out of all possible WC boundary segments is similar between the standard (46 %) and chromium doped (43 %) samples. Thus, this explanation cannot account for the increasing area fraction of $\Sigma 2$ twist boundaries from standard to chromium doped samples out of all possible WC boundaries. Finally, analogous to the observation made in the misorientation angle distribution, the fraction of $\Sigma 2$ twist boundaries is greater within WC/WC boundaries compared to all possible WC boundaries regardless of chromium doping.

8.4.3 Discussion

The fraction of $\Sigma 2$ boundaries measured in this work (5.1 %) is lower than the value reported by Kim et al. (11-14 %) for WC-Co [64]. This could be due to the difference in WC grain sizes (1.4-5.3 μm) and cobalt content (7-20 %) of the samples used for study by Kim et al. compared to the current work (13.6 μm mean grain size and 10wt% cobalt content). In this section, the wording $\Sigma 2$ boundaries is used instead of $\Sigma 2$ twist boundaries as the fraction of $\Sigma 2$ tilt boundaries was negligible. Yuan showed that that the fraction of $\Sigma 2$ and $\Sigma 13$ boundaries reduced with increasing WC grain size from 0.5 μm , 1 μm to 2 μm [233]. Grain sizes were increased in this study by increasing the sintering times. The author reported the fraction of $\Sigma 2$ and $\Sigma 13$ boundaries as line and number fractions. Yuan determined that the number and line fractions reduced from 10.4 % to 6.2 % and 38.9 % to 28.3 % respectively for $\Sigma 2$ boundaries while these parameters reduced from 2.8 % to 1.1 % for $\Sigma 13$ boundaries. It was speculated

that the migration and elimination of $\Sigma 2$ boundaries occurs at the early stage of sintering and this procedure proceeds at a higher speed than coarsening of carbide grains. Hence, the reduction of $\Sigma 2$ boundaries with increasing grain size. In another work, Yuan showed that population of $\Sigma 2$ boundaries decreases with increasing cobalt volume fraction when studying WC-Co samples with 6 wt%, 8 wt% and 10 wt% cobalt fractions [234]. However, peculiarly Kim et al. had reported that the variations in boundary fraction measured for $\Sigma 2$ and $\Sigma 13$ boundaries were not sensitive to varying carbide grain sizes and cobalt volume fractions [64].

Furthermore, Kim et al. determined that the fraction of $\Sigma 13$ boundaries was to be 2-3 % [64]. However, in the present work, the MRD values in the axis-angle distribution for the 30° misorientation were too low (close to a random distribution) to statistically determine the area fraction of the $\Sigma 13$ boundaries. This could be the result of large WC grain sizes in the present study than those reported in the work of Kim et al. Interestingly, in most works, the twist variant of the $\Sigma 13$ boundaries are found to be the most abundant unlike the current work where tilt boundaries were found to be the most abundant in the samples studied [64, 233].

Even though studies on the effect of chromium doping in WC-Co have not been carried out in the literature, the effect of other grain growth inhibitors such as vanadium has been examined [235]. In the work by Liu et al., vanadium was added in the form 1 wt% vanadium carbide (VC) to a WC-10wt%Co sample. The fraction of $\Sigma 2$ boundaries reached a maximum of 18% with the addition of vanadium at 1390°C . This was attributed to finer grain sizes and increased carbide contiguity resulting from improved inhibition of vanadium against grain growth. Grain growth inhibition is facilitated by the formation of $(\text{W,V})\text{C}_x$ at the WC grain terminating planes impeding WC grain growth. The study concluded that as the sintering temperature is increased, $(\text{W,V})\text{C}_x$ destabilises allowing WC grains to grow and coalesce leading to reduced $\Sigma 2$ boundaries.

However, since the mean grain size of the standard ($13.6\text{ }\mu\text{m}$) and chromium doped ($13.8\text{ }\mu\text{m}$) samples are similar in the present work, increase in $\Sigma 2$ boundaries cannot be assigned to the grain inhibition effect of chromium. Yuan et al. examined the effect of different binders (6 wt% cobalt and 6 wt% nickel) on the fraction of $\Sigma 2$ boundaries in WC-Co [236]. It was found that the population of $\Sigma 2$ boundaries increased when a nickel binder was used instead of a cobalt binder. This observation was explained to be a result of the change in the interfacial energy at the $\Sigma 2$ boundary.

Likewise, chromium doping is likely to alter carbide boundary chemistry (such as the formation of cubic $(\text{Cr,W})\text{C}$ at WC/Co boundaries) which in turn affects the grain boundary energy and preference for certain boundary types as was seen with the increased fraction of $\Sigma 2$ twist boundaries. The modified boundary chemistry resulting from chromium doping is likely to change the fracture toughness of the $\Sigma 2$ twist boundaries. It can be hypothesised that the reduced grain boundary energy

alludes to the increased fracture toughness of $\Sigma 2$ twist boundaries. This agrees well with the difficulty in performing successful DCB tests at $\Sigma 2$ twist boundaries on the chromium doped sample compared to the standard sample as was reported in the previous chapter.

8.5 Summary

The WC grain size distribution and extremities in the WC grain size distribution were examined for the standard and the chromium doped WC-Co samples. It was found that even though mean grain sizes between the samples were similar (13.6-13.8 μm), a substantial difference in grain size dispersion existed between the standard ($\sim 43.6 \mu\text{m}$) and the chromium doped samples ($\sim 51.7 \mu\text{m}$). This was suggested to lead to difference in material performance between the two samples. Both samples were found to have lognormal grain size distributions as expected. The outliers that were observed from plotting the probability plots of the lognormal distributions were postulated to affect the physical properties of WC-Co in an unknown manner.

GBCD analysis for the most abundant boundary types ($\Sigma 2$ and $\Sigma 13$) was performed on the standard and the chromium doped samples. $\Sigma 2$ boundary fraction (5.1 %) measured in this work is smaller than the values reported in the literature. This was attributed to the difference in carbide grain sizes and cobalt volume fractions of the samples used compared to those described in the literature. Furthermore, it was found that the area fraction of $\Sigma 2$ boundaries was greater within WC/WC boundaries compared to all possible WC boundaries. In contrast, the area fraction of $\Sigma 13$ boundaries could not be reliably determined due to the low MRD values (close to unity) for the 30° axis-angle distribution. Contrary to the literature, it was deduced that the $\Sigma 13$ tilt boundaries were present in greater number relative to $\Sigma 13$ twist boundaries.

Finally, it was determined that the area fraction of the $\Sigma 2$ boundaries increased threefold with the addition of chromium. This was due to the change in the boundary chemistry of the $\Sigma 2$ boundaries. Increased boundary fraction implies better cohesion at the boundary. Thus, it was proposed that the chromium doping increased the fracture toughness of the $\Sigma 2$ boundaries. This explains the difficulty in performing DCB tests at the $\Sigma 2$ twist boundaries in the chromium doped sample.

9 Conclusions and Outlook

9.1 Conclusions

Fracture is an important aspect that dictates WC-Co tool performance and lifetime during operation. Yet, knowledge about the contribution of microstructural features for fracture toughness of the WC-Co is lacking. This knowledge is useful for controlling WC-Co microstructure during GBE to produce superior WC-Co tools.

This work was dedicated to deciphering the effect of WC/WC boundaries in crack propagation within WC-Co as most of the fracture path has been shown to be intergranular with respect to the carbide grains.

Preliminary DCB tests performed on the lowest energy plane of WC– type II $\{10\bar{1}0\}$ planes showed that DCB tests on polycrystalline WC-Co are achievable. Furthermore, measured fracture energy values for cleaving type II $\{10\bar{1}0\}$ planes were in agreement with those deduced from DFT calculations in the literature. This conveyed the validity and reliability of the DCB tests for measuring fracture energy of microstructural features in WC-Co.

A novel method was devised to identify ideal CSL boundaries within the WC-Co microstructure, perpendicular to the surface from analysis of acquired EBSD data. This was necessary for performing DCB tests at boundary sites as such an ideal boundary will need to lie along the middle of the DCB with the DCB itself milled perpendicular to the sample surface: this ensures that during a test, the crack propagates along the boundary making fracture energy measurements of the boundary possible.

$\Sigma 2$ twist boundaries were chosen for DCB testing owing to their abundance across the WC-Co microstructure. Measured fracture energy values for type II $\{10\bar{1}0\}$ planes ($7.04 \pm 0.36 \text{ Jm}^{-2}$) were shown to be twice that of $\Sigma 2$ twist boundaries ($3.57 \pm 0.28 \text{ Jm}^{-2}$). This corresponds with the observation that the largest fraction of the crack path in WC-Co is intergranular.

Rohrer et al.'s five parameter GBCD analysis of a WC-10wt%Co sample showed that area fractions of $\Sigma 2$ and $\Sigma 13$ boundaries were different to those reported in the literature. This was attributed to the difference in carbide grain sizes and cobalt volume fractions compared to that of the WC-Co samples reported in the literature.

The GBCD analysis also found that the chromium doped samples (WC-10wt%Co-1wt%Cr) had an area fraction of $\Sigma 2$ boundaries that was three times higher than the standard sample. This was hypothesised to be a result of the change in $\Sigma 2$ boundary chemistry as a consequence of doping which in turn reduces the $\Sigma 2$ grain boundary energy. This observation was also linked to unsuccessful DCB tests at the $\Sigma 2$ boundaries on the chromium doped sample where changed $\Sigma 2$ boundary chemistry is likely to have increased fracture toughness of the said boundary. Hence, addition of chromium as a dopant to WC-Co is likely to improve fracture toughness of WC-Co by virtue of increasing the area

fraction of $\Sigma 2$ boundaries (boundaries with high stability to cobalt infiltration and high work of separation) and modifying the chemistry of $\Sigma 2$ boundaries to increase their fracture toughness.

9.2 Outlook

The role of WC/WC boundaries in WC-Co tool fracture was somewhat successfully analysed in this work by fracture energy measurements of the most abundant boundaries ($\Sigma 2$ twist) via DCB tests. Yet, the role of other special WC boundaries in fracture was not investigated. This will be an interesting avenue to explore in future work. However, finding sufficient ideal boundaries (perpendicular to the surface) of a given boundary type for DCB testing is likely to be difficult like in the case of $\Sigma 2$ tilt boundaries as mentioned in chapter 6. This means larger areas of the sample surface must be EBSD mapped. But this limitation can potentially be overcome using current rapid EBSD systems allowing for mapping of large areas in a short span of time.

It will also be useful to perform DCB tests at WC/Co phase boundaries and compare their fracture energy values to those measured for the type II $\{10\bar{1}0\}$ planes and $\Sigma 2$ twist boundaries.

The service temperatures of WC-Co tools (cutting and drilling) are high. Therefore, it will be beneficial to perform DCB tests at WC/WC and WC/Co boundaries as well as pillar compression tests on smaller volume of WC-Co material at high temperatures in situ in a SEM to investigate the effect of elevated temperatures on interface fracture properties and material behaviour.

Even though the effect of chromium doping (in the form of Cr_2C_3) on the WC boundary ($\Sigma 2$ and $\Sigma 13$) population was determined, the fracture energy of $\Sigma 2$ twist boundaries on the chromium doped sample could not be measured owing to unsuccessful DCB tests. This was attributed to toughening of the $\Sigma 2$ twist boundary via chromium doping. Hence, it might be useful to study the effect of the addition of other grain growth inhibitors (VC, NbC, TaC and TiC) on grain boundary populations and toughness of $\Sigma 2$ twist boundaries.

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