

Department of Materials
Imperial College

B_4C - SiC Composites for Armour

Henry Alexander Payne

Thesis submitted for the degree of Doctor of Philosophy

Supervisors: Professor Luc Vandeperre, Professor Finn Giuliani and Dr Florian Bouville

Declaration

I hereby confirm that this thesis is my own work. Works by collaborators and from the literature have been acknowledged and referenced.

Henry Payne

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Abstract

Armours form a key component of the modern soldier's protective equipment. Ceramics have higher hardness and lower density than traditional metals, providing a more capable and lighter armour. Armour can however decrease mobility and increase soldier fatigue. Boron carbide (B_4C) has a high hardness, with a density lower than other ceramic armours such as silicon carbide (SiC), suggesting it has good potential as an armour material. However, under high impact pressures it is seen to undergo a polytype breakdown resulting in an amorphous phase. This culminates in a loss of mechanical properties. It has been suggested that a composite of B_4C and SiC could have an increased amorphisation resistance. To investigate this, microemulsion silica (SiO_2) was combined with a carbon source to produce SiC precursor powders. These were used to develop B_4C - SiC composites with a range of microstructures. A 3D non-destructive Raman method was developed to investigate the amorphous region generated by indentation hardness experiments.

Microemulsion produced SiO_2 was found to have a well controlled particle size distribution with a mean size of 65 nm. The conversion of SiO_2 to SiC was found to produce β - SiC from a range of reactions. B_4C - SiC composites were then developed, in an 88:10 ratio. Starting powders containing microemulsion SiO_2 , commercial B_4C and a carbon source produced composites with a high relative density of 97.7 % and a homogeneous dispersion of the SiC phase. This was achieved when the SiO_2 and carbon source were intimately mixed, before being added to other components. These composites exhibited a higher than expected hardness of 39 GPa. A non-destructive 3D Raman method was developed to probe the amorphous zone under indents. This indicated that it is unlikely that SiC can prevent the amorphous breakdown of B_4C when added as a majority or minority phase.

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1 Introduction

Ever since humans have gone to war, there has been a drive for more powerful weapons and better protection. Looking back this has seen the use of swords and chain mail, whilst in modern times bullets and ceramic or composite armour plates are used. All armours have benefits and drawbacks, with their characteristics dependent on the threat they are designed to counter. A problem facing modern armour is weight; between the Battle of the Somme and the Invasion of Kuwait [1], the infantry soldier's standard loadout has increased by 25 kg. This increase in weight leads to an evident decrease in mobility and increase in soldier fatigue [2–4]. Body armours currently exist in two parts; a plate carrier, usually made of textile based materials, is used to defeat shrapnel and low velocity rounds. A heavy and bulky ceramic or metal plate can be inserted to provide protection from higher velocity threats such as that from the prevalent AK-47.

Advanced ceramics have several benefits over traditional metals for use in armour. Ceramic materials considered in armour have lower density than that of an equivalent metal [5, 6]. These also benefit from a higher hardness, which increases the chance of projectile fracture during the surface dwell period. Projectile fracture and erosion reduces its ability to penetrate, hence improving ballistic performance [7, 8]. A lighter, more capable, armour can hence be produced using ceramics [7]. However, armour ceramics have a lower fracture toughness than that of metals due to the nature of ceramic brittle failure [7]. Damage during handling is therefore more likely, reducing the functionality of such an armour.

Traditional ballistic ceramic armour consists of alumina (Al_2O_3) or silicon carbide (SiC). These have shown good ballistic properties, with Al_2O_3 being the cheapest to produce [6]. SiC requires higher processing temperatures, thus increasing cost, but does demonstrate a higher hardness. Boron Carbide (B_4C) exhibits a greater hardness compared to SiC [9–11] with a 22% lower density [12]. B_4C based armours could hence provide a lighter armour. However, it is known to undergo an amorphous breakdown at high pressures, resulting in a loss of mechanical properties [13–19]. B_4C has a rhombohedral structure which comprises of 12 atom isocahedra linked with chains [19]. It is thought that a shear stress bends these chains, along with potentially fracturing the isocahedra. This leads to the breakdown of the polytype and results in an amorphous structure [13, 17, 20].

Recent work has sought to reduce amorphisation by either reducing grain size [21], introducing carbon at the grain boundaries [22], or doping the structure with silicon (Si) or boron (B) [13, 23–26]. The reduction in grain size and the addition of carbon have been hypothesised to increase the resistance to amorphisation by allowing grain boundary sliding. This prevents the build up of high pressures needed for amorphisation. However, this theory was not proven in these works. Addition of Si or B has also been shown to reduce amorphisation, although the reason for this is unclear. Understanding

of the amorphous breakdown in an alternative material must be fully understood for it to be widely adopted.

The combination of SiC and B₄C has been used in the literature to improve material properties such as fracture toughness [27–30]. In a similar way to other methods, it can be hypothesised that the addition of a second phase could alter the stress state within the material. The more ductile SiC may deform, reducing the stress buildup within the B₄C as the ballistic pressure wave progresses. This may then limit the progress of the amorphous breakdown of the B₄C, maintaining the desirable properties of B₄C whilst greatly improving ballistic reliability. The successful use of B₄C-SiC composites for other applications suggests it is ideal for achieving this goal. This composite could either exist as a homogeneous dispersion of similar sized grains or with SiC forming an intergranular phase. The design of various microstructures will be crucial in designing a composite with increased amorphisation resistance.

This work will focus on understanding the amorphous breakdown in B₄C-SiC composites. A range of microstructures will be used to understand how a composite can be tailored to increase amorphisation resistance. To do this a robust method for analysing the amorphous breakdown must be developed for these composites. The microstructure of a composite can then be altered, and the effect investigated. Tailoring the microstructure will be achieved by producing a range of ceramic precursor powders which will be processed into composites through several methods. These studies will allow the amorphisation resistance of B₄C-SiC composites to be determined.

This thesis will continue by discussing the literature including; defining a good ballistic ceramic, understanding the amorphous breakdown mechanism, and methods for developing and producing a range of composite microstructures. From this the aims of this work will be defined. Next the general composite and powder production methods will be described along with characterisation techniques and the properties of commercial raw materials. The production of ceramic precursor powders will then be investigated, followed by characterising the composites they produce. The amorphisation resistance of these composites will then be considered, alongside the method for determining this. Conclusions on the use of B₄C-SiC composites for amorphisation resistant armour will then precede discussion on further work needed in this area.

2 Literature Review

The production of B_4C - SiC composites for armour is a novel concept based upon principles from a variety of industries and literature. This review will begin by discussing current ballistic armours as well as demonstrating the need for advancement in the field. The factors affecting materials selection for armour, such as weight, cost and mechanical properties, will then be discussed. The structure of B_4C will be considered along with the characteristic amorphous breakdown observed throughout the literature. This will be concluded by discussing possible ways of combating the reduction in mechanical properties resulting from amorphisation. Next the production of nano SiC and B_4C will be considered, along with the sintering of these to produce a final composite. Finally, conclusions will be made that inform the best route for production of B_4C -SiC composites, with microstructures that reduce amorphisation.

2.1 Defining a ballistic ceramic

Ceramic armour has become an important component in the defence of both personnel and vehicles. Currently there are three key considerations when proposing a material as an armour: the weight of the armour tiles, their cost to manufacture and their ballistic properties. Ceramics are excellent materials for armour; they have lower density than traditional metals and good ballistic performance due to high strength and hardness [6, 9, 31–37]. They are, however, often expensive to produce. This section will begin by understanding the weight burden of various ceramics, as well as their production cost. A method of measuring the ballistic capabilities will then be introduced and the general ballistic performance analysed. This will then be linked to material properties, such as hardness. This will give understanding of how each material responds to an impact and what can be done to mitigate any damage.

Importance of the weight

Ricciardi *et al* have shown that metabolic cost of walking at a tactical pace is increased by 126 kcal/hour [2] when wearing body armour (BA). This was followed by identifying a 68% increase in blood lactate levels, which indicates the onset of muscle fatigue. This view is echoed by Knapic *et al* who notes that the reduction of weight can reduce stress related injuries, hence increasing soldier effectiveness and reducing downtime [1]. Hasselquist *et al* considers the weight of body armour as a proportion of the body mass of the soldier. It was seen that the addition of military clothing and body armour added a mass equal to 19% of the individual's body mass [4]. The need for protection must be balanced against the detrimental effects of armours, such that maximum survivability is obtained. This can be achieved by determining a robust set of material requirements.

It is clear that an armour must be light to increase soldier mobility and survivability, and to reduce

fatigue. Current ceramics such as alumina (Al_2O_3) and SiC have a density of 3.8 g/cm^3 [38] and 3.2 g/cm^3 [39] respectively. The progression of armour towards ceramics with lower densities can therefore have a weight advantage, assuming ballistic performance is maintained. B_4C provides a natural follow on to this with a density of 2.5 g/cm^3 [40]. The use of B_4C could therefore significantly reduce the weight burden of armour on a system or soldier.

Cost

The cost of ceramic armour is centred around the cost incurred during production. An armour that is very expensive is unlikely to see widespread use, hence not providing a major advantage. Roberson *et al* summarises the variation in cost across these armour systems as can be seen in Table 1 [6]. Al_2O_3 is the cheapest ceramic armour currently being produced. This is likely due to the low temperatures required for sintering [31]. Reaction Bonded (RB) SiC and Sintered SiC see a slight increase in cost. This is likely due to the increase in temperatures required to see successful sintering as discussed later in this review. A large increase in cost is seen when moving from traditional sintering of SiC to Hot Pressing. An increase of 200% gives an insight into the true cost of operating a highly specific device at high temperatures and pressures for prolonged periods of time. The sintering of B_4C without pressure has had limited success and requires the use of sintering aids which can make it unsuitable for use with ballistic armour [41, 42]. Using hot pressing is therefore essential if B_4C is to be used, which carries the increase in cost. Additionally, only 1000 to 2000 metric tons of B_4C powder are produced annually [32]; this is in stark contrast to Al_2O_3 where it is estimated 603,000 metric tons were produced in February 2020 alone [43]. This limited supply drives up cost and a reliance on a small number of manufacturers. There is a need to understand B_4C production, and how it may be optimised. This should aim to reduce processing temperatures whilst increasing powder production, hence driving down cost.

Table 1: Table displaying the cost of production of a ceramic armour relative to Al_2O_3 . Here Reaction bonded (RB), sintered and Hot Pressed (HP) ceramics are considered. A clear increase in the cost of the armour can be seen when B_4C is used.[6]

Ceramic	Relative Cost
98% Al_2O_3	1
RB SiC	2.5
Sintered SiC	4.5
HP SiC	9
HP B_4C	16

Estimating the ballistic capabilities of ceramics

Hazel *et al* note that ceramic armour by its nature is parasitic; it cannot currently be integrated into a vest or vehicle to replace another material [7]. It is therefore important to gain a good understanding of

ballistic performance, since the ceramic only provides ballistic protection. It is common for authors to define their own experiments and use them to infer the suitability of the ceramic for armour. Literature defines several parameters and measures of ballistic performance dependent on experimental setup. The majority of literature [12, 33, 35–37, 44] looks to examine ballistic performance using a tile-reference setup. Commonly known as a Depth of Penetration (DOP) test, a ceramic tile is mounted in front of an aluminium alloy or polycarbonate reference material. The projectile penetration depth into the alloy is measured both with and without the ceramic present. The method then determines how much ceramic is needed to significantly reduce penetration. If a ceramic results in less penetration with a smaller tile thickness, it is performing better.

A simple solution to increase protection is to increase tile thickness. It does however increase the weight burden on the soldier by adding extra material. Authors seek to quantify this relationship using a defined factor. However, the definition of this varies and hence comparisons must be carefully selected. The Density Efficiency Factor (DEF) weighs up the negative requirement to increase tile thickness and the positive effect of decreasing penetration. This factor reports a saturation point. The thickness at saturation is the minimum thickness at which a relatively high ballistic performance can be achieved. The DEF shows promise as a definition of ballistic performance as it allows comparison between materials if the same projectile, thickness and backing material are used. However, it does not consider the quality of the ceramic after impact and hence multi hit capability. This is a major drawback when developing a multi-hit capable armour [37].

The Mass Efficiency Factor (MEF) provides an alternative. When this factor is greater than 1, the armour is performing better than the reference backing plate. A value of 4 for example would indicate that the reference would require 4 times the areal density to perform as well as the armour [12]. Both factors have the same drawback, they are heavily affected by the experimental setup, specifically the backing plate used. Rosenberg *et al* [45] discusses that the use of a harder backing plate can significantly change the values reported as the armour is less likely to fail from bending. However, literature values can be compared using these factors, giving a general understanding of the performance of several ceramics. In order to examine the literature, sources were reviewed and the results were summarised in Table 2 for several ceramic materials

Comparison directly between values of DEF of different materials can be conducted. It is seen that Al_2O_3 has a significantly lower DEF at both 6 mm and 10 mm tile thickness compared to SiC and B_4C . This suggests that, when weight and penetration resistance are considered, SiC and B_4C perform better than Al_2O_3 . However, when comparing results for a 7.62 mm projectile, it can be seen that the maximum in the DEF occurs at 5 mm for Al_2O_3 , 4 mm for SiC, but 7.5 mm for B_4C . These result in areal densities of 19.0 kgm^{-2} for Al_2O_3 , 12.8 kgm^{-2} for SiC and 18.8 kgm^{-2} for B_4C . Compared to SiC, a larger mass of B_4C is needed to defeat the projectile hence effectively negating the low density

benefit that B_4C has. If the thickness of B_4C needed could be reduced, a significant decrease in the DEF, and areal density required, could be achieved.

Considering these trends it can be concluded that an increase in tile thickness for Al_2O_3 , SiC and B_4C increases ballistic performance to a point, at which point further increases in thickness adds weight with limited reductions in penetration. Further to this, B_4C requires a greater tile thickness, and hence areal density, to achieve the same performance as SiC. This negates its density advantage and suggests that the material reacts differently under a ballistic impact.

Table 2: Table showing the effect of tile thickness (t) on the Differential Efficiency Factor, DEF, and Mass Efficiency Factor, MEF, for Al_2O_3 , SiC and B_4C . * denotes values that were calculated by the addition of a trendline.

Material	Investigation	Round	Parameter	Value at 6mm	Value at 10 mm	Effect of t on parameter
Al_2O_3	Savio <i>et al</i> [44]	7.62 AP	DEF	-	-	Increase to a constant at 5.6 mm
95% Al_2O_3	Madhu <i>et al</i> [46]	12.7 AP	DEF	-	4.44	Increase
99% Al_2O_3	Madhu <i>et al</i>	12.7 AP	DEF	-	2.32	Decrease
Al_2O_3	Cui <i>et al</i> [37]	Various	DEF	3.8	3.4	Increase to 5 mm then decrease
SiC	Roberson <i>et al</i> [12]	7.62 AP	MEF	2.8	-	Increase to a constant at 5 mm
SiC	Nanda <i>et al</i> [33]	7.62	MEF	-	1.2	Increase
SiC	Cui <i>et al</i>	Various	DEF	6.4	6.0	Increase to 4mm then decrease
B_4C	Cui <i>et al</i>	Various	DEF	6.0	-	Increase
B_4C	Savio <i>et al</i>	7.62 AP	DEF	6.85*	-	Increase to 7.5 mm then decrease
B_4C	Savio <i>et al</i>	12.7 AP	DEF	-	6.1*	Increase to 9 mm then decrease

Hardness

Hardness provides an understanding of how a material deals with a ballistic impact. This is especially true in ceramics, which cannot undergo a significant amount of plastic deformation before fracture. A high hardness allows the material to damage the projectile before it fails during the dwell period. Dwell is the initial stage of the projectile-armour interaction, during which limited penetration into the armour is achieved [47, 48]. The projectile undergoes significant erosion and fracture due to the high strength, and hence hardness, of the ceramic armour. This is a key event, with successful fracture reducing or preventing projectile penetration into the armour [49]. An increase in the hardness of an armour will therefore increase ballistic performance and the range of threats that can be defeated.

Hardness experiments are used throughout the literature to examine the damage caused by an impact which creates high pressure within the ceramic. Before examining hardness, it is necessary to define the experiments used to determine its value. Hardness is measured through indentation of the ceramic with either a Vickers, Bercovich or Knoop indenter [7]. The Vickers indenter is a 4 sided pyramid with an apex angle of 68° . The size of the indent created is a direct measure of the hardness. The Knoop indenter is diamond in shape whilst a Bercovich is a 3 sided pyramid. These are often used for hard ceramics as they reduce cracking which complicates hardness calculations [7]. To compare the literature, a Vickers Hardness Number (VHN) and Knoop Hardness Number (KHN) are defined.

$$\text{VHN} = 1.854 \frac{F}{d^2} \quad (1)$$

where F is the load applied and d is the length defined in Figure 1.

$$\text{KHN} = 14.2 \frac{F}{l^2} \quad (2)$$

where l is the length defined in Figure 1

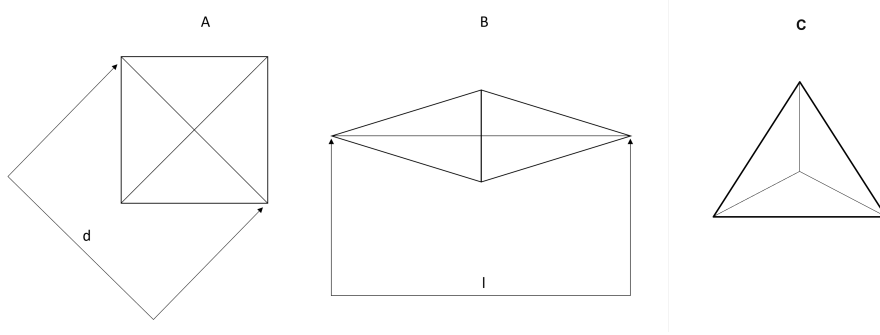


Figure 1: A diagram showing the a) Vickers, b) Knoop and c) Berkovich indenters used to measure the hardness of ceramics. Redrawn from [7]

The literature, as compared in Table 3, tends to be in general agreement about the hierarchy of hardness when comparing Al_2O_3 , SiC and B_4C . Al_2O_3 has the lowest hardness for both VHN and KHN. SiC and B_4C have similar values of hardness with the exact value varying depending on author and test conducted. It was noted by Swab that a large degree of cracking occurs during indentation which can make hardness values inaccurate. This is echoed by Hallam; Knoop is often preferred as it induces less cracking, or at least less cracking detrimental to measuring the hardness. These values align well with ballistic performance predicted by DEF. The higher hardness of SiC and B_4C will increase ballistic performance.

Analysis of damage incurred during indentation allows for discussion on the possible failure mechanism of a ceramic during a ballistic impact. Hallam investigated the sub surface cracking of SiC-4wt% B_4C and B_4C under a 19.6N Vickers indentation [9]. The surface and subsurface micrographs are seen in Figure 2 & 3. Hallam explains that crack propagation in both the SiC-4wt% B_4C composite and B_4C samples occurs through transgranular cracking. This was shown to decrease crack propagation resistance when compared to a SiC-AlN-C benchmark sample which undergoes intergranular crack deflection. Comparing the micrographs, SiC-4wt% B_4C is seen to have a significantly shallower region of damage when compared to B_4C but does exhibit a 'half penny' shaped crack extending down to similar depths. Further analysis shows a heavily fragmented hemispherical zone in B_4C , with the larger region of damage evident in Figure 4c. These differences give a clear indication that SiC and B_4C act very differently under load. The plastic and fracture zone in B_4C appears much more extensive

than the SiC majority composite. This is surprising when considering the relatively similar values of hardness. It has been noted in various studies that this may be caused by an amorphous breakdown [13, 15, 18, 19, 50, 51]. This likely leads to decrease in yield strength, hence more damage is sustained. This loss of mechanical properties will reduce the ability of a B₄C armour to withstand further impacts.

Table 3: Table showing literature hardness values achieved through knoop indentation from various literature studies.

Investigation	Material	Value at constant (GPa)	Density (g/cm ³)
Swab <i>et al</i> [10]	Al ₂ O ₃	13.0	3.90
	SiC	18.2	3.20
	B ₄ C	18.4	2.49
Hallam <i>et al</i> [9]	Al ₂ O ₃	-	-
	SiC- 5wt% B ₄ C	20.4	3.21
	B ₄ C	20.0	2.49
Vargas-Gonzalez <i>et al</i> [11]	Pressureless SiC	21.0	2.52
	Pressureless B ₄ C	22.2	3.20
	Hot Pressed SiC	19.6	3.20
	Hot Pressed B ₄ C	20.2	2.50

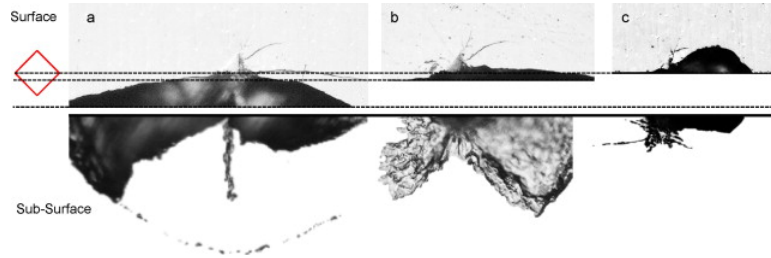


Figure 2: Reflected light micrographs showing the surface and subsurface damage occurring in a sample of SiC-4wt% B₄C during a Vickers indentation under 19.6 N. From a) to c) the micrographs move inwards from the edge of the indent to the centre. The surface images are offset to where they refer to spatially when compared to each other. The position of the indenter is displayed by a red diamond on the left of the image. Reproduced with permission [9].

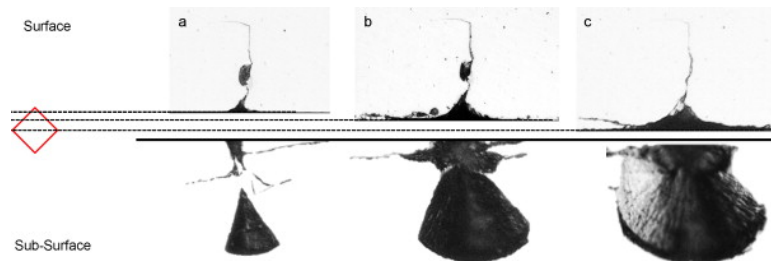


Figure 3: Reflected light micrographs showing the surface and subsurface damage occurring in a sample of B₄C during a Vickers indentation under 19.6 N. From a) to c) the micrographs move inwards from the edge of the indent to the centre. The surface images are offset to where they refer to spatially when compared to each other. Reproduced with permission [9].

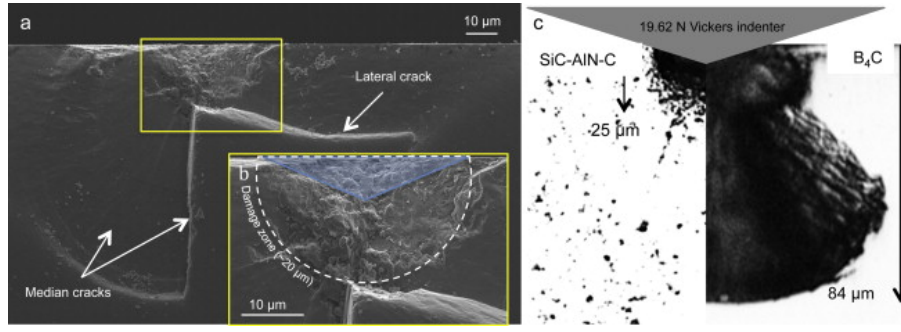


Figure 4: a) SEM SE micrograph showing median and lateral cracking resulting from a 19.62 N Vickers indent onto a B₄C sample. b) Micrograph showing an extensive fragmentation damage in a hemispherical region. c) Reflected light micrographs showing a comparison between the sub surface damage post indentation for B₄C in comparison to a reference SiC-AlN-C sample. Reproduced with permission [9].

Conclusion

The weight of an armour can have significant impact on a soldier or system. B₄C shows promise in this area, with its lower density than traditional armour ceramics. It can be seen that the cost of armour varies significantly across ceramics, with B₄C incurring the highest cost. A lower cost increases the chance an armour can be mass produced. B₄C and SiC require higher temperatures and pressures for sintering to a ballistic quality and hence cost more to produce. For carbides to be used, it is prudent to consider the powder production methods such that a lower cost of production may be achieved.

The tile thickness required to achieve a set ballistic performance gives an indicator as to which ceramic makes the best armour. Al₂O₃, SiC and B₄C show similar trends in DEF, with these factors increasing to a saturation point. Using these, SiC and B₄C show consistently greater ballistic performance than Al₂O₃. The saturation point in B₄C occurs at higher thicknesses than SiC. This suggests B₄C is responding to the impact differently and is not reaching its full potential. The extra thickness needed adds more weight negating the lower density benefit of B₄C. This reduces soldier mobility hence reducing the armour's effectiveness. Hardness can be used to investigate the material response to a ballistic impact. It is seen that B₄C has a significantly larger zone of damage than SiC despite similar ballistic performance. It is suggested that a unique amorphous breakdown is occurring in B₄C which results in poorer than expected ballistic properties. Investigation into the cause and mitigation of this breakdown is vital in understanding how to improve the ballistic performance of B₄C.

2.2 Boron Carbide as a ballistic ceramic

B₄C has been a material of significant interest in the field of armour. Its high hardness, up to 40 GPa, and low density of 2.54 g/cm³ provide great potential for use as an armour [34, 52]. It is noted that the material has a tendency to become amorphous under load, hence reducing favourable mechanical properties.

This section will begin by considering the structure of B₄C across the phase diagram. Next, the

ways in which studies have investigated the amorphous breakdown will be discussed, followed by the proposed mechanisms of amorphous breakdown. Finally, current solutions for reducing amorphisation will be considered and conclusions drawn on potential research avenues.

Structure of Boron Carbide

In order to understand the breakdown of boron carbide, it is first necessary to consider its crystal structure. The definition of the structure as B_4C , whilst widely used, has been noted by some to be fundamentally inaccurate [13]. Clark *et al* proposed an ideal stoichiometric structure of $B_{12}(CCC)$. The (CCC) part of the formula denotes the composition of a chain that links icosahedra within the structure along the (111) direction (the exact direction varies depending on overall structure)[13, 50, 51, 53–55]. Besnard *et al* discuss this in depth when considering the possible structures of B_4C . These can be seen in Figure 5 and draw on the work of Clark *et al*. It can be seen that fundamentally the boron carbide can exist as either a rhombohedral lattice with trigonal symmetry ($R\bar{3}m$) or a hexagonal lattice [13]. Within these there exist atoms that are either in polar, non polar or equatorial positions.

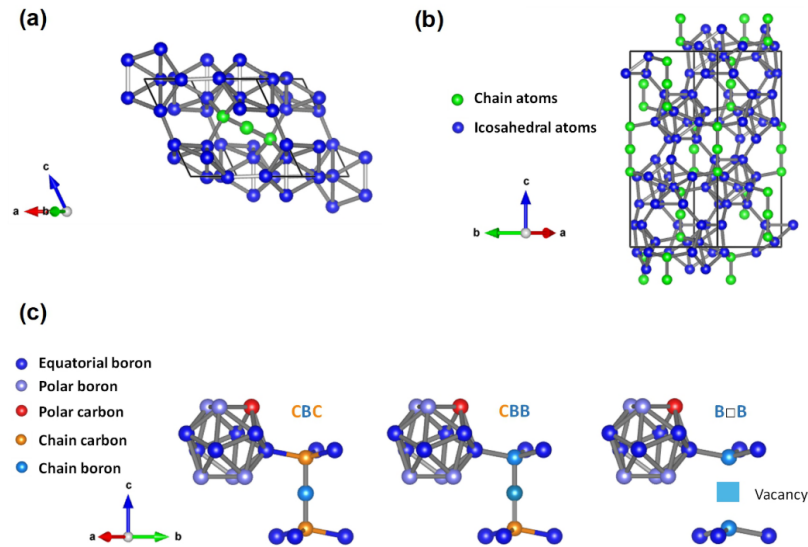


Figure 5: a) Crystal structure of B_4C with a rhombohedral lattice b) Crystal structure of B_4C with a hexagonal lattice c) Various inter icosahedra chain configurations based on the work of Clark *et al* [56]. Reproduced with permission [13].

The range of structures that exist for boron carbide are likely to depend on the ratio of boron and carbon within the structure. This hypothesis was confirmed by Thevenot and Aselage *et al* who note that the structure of boron carbide varies between a boron rich structure of $B_{10.4}C$ at ~ 9 at% C to a carbon rich structure of B_4C ($B_{12}(CCC)$ stoichiometrically) at 20 at% C [53, 57]. This was corroborated by Schwetz *et al* who deduced the phase diagram for boron carbide using electron probe microanalysis along with chemical analysis. As seen in Figure 6, the structure evolves from one containing extra boron to another containing extra carbon as graphite [58]. Which exact structure exists at a point in the phase diagram has been a matter of some debate. Werheit and Shalamberidze

[54] conducted a study into the evolution of the structure with carbon content ($[C]$) using infrared spectroscopy (IR). Their work shows a decrease in B_{12} icosahedra with carbon content along with a rise in $B_{11}C$ icosahedra. These both move from 0.01% to 100% or vice versa with a crossover at $[C]=0.13$. Analysis of the chain shows an increase of CBC and $B\Box B$ with $[C]$ whilst CBB decreases with $\Box$ denoting a vacancy which produces a 'chain free' structure. Vast *et al* [59], Lazzarri *et al* [55] and Werheit *et al* conclude that the most likely structure is $B_{11}C_p$ (CBC) with p denoting the polar position. However, the authors differ on the exact structure in the carbon rich region, with Werheit showing it to be 100% $B_{11}C_p$ with 91% CBC and 9% $B\Box B$. Vast shows this to be mainly $B_{11}C_p$ (CBC) with 2.5% having the B_{12} and $B_{10}C_2$ icosahedra. There is little experimental evidence that the ideal B_{12} (CCC) structure, proposed by Clark, exists at high $[C]$ with Werheit hypothesising it is lost in high noise regions of the IR spectra [60]. B_4C should therefore not only be associated with the B_{12} (CCC) structure and instead expand to include $B_{11}C_p$ (CBC).

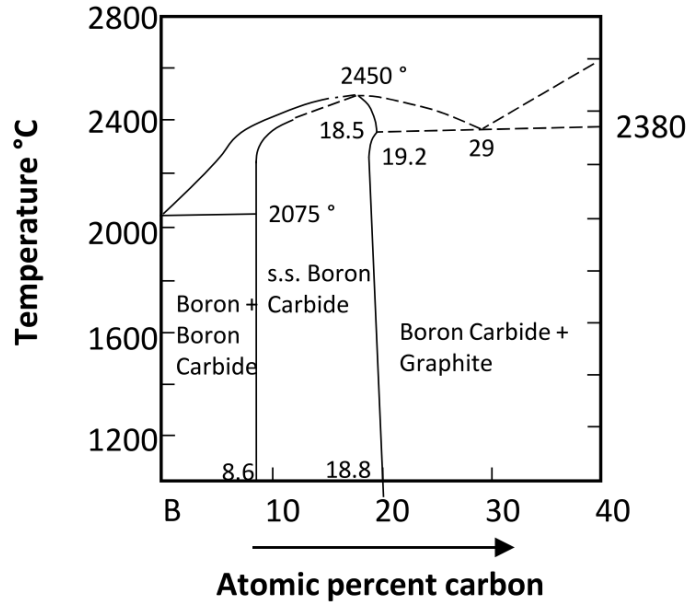


Figure 6: The phase diagram of boron carbide proposed by Schwetz *et al*. The structure is seen to range from a boron rich to a carbon rich structure. Reproduced with permission [61].

Investigating amorphous breakdown of boron carbide

As discussed previously, boron carbide has unexpectedly poor ballistic performance against certain threats; it is thought that the structure of B_4C breaks down and forms amorphous bands leading to a loss in mechanical properties[13–19]. This significantly reduces ballistic performance after the first impact. Analysis of amorphisation directly often uses Transmission Electron Microscopy (TEM) whilst Raman spectroscopy is used as a low resolution, non destructive method [15, 18, 22, 62]. TEM is used sparingly in the literature to consider the atomic level structure of amorphous regions and verify hypotheses generated from computational work. Focused Ion Beam (FIB) techniques are

used to prepare thin lamella for inspection within the TEM, usually on indents produced using a Berkovich tip [22, 24, 63, 64]. It should be noted that single crystals grown along certain directions are often used, hence allowing analysis of preferential amorphous directions. Further work in the field of polycrystalline B_4C will be needed to determine if these observations are consistent across a range of microstructures.

Studies have been conducted to determine the mechanism of amorphous band formation. Ge *et al* used nanoindentation and mechanical scratching [18]. This was coupled with Raman spectroscopy. Analysis post-indentation showed the appearance of peaks at 1330 cm^{-1} , 1350 cm^{-1} , 1520 cm^{-1} and 1550 cm^{-1} . These were attributed to D (disordered) and G (crystalline) bands of graphite. The observations were verified by electron energy loss spectroscopy (EELS) and TEM analysis which showed a clear amorphous region in the indent. Amorphous bands form along the $\langle 11\bar{3} \rangle$ direction; it is noted that these are likely caused by shear in the (120) plane suggesting that amorphisation results from shear. Subhash *et al* showed the extent of amorphous breakdown in the 0.69 N indent using sequential Raman and polishing [15]. A visualisation of the Raman shift can be seen in Figure 7. The amorphisation occurs further into the material than just below the indenter. It can also be noted that a plastic zone exists around the amorphous bands. This suggests that the stress required for amorphisation is higher than that required for plastic deformation. Parsard *et al* considered a similar study except with indents at larger forces of between 1.7-13.7 N [65]. The amorphous region is seen to increase to a peak, with the spatial position similar to the location of maximum shear stress determined from Hertzian contact theory. Additionally, finite element simulations (FES), were used to relate the amorphous region to the stress and strain fields below the indent. These predict a similar half-penny shape to those determined experimentally. They note that there are potential issues with this method, such as the precision of polishing depth, although attempts to mitigate this using reference indents were trialled. Additionally, polishing is noted to remove extra materials around cracks, an area where amorphous bands are known to form, which could impede the accuracy of the zone calculations.

Both studies note a relationship between the amorphous zone and a critical stress, greater than that required for plastic deformation. The stress is seen to approach the same value as the Hugoniot Elastic Limit (HEL), a value that is analogous with the yield strength at high strain rate [7] and is often used to characterise ballistic ceramics. Ghosh *et al* argues that the HEL is also the global pressure required to initiate amorphisation [14] with a value of around 17 GPa. A similar observation was made by Grady who calculated a value of 18 GPa in uniaxial strain [66]. This requirement for high stress is echoed by Chen *et al* who showed that a stress of 23.3 GPa was required to initiate amorphisation [19] under ballistic conditions. This suggests that B_4C could perform well until a critical stress is reached.

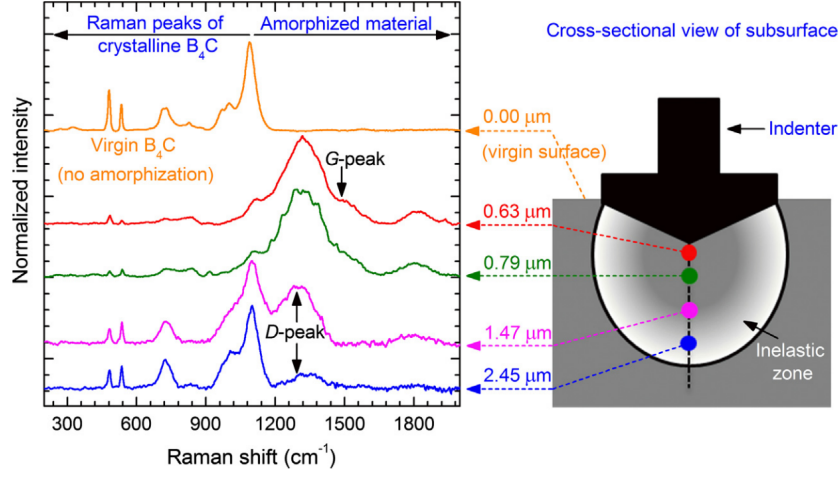


Figure 7: Raman pattern showing a clear shift resulting from G and D bands of graphite. Reproduced with permission [15].

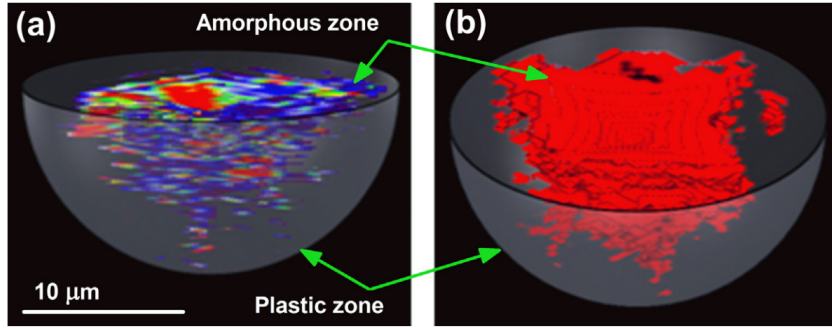


Figure 8: 3D visualisation of the amorphous region under an indenter tip. The samples were analysed under a Raman microscope before being polished. This occurred sequentially until a 3D image was achieved. Reproduced with permission [15].

Mechanism of Amorphous Breakdown

To understand the process by which boron carbide breaks down, initial studies focused on in situ, high pressure, diamond anvil cell (DAC) experiments [16]. These were conducted within a Raman microscope allowing the evolution of the amorphous region with time to be investigated. Yan *et al* reports on this whilst observing how the intensity of peaks associated with amorphisation change with time [50]. Amorphisation occurred on depressurisation if the initial pressure applied was $\gtrsim 25$ GPa. This agrees with the ballistic tests conducted by Chen *et al* who showed a threshold pressure had to be exceeded to cause amorphisation [19]. It was also noted that the pressure had to be decreased to below 20 GPa to allow amorphisation to occur. In later work, Yan *et al* proposed a method of amorphous breakdown [16]. Raman spectroscopy at low and high temperature suggest that the CBC chain breaks down leaving the icosahedra intact. It was suggested that the boron in the chain bonds to another atom in the icosahedra when the chain is bent under pressure. This leads to collapse of the chains when pressure is removed. Gosh *et al* propose a similar mechanism where the isocahedron remains intact but the chain breaks apart. Raman spectroscopy, FTIR and photoluminescence were

used to show the CBC chain initially breaks down into atoms, followed by a substitution with the icosahedra. This results in B_{12} icosahedra along with disorganised carbon. This can be seen in Figure 9a.

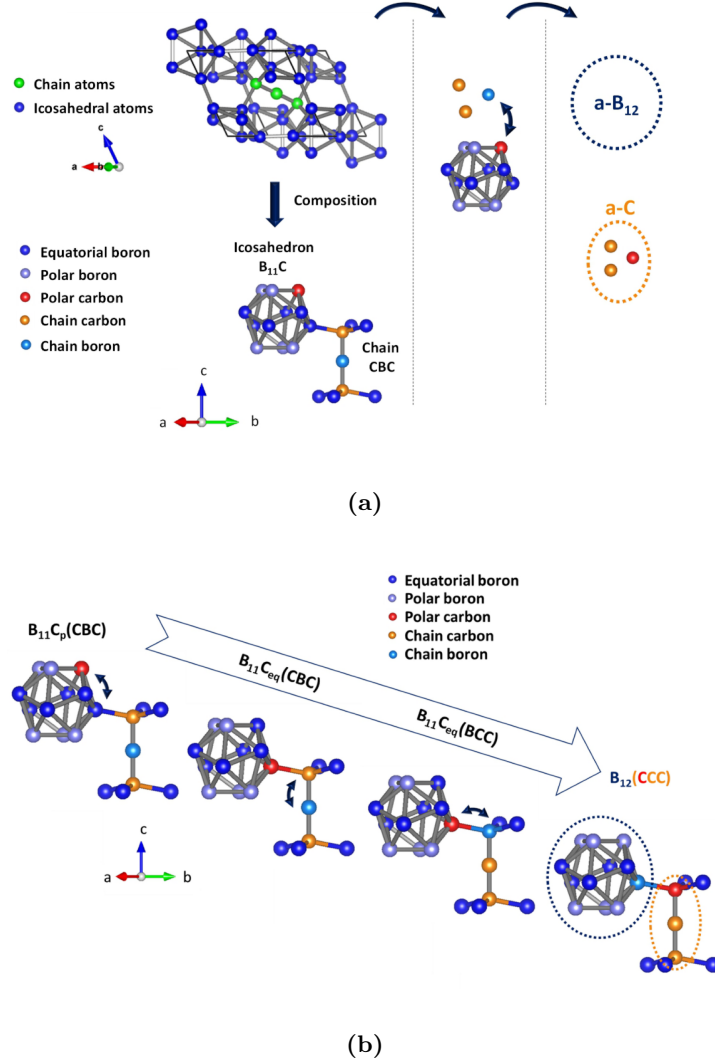


Figure 9: a) Schematic showing the amorphisation mechanism proposed by Ghosh *et al* [14]. Here the CBC chain decomposes to carbon and boron atoms. Boron then substitutes with the polar carbon in the icosahedra. Reproduced with permission [13]. b) Schematic showing the amorphisation mechanism proposed by Fanchini *et al* [20, 67]. Here the structure forms a CCC chain which in turn forms amorphous graphite. Reproduced with permission [13].

Finachini *et al* considers a mechanism with similar steps; adaptation of the icosahedra and break down of the chain. This work proposed that the polar carbon in the icosahedra becomes part of the CBC chain to form a CCC chain [20]. This is described in Figure 9b. These chains are known to concentrate along the (113) direction and it is proposed that these form amorphous carbon when the polytype collapses. However, there is no clear explanation as to how this polytype collapses. Chen *et al* seem to show agreement [19]. Their experiments show that the amorphous band primarily forms along the (113) and $(2\bar{1}3)$ planes. Ge *et al* also showed that shear bands form along the (113) plane but it was noted that this direction did vary, suggesting it was correlated to a shear condition rather

than preferred orientation[18]. This was echoed by Zhao *et al* who showed that amorphous bands consistently orientate along the direction of maximum shear stress [17]. They did note a variation in this direction based on the grain orientation. This further verifies that shear direction, rather than crystallographic orientation, is determining the amorphous band direction.

Analysis of the amorphous region directly can help verify these hypotheses. Reddy *et al* used TEM to analyse thin specimens post indentation [62]. An indentation schedule, with a slow loading rate of 0.125 mN/s up to 25 mN, showed unique pop-in events. Here a decrease in instantaneous stiffness is seen, with a plateau in the hysteresis curve. This event was investigated using the TEM for the (214) crystal and shows bands of length ≈ 300 nm and width ≈ 1 -4 nm occurring on the (122) plane as seen in Figure 10. This is coupled with an observation of an amorphous peak in the associated Raman spectra. It was found that the activation volume of the pop in was ≈ 1.8 -2.8 Å which is similar to that of dislocation activation in other metal and ceramic indentations. It is proposed that the lattice displaces under shear before forming dislocation kinks, which in turn nucleate amorphous bands as seen in Figure 11.

Reddy *et al*'s earlier work shows a different possible mechanism for band formation [22]. This work noted that the amorphisation occurs along a direction where dislocation motion is energetically unfavourable due to a large Burgers vector. The shear stress is instead accommodated by the bending and breaking of the inter icosahedra chain. Work by An *et al* sought to analyse this further using reactive-molecular-dynamics simulations [68]. Here, they conclude that the break up of the icosahedra gives enough free volume for amorphous band formation. The chain was seen to break, leaving a lone electron pair on the carbon within the icosahedra; this could then bond to a boron in the icosahedra leading to the icosahedra breaking apart [23]. This went further to show that the introduction of twins into the structure leads to faster development of amorphous bands and results in a reduction in shear strength [69]. The twins were seen to form under shear and coalesce before amorphous bands formed which in turn initiated cracking. It is clear that amorphisation is a shear related event and that there is disagreement between authors on the exact method of amorphous breakdown.

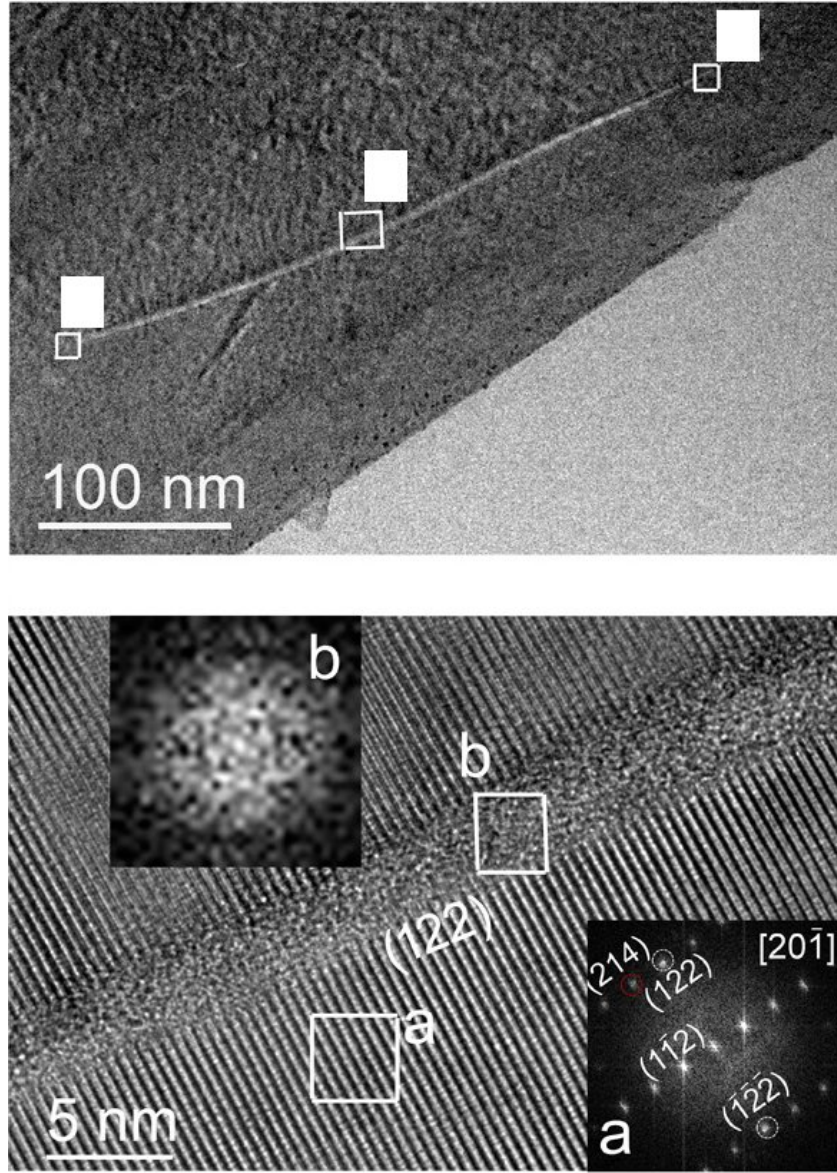


Figure 10: TEM micrograph showing a high level view of an amorphous band (top) and a high resolution micrograph (bottom) with Fast Fourier Transform (FTT) analysis showing amorphous nature of the band. Reproduced with permission [62].

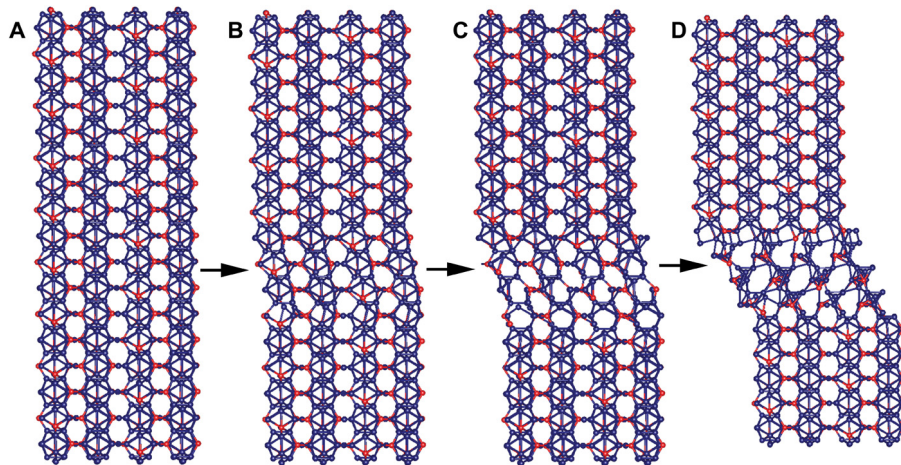


Figure 11: Diagram explaining how amorphous bands form. From A to D the lattice is strained (B) a dislocation kink is formed (C) and an amorphous breakdown occurs (D). Reproduced with permission [62].

Reducing Amorphisation

Amorphisation mitigation has been studied in relatively little detail compared to the amount of literature that exists on the mechanism of its formation. In this review two prevalent methods will be considered: 1) Changing Microstructure and 2) Doping.

1) Changing the Microstructure

Few studies have considered the effect of microstructure on the amorphisation of B_4C . DeVries *et al* observed higher compressive strength and hardness along with a decrease in cracking about the indenter tip when grain size was decreased [21]. This was taken further to see an increase in an estimate of fracture toughness. A decrease in the volume of the amorphous region was also seen for nanocrystalline B_4C but this could not be completely mitigated. Reddy *et al* analysed the effect of adding amorphous carbon in the grain boundaries between nano grains of B_4C [22]. This showed that fracture toughness can be increased by promoting grain boundary sliding using the amorphous carbon. This also led to a decrease in the extent of amorphisation. It could be hypothesised, in both of these methods, that increased grain boundary sliding reduces the pressure build up within the material. This reduces the amorphous breakdown. However this could not be proven in these works.

2) Si and B Doping

The addition of Si is proposed as a way of preventing polytype breakdown. Whilst studies have shown a reduction in amorphisation can be achieved, the disagreement between the exact mechanism of amorphous breakdown means explanations need to be examined carefully. An *et al* considered the replacement of the CBC chain with a Si-Si chain [23]. This was shown to increase ductility allowing it to accommodate shear up to twice the value of undoped B_4C . It was suggested that the Si allows the icosahedra to rotate and prevents chain bending and breaking. It is therefore able to accommodate more shear before breakdown. This computational study noted the issue with synthesising the required structures, specifically with ensuring silicon diffusion to the correct location. Besnard *et al* conducted a comprehensive study and found similar issues to be prevalent [13]. Here it was shown that amorphisation could be reduced by the production of Si doped B_4C . However, this work was unable to verify the exact location of the Si within the structure, making it difficult to verify the exact mechanism by which it prevents amorphous breakdown.

Proctor *et al* considered the reduction in the $B_{12}(CCC)$ polytype with the addition of Si [25]. Some have noted that the breakdown of the $B_{12}(CCC)$ polytype, either native in the B_4C or formed under pressure, is the cause of amorphous breakdown [20]. It was shown that the addition of Si reduced the native $B_{12}(CCC)$ by 10%. Further to this, it was hypothesised that the addition of Si reduced the

formation of $B_{12}(CCC)$ under pressure. However, much like Besnard, the study was unable to define the location of the Si. Along with this, some studies do show evidence that the $B_{12}(CCC)$ polytype does not exist natively and that the breakdown of CBC chains is responsible for the amorphous breakdown of B_4C [70, 71].

Chauhan *et al* builds on the idea of chain and icosahedra alterations to investigate if doping with boron can reduce the extent of amorphous breakdown [24]. Here, a structure of $B_{6.3}C$ was produced with B substituting into both the icosahedra and chain. This work is in agreement with Reddy *et al* on the shape and size of amorphous bands observed using TEM. A 30% reduction in amorphous bands was noted along with crack initiation from amorphous bands. No particular mechanism is proposed for this improvement but a decrease in hardness is noted on doping. Potential increases in flexibility of the structure could be reducing the ease with which amorphous bands form, similar to that of Si doping.

2.2.1 Using composites of B_4C to reduce amorphisation

Carbide composites containing B_4C have been considered in the literature and provide a potential route to decreasing amorphisation. If the problematic B_4C phase can be removed, or the stress state altered, then amorphisation may be affected. For this to be successful, ballistic performance must be improved or maintained. The majority of literature aims to identify an optimal processing condition and composite composition, usually to maximise properties such as ease of sintering, fracture toughness or hardness [27–30]. Matovic *et al* investigated the development of a low temperature, high pressure, sintering apparatus. It has already been seen that the processing conditions of B_4C can significantly increase its cost. The addition of a phase that sinters at lower temperatures, such as Silicon Carbide (SiC) can aid this [29]. This work produced composites with densities above 95% and a Vickers hardness up to 31 GPa for a 75:25 (B_4C :SiC) composite. So *et al* considered a sintering aid-free method. B_4C often requires sintering aids due to its difficulty in sintering [27]. These aim to lower the temperature of processing, hence potentially decreasing cost, but often result in unwanted secondary phases. The addition of SiC can lower the sintering temperature whilst providing a well controlled carbide phase with similar mechanical properties. In this work dense B_4C -SiC composites were achieved at 2000 °C and 40 MPa pressure. It was noted that the hardness and flexural strength increases with B_4C content whilst fracture toughness decreases. This is expected due to the increased hardness of B_4C over SiC. A similar trend was observed by Hwang *et al* who produced similar composites via a polymer processing route [28]. These studies suggest that B_4C and SiC can bring mutual benefits to a ballistic composite, especially by decreasing processing costs and increasing favourable mechanical properties. However, the effect of adding an additional phase on amorphisation has not been widely investigated.

Conclusion

Boron carbide has shown promise as an armour due to its low density and high hardness. However, it undergoes shear induced amorphous breakdown that results in poor mechanical properties at high pressures. Work has shown the presence of amorphous bands below indents in B_4C . These are studied using a combination of Raman spectroscopy, TEM and optical microscopy. Determining the 3D structure of the amorphous zone requires precise polishing, combined with Raman mapping. However, the process is lengthy and additional amorphisation can be introduced during processing. Improvements to these methods are needed, such that the amorphous zone can be investigated accurately in a timely manner.

Several mechanisms of breakdown have been proposed; a general consensus shows that the inter icosahedra chain breaks during shear but in which polytype this occurs is a source of contention. This is added to by the disagreement in the exact polytype structure at each section of the phase diagram. It is possible to alleviate the effects of amorphisation by reducing grain size, adding inter granular phases and doping with silicon or boron. It can be theorised that changes to the stress state around the B_4C can alter its response to shear, and hence the extent of amorphous breakdown. However, the exact mechanism behind these observations is not clear to date.

Composites with other carbide materials, such as SiC, have shown a precedent for providing a good balance of sinterability and mechanical properties. However, despite this, little work has been undertaken to understand how the addition of a SiC phase affects amorphisation. This leaves room for significant study, with the potential to link mechanical properties to the amorphous breakdown in these materials.

2.3 Powder production techniques

Literature lacks understanding on the effect of SiC inclusions on amorphisation. It could be theorised that by combining B_4C with SiC, using nano sized grains, amorphisation may be reduced. However, the production of nanoparticles of SiC and B_4C materials is not wide spread amongst industry. For a ballistic composite to be usable, it must be accompanied by a well understood, low cost and scalable production method. Whilst there is some literature on the subject, it is often limited to producing intermediates and not the final product. The overall production method can generally be described by the flow chart in Figure 12.

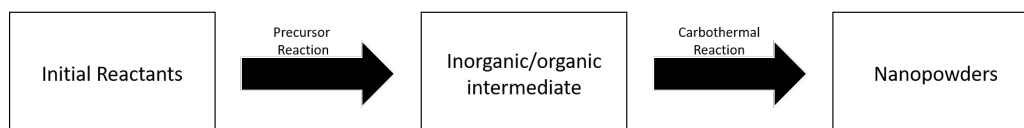


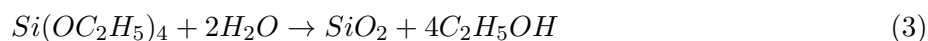
Figure 12: Flowchart describing the typical reaction route to produce nanopowders

This chapter will begin by discussing the routes to SiC nanopowders, followed by discussion on how to produce B₄C nanopowders. Sintering conditions and requirements will then be considered to determine areas of investigation.

2.3.1 Silicon Carbide

SiC nanopowders are typically produced by creating a silicon based SiC precursor, which in turn undergoes a carbothermal reaction to form SiC. The sol-gel method is most commonly used to produce the SiC precursor and can be broken down into: 1) Traditional sol-gel production and 2) Microemulsion controlled production. Both methods aim to produce particles consisting of a well connected silica (SiO₂) network. Microemulsions seek to control the production of particles further by changing the environment in which the sol-gel reaction is undertaken.

The sol-gel method is well established in chemical science and can be considered in the context of the Stöber process [72]. In this work a sol, particles suspended as a colloid, is produced which in turn undergoes a gelification reaction [73]. In this case a precursor such as a tetraalkyl silicate reacts to form a sol of small particles, which undergo gelation in the presence of a catalyst to produce SiO₂. An example of this reaction can be seen in Equation 3. Stöber *et al* noted that monodisperse particles in the range of 0.02 µm to 2 µm could be produced by changing the solvent and catalyst used [72].



Following the production of the Si precursor, a carbothermal reduction is conducted where the particles are reacted with a carbon source at high temperature. Literature usually aims to produce the low temperature, cubic β-SiC, but some do focus on producing the high temperature, hexagonal α-SiC [74, 75].

Traditional Sol-Gel Production of nano-silica

Sol-gel reactions have been used to create a range of ceramic powders including barium titanate [76] and porous SiC structures [77]. SiC particles have also been studied with some considering the use of the process to produce whiskers [73] and others focusing on the production of nanopowders [73, 78–80].

Seog *et al* consider the silane-H₂O-Catalyst route to produce monodisperse spherical β-SiC nanoparticles [79]. Phenyltrimethoxysilane (PTMS) or Tetraethylorthosilicate (TEOS) were reacted with water and a NH₄OH catalyst. These were aged for 24 hrs at 20°C followed by drying under vacuum. The resulting gel powder was then reacted with carbon at 1400-1500 °C in an inert atmosphere. The particles produced were monodisperse and spherical suggesting that the method was successful. In

addition to this, Seog discusses ways to control particle size. It is noted that using TEOS produces smaller particles of $\sim 0.2 \mu\text{m}$ compared to $1 \mu\text{m}$ when PTMS is used. This is due to a decrease in the zeta potential for PTMS derived particles from -80 mV to 20 mV . Benzene rings exist on the surface of these particles; as these can not interact with the water they do not become charged, hence do not form a charged double layer. The neutral particles aggregate as there is no electrostatic repulsion to keep them apart. This shows that the size of particles can be affected by altering their surface chemistry. It is noted that the addition of an alcohol to the solution can also increase particle size. This is due to a reduction in the dielectric constant (ϵ). Equation 4 demonstrates how repulsive and attractive interactions can affect the energy barrier to agglomeration, V_B :

$$V_B = -\frac{A\kappa a}{12} + 2\pi\epsilon a\psi^2 \quad (4)$$

where κ is the Debye-Huckel parameter, a is the particle diameter, A is the Hamaker constant and Ψ is the surface potential [79]. The negative term results from attractive van der Waals forces whilst the positive term relates to electrostatic repulsion. This formula does vary between authors and the exact system being used [81]. However, control of each parameter can be seen to allow precise control of particle size by inhibiting or allowing agglomeration. Hatakeyama and Kanzaki undertook similar work to produce SiO_2 using TEOS and phenyltriethoxysilane (PTES) [80]. They, alongside Stöber *et al* [72], additionally note that varying the concentration of NH_4OH can affect particle size. It was seen that the more NH_4OH that was added, the greater the monodispersity of the particles. It is thought that the larger the amount of catalyst, the more nuclei that form. As there are more nuclei, each undergoes a relatively small growth compared to if there were few nuclei. This reduced growth reduces the chance that particles will be significantly different in size. This also reduces the driving force for Oswald Ripening as there is limited difference in the radius of curvature across the gel. This then reduces the variation in particle size.

Najafi *et al* and Li *et al* consider an adaptation of the silane- H_2O -Catalyst route [73, 82]. Here TEOS is prehydrolysed in an acid catalyst to form SiO_4 . This is then aged with the optional addition of an alkali catalyst. In addition to this, phenolic resin is mixed in during the hydrolysis stage to act as a carbon source during the carbothermal reaction. Both authors note a narrow particle size distribution around $0.1 \mu\text{m}$ in size. These results are similar to using the silane- H_2O -Catalyst route discussed above.

Microemulsion controlled production of nano-silica

Microemulsions provide an alternative to the use of traditional sol-gels. A microemulsion is defined as a thermodynamically stable emulsion with a droplet size of $5\text{-}50 \text{ nm}$. This structure is achieved using a combination of surfactants which result in an ultra low interfacial tension [83]. The reaction

environment this provide allow greater control of the resultant particle size and shapes [84–86]. Microemulsion methods have been used in various applications including the preparation of Selenium nanoparticles [87], Titanium Oxide photocatalysts [88] and Cerium nanocomposites [89, 90]. The most relevant work for this project however is the production of silica nanoparticles by microemulsions using TEOS as explained by Equation 3. These have been investigated in the literature and yield similar particles to those produced by the sol-gel method before the carbothermal reaction [84–86].

A water in oil (W/O) reverse microemulsion exists when a continuous oil phase contains nano-scale droplets of water stabilised with a surfactant [91]. This provides a unique environment in which to form SiO_2 nanoparticles. Figure 13 shows the mechanism by which a W/O micro emulsion containing TEOS, water and a catalyst forms SiO_2 nanoparticles. This can be described in 4 steps [84, 92, 93]:

1. TEOS diffusion to W/O interface.
2. TEOS reaction with H_2O to form a single silanol group.
3. Further TEOS reaction with H_2O to form SiO_4 monomer.
4. Monomers react to nucleate a SiO_2 nanoparticle. Particle growth continues until monomers are depleted.

This is seen to occur initially as an intramicellar reaction. In order for nucleation to occur a critical concentration of monomers must be achieved [84]. It is therefore necessary to maximise the formation of monomers as well as allowing these to come together in a high enough concentration to cause nucleation.

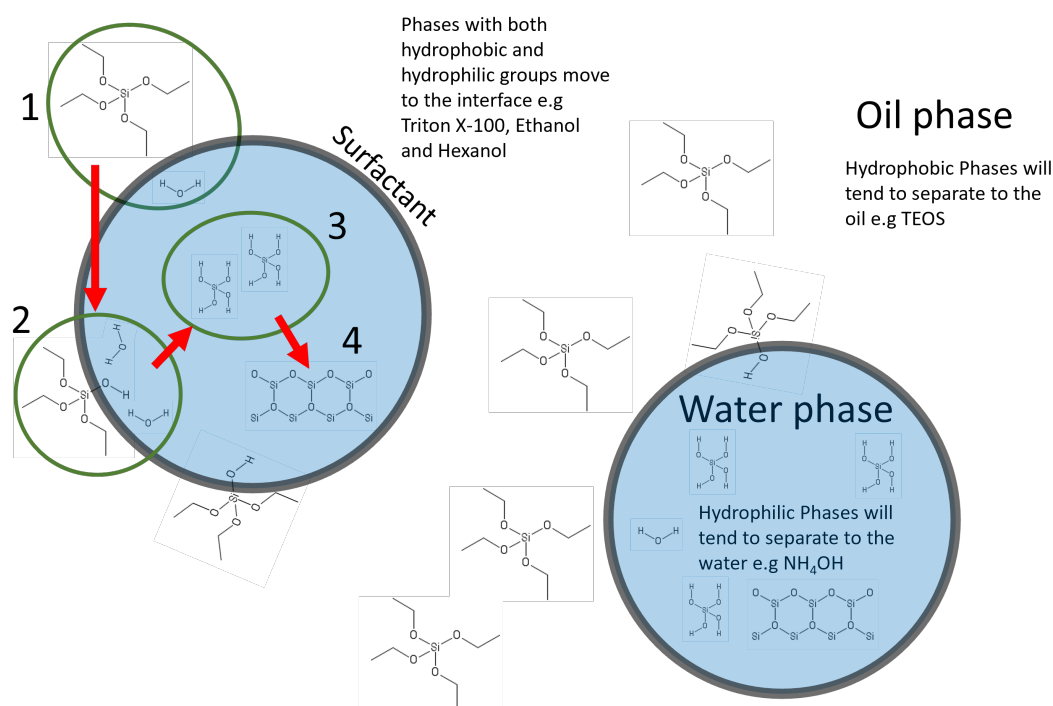


Figure 13: Schematic describing the production of a silica nanoparticle using TEOS-Catalyst- H_2O reverse microemulsion. Reactions 1-4 are described above.

The factors affecting the nanoparticles that result from this process have been studied within the literature by Bagwe *et al* [84]. These include: the concentration of catalyst ($[\text{NH}_4]$), the type and concentration of surfactant and co-surfactant, the concentration of TEOS ($[\text{TEOS}]$) and the ratio of water to oil (O). $[\text{NH}_4]$ defines the rate of hydrolysis of TEOS to form SiO_4 . It does this by providing OH^- ions. Increasing $[\text{OH}^-]$ leads to a greater number of smaller particles. The more catalyst, the higher the rate of hydrolysis and hence the greater the number of monomers per micelle. More micelles will contain enough monomers for particle nucleation, increasing nucleation whilst decreasing particle growth. Particle growth is likely easier when there are free monomers to adjoin to the surface, whereas particles would need to Ostwald ripen to achieve growth without free monomers. This reaction is also linked to the effect of adding a co-surfactant. The hydrolysis of TEOS produces ethanol, a co-surfactant that moves into the surfactant layer surrounding the micelles. This is thought to decrease micelle rigidity whilst altering the packing parameter of the surfactant molecules [84, 94]. This in turn increases the number of micelles, by changing the preferred radius of curvature of the film, whilst also increasing intermicelle reactions though decreased rigidity. A larger number of micelles were seen to exist leading to a larger surface area available for TEOS hydrolysis. This increases the number of monomers and the likelihood of nucleation occurring. The decreased rigidity allows micelle collision and coalescence which increases the chance that a micelle contains significant monomers to nucleate a particle. Similar effects are seen when a different surfactant is used or the ratio of water to surfactant is altered. To achieve nano sized particles which are monodisperse it is crucial to maximise nucleation whilst minimising the extent of particle growth.

The concentration of TEOS ($[\text{TEOS}]$) is seen to have limited effect on particle size and morphology. This is explained as the $[\text{TEOS}]$ used is in excess [84] with no literature considering the effect of limiting TEOS. The use of TEOS in excess does allow for better analysis of other factors by removing a variable. The excess TEOS will remain in the oil phase as the available water is reduced. The ratio of water to oil and water to surfactant is also an important factor to consider although there is little literature on the subject. Chang *et al* notes that there must be sufficient surfactant to sustain the microemulsion [91]. It can be said that if too much co-surfactant is used, the extent of coalescence may break the microemulsion which would separate into water and oil phases. The specific surfactant and oil phase used defines this. The interaction between these can define particle size. For example, hexane is seen to penetrate micelles less than cyclohexane as it is less polar. This results in a larger micelle with more surface area available for hydrolysis. The greater number of monomers leads to greater nucleation and hence smaller particles [86]. This is in agreement with Bagwe who instead uses smaller initial micelles to promote hydrolysis and then coalescence to achieve nucleation. Both methods are seen to achieve monodisperse particles of nano size.

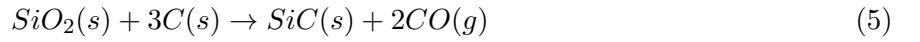
These results indicate that the additional variables introduced by controlling the sol-gel environment,

through the use of a microemulsion, can lead to greater control of particle size and dispersion. This control could allow a range of different SiO₂ powder dispersions to be produced in situ, rather than mixing powders of varying sizes.

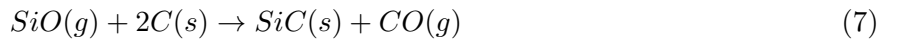
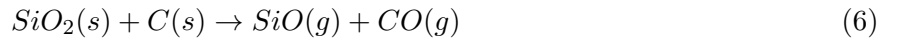
Carbothermal Reaction

In addition to discussing silica particle production, it is necessary to consider the effect of the carbothermal reaction on the resulting particles. Some studies involving traditional sol-gel produced silica consider the production of final SiC powder; these studies are not seen for microemulsion SiO₂. However, the similarities between the silica produced in both methods is significant enough for discussions on the final carbothermal reaction to apply to both.

Li *et al* discuss the reactions that occur to form SiC from SiO₂ [82]. Overall the most favourable reaction progresses as seen in Equation 5; it was observed at both 1550 °C and 1650 °C [95].



It is believed that this is completed in a two step reaction:



These temperatures are lower than those predicted by Hagan *et al*, who calculated the Ellingham diagram, as seen in Figure 14 [96]. Here it is noted that carbon can reduce SiO₂ to SiC at around 1780 °C. It can also be seen that carbon can reduce SiO₂ to metallic Si at temperatures above 1900 °C. The heating and hold temperatures of the SiO₂/C mix must be designed to prevent this.

The SiO gas formed during this process diffuses through the silica to the surface of the particle at which point it is able to react with the carbon source. The formation of this gas is seen to be fast with the reaction predicted to be occurring in a few seconds [95]. The reaction to form SiC also depends on the exact scenario in which the particles are found. Various mechanisms have been proposed depending on conditions such as temperature, pressure and particle contact [95]. However, all these reactions depend on the SiO gas formation which can be seen as the common factor across the system. It is noted by Li *et al* that the outside of SiO₂ blocks reacted in a carbon environment went green and formed SiC. The centre of the blocks remained hard and black, and was identified as carbon [82]. It is likely that the SiO gas moves rapidly to the surface where it reacts, hence leaving unreacted carbon in the centre. From this it can be seen that a fine control of carbon content and dispersion is needed to prevent inhomogeneity from occurring.

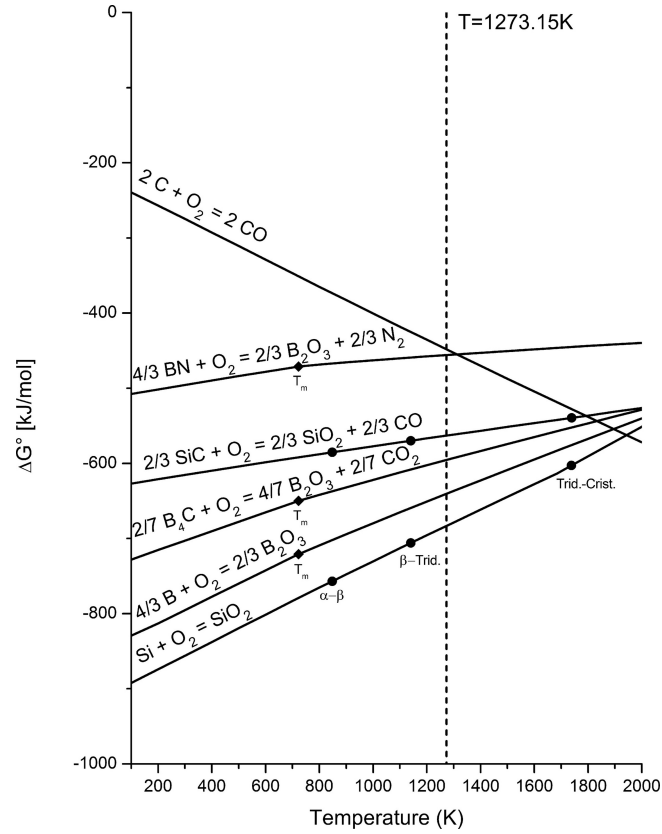


Figure 14: Ellingham diagram demonstrating the ability of solid C to reduce SiO_2 to SiC. Reproduced with permission [96]

A number of studies note that a degree of free carbon is left in the powder after the reaction [73, 80, 82]. This is seen to range from 0.25% to 2.7%. Lower values are achieved when the TEOS is pre-hydrolysed and phenolic resin is added as a carbon source [73, 82]. It is likely that the production of the gel within the phenolic resin allows the majority of the silica to react due to the fine dispersion of carbon. Najafi *et al* discuss the effect of temperature on the resulting SiC powder using X-Ray diffraction (XRD), FTIR and SEM [73]. It can be seen that pyrolysing at 700 °C leads to an amorphous structure of silicon and carbon. It is unlikely that this temperature is significant enough to initiate the formation of SiC. It was instead found that a minimum temperature of 1400 °C was needed to successfully form β -SiC, a view echoed across the literature [73, 80, 82]. It is also noted that a temperature of above 1600 °C is needed to fully remove the remaining silica [80, 82]. This does however come at a cost; as temperature is increased, grain growth is seen and size control is lost. As the temperature is increased, mass transport will become more prevalent and particles will begin to coarsen. This shows that temperature must be finely controlled such to reduce the silica phase but prevent coarsening.

Conclusion

Sol-gel and microemulsion production of silica can be used to produce spherical silica nanoparticles with a high degree of monodispersity. Achieving this requires the careful selection of chemicals and prevention of agglomeration. Silica nanoparticles must be reacted with carbon to produce SiC. It can

be seen that temperatures above 1600 °C are required to remove all silica. A carbon source must be well dispersed throughout the powder to achieve homogeneous SiC. Additionally the conversion temperature and hold time must be carefully chosen to prevent significant grain growth.

2.3.2 Boron Carbide

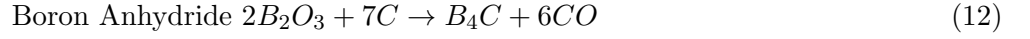
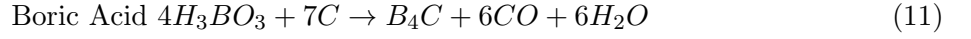
Boron carbide is not as widely produced as SiC [32, 43]. The methods for production can therefore be separated into industry and research. Industry reactions are based around a basic carbothermal reaction. Research methods aim to produce specific sizes and stoichiometries of B₄C. These include magnesothermal reduction, synthesis from elements, vapour phase reactions and polymer precursor reactions [97]. Magnesothermal and synthesis from element routes are known to be of high cost due to the price of elemental boron and magnesium. Vapour phase reactions, on the other hand, are known to produce high quality thin films, whiskers and fine powders. It is however noted that the products are non-stoichiometric and would not be suitable for the production of a dense ceramic [97]. This review will therefore consider the industry preferred carbothermal reactions, along with the polymer precursor routes.

Industrial synthesis routes

Industrial routes to powder production involve the reduction of boric acid and boron trioxide in a carbon environment [97]. These methods do not produce powders directly; instead boron carbide is produced as blocks which in turn must be ground into powder. These extra steps are known to cause contamination due to the chipping of grinding material. The reaction is seen to take place in 3 steps if boric acid is used.



If an anhydride is used then the reaction proceeds via Equation 9 & 10. The overall reactions for boric acid and anhydride are given below [97, 98]:



Both the reactions commonly used in this process are highly endothermic and require high temperatures, usually >2000 °C for successful reduction [97, 98]. Tube Furnaces, arc furnaces and Acheson type furnaces are used to achieve this. Tube furnaces can be used with a protective atmosphere. However, the yield is known to be lower than arc furnaces and limited in size by the dimensions of the graphite tubes that can be purchased. These are therefore not used on an industrial scale. Arc furnaces achieve high temperatures by producing an arc between two graphite electrodes. Boric acid and petroleum coke are used as the reactants. It is noted in the original patent that extra boron is required. This is because gaseous boron oxides can form leading to a significant loss of boron during the process [99]. This is an issue that plagues high temperature routes to B_4C . The loss of boron also leads to unreacted carbon in the boron carbide that is produced, usually as graphite. This can be in the region of 5% or greater [99] but can be reduced, through conditions and reactant optimisation, to 0.65% [100]. Acheson type furnaces undergo the same processes as an arc furnace except with more varied heating rates and a different apparatus. Here a graphite rod is used to heat the reactants. The furnace is then opened and the B_4C that forms around the rod is collected. Excess B_2O_3 , which forms a glassy film at high temperatures, is left when the reaction is not completed [99]. This is left in the furnace for the next run. Continuous production can therefore be achieved by simply restocking the furnace; this has resulted in this method being the most common in industry. The removal process is likely to introduce the B_2O_3 as a contaminant. Suri *et al* notes, when reviewing the process, that this can somewhat be mitigated by operator experience but is still a common issue [97].

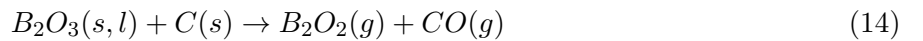
The reaction kinetics provide an insight into how to optimise the process to produce nanopowders. Weimer *et al* conducted experiments to examine the effect of different reaction temperatures on the final product [95]. It was seen that, at temperatures of 1530 °C, the B_4C crystallites had a wide size distribution which narrowed as temperatures rose. At temperatures beyond 1900 °C the crystallites were near-monosized, as seen by SEM observation. Further analysis showed that particle size decreased as temperatures were increased to around 300 nm at 1680 °C, after which wide spread agglomeration and sintering occurred. These findings can be combined with the effect of heating rate to understand what conditions are required to produce nanoparticles. At slow heating rates (<100 °C/s) the reactions occur with the B_2O_3 in the liquid phase. This leads to nucleation and growth which is limited by diffusion and heat exchange. This results in larger crystallites with sizes in the 100s of microns. As the rate is increased (10^3 to 10^5 °C/s) the reaction continues in the liquid phase but submicron

crystallites begin to form as the overall temperature approaches the boiling point of B_2O_3 . Gaseous B_2O_3 undergoes an instantaneous reaction through an oxide intermediate to produce clusters of boron carbide molecules. These then coagulate and sinter to form particles. At higher heating rates ($>10^5$ °C/s) there is very little liquid phase reaction and B_4C particles of around 0.05 μm to 0.1 μm form. Much like in an arc furnace, the gaseous nature of the reaction will lead to significant loss of boron. Whilst the crystallites are small, the resultant block of B_4C must still be ground to produce the final product.

High heating rates and temperatures of around 1700 °C must be used to produce nanoparticles. However industrial methods often lead to excess carbon as graphite in the final product as well as reactant contamination. In addition, whilst crystallites are small, the requirement to grind the B_4C block into particles means these sizes are not always achieved. This reduces their usefulness in producing finely controlled nanosized powders.

Polymer precursor routes

Low temperature synthesis routes involve the use of boric acid as a boron source by either chemically adding it to a polymer chain, or mixing to form a hybrid [101]. A hybrid exists when the two materials are finely mixed to form a single phase final product [102]. The result of this is that the boron source and carbon source are homogeneously dispersed. This is then, optionally, pyrolysed in an inert atmosphere to produce precursors. The final step is a carbothermal reaction under an inert atmosphere as described by Equation 9. B_4C was seen to form at around 1500 °C, significantly less than the 1700 °C needed in industrial processing. This reduces the loss of boron through gaseous oxide species which often occurs via reactions seen in Equations 13,14 & 15 [103]. The coarsening of B_4C also occurs at high temperature [104]. The homogeneity dispersion of carbon in the precursor is a double edge sword as Tahara *et al* note [104]. Whilst a more homogeneous product is formed, there is significantly more carbon used than is required for the reaction (Equation 9) which can result in excess carbon species. The literature therefore focuses on the use of different organic components and the extent of control over the product their use brings.



Various organic molecules have been used as the polymer component of the polymer precursor. These include saccharides [105], citric acid [103, 106, 107], phenolic resin [108, 109], poly (vinyl alcohol) (PVA) [110, 111] and glycerin [112]. Sudoh *et al* considers the use of saccharides as the base for a polymer precursor [105]. Cellulose and glucose were reacted, independently, with boric acid. It was seen that when the components are simply mixed the reaction occurs as per Equation 9. A significant amount of B_2O_3 contamination was found in the product. To prevent this, the organic component and boric acid underwent a hydrothermal reaction at 120 °C for 2 hours to promote ester bond formation. When a hydrothermal reaction is undertaken it is thought that a $H_2[(C_6H_8O_{10})(B(OH)_2)_2]$ structure forms, if a ratio of boric acid to glucose of 2:1 is used. The intimate dispersion of B and carbon source that is achieved through esterification either allows a more direct route to B_4C or the reaction as per Equation 9 occurs more completely. This is not decided in this work. Precursors using glucose, both simply mixed or which undergo esterification, yield crystallites of around 10 μm . When cellulose is used the particles are seen to be <10 μm but the reason for this was not investigated. This work occurred using temperatures of 1400 °C and yielded particles with lower carbon content than industrial methods, with the final product depending on the exact organic component and processing used.

Citric acid can also be used to produce B_4C [107]. Citric acid and boric acid are reacted to form a gel using the sol-gel method. It is thought that the boric acid becomes dispersed in a gel formed from citric acid, hence forming a hybrid. The resultant gel is pyrolised to form B_2O_3 and amorphous carbon. Khanra *et al* considers the specific reaction that makes boron carbide [106]. It is thought that the boric acid decomposes as per Equation 8 and the citric acid decomposes as per Equation 16.



Hadian *et al* discuss the conditions required to produce B_4C [107]. It was seen that a temperature of greater than 1450 °C was needed to remove B_2O_3 contamination. It was noted by Khanra that this method reduced the amount of free carbon compared to industrial methods, as well as shortening reaction times [106]. The excess carbon found in the product is reduced by using lower temperatures than those found in industry, hence reducing boron loss through gaseous species. In addition, the use of excess boric acid reduces the amount of free carbon, and the intimate dispersion of the boron and carbon allowed a more complete reaction. Intimate dispersion was able to reduce the amount of free carbon in the final product to 2.38% when the ratio of boric acid to citric acid is raised to 1:2.2. The final D_{50} value was found to be around 1.5 μm with the particle size being larger when the ratio of boric acid to citric acid was increased. This is similar to the results seen for cellulose and does suggest that some nanoparticles can be formed via this reaction.

Phenolic resins come in a range of forms and can be used as carbon sources due to their benzene

rings [113]. Hasegawa *et al* consider the use of boric acid and 2-hydroxybenzyl alcohol (HBA) in N,N-dimethylformamide (DMF) to produce a hybrid gel [109]. The mixing of these results in a phenolic resin as the carbon source and B_2O_3 as the boron source. This hybrid nature ensures homogeneity in the powder before it undergoes the carbothermal reaction at 1500 °C after a dehydration step at 300 °C. Powders were produced containing small amounts of B_2O_3 contamination. The excess carbon content was reduced to 5 wt% by reducing the carbon to boron ratio to 1:2.0. This is not as low as those achieved using citric acid. No analysis was done on the final particle size. Najafi *et al* discuss the use of a phenolic resin and Tetramethyl/borate (TMB). An acidic catalyst and dispersant was used to stabilise the precursor particles. This was found to reduce final B_4C particles to a size of 10-30 nm. This is significantly less than both saccharides and citric acid precursors. The work also showed that when a temperature of 1270 °C is used, the carbon content can be reduced by increasing time held at that temperature. The free carbon content was only reduced to 6 wt% however, suggesting increased temperature or a different precursor may be more effective at reducing excess carbon.

Unlike phenolic resin precursors, PVA precursors react directly with the boron to form poly(vinylborate) (PVBO) [111]. This then breaks down under pyrolysis conditions to form carbon and B_2O_3 which is reacted at temperatures between 1300 °C and 1500 °C to form B_4C . The work by Murray considers this [111]. It was noted that careful tailoring of the C/B molar ratio is required to reduce contamination from B_2O_3 or carbon. It was found that the reduction of the C/B ratio led to more B_2O_3 contamination. When the ratio was increased, excess carbon become more prevalent. The exact quantities of these are, however, not disclosed; the author does note them as small. Lower final reaction temperatures can be used to achieve different boron carbide stoichiometries, such as $B_{2.5}C$; this is possible due to reduced boron loss at lower temperatures. This gives the method flexibility, not seen with other organic precursors, but a large degree of both B_2O_3 and carbon contamination were found in the sample. The limited work on this method makes it hard to quantify its usefulness for producing B_4C particles on a large scale and in a range of sizes.

Conclusion

Industrial routes to B_4C involve direct reaction between boric acid, or boron anhydride, and a carbon source, such as carbon black. Whilst a continuous process using the Acheson furnace is the primary route for B_4C production, it is unable to produce small particle sizes and often contains reactant contamination. Polymer precursor routes seek to reduce contamination by using lower temperatures. This has the added benefit of a potential decrease in production costs. Lower temperatures reduce boron loss through vaporisation, hence increasing reaction control. Phenolic resin hybrids are able to produce the smallest particles, with a range of 10-30 nm. However, it is citric acid-boric acid precursors that reduce free carbon contamination to its lowest at 2.38%. Control of the C/B ratio,

dwel temperature, dwell time and heating rate are all noted as key to the production of a specific powder with low contamination.

The current use of non-industrial precursor powders for both SiC and B₄C increases control over the final powder properties and processing conditions. This can have added benefits such as reduced contamination in the final part. However, these precursors are often tailored for specific uses and the conversion of precursors to SiC is not widely investigated. There is room for further work in this field by tailoring a precursor to a wider range of uses. Additionally, the combination of several precursors has not been widely studied and could open up avenues to composite precursor powders.

2.4 Sintering of powders

High temperature processing, required to produce successful carbide armours, is a source of increased processing cost and complexity. This reduces the likelihood that an armour will be widely used. Sintering of boron carbide usually requires high temperatures and pressures along with additives [42, 114–121]. Similar to SiC, B₄C has a very high bond strength, resulting in these extreme requirements. Understanding of this process is crucial, such that a successful and reliable composite processing method can be developed.

Initial attempts to sinter B₄C to full density included using temperatures up to 2300 °C, close to the melting point of B₄C. A key observation was the requirement for an inert atmosphere to prevent oxidation of the resulting mix. Initial work focused on the use of pressureless sintering environments but the poor resulting densification of 80% spurred further investigation. These focused on decreasing temperatures, to improve commercial viability [122, 123]

Understanding moved forward in the 1970s and 80s to show that the addition of additives was necessary to increase densification. Carbon addition was shown to decrease surface mobility during sintering. The B₂O₃ oxide layer is lost through a reaction with carbon. Both the presence of carbon and the loss of the oxide layer increase the surface potential [124]. The reduction of surface diffusion and increase in grain boundary mobility promotes densification over coarsening [125]. Schewetz *et al* showed that an increase in bulk density is obtained for up to 2 wt% C inclusions, significantly less than the 4-6 wt% used by others [126]. This was still greater than when C additions are not used. This improvement was linked to the specific surface area (SSA) of the powder. For the same wt% C, increasing the SSA of the powder to 22 m²/g could increase bulk density without increasing temperature. In this work, the highest bulk density was achieved with an inclusion of 3% C, SSA of 22 m²/g and a temperature between 2100 °C and 2150 °C. It is noted that a fine grain structure is required, but is not sufficient alone, to produce high density parts. The smaller initial powder size also serves to disperse the carbon allowing its more effective use. When no carbon is used, grains of 20 µm-50 µm are seen with a dispersed, porous, network of smaller grains at the grain boundaries.

Additives continue to be a source of investigation in the recent literature, though their use has decreased as hot pressing (HP) and spark plasma sintering (SPS) have become more prevalent. Aluminium (Al) additions were studied by Mashhadi *et al* with the aim of reducing sintering temperatures [41]. This work showed that the use of 4 wt% Al can lead to a decrease in pore size and increase in density, through a liquid phase sintering (LPS) method. Despite this improvement, only a 94% relative density (RD) could be achieved with a range of Al-B phases present throughout the material. Notably, these additions did lead to an increase in hardness and fracture toughness up to the optimum value, followed by a decrease. This was attributed to increased crack bridging and deflection which may increase the attractiveness of the additive. Cr_3C_2 has also been shown as a potential pressureless sintering additive [42]. Li *et al* conducted work showing that 25 wt% Cr_3C_2 was the optimum condition for improved density of 95%. As an LPS method, similar drawbacks to Al additives are seen. Above temperatures of 2080 °C, the temperature at which the liquid phase is completely melted, CrB_2 forms and abnormal grain growth occurs. Additionally, a decrease in flexural strength was seen above 2080 °C, with the effect greatest for higher Cr_3C_2 contents. This was attributed to the abnormal grain growth, making its formation unfavourable. This reduces the usefulness of this method, although its full effect on mechanical properties has not been studied.

The increasing prevalence of HP and SPS methods have opened up other avenues to achieving higher densities of B_4C , without the need for excessive use of additives. HP and SPS methods utilise similar principles. The application of high temperature, combined with uniaxial pressing, increases the sintering pressure between particles, leading to increased densification. SPS, building on from HP, increases heating rates from around 10 °C/min in HP to around 100 °C/min in SPS using high currents [115, 127]. Angers *et al* demonstrated the first comprehensive work into hot press sintering of B_4C [127]. The effect 6 key parameters have on the resulting B_4C were investigated; hot pressing time, temperature, pressure, heating rate, cooling rate and lining of the die. The time to achieve maximum theoretical density was shown to decrease with temperature; at 2100 °C this was around 120 minutes whilst at 2300 °C this was around 8 minutes when a constant pressure of 34.3 MPa was used. For the same powder, an increase in temperature leads to an increase in density. Here, maximum density was achieved around 2050 °C but it is noted that this varied depending on initial powder properties.

Pressure shows a similar effect; densities at hold temperatures below 2000 °C are greater when higher pressure is used. As temperatures approach 2050 °C, the effect of pressure is seen to decrease, with 34.4 MPa showing the highest relative density. Whilst there is limited data around the plateau in density, as seen in Figure 15a, it can be said that a balance can be struck where lower pressures are used in favour of slight increases in hold temperatures. Heating rate data indicated that a slower rate leads to increased densification at lower hold temperatures, due to the increased time available for densification. However, if allowed to achieve a higher hold temperature, the same density can

be achieved for faster heating rates [127]. Similarly, it can be said that a lower heating rate can be used in turn with a decrease in hold temperature. The cooling rate needs to be closely considered, whilst likely heavily affected by initial powder composition, a very slow cooling rate below 7.5 °C/min can lead to a significant increase in porosity. It was hypothesised, supported by annealing and mass loss experiments, that the B_4C decomposes to secondary B and C phases although this could not be verified directly [127]. Therefore, consideration should be taken to ensure a high enough cooling rate is used, depending on factors of the initial powder, such as contaminant concentrations. The liner of the die was shown to have some effect; BN liners exhibited densities 3-10% greater when low cooling rates were used, compared to a graphite lining. It was noted that there was some reaction between the B_4C and graphite. It can therefore be deduced that, as long as cooling rates are not significantly low, graphite paper can be used to line a die, with BN liners allowing a greater range of cooling rates to be used.

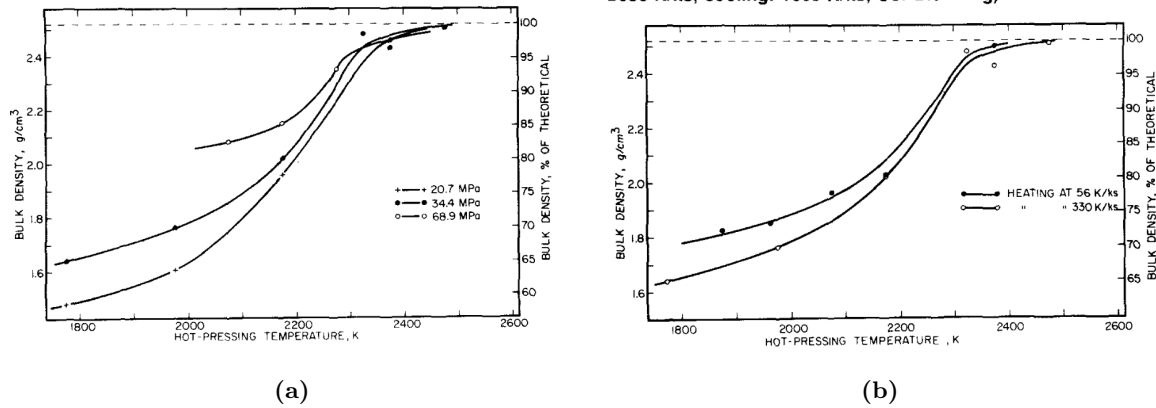


Figure 15: a) graph showing the effect of pressure on the density of B_4C when various hold temperatures are used b) Graph showing the effect of heating rate on the density of B_4C when various hold temperatures are used. Reproduced with permission [127]

The use of the SPS has similar considerations, but the difference in heating mechanism is of particular note. As B_4C is electrically conductive, the current applied leads to direct Joule heating at the particle-particle interface, differentiating itself from hot pressing. Work by Moshtaghioun *et al* showed that the sintering temperature, compared to hot pressing, can be decreased to 1800 °C when a uniaxial pressure of 75 MPa is used [115, 116], confirming results seen previously [128, 129]. However, it was noted that densification was initially poor when temperatures below 1600 °C were used. It is likely that B_2O_3 , which forms on the surface of the powder, is not removed due to the rapid heating in an SPS. This promotes coarsening through surface or vapour phase transport [130]. This can be removed by ex-situ annealing which reduced the temperature at which full density could be achieved to 1700 °C as supported by Li *et al* [117]. Li *et al* also conducted work to determine why a stark increase in densification is seen when the hold temperature is increased from 1450 °C to 1675 °C. It was noted that planar defects, such as stacking faults and twins become more common at higher temperatures.

These features increase densification by improving diffusion pathways [117]. Whilst the SPS method uses lower temperatures during sintering, the effects of surface oxides and defects must be closely monitored to achieve high densities.

SiC has a similar sintering regime to B_4C due to its similarly high bond strength. Pressureless, HP and SPS sintering methods can all be used, with similar considerations to B_4C . Additives such as C and Al can be used to enhance diffusion without entering the liquid state [131, 132] whilst liquid phase additives such as Al_2O_3 and Y_2O_3 can also be used [133–135]. Similar to B_4C , these aim to decrease processing temperature but can increase the impurities within the final ceramic. For pressureless sintering, maximum density is achieved at around 2150 °C [131]; Al reduces this to 2050 °C [133] and LPS additives can go further, to around 1600 °C [136]. HP on the other hand can reduce temperatures to below 1700 °C if high pressures of 350 MPa are used in an isostatic pressing setup with some B and C additives [137]. SPS can be used to decrease temperatures to around 1850 °C when forces of 75 MPa are used [138]. Similarly to B_4C , SiC often oxidises on the surface to form SiO_2 which can become volatile and reduce densification during sintering. Reduction steps can help to react SiO_2 with free carbon to remove this layer, although LPS additives often lead to re-oxidation. If cubic β -SiC is used as a source, additives can also promote the formation of hexagonal α -SiC at lower temperatures [131]. Whilst normally occurring at temperatures >1900 °C, this leads to elongated grain structures which alters the mechanical properties. These parameters demonstrate that systems using pressure have advantage over pressureless systems but ultimately the final setup used depends on starting powders, experimental aims and target composition.

B_4C -SiC composites sinter in a similar way to their constituent parts. So *et al* observed that maximum densification can be achieved at around 2000 °C when 40 MPa is used in a HP device [27]. It was noted that some 6H to 4H polytype transition can occur if α -SiC is used, due to the higher temperatures required to sinter the B_4C phase. This can lead to abnormal grain growth. To mitigate this, SPS can be used as it reduces heating and dwell times, limiting grain growth. Matovic *et al* consider the use of a ultra high pressure setup where 100 MPa is applied at around 1500 °C. This method achieved 98% RD at low temperatures [29]. This further verifies the need to tailor a sintering process, using the observed trends, to the given use case.

2.4.1 Conclusion

The sintering of B_4C and SiC can be completed using pressureless, HP and SPS methods. Sintering additives are required during pressureless sintering to lower the sintering temperature and improve densification. HP and SPS methods achieve the same effect using the application of pressure and hence do not normally require additives. This mitigates the extra phases in the final composite, which are present if additives are used. The SPS method has a significantly higher heating rate than HP and,

in B_4C and SiC , works by applying direct heat to the powder particle interfaces. The same trends as HP are seen with extra consideration needed to optimise the process for the rapid heating rates and different heating methods.

B_4C and SiC are both easily oxidised which can lead to oxide species at the particle surface which must be removed to achieve full densification, as they promote coarsening. To sinter a B_4C - SiC composite, it is necessary to consider best practices seen in the sintering of the constituent components. On doing this, it become possible to tailor an ideal sintering regime from a robust starting point.

3 Aims of this work

B₄C shows good potential as a ceramic armour due to its low density and high hardness. It however, suffers an amorphous breakdown under load, reducing its usability. Understanding of the amorphous breakdown in B₄C has improved, however reduction of amorphisation remains an area that is poorly understood. It is clear that, in order to deduce the effect of microstructural changes on the amorphous breakdown, there must be improvements in the methods used to analyse amorphisation. The generation of a reliable, fast and non-destructive Raman based method would appear an obvious avenue of work. B₄C-SiC composites have been used previously to balance sinterability and mechanical properties to bring mutual benefits to both materials. However, their amorphous behaviour is not widely investigated, with production methods also focusing on specific use cases. The production of, and characterisation of amorphous behaviour in, B₄C rich composites could allow amorphisation resistant microstructures to be developed. The use of ceramic precursors has been shown to potentially decrease production cost, as well as providing control over powder size and morphology. The understanding surrounding the formation of SiC from SiO₂ precursors appears poorly understood. Investigation in this field could allow greater control over final composite microstructure. Hence composites can be tailored to reduce amorphisation based on analysis by a novel Raman method.

In order to achieve this goal, this thesis will consist of three main studies.

- Firstly, methods for the production of SiC from nano-SiO₂ precursors will be investigated. This will allow control over the final composite along with understanding of the suitability of the composite for industrial scale production. Microemulsions show the most promising route for SiC as the additional control provided by these has been shown to produce a range of nano-SiO₂ particles. Nanopowders are not widely produced and a range of these will be needed to allow the formation of various microstructures.
- Secondly, B₄C-SiC composites will be produced and characterised. This will focus on determining the quality of the composites produced using a range of methods. This will include factors such as sinterability, density and carbon content. The analysis of hardness information can then be used to determine the potential for each composite to be resistant to amorphous breakdown.
- Finally, a novel Raman method, that is able to analyse amorphisation in B₄C rapidly, reliably and non destructively, will be developed. This method can be combined with traditional TEM observation to determine its usefulness. It will then be used to analyse amorphisation in both B₄C and B₄C-SiC composites.

The completion of these studies will allow conclusions to be drawn on the effect SiC has on the amorphous breakdown of B₄C, how to best produce B₄C-SiC composites from precursor powders and the usability of the novel Raman method.

This thesis will continue by discussing the materials and methodology used in this work. The three studies will then be considered individually before conclusions are drawn. Future work that is required to advance understanding will then be discussed.

4 Production Methods and Characterisation Techniques

In order to investigate how amorphisation in B_4C is affected by SiC , it was first necessary to prepare an SiO_2 -based ceramic precursor powder. This was then characterised and compared to a set of criteria which will be discussed in Chapter 5. Once the characteristics of these powders were understood, they could be used to produce composites. Similarly to the powders, a collection of criteria were established to define an optimal composite, against which different composites could be compared. This process is detailed in Chapter 6. The amorphous response of selected composites was then examined, as seen in Chapter 7.

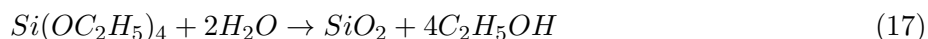
This chapter will begin by describing key methods used in the proceeding chapters. Next, analytical techniques will be discussed followed by characterisation of the commercial powders used.

4.1 Synthesis of Silica nanoparticles

A key objective of this work was to investigate the viability of using SiO_2 nanoparticles as a precursor for SiC . It was theorised that the use of an in-house precursor powder could give greater control over the final powder and hence the microstructure of the composite. Additionally, alternative production methods were of interest to the sponsor of this work.

Powders were produced using a microemulsion method, building from the work of Bagwe *et al* [84]. This focused on determining the effect of differing reactant ratios on particle size, the effect and viability of scaling up to larger production volumes and the reactions between SiO_2 and phenolic resin to produce SiC .

A water in oil (W/O) or reverse microemulsion was used to produce SiO_2 nanoparticles. The production of nanoparticles using this method is covered in detail in Chapter 2 of this thesis. Fundamentally, a SiO_2 precursor, such as tetraethyl orthosilicate (TEOS) is reacted in an emulsion containing H_2O droplets with controlled size and rigidity. This produces SiO_2 nanoparticles of spherical geometries. The reaction proceeds as per Equation 17.



The methodology of this reaction process is illustrated in Figure 16. Initially, 7.5 mL cyclohexane (MERCK, USA), 1.6 mL 1-hexanol (MERCK, USA) and 1.77 g Triton X-100 (MERCK, USA) were mixed for 15 minutes. This forms the oil phase of the microemulsion wherein the Triton acts as a surfactant to stabilise the water in the oil phase. 0.4 mL deionised (DI) water was added and the solution mixed for 15 minutes, completing the formation of the microemulsion. 0.1 mL TEOS (MERCK, USA) was then added to the reaction vessel. After a further 15 minutes of agitation, 0.06

mL aqueous ammonia solution (NH_4OH) (MERCK, USA) was added as a catalyst. The solution was then mixed for 24 hours, after which a volume of ethanol, equal to 25% of the total volume was added. This was mixed for a further hour before centrifuging the solution at 9000 rpm for 20 minutes with a slow deceleration. The supernatant was removed and ethanol added for storage. Before analysis, the samples were dispersed using a UP200s sonicator (Hielscher, Germany) for 20 minutes in 1 second pulses at 120 W.

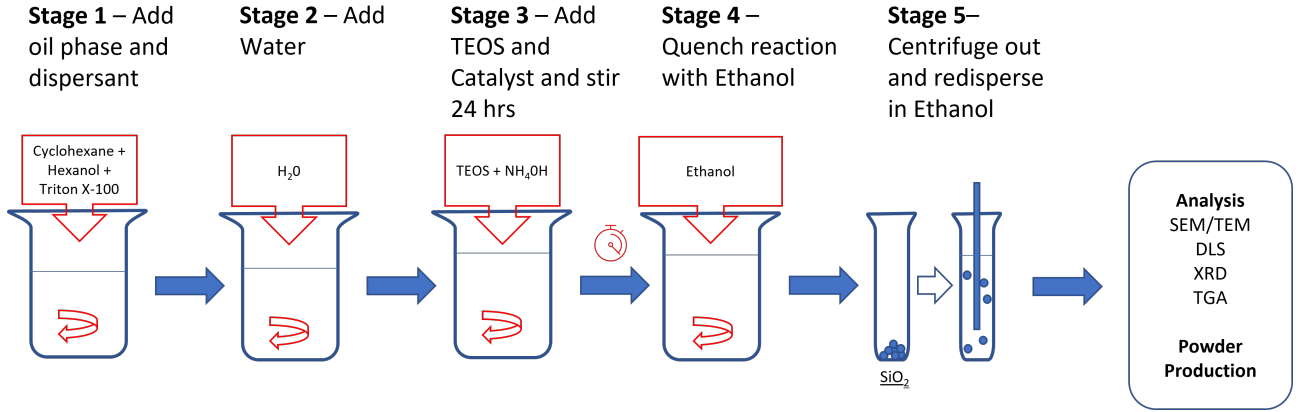


Figure 16: Diagram explaining the production process for microemulsion SiO_2 particles.

It is possible to define the microemulsion solutions through four ratios:

$$R = V_{\text{TEOS}} : V_{\text{H}_2\text{O}} \quad (18)$$

$$S = V_{\text{NH}_4\text{OH}} : V_{\text{H}_2\text{O}} \quad (19)$$

$$O = V_{\text{Oil}} : V_{\text{H}_2\text{O}} \quad (20)$$

Where V is the volume present and the oil phase is defined as the sum of the volume of hexanol and cyclohexane.

$$E = V_{\text{Triton X-100}} : V_{\text{H}_2\text{O}} \quad (21)$$

From these it was possible to formulate a range of solutions that could be used to investigate the use of silica nanoparticles as a SiC precursor. These are shown in Table 4 with each solution being produced several times and at various scales for a range of experiments.

Table 4: Definition of Ratio set A, B, C and D from ratios R, S, O and E.

Ratio Set	Ratios				Change vs Standard Ratio Set
	R	S	O	E	
A	0.25	0.15	22.8	4.43	Standard Ratio Set
B	0.50	0.15	22.8	4.43	TEOS $\times$ 2
C	0.25	0.30	22.8	4.43	NH ₄ OH $\times$ 2
D	0.25	0.45	22.8	4.43	NH ₄ OH $\times$ 3

Calculating SiO₂ yield

When using SiO₂ in a ceramic precursor powder, the yield of the reaction needs to be understood. This allows the quantity of other components to be calculated such that the desired powder composition is achieved. Dried SiO₂ was found to be difficult to disperse with other components hence yield experiments sought to predict the quantity of centrifuged, but not dried, SiO₂. This was found to be easier to handle and disperse than its dried alternative. Method I was initially used to achieve this. The SiO₂ was centrifuged from its storage solution and the supernatant, removed. The amount of ‘wet’ SiO₂ produced was determined by comparing the weight of the centrifuge tube pre and post this process. The SiO₂ is considered ‘wet’ as it still contains ethanol or residual reactants from the storage solution and appears a milky white colour. A separate batch of SiO₂ was produced and analysed using Thermogravimetric Analysis - Differential Thermal Analysis (TGA-DTA) using a 10 °C/min to 1580 °C programme. This allowed the mass loss due to solvent evaporation to be determined. By combining this with the mass of ‘wet’ SiO₂, a mass of ‘dry’ SiO₂ could be calculated. This method assumes that all SiO₂ batches have the same degree of mass loss during drying and that there is batch-batch yield variability.

To calculate a yield, the data was compared to the theoretical maximum yield of the TEOS to SiO₂ reaction. Knowing the volume of TEOS used, and that it is a limiting reagent, allows molar calculations to show the maximum possible mass of SiO₂ that can be produced if the reaction goes to completion. This was compared to the mass of dry SiO₂ produced, using each method, and a yield could be obtained.

Method I, which is used throughout Chapter 5, was seen to be unreliable with a wide spread of values as seen in Figure 17. This is likely due to variations in how wet the SiO₂ was before weighing; variations in measurement time and room temperature could lead to the evaporation of solvents. To improve upon this, a second method was developed. In Method II, four standard batches were produced on the same day and removed from their storage solutions. Alumina crucibles were weighed on a high precision balance after which the wet SiO₂ was added. These were heated to 1000 °C at an unspecified rate in a box furnace (Carbolite, UK) under atmospheric conditions. This allows any volatiles such as ethanol or residual reactants to evaporate. The mass of the crucible was then weighed and hence

the yield of dry SiO_2 was determined directly. Care was taken to use sterile crucibles that had been pre-heat treated to $1000\text{ }^\circ\text{C}$ to remove any external reactants, such as carbon. Method II, which directly measures the mass of ‘dry’ SiO_2 , shows only small error in calculating the yield of the SiO_2 reaction and led to a yield of 70%. This is because it does not rely on the weighing or TGA analysis of ‘wet’ SiO_2 , as is used in Method I. Method II does not measure yield on a batch by batch basis however. Hence, it will be necessary to monitor the composites and confirm their final composition.

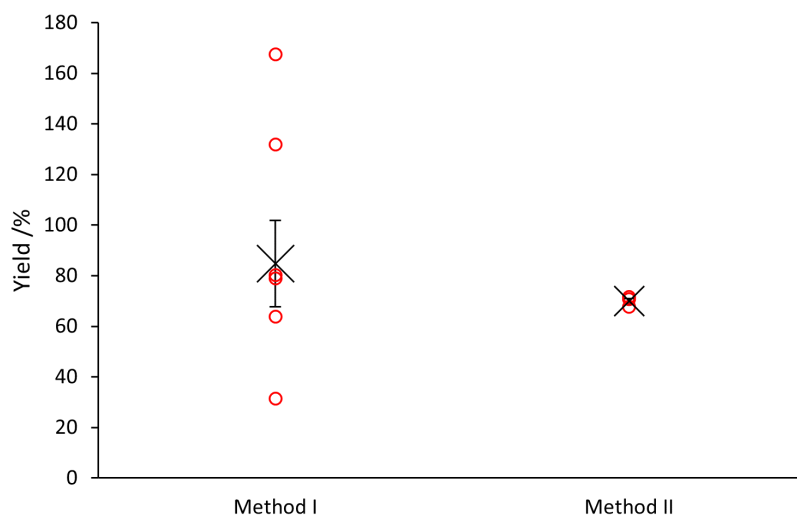


Figure 17: Graph showing the results for yield experiments conducted by Method I, where measurement of ‘dry’ SiO_2 was predicted using differential weighing and DTA-TGA analysis. Method II directly measures the amount of ‘dry’ SiO_2 obtained by heat treatment. These are then combined with theoretical molar yield to produce a yield value. The error bars were obtained by calculating the standard error of the mean.

4.2 Production of Composites

A key component of this work was to consider the effect of microstructure on amorphisation. Hence it was important to determine the range of microstructures that could be produced using commercial powders alongside those made using microemulsion SiO_2 . A commercial B_4C sample was produced to act as a reference for all analysis conducted on composite samples. Composite 1 consisted of B_4C (Houganas, Germany), SiC (Houganas, Germany) and phenolic resin (Sumitomo Bakelite, Japan), and was synthesised in order to identify the microstructures produced when commercial ceramic powders were simply sintered together. Composite 2 built on this by identifying how converting commercial SiO_2 (Evonik Industries, Germany) to SiC *in situ* could alter the microstructure. Composite 3 furthered this investigation by using SiO_2 produced using the microemulsion method described above. This allowed comparison between composites consisting of commercial and in-house SiO_2 . Throughout these investigations, samples were monitored for phase homogeneity and ease of production. Iterative improvements were made to production methods to optimise homogeneity and improve density. Table 5 shows the compositions produced during this work and the analysis carried out. The production methods for each of these composites is defined below.

Table 5: Composite types are separated into 1-commercial B₄C, SiC and phenolic resin; 2-commercial B₄C, phenolic resin and commercial SiO₂; 3-commercial B₄C, phenolic resin and microemulsion SiO₂. Production methods X, Y and Z are defined in the composite powder production section below. Characterisation studies are found in Chapter 6 of this thesis. Amorphisation studies are found in Chapter 7 of this thesis.

Target Composition (B ₄ C:SiC:C)	Composite Type	Production Method	Studies	
			Characterisation	Amorphisation
100:00:00	-	X	•	•
88:10:02	1	X	•	•
88:10:02	2	Y&Z	•	•
88:10:02	3	Y&Z	•	•
10:88:02	1	X		•

Composite powder production

The production method for B₄C and Composite 1, Method X, can be seen in Figure 18. Here the powders are simply mixed in MEK, which assists with the breakdown of the coarse phenolic pellets, then dried and milled before being hot pressed. An ARE 250 (Thinky, USA) was used for the planetary mix stage whilst a Turbula mixer (WAB, Switzerland) was used for the milling steps. The process was monitored throughout to identify any poor mixing or agglomeration. The powders were seen to disperse well, forming a smooth paste which was dried to a fine powder.

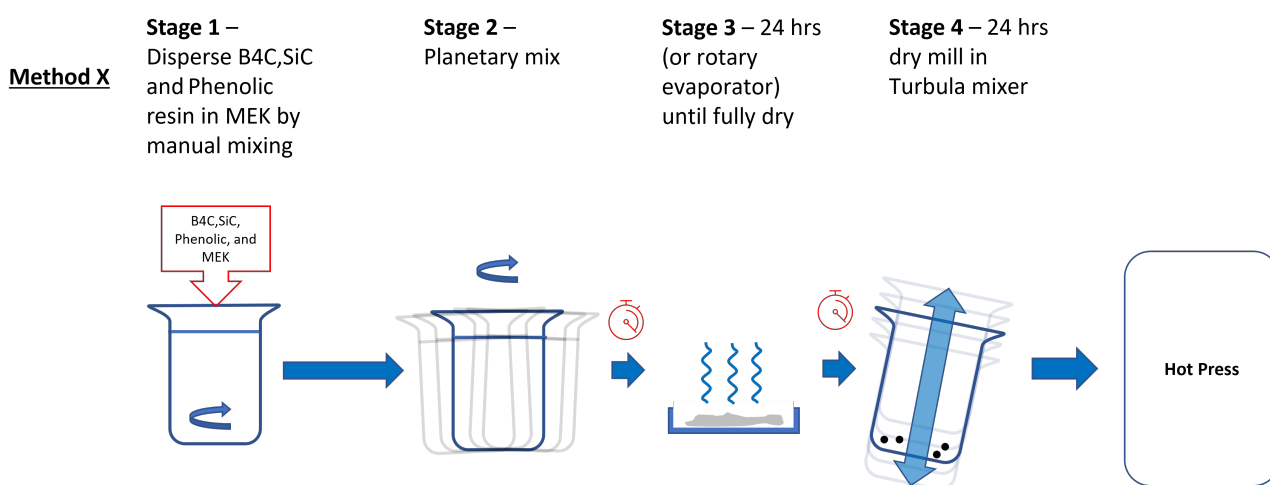


Figure 18: Method X - Diagram explaining the production process for a sample of commercial B₄C or Composite 1.

Composites 2 and 3 required additional processing to produce well dispersed starting powders. SiO₂ was seen to clump if Method X was used, with agglomerates visible to the naked eye. This would reduce the homogeneity of a final composite. Two reaction methods were developed to improved the SiO₂ dispersion. In Method Y, seen in Figure 19, SiO₂ was sonicated in the MEK. Commercial SiO₂ was added as a dry powder, whilst in-house SiO₂ was centrifuged from its storage solution and then dispersed. This was followed by wet mixing with the remaining components.

Having analysed composites made using Method Y, it was hypothesised that intimate mixing of the

the carbon source and SiO_2 could increase the composite density and homogeneity. Hence Method Z was developed, wherein the phenolic resin and SiO_2 were mixed and dried before other components were added. These methods were compared to determine their effectiveness for producing a dense, homogeneous composite.

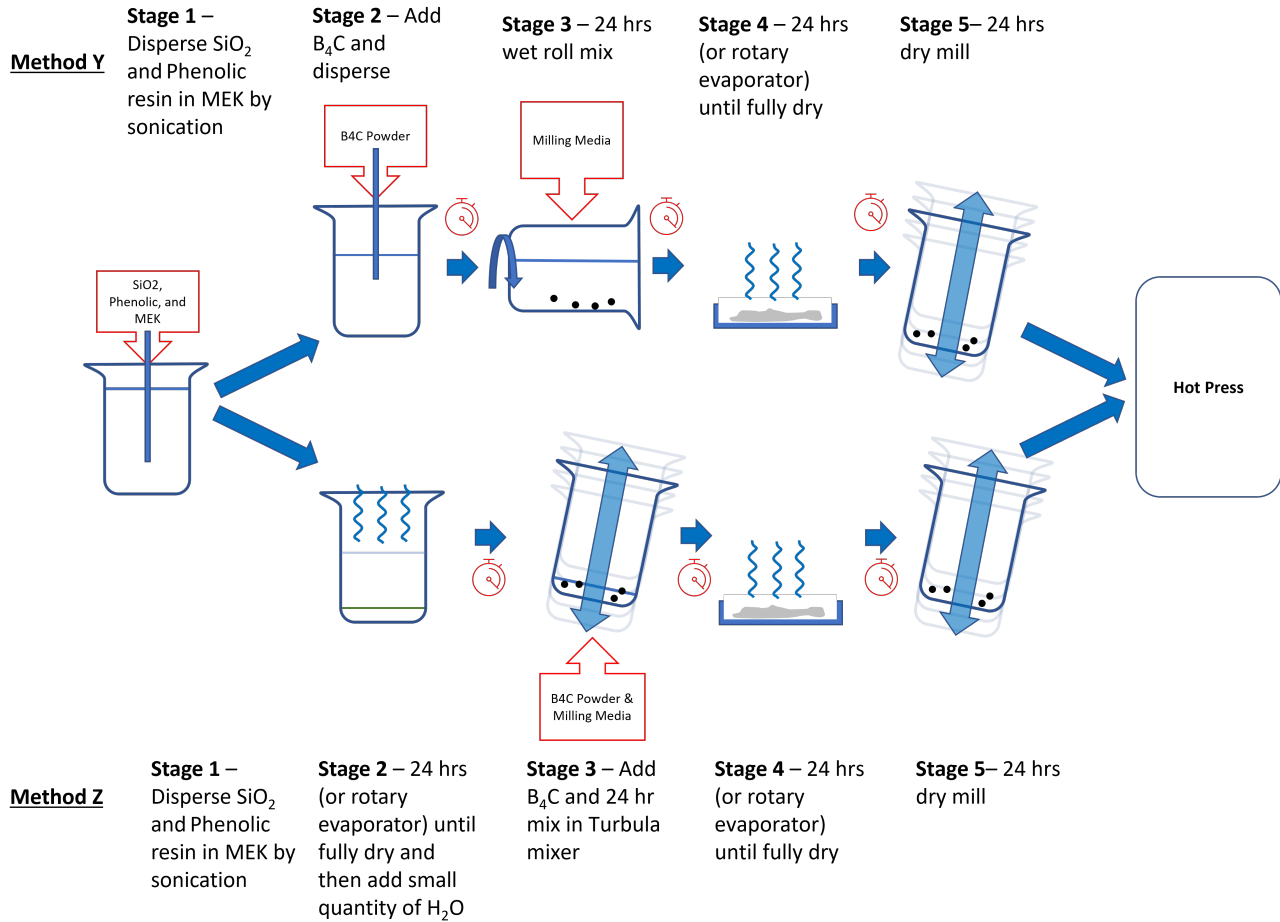


Figure 19: Method Y and Z - Diagram explaining the production processes for Composite 2 and Composite 3. Either of these methods are suitable for these composites; Z was developed from Y to ensure intimate mixing between the SiO_2 and phenolic resin.

For all samples and initial commercial powders, a dry milling step was used. Here, SiN milling media was mixed vigorously with the powder using a Turbula (WAB, Switzerland) mixer. Powders were then sieved to below $100\ \mu\text{m}$ before use. This helped improve homogeneity and increase powder packing, hence reducing the chance of pores developing in the final composite.

Sintering of powders

The sintering of samples can affect the properties of the final ceramic. However, due to equipment availability, this variable was not investigated in depth. Reaction conditions were based on literature knowledge [98, 127, 139] and can be found in Figure 20. The powders were pre-compacted using a 1 ton press for 5 minutes after which an FCT hot press (FCT, Germany) was used. A heating rate of $10\ ^\circ\text{C}/\text{min}$ was used up to $1200\ ^\circ\text{C}$ followed by $5\ ^\circ\text{C}/\text{min}$ to $1600\ ^\circ\text{C}$, $10\ ^\circ\text{C}/\text{min}$ to $1800\ ^\circ\text{C}$, $5\ ^\circ\text{C}/\text{min}$

to 2100 °C and 2 °C/min to 2150 °C. A 30 minute hold was added to allow phenolic pyrolysis at 500 °C and SiO₂ reduction to SiC at 1600 °C. The latter hold was accompanied by a reduced heating rate due to the range of temperatures over which the reaction can occur. The heating rate at high temperatures was lowered as a safety measure by the device with a 120 minute hold being used at the maximum temperature to promote sintering. A maximum load of 57 MPa was used with the maximum temperature being 2050 °C and 2150 °C for SiC and B₄C majority samples respectively. An inert 1 atm Ar atmosphere was used up to 2050 °C and Ar- 10% H₂ was used to 2150 °C as specified by the manufacturer.

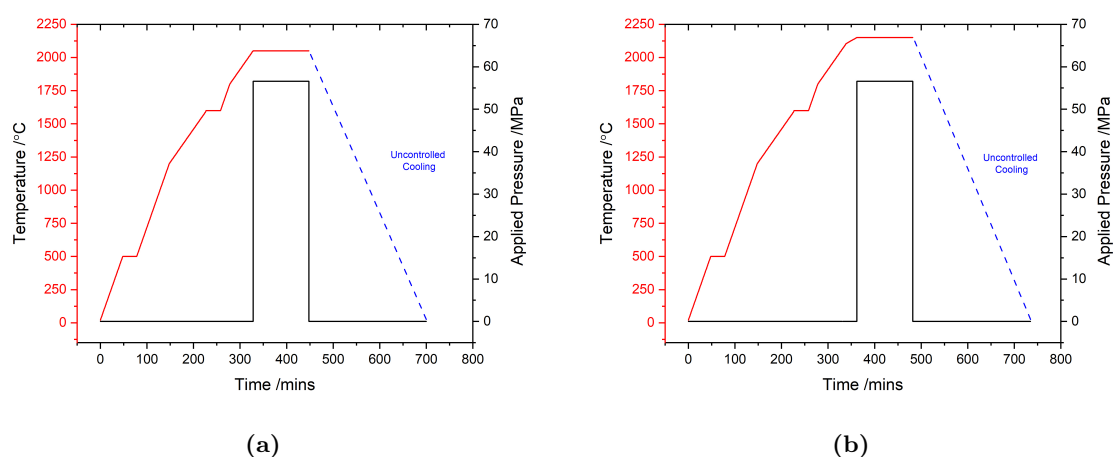


Figure 20: Sintering in a hot press. a) Graph showing the sintering regime used when a sample has SiC majority b) Graph showing the sintering regime used when a sample has a B₄C majority

4.3 Characterisation techniques

The techniques used for characterisation can broadly be categorised by the three studies that were conducted. In characterising the production of microemulsion SiO₂, DLS and SEM were employed for particle size and morphology analysis. TGA-DTA was utilised to probe the reaction during which SiC forms. Composites were investigated in two separate studies. The first aimed to understand the density, homogeneity and hardness of produced composites, utilising techniques including SEM, XRD, carbon analysis and indentation. The second study aimed to characterise the extent of amorphous breakdown in the material, which required the use of Raman Spectroscopy and TEM.

4.3.1 Characterisation of SiC precursors and SiO₂ powders

In order to determine the effect of changing reactant ratios and conditions, the size and morphology of the resulting SiO₂ was studied. The particle size distributions were investigated by DLS analysis, and SEM or TEM analysis was employed to determine particle shape. From this, the effect of altering the reactant ratios or conditions on particle size could be determined. The production of SiC from SiO₂ powders and a carbon source was a critical objective of this work. Its initial viability was determined,

prior to full composite production, by the mixing of SiO₂ particles with phenolic resin and analysis of the resulting reactions at various temperatures using a TGA-DSC device. This data was used to inform the final composite production methods.

Dynamic Light Scattering

SiO₂ nanoparticle dispersion and subsequent size distribution analysis were achieved using dynamic light scattering (DLS) on a Malvern Zetasizer (Malvern Panalytical, UK). DLS works by evaluation of the particular Brownian motion: a sample is illuminated by a laser, and a photon detector performs nanosecond scans, separated by time delay τ , to map the interference between the waves scattered by the sample[140]. The scans are compared to the original for each τ and assigned a correlation factor (G). Larger particles have more inertia, which is seen as a smaller change in G as a function of τ ; thus, from the correlation factor, the particle diffusion coefficient D can be deduced[141]. The Stokes-Einstein equation (22) facilitates the calculation of the hydrodynamic diameter (d) of the particles, where d is defined as the diameter of a hard sphere that is diffusing at the same rate as the particle being analysed[141]. This definition can under- or overestimate particle size and includes any absorbed species, such as polymers, in the value.

$$d = \frac{kT}{6\pi\eta D} \quad (22)$$

where k is the Boltzman constant, T the temperature (K) and η the solvent viscosity (kg mm⁻²). The device completes three analysis runs of the same sample. A minimum of two samples were analysed for each experiment repeat. Usefully, agglomeration or sedimentation of particles during measurement, which reduces data accuracy, can be identified in the correlation function. Data involving these effects were noted; those that did not were averaged and error analysed.

The size distributions of particles that can be achieved from a reaction is crucial information for a project such as this, which necessitates the production of specific particle sizes in order to tailor the microstructure of a final product. The distributions in this project were fitted to descriptive functions; herein, a log normal distribution was used as described by Equation 23:

$$f(x) = L \frac{1}{x\sigma\sqrt{2\pi}} \exp\left(-\frac{1}{2}\left(\frac{\ln(x) - \mu}{\sigma}\right)^2\right) \quad (23)$$

where σ is the standard deviation, μ the mean and L a scaling factor. This model uses regression analysis to produce a fitting with an R^2 value as close to 1 as possible. Figures 21a & 21b show the fitting function when compared to original data and the associated standard deviation. It can be seen that, for a good fit, the fit matches the data well and is generally within the error bars of each point. When a more complicated particle distribution exists, as seen in Figure 21b, the fit is within the error bars of each point at higher volume %, but over- or under-estimates points at lower volume %. When a second peak is clearly observed, a second fitting could be done. However, the majority of data had

a similar distribution shape to that in Figure 21a. In this work, a μ and σ value will be reported. Further analysis of particle size and morphology could be achieved using SEM or TEM in the setups described below.

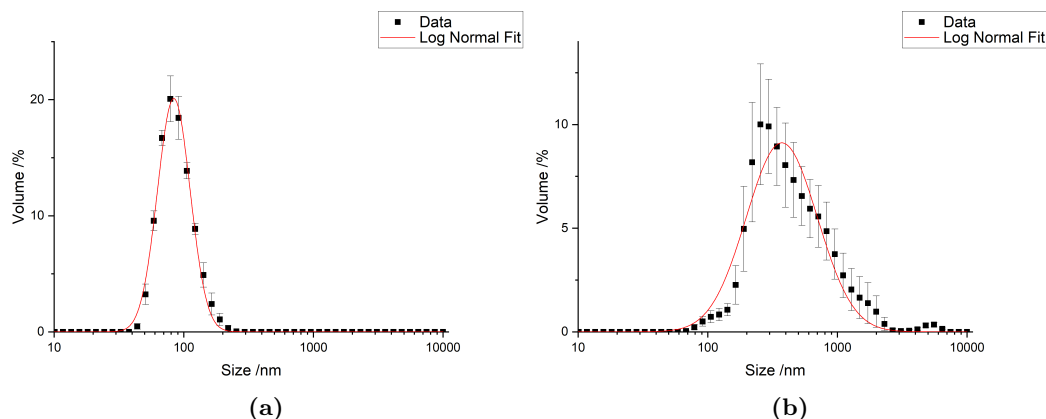


Figure 21: a) Data plotted alongside a log normal fit. This would be considered a good fit with an R^2 value of 0.99. b) Data plotted alongside a log normal fit. This would be considered a lower quality fit with an R^2 value of 0.94. However, the fit does still pass within error of all the points. Error bars shown are calculated using the standard error of the mean.

TGA-DTA analysis

Thermogravimetric analysis (TGA) was used to investigate reactions occurring in prepared powders such as the formation of SiC. A NETZSCH STA 449F1 (NETZSCH, Germany) device, with an Al_2O_3 crucible and chamber, was used at a ramp rate of $10\text{ }^\circ\text{C}/\text{min}$ up to $1580\text{ }^\circ\text{C}$ in an inert Ar atmosphere with a $50\text{ ml}/\text{min}$ flow rate. This allowed analysis of all the likely reactions occurring within the powder, whilst operating within the safety limits of the device. TGA measures the variation in the mass of a sample with temperature, and is coupled with Differential Thermal Analysis (DTA), which measures the difference in temperature between the sample and a reference. This yields information about the reactions occurring within the sample. Such techniques could be combined with x-ray diffraction (XRD) and carbon analysis (CA) studies to provide full insight into the carbothermal reduction mechanism.

4.3.2 Characterisation of produced B_4C -SiC composites

When developing a composite production method, it is important to determine the compositions and phases of both the starting powder and the final sintered part. Fundamentally, this involves comparing the initial powder composition (C_P), targeted final part composition (C_{TF}) and observed final part composition (C_{OF}). C_{TF} is the composition that is expected if the mass losses and reactions within the composite match those of the individual components.

XRD analysis was used to determine the phases present in the samples. Additionally, it provided some

qualitative understanding of the composition of the sample. SEM analysis was then used to investigate the ratio of phases using micrograph analysis and hence calculate a final observed composition. Carbon analysis was employed to validate the carbon quantities predicted by both SEM and XRD data, thus evaluating the accuracy of the final theoretical and observed compositions predicted by the former two techniques. This approach generated good confidence in the final observed compositions, which can in turn be used to discuss compositional effects on amorphisation.

It was key for this study to fully characterise the microstructure of the final composite. This involved SEM analysis to investigate grain sizes and homogeneity; XRD analysis to investigate the texturing in the sample and compositional analysis to determine the elemental ratios.

X-Ray Diffraction

X-ray diffraction (XRD) was employed to analyse the crystal structures of the nanopowders produced throughout this work. A Bruker D2 Phaser diffractometer was used between a 2θ value of 10° and 80° . The step size was 0.018° with a time per step of 0.5 s using a Cu K α radiation with a wavelength of $1.54060 \text{ \AA}(\alpha_1)$ and $1.54443 \text{ \AA}(\alpha_2)$. The International Centre for Diffraction Data (ICDD) database was used, through the XpertHighscore software, to identify phases.

Scanning Electron Microscopy

A Leo Gemini 1525 (Zeiss, UK) SEM was used to analyse powder samples, final sintered samples and indents. Powders were dispersed in ethanol and added drop wise onto either an aluminium stub or a glass slide attached with carbon tape to an aluminium stub. The latter provides higher resolution whereas the former provides higher contrast due to charging. Secondary electron imaging (SEI), electron dispersive x-ray spectroscopy (EDX) and backscattered electron imaging (BSE) were used to investigate samples. An InLens SEI detector was used at an accelerating voltage of 5 kV for general imaging. An x-act EDX (Oxford Instruments, UK) was used at 10 kV to investigate the chemical compositions of samples. A BSE detector was used to give qualitative composition information: whilst SiC, B₄C and SiO₂ show some contrast differences in SEI imaging, BSE imaging can significantly enhance this. A 5 nm coating of gold was generally used to prevent charging on composite samples.

Micrograph analysis was used to determine the composition of the sample. Micrographs were thresholded, using ImageJ software, to pick out individual phases. The % area taken up by each phase was calculated and the observed final composition, C_{OF}, determined. This was conducted on 1k magnification micrographs, such that the largest area possible could be analysed. However, as is a limitation of SEM, phases that exists outside of the SEM resolution limit cannot be added to the composition. Hence, it is important to consider SEM, XRD and CA data holistically.

A homogeneous dispersion of the SiC phase in the composites is crucial in this work. It prevents

mechanical properties or amorphisation resistance differing across the sample. A Python script, found in the appendix section 11.1, was used to calculate a homogeneity value. The image was thresholded, after which the script determined the composition as described above. The area analysed was then decreased in size by 1 pixel in x and y directions and the composition was recalculated. This was repeated until only a 5 px x 5 px image remains. The resulting data was then plotted to produce the graph seen in Figure 22. This can be split into two distinct regions. To the right of the grey line the data is either flat or oscillates about a mean value, thus a consistent mean and standard deviation can be calculated. A smaller standard deviation indicates a more homogeneous dispersion of SiC, with limited agglomeration and a more constant composition. To the left of the grey line, the data trends down to 0% SiC; in this region the sensitivity of the method, and hence its resolution, is low hence it is discounted. Comparison of the standard deviation across compositions and processing methods was conducted to identify the most suitable composite. The mean value was used to determine the quantity of SiC in the composite. This analysis was completed four times on each micrograph with the area shrinking to a different final location each time.

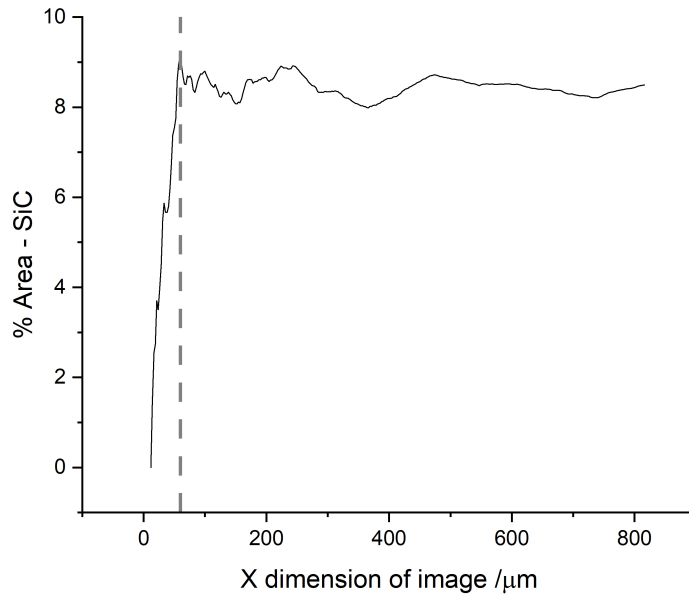


Figure 22: Graph showing the relation between the X dimension of the area being analysed and the % Area of SiC. Two regions can be seen, a flat or oscillating region to the right of the line and a decreasing region to the left. The right side region gives understanding of the sample composition and homogeneity.

Micrograph analysis was also used to characterise grain size and shape of the SiC phase. ImageJ was used to determine grain area, aspect ratio and size. Here, size was determined by fitting an ellipse to the grain and reporting the maximum vertex (major axis) [142]. The aspect ratio was determined by dividing the maximum vertex by the minimum vertex.

Argus imaging was necessary to characterise grain size and shape in B_4C , due to the inability of SEI to identify grain boundaries without etching. Argus imaging utilises the same working principle as

electron backscatter diffraction (EBSD). When the electron beam interacts with the sample, some primary electrons are scattered back towards the detector. The number of these depends on the atomic mass of the sample, which is the origin of contrast in BSE imaging. Some of these electrons can be diffracted by crystallographic planes and hence provide lattice orientation information. An Argus detector, consisting of three detectors each allocated a colour, shows this as an RGB image as seen in Figure 23. This highlights the grain boundaries in B_4C and, as it does not index the diffraction patterns, is much faster than EBSD. Particle size and shape analysis as described above can then be done on B_4C by outlining the grains in the Argus image. An e-flash HD EBSD detector (Bruker, Germany) using Espirit 2.3 (Bruker, Germany) was used within a Quanta FEG 650 (FEI,US) SEM microscope.

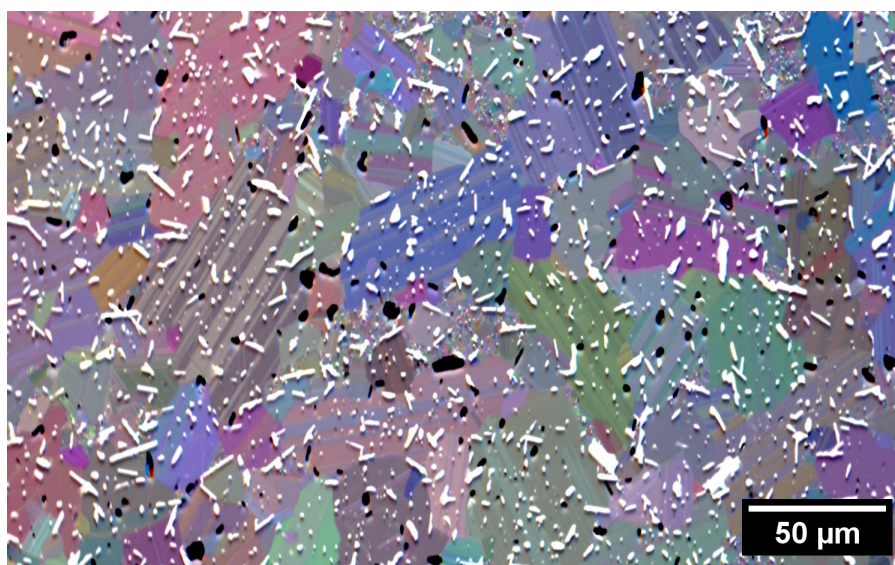


Figure 23: Argus micrograph showing the typical signal seen from a B_4C -SiC composite. The bright white regions are SiC grains whilst black areas are grain pullout and pitting caused by sample preparation.

Carbon Analysis

Carbon analysis (CA) was used to determine the carbon content of produced powders and sintered samples, such that their content could be compared to predicted values. The technique involves the combustion of a sample in an oxygen-rich atmosphere, and quantification of the resultant CO and CO_2 . Figure 24 describes the working principle of the device. An EMIA-320V2 (Horiba, Japan) was employed in this work.

The device was calibrated to use 1 g of copper 20 - 60 mesh powder (Horiba, Japan) and 1 g of iron powder (Horiba, Japan). It is essential to calibrate the detectors against a recognised carbon standard. Tungsten carbide (WC) BCS-CRM 352/1 (Horiba, Japan) with a fixed carbon content of 6.154 wt% was used in this work. The mass of WC was varied in order to vary the volume of CO_2 and CO produced ($V_{CO_2 + CO}$). The mass of carbon in the sample ($[C_s]$) can then be plotted

against $V_{\text{CO}_2 + \text{CO}}$. The resulting trend can be applied to any sample so $[\text{C}_s]$ can be determined. It is key to vary the mass of WC across a wide range such that the trend is accurate for the widest range of $[\text{C}_s]$. Before each run the device was calibrated using at least five calibration points. The calibration was applied and a blank, WC and stock powder sample was then run to confirm accuracy. The manufacturer expects an accuracy of 0.5% for the measurement, although this can be reduced using a robust calibration method. Sintered samples were ground to a coarse powder whilst powder samples were used as produced. Three runs were completed for each sample with the exception of those produced after TGA; TGA produces very small quantities of powder and hence usually only one sample could be run.

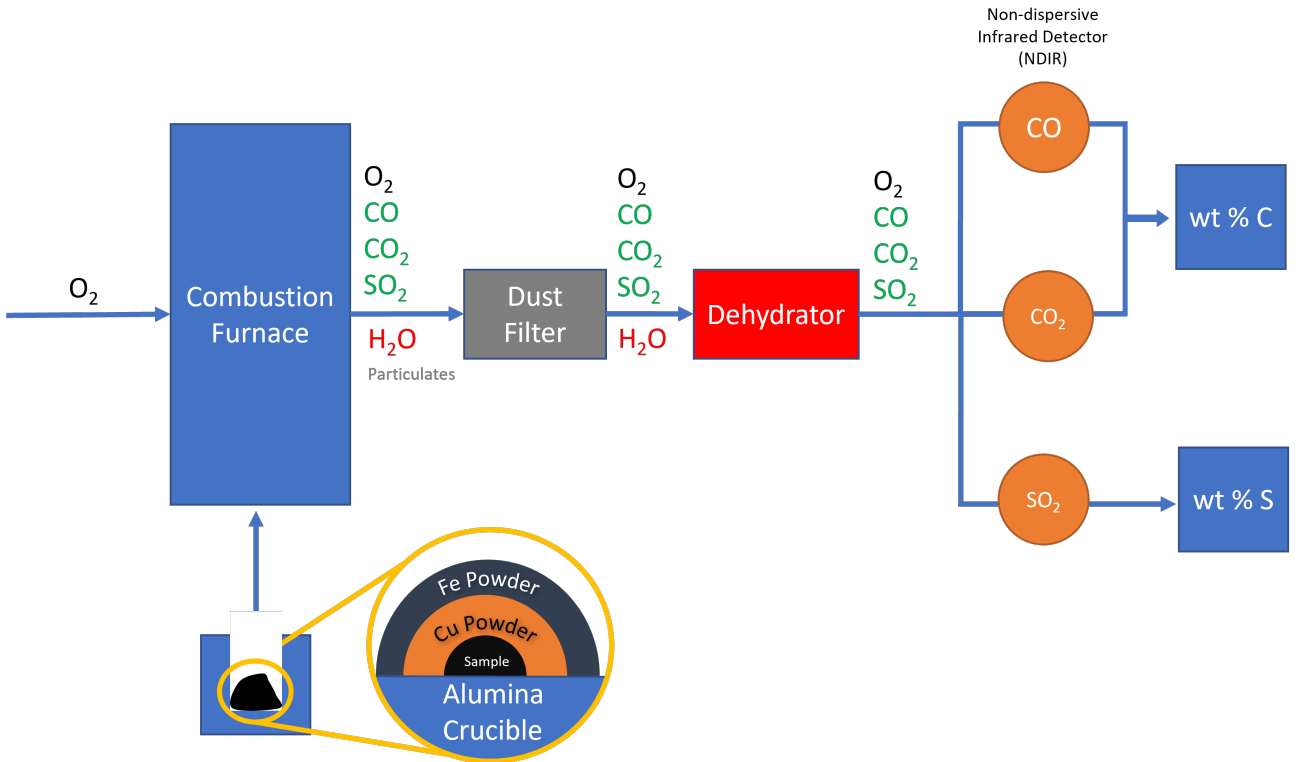


Figure 24: Schematic showing the working principle of a Horiba EMIA-320V2 Carbon and Sulphur analyser

Determining composition

The data collected from these methods can be used to calculate C_{TF} . This is done by considering the pre and post sintering carbon compositions, mass loss data from TGA-DTA and molar calculations for the reactions that are occurring. This results in a predicted amount of B_4C , SiC and carbon in the final composite. It is also important to understand how C_{TF} and C_{OF} differ, the latter of which can be determined by SEM and CA observations. Additionally, the difference in $[\text{C}_s]$ between the two compositions can provide insight on the reactions occurring within the samples.

Density

The Archimedes method was used to determine the density of final sintered parts. Data from this was compared to C_{TF} and C_{OF} to inform improvements in the processing methods. Using the rule

of mixtures and literature values for densities of components, a maximum composite density can be obtained, which was compared with the observed density to report a relative density. A balance and density kit were used to measure the mass of dry (m_d), submerged (m_{sub}) and saturated (m_{sat}) samples. Samples were saturated in deionised (DI) water and left in a desiccator under negative pressure for 12 hours. The mass of the saturated sample was then measured submerged (m_{sub}) and in air (m_{sat}). When measuring m_{sat} , excess water was removed from the surface using a damp cloth. Equation 24 outlines how density is calculated:

$$\rho_s = \frac{m_d}{m_{sat} - m_{sub}} \rho_w \quad (24)$$

where ρ_s is the density of sample and ρ_w is the density of water during measurement.

Each mass was measured 3 times for each sample. Care was taken to ensure the DI water used was at a stable temperature during measurement.

4.3.3 Characterisation of amorphisation in produced B₄C-SiC composites

The investigation of amorphisation was crucial in determining the effect of microstructure on the amorphous breakdown that occurs in B₄C. This method consisted of four parts each involving their own optimisation stages. Samples were indented using nano/micro indentation to induce amorphous breakdown. Raman spectroscopy mapping was then used to investigate the extent and location of the amorphous zone. Indents were subsequently prepared for TEM using a Focused Ion Beam (FIB) technique to produce thin samples. Finally, the amorphous region was mapped in TEM using high resolution (HR) montaging techniques.

Nanoindentation

Samples were cut into $10 \times 10 \times 2$ mm squares and polished down to $0.05 \mu\text{m}$ using diamond suspensions. An indenter (Micromaterials, UK) was used to instigate amorphisation in B₄C and B₄C-SiC composites. A low load Berkovich tip was used to indent the sample with a maximum load ranging from 100 mN to 500 mN in 50 mN steps. At least 10 indents were produced per maximum load. The nanoindentation pendulum was used at a $10 \mu\text{m/s}$ displacement rate with a 60 s dwell at maximum load. During unloading, a 60 s dwell was added at 10% of maximum force which was used to account for thermal drift.

The Oliver-Pharr method [143] was utilised to determine the hardness (H) and reduced modulus (E_r) of a sample. These can be defined as:

$$H = \frac{P_{max}}{A_c} \quad (25)$$

where P_{max} is the maximum load applied to the sample and A_c is the contact area at maximum load, and:

$$E_r = \left(\frac{\sqrt{\pi}}{2}\right)\left(\frac{S}{A_c}\right) \quad (26)$$

where S is the stiffness.

This method assumes that the initial unloading of a pyrimidal indenter is the same as elastically unloading a cylindrical one and hence the unloading curve follows a power law relation. S can be calculated by taking the derivative of the power law fitting at a given load. Here, several depths (h) can be defined; h_{max} corresponds to the depth at maximum load, h_f the final depth and h_c is the ‘vertical distance along which contact is made’ or the contact depth at maximum load. On loading, the surface elastically deforms before undergoing plastic deformation, on unloading elastic relaxation occurs resulting in $h_f < h_c < h_{max}$. Figure 25 shows a typical hysteresis curve of a hard ceramic, and how the parameters may be calculated.

It is trivial to calculate the contact area at maximum load, A_c , of a Bercovich tip due to its set geometry, with A_c being related to h_c by Equation 27.

$$A_c = 3\sqrt{3}h_c^2 \tan^2 \theta \quad (27)$$

where θ is the angle between the surface normal and the indenter face; for an ideal Bercovich this is 65.27° . However, in the case of hard ceramics, damage to the tip is common during indentation, which alters A_c . To account for this change, a diamond area function (DAF) was used to calculate A_c . This involves the placement of indents into a polished piece of fused SiO_2 ; from the resulting hysteresis curve S and h_c can be calculated. As the elastic modulus, E , and hence E_r , of fused SiO_2 are known, it is possible to calculate A_c using Equation 26 for each P_{max} . The final DAF then relates A_c to h_c . The resulting formula can be used to determine A_c during indentation and hence H can be calculated for a sample. DAFs were conducted before each indentation experiment.

E of the sample which can be related to E_r :

$$\frac{1}{E_r} = \frac{1 - \nu^2}{E} + \frac{1 - \nu'^2}{E'} \quad (28)$$

where E and E' are the elastic modulus of the sample and indenter respectively. ν and ν' are the

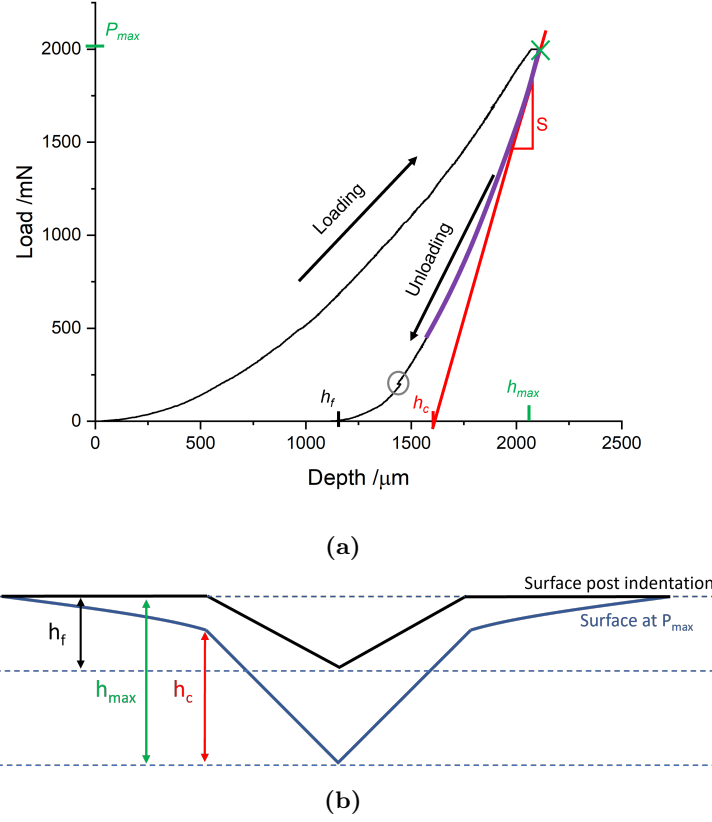


Figure 25: a) Graph showing a typical indentation hysteresis curve of a hard ceramic. Key values used in calculating hardness and reduced modulus are labelled. The purple line shows a power law fitting. A small dwell used to calculate thermal drift is circled in grey b) Diagram showing depths that can be defined as part of the indentation hysteresis

Poisson ratio of the sample and indenter. This expression is based on Hertz contact theory which models two spheres contacting elastically, or an equivalent sphere contacting a rigid surface. E_r can be calculated from indentation data using Equation 26. The above calculations presume that cracking, after plastic deformation, has not occurred and hence, where cracking is observed the limitations of the results must be noted.

Microindentation

Samples used for nanoindentation also underwent microindentation. Here a high load-Berkovich tip was used with maximum loads of 500 mN to 2000 mN in 250 mN steps. The displacement rate was 10 mN/s with a 60 s dwell at maximum load. At least 10 indents were produced per maximum load with a 30 s dwell at 10% of maximum load to allow thermal drift to be calculated. Due to the heavy cracking of the samples, H and E_r calculations should be considered alongside the extent of cracking.

Raman Spectroscopy

Raman spectroscopy was used to identify amorphous regions under indents as discussed fully in Chapter 7. The temporary excitation of electrons within bonds *via* a laser leads to inelastic Raman scatter-

ing of the beam. Figure 26 shows the working principles of Raman spectroscopy as well as the setup of a true confocal Raman microscope. Confocal microscopes block returning signal from out of focal plane excitations using a pinhole. An InVia Raman microscope (Renishaw, UK) was used with a 43 mW, 532 nm laser in confocal mode with a 2400 l/mm grating. A 100 $\times$ magnification objective lens was used throughout this work.

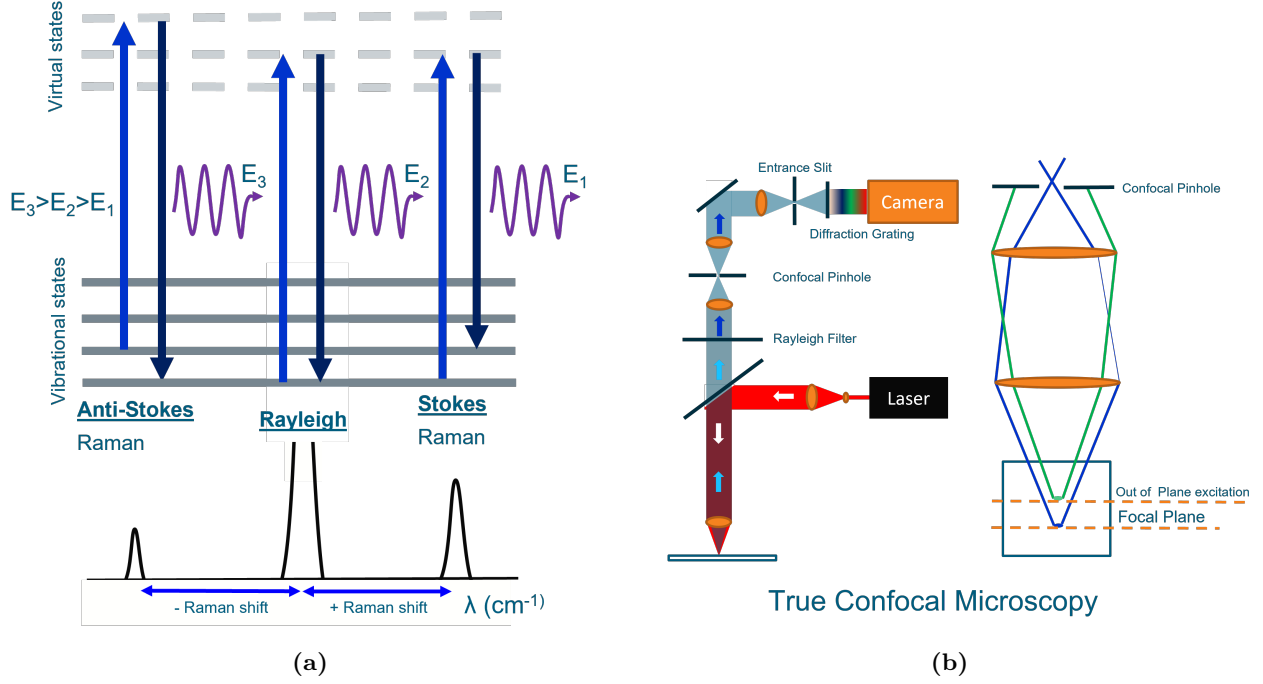


Figure 26: a) Energy level diagram explaining how Raman signal is produced when bonds within the material are excited by laser radiation. b) Schematic showing the setup of a true confocal Raman microscope

A series of single surface scans were completed before each experiment to check the focus. When a high signal to noise ratio is achieved, the sample is in focus. The laser was set to deliver 50% intensity in 3 s pulses with 3 iterations combined to produce 1 spectrum. The key materials investigated were B_4C and amorphous B_4C . The typical spectra for these can be seen in Figure 27a. The key peaks used for identifying phases are seen in Table 6. A scan range of 665 cm^{-1} - 1825 cm^{-1} (1275 cm^{-1} scan centre) was used as it includes these peaks.

During this work, a novel depth scanning method was developed. To scan in depth, the sample surface was brought into focus and the stage moved upwards. This moves the focal plane into the material; the Z movement of the stage is termed the scan depth. Figure 27b shows a typical depth scan for an indent when the sample is in good focus. It can be seen that at $0 \text{ }\mu\text{m}$ the peaks are clear with a good signal:noise ratio. At $5 \text{ }\mu\text{m}$ there is significantly more noise, but the peak is still identifiable.

Area mapping was used to investigate the extent of amorphisation around and under the indent. Spectra were analysed and a peak was assigned a value of 0 (absent), 1 (weak) or 2 (strong). Weak was defined as below the 20th percentile of the maximum spectra intensity. These values were then

plotted as an area map. Maps were varied in size depending on the size of indent with the intention being to fully incorporate the indent and surrounding material. A horizontal step size of $0.7\text{ }\mu\text{m}$ was used as specified by the manufacturer. It was noted that due to the small size of SiC grains, and peak overlap, SiC was hard to identify. Mapping of SiC was therefore not completed.

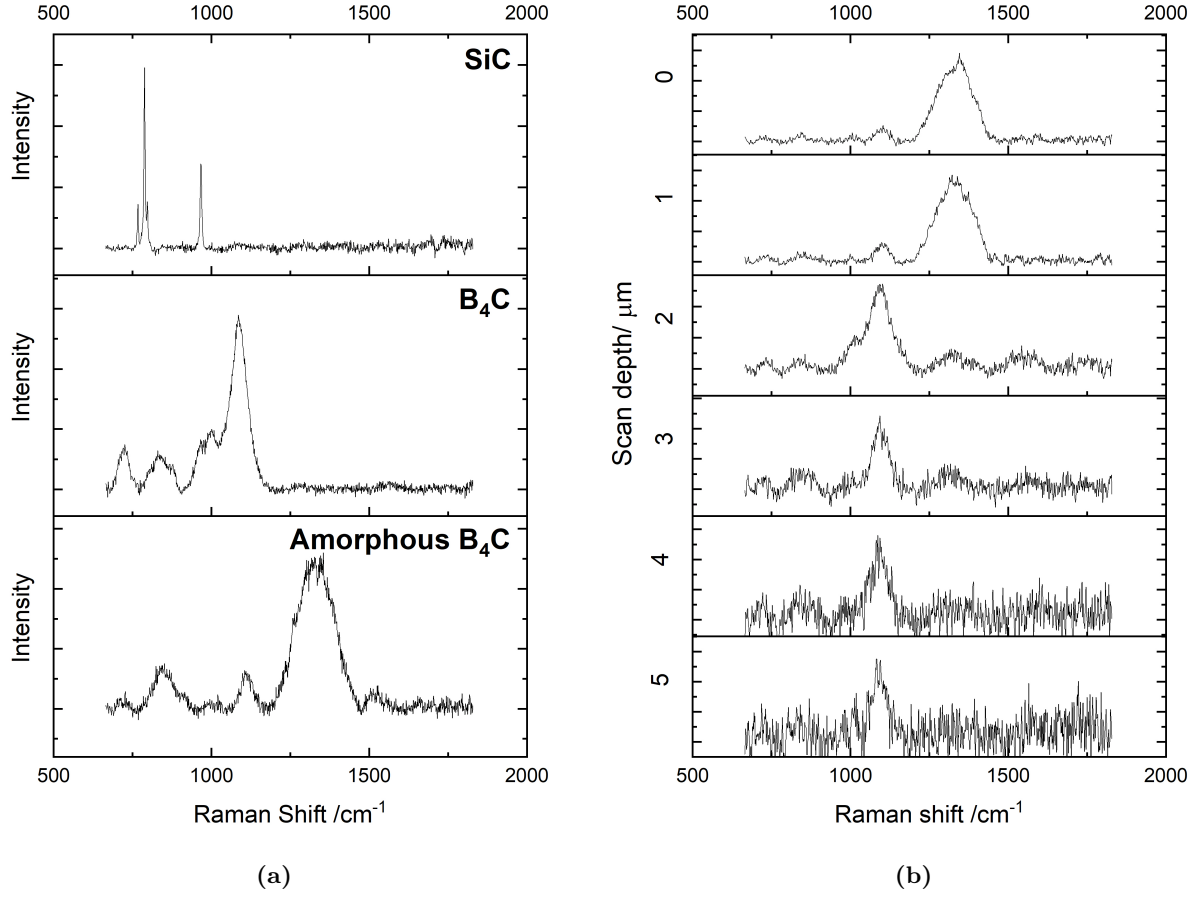


Figure 27: a) Raman spectra showing the expected signal for SiC, B₄C and amorphous B₄C. b) Raman spectra at various scan depths

Table 6: Raman peaks that are present in the key phases found in this work

Material	Peak /cm ⁻¹	Reason
SiC	766	Si-C bond Transverse optical peak 1 [144, 145]
	788	Si- C bond Transverse optical peak 2 [144, 145]
	966	Si-C bond Longitudinal optical peak [144, 145]
B ₄ C	725	Icosahedra-Equitorial atoms [60]
	828	Icosahedra-Polar and Equitorial atoms [146]
	965	Chain atoms [60, 146, 147]
	998	Chain and icosahedra atoms [146, 147]
	1085	Icosahedra-Polar atoms and chain atoms [146, 148]
Amorphous Zone	1105	Icosahedra shift due to loss of carbon [149, 150]
	1340	Carbon- D peak [50, 51]
B ₄ C	1550	Carbon - G Peak [50, 51]
	1810	Amorphous peak [18, 50, 51]

TEM Sample Preparation: Focused Ion Beam

A Helios NanoLab 600 Focused Ion Beam-Secondary Electron Microscope (FIB-SEM) (ThermoFisher Scientific, USA) was used to prepare indented samples for Transmission Electron Microscopy (TEM). Samples were prepared using a combination of AutoTEM (ThermoFisher Scientific, USA) and manual techniques. AutoTEM is a software designed to automate the production of TEM specimens using a set of pre-designed protocols; this was originally purposed for wafer inspection at fabrication facilities. Protocols were iteratively trialled with different parameters to optimise for B₄C-SiC composites. A number of key parameters must be defined to ensure ion (i) beam milling and thinning occurs effectively. Initially TEM specimen size (X,Y) and depth are defined along with a milling current. To determine the milling current of a sample, a series of trenches were manually milled to a constant depth. The current that produces a trench of the target depth would be the optimum milling current.

In AutoTEM, fiducial markings are employed to optimise focus and to determine the correct locations for trench milling. Once the milling and polishing currents are selected, the focus must be calibrated to allow accurate fiducial recognition. Initially, 21 nA was determined as the best milling current; however, it suffered from poor fiducial matching (defined as < 95% matching parameter). Instead, a lower current of 9.3 nA was chosen.

The milling current is combined with a correction factor and depth percentage which alters the depth of milling relative to a silicon reference. For example, a correction factor of 1 and depth percentage of 100% applied to a 7 µm deep trench programme will produce a trench of that depth in silicon. This factor was therefore increased to 3.0, due to the increased milling difficulty of B₄C-SiC relative to Si. The depth percentage was also increased to 300% consider the lower current used for reasons discussed above.

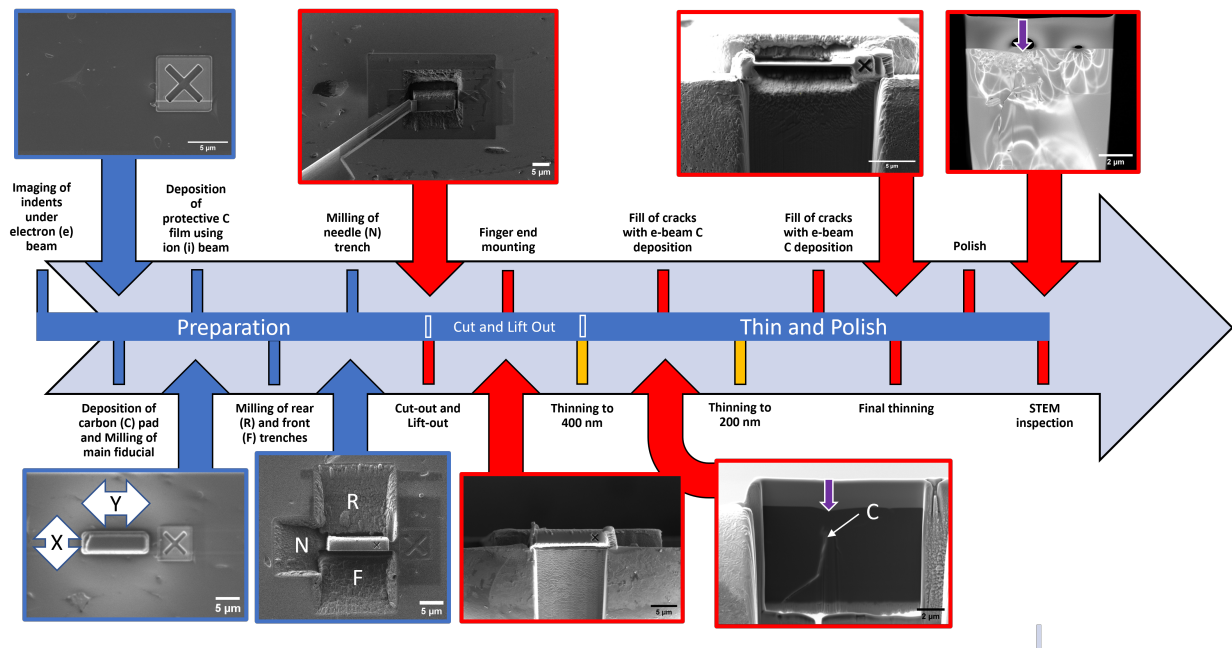


Figure 28: Diagram explaining the FIB process undertaken for heavily cracked samples. The meaning of X and Y are defined. Blue steps were automated, red had to be completed manually and orange could be either, depending on user experience. Purple arrows indicate the location of the indent centre. Carbon, used to fill cracks is identified as C.

Specimen lift-out was conducted manually with a top down finger method. Such specimens are typically mounted to the side of a copper grid with one edge attached by platinum (Pt) deposits. However, indentation samples contain a significant amount of cracking at higher loads. Consequently, specimens were mounted to the top of a copper ‘finger’ with a channel dug out to allow TEM to be conducted. The sample was attached at both ends to the copper grid in order to reduce the risk of sample twist or further crack propagation during thinning. It was determined that the highest load indent that could be successfully lifted out and thinned was 1000 mN. The samples had an approximate survival rate of 1 in 20 under these conditions, a probability which was affected by factors such as residual stresses, cracking and user experience.

To mitigate the likelihood of specimen failure due to cracking, electron (e) beam deposition was utilised to fill in the cracks with carbon. This process was necessary for samples which bore cracks, and it significantly improved their survival. e-beam decomposition works by depositing carbon through chemical vapour deposition, wherein a reactant gas is pushed towards a surface and reacted by a rastering e (or i) beam. In this case, samples underwent deposition for a dwell time of 50 ns using a beam of 2 kV voltage and 2.8 nA current. The exact thickness at which crack filling occurred varied between samples. However, the depth of penetration of carbon into the cracks was limited and hence had to be completed at sample thicknesses of 400 nm and 200 nm. Beyond this, filling was avoided such as not to implant carbon into the bulk sample. Crucially, a large area of deposition was required in tandem with a very short dwell time. The larger the area, the more time the gas had to impregnate

the crack before the beam returned, improving crack filling. The reduced dwell time also led to the production of small crystallites, which better impregnate the cracks. The entire specimen hence underwent e-beam deposition with a dwell time of 50 ns.

Thinning was conducted using 30 kV, 2.5 nA - 0.79 nA for a rough thin, followed by 5 kV, 0.17 nA for fine thinning. This reduced the damage to the specimen during thinning and prevented ion implantation. A final thickness of between 100 nm and 80 nm was targeted. A polish was conducted at 2 kV, 39 pA to remove any amorphisation caused by the i-beam. Finally, the sample was investigated using the scanning transmission electron microscopy (STEM) 3+ detector to verify electron transparency.

Transmission Electron Microscopy

A Joel 2100 Plus TEM (Joel, Japan) was used to analyse both powder and indentation samples. Powder samples were dispersed in ethanol and placed on copper grids. The solutions were heavily diluted, until transparent to the eye, to ensure electron transparency of the resulting sample. Indentation samples were prepared utilising the FIB-SEM process described above.

Analysis of indentation samples requires an appreciation of the position of features relative to the indent. These features can then be investigated at higher magnifications to determine their identity. Montaging was used to produce high resolution maps of the area surrounding the indent and identify key features. SerieLEM (University of Colorado Boulder, USA) was used in this work to collect a montage of 18×18 frames at $100k \times$ magnification. These were converted into a map with a 10% overlap between each frame, which could then be combined into larger maps using a digital micrograph (Gatan, US). The final micrographs were inspected and compared between samples and indent forces to determine the location and extent of amorphisation. Amorphous bands and the resulting closed cracks appear bright when objective under focus is used; this was used to enhance contrast in the mapping. Processing was also conducted where light areas were separated from the main image using thresholding and Sobel filtering in ImageJ.

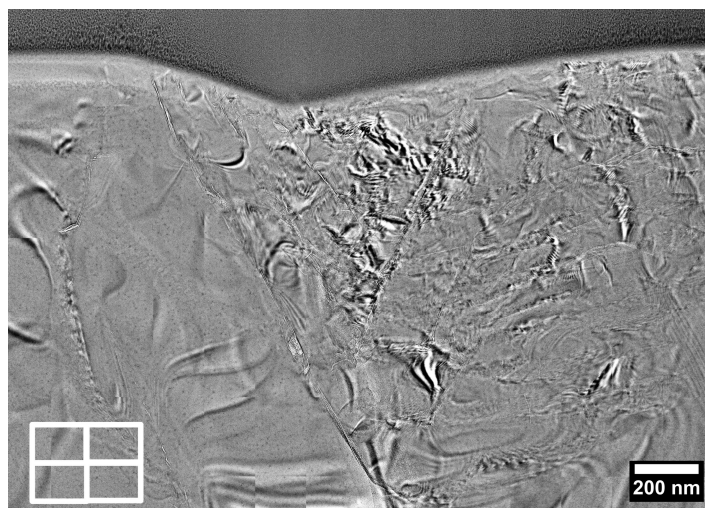


Figure 29: TEM micrograph produced using high resolution montage. The average size of each frame is shown on the bottom left.

4.4 Properties of commercial materials

During this work four key standard materials were used. A commercially available SiO_2 , B_4C , SiC and a phenolic resin were purchased for use in the composite production. The phenolic resin was used as a carbon source whilst the remainder were used to produce reference composites. This facilitated the critical evaluation of microemulsion SiO_2 as a precursor to SiC .

Commercial SiC and SiO_2 were analysed to understand how they compare to microemulsion SiO_2 in both size and reactivity during heat treatment. DLS analysis was used to determine the particle size distribution whilst SEM was used to investigate the particle morphology. TGA-DTA analysis was used to understand how the powders react to heat treatment. This can identify mass losses and phase changes, which was used to predict the reactions that could occur during composite production. From this the most suitable SiC precursor could be identified.

Commercial powders were also mixed, as described above, to produce a composite powder. It was important to understand the C_{TF} , C_{OF} and crystallography of the composite, which was achieved using XRD and CA. Combining these with SEM analysis, it was possible to predict the composition and crystallography of the final composite whilst also calculating an observed composition. To achieve this, the carbon content and crystallography of the starting commercial powders must be known. XRD and CA analysis were therefore completed on the as-received commercial powder, after hot press sintering and post TGA-DTA analysis.

Commercial Silica

The particle size distribution of amorphous Aerosil 200 (Evonik Industries, Germany) SiO_2 powder is illustrated in Figure 30c. These particles have a μ of 98 nm. Figure 30d shows a typical SEM micrograph of the SiO_2 . It can be noted that the primary particle size is of the nanometre scale.

The manufacturer's specification identifies that the particles have a spherical morphology. From TGA-DTA, it noted that there is very little mass loss or gain associated with SiO_2 heat treatment. Nevertheless, a sizeable exothermic reaction occurs during heat treatment, beginning at around 400 °C and continuing to 1400 °C. Within this temperature range SiO_2 is known to undergo a range of phase changes, although these are not widely investigated from an amorphous initial state. Initially, quartz can form up to temperatures of 1200 °C. At 1200 °C, the quartz can undergo a phase-change to cristabolite[151, 152], to which the exothermic reaction can likely be attributed. The literature does note that the temperature and exact route of phase transformation changes based on initial crystallinity, contaminants and production method.

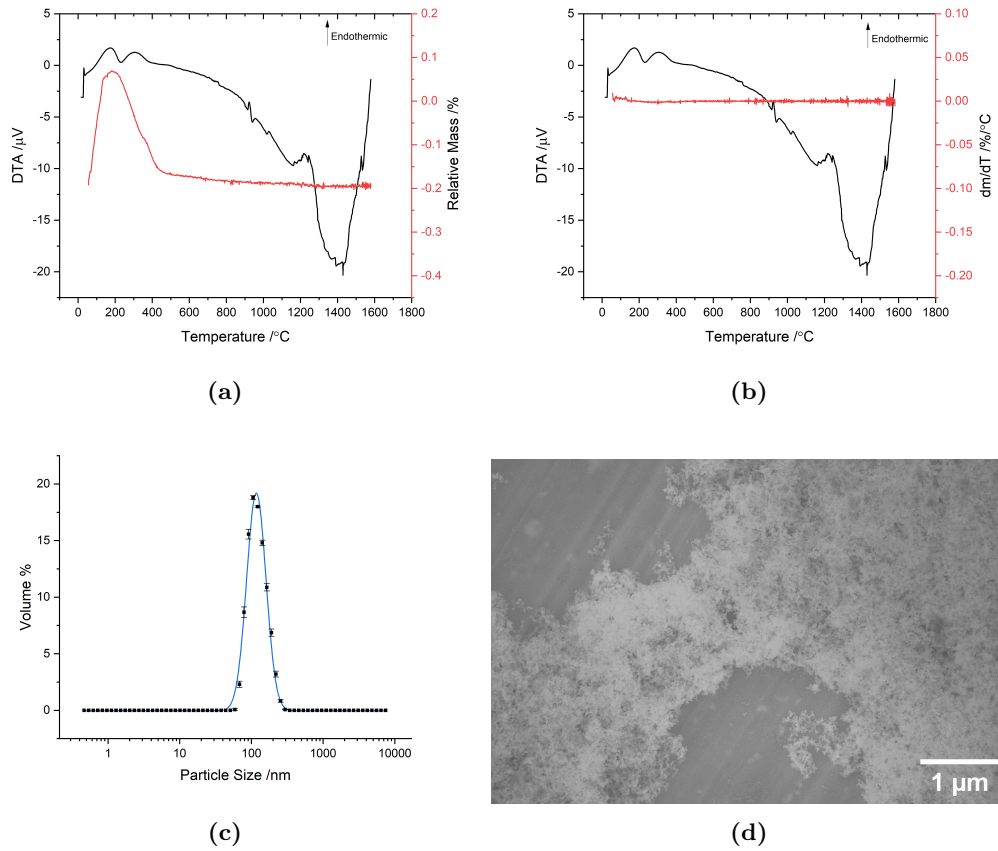
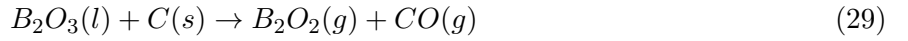


Figure 30: Summary of the characteristics of commercial SiO_2 powders. a) DTA-TGA data showing the changes in mass and DTA signal with temperature. b) DTA-DTG signal showing the change in the derivative of mass signal and DTA signal with temperature c) DLS determined particle size distribution of commercial SiO_2 powder. d) SEM micrograph of commercial SiO_2 powder.

Boron Carbide

Commercial boron carbide (Houganas, Germany) was a key component of the composites produced during this work. XRD patterns for before and after hot pressing can be seen in Figure 31. Peaks associated with B_4C (ICDD-00-035-0798), B_2O_3 (ICDD-00-006-0297) and crystalline carbon (ICDD-01-075-0444) are seen. A sharpening of the carbon peak suggests smaller carbon grains combine, hence reducing the variability in the diffraction peak. There is also a clear loss of B_2O_3 , which

was attributed to the reduction of the surface B_2O_3 groups into B_4C . The reaction proceeds as per Equation 29 followed by Equation 30 [153]. TGA-DTA analysis showed a mass loss beginning at 1250 °C as can be seen in Figure 32b. The loss of CO or B_2O_2 species leads to the drop in mass. The final mass of B_4C after being held at 1580 °C was 92.4% of the original mass. This mass loss was taken into account during composite composition calculations. It is noted by the supplier that the powder can contain some contaminants which are summarised in Table 8. Oxygen is a significant part of this, further verifying the presence of B_2O_3 in the starting powder.



The carbon contents of the the initial powder, post TGA-DTA powder, and hot pressed sample are detailed in Table 7. A significant reduction in carbon content is seen post TGA-DTA. As this is environment contains oxide species, with alumina crucibles and furnaces being used, it is likely that oxidation of the powder occurs. This observation is supported by the observed mass increase and subsequent decrease in the TGA-DTA plot. This oxidation of the powder led to a slight mass increase between 500 °C and 1100 °C [154]. The oxidised B_4C may then react; free-carbon could be lost as CO whilst any B_2O_3 reacts as described above. Owing to the carbon rich environment, and the relatively limited gas flow, a large drop in carbon content is not seen post-hot pressing. This is likely due to a balance between mass loss as CO and B_2O_3 , and carbon contamination from the device. Thus, for evaluation of compositional changes, those produced in the hot press should only be compared with hot press CA data for commercial B_4C .

DLS analysis was used to examine the powder size distribution. Figure 32c shows the powder size distribution of B_4C when dispersed in ethanol using a UP200s sonicator (Hielscher, Germany). These particles have a μ of 196 nm. SEM analysis was used to determine initial powder morphology and micrographs can be seen in Figure 32d. The powder has a non spherical morphology with no particular defined shape. It is noted that the DLS appears to underestimate the particle size, when compared to SEM analysis. This is likely due to the larger micron sized particles being on the edge of the resolution range of the device. Alternatively, sonication which is required for DLS may break up agglomerates or favourably disperse smaller particles. This highlights the necessity to analyse samples using both SEM and DLS analysis.

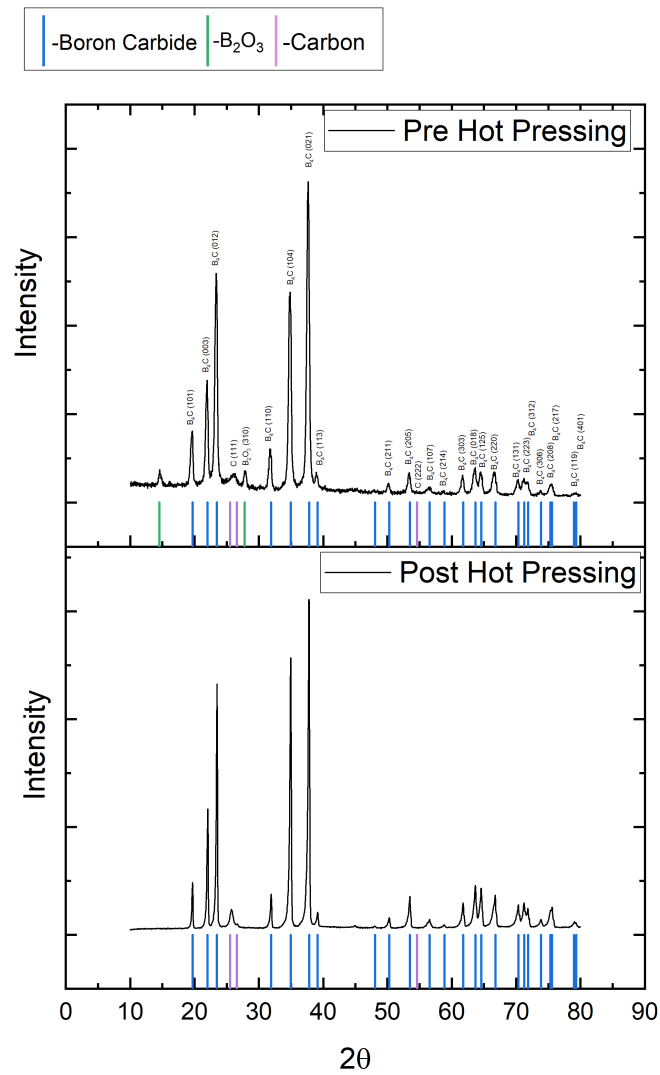


Figure 31: XRD pattern for commercial Boron Carbide before and after hot pressing.

Table 7: Carbon content for commercial B_4C powder after several heat treatments

Condition	C wt%
As-Received	23.0 ± 0.3
Post-TGA	17.5
Post Hot Pressing	22.4 ± 0.1

Table 8: Contamination found in commercial B_4C powder as described by the manufacturer

Contaminant	Max wt%
N	0.7
O	2.6
Fe	0.1
Si	0.15
Al	0.05
Other	0.1

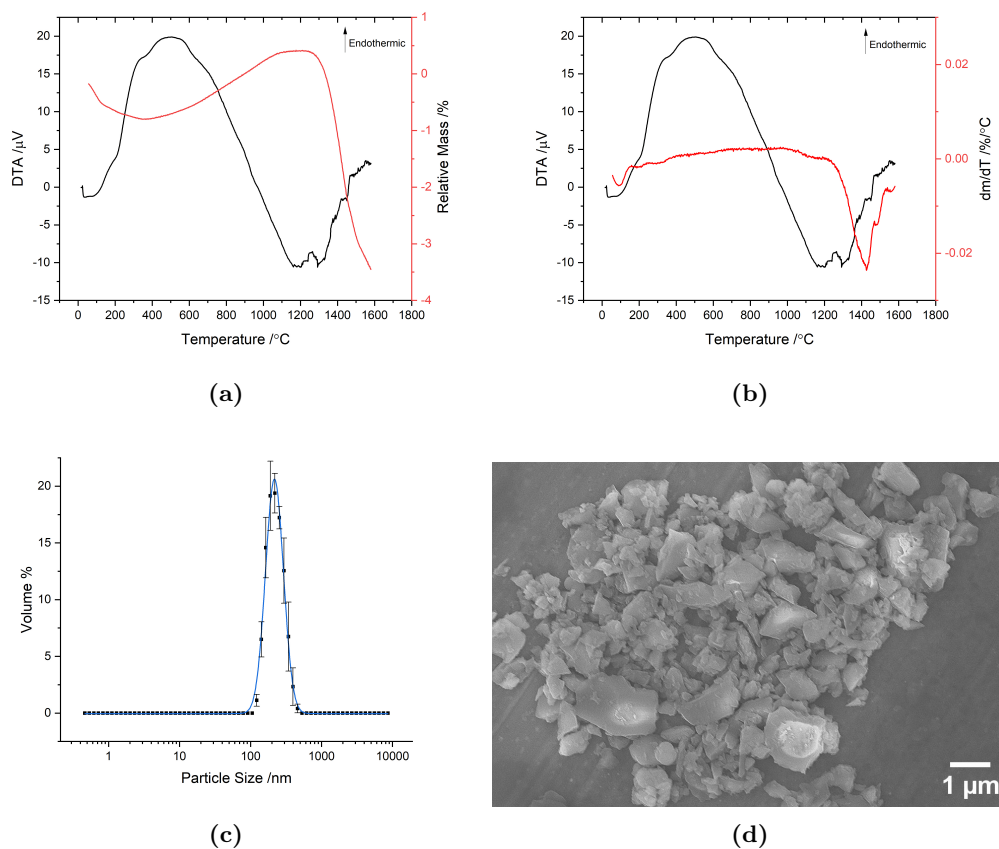
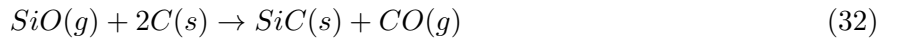
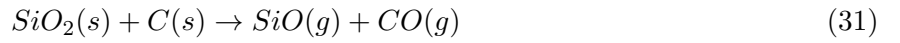


Figure 32: Summary of the characteristics of commercially available B_4C powder. a) TGA-DTA graph showing the response of the powder up to 1580 °C. b) DTA-DTG signal showing the change in the derivative of mass signal and DTA signal with temperature. c) DLS determined particle size distribution of commercial B_4C powder. d) SEM micrograph showing morphology of commercial B_4C powder

Silicon Carbide

Similar to commercial B_4C , UF-25 commercial α -SiC (Houganas, Germany) was procured for use in a limited number of samples. The as-received powder was also subject to XRD, TGA-DTA, CA, SEM and DLS analysis with the results seen below. XRD patterns shown in Figure 33 indicate that this powder is hexagonal (α) in nature (ICDD-00-031-1232), confirming the manufacturer's specification. TGA-DTA analysis, seen in Figure 34b, shows a slight mass increase at between 600 °C and 1200 °C. Similar to B_4C , the oxidation of some powder to SiO_2 groups results in a mass increase. A mass loss was observed at 1450 °C although significantly less than was seen in B_4C . This was attributed to the reduction of these groups to SiC, and proceeds as per Equation 31 & 32 with the loss of CO or SiO reducing the overall mass of the sample. The final mass of SiC after being held at 1580 °C was 97.0% of the original mass. This mass loss was taken into account during composite composition calculations.



The oxygen rich environment of TGA-DTA led to a decrease in carbon content during heat treatment as seen in Table 10. Similar to B_4C , this is likely due to oxidation of the powder, resulting in greater reduction by free carbon, and hence more carbon loss. However, a slight increase in carbon content was observed post-hot pressing. It can be theorised that carbon contamination from the hot press was balanced by a loss of carbon during powder reduction. By contrast, in SiC, the carbon lost during reduction may be less than the carbon added by contamination, leading to an increase in carbon content.

The DLS particle size distribution can be seen in Figure 34c. This powder has a μ of 195 nm . SiC is more stable in DI water than ethanol hence DLS analysis was conducted in DI water. Figure 34 shows the morphology of the initial powder. Similar to B_4C , this powder has a non-spherical morphology with no specific shape. Similar to B_4C , it is noted that the DLS appears to underestimate the particle size, when compared to SEM analysis. This is likely due to the larger micron sized particles being on the edge of the resolution range of the device. Alternatively, sonication which is required for DLS may break up agglomerates or favourably disperse smaller particles. This highlights the necessity to analyse samples using both SEM and DLS analysis.

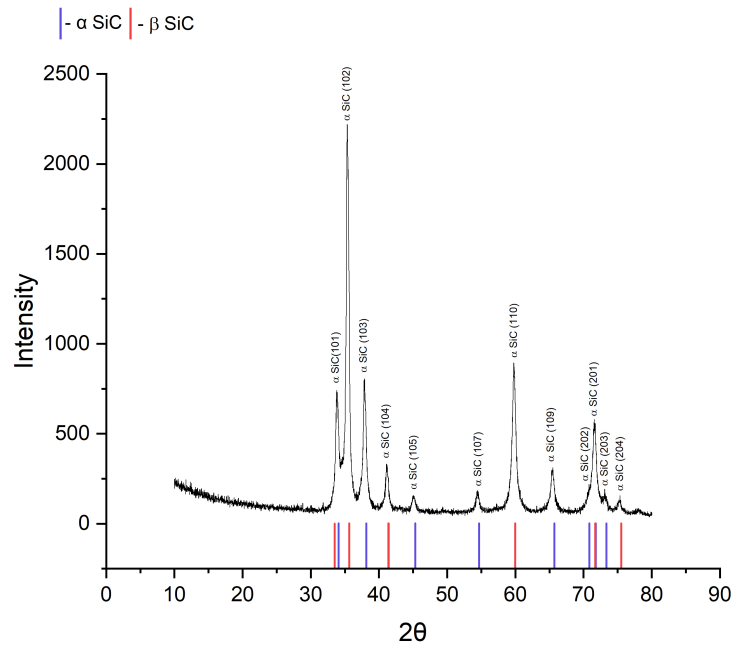


Figure 33: XRD pattern for commercial α -SiC before hot pressing.

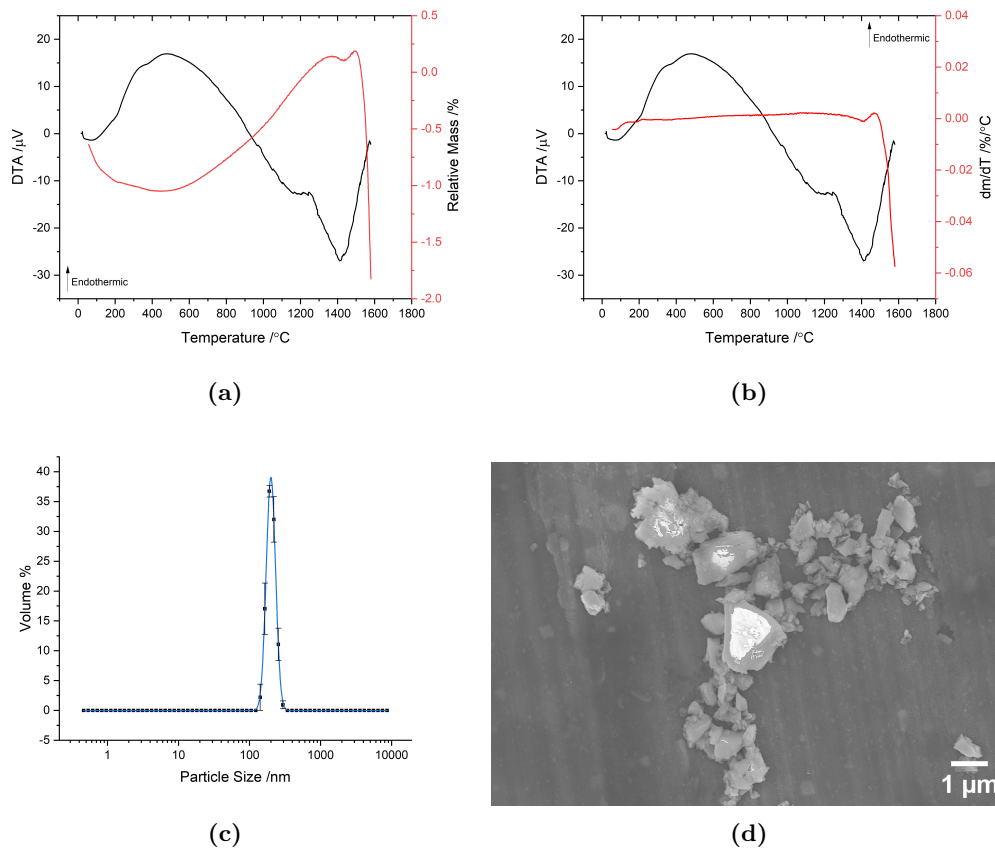


Figure 34: Summary of the characteristics of commercially available SiC powder. a) TGA-DTA graph showing the response of the powder up to 1580 °C. b) DTA-DTG signal showing the change in the derivative of mass signal and DTA signal with temperature. c) DLS determined particle size distribution of commercial SiC powder. d) SEM micrograph showing morphology of commercial SiC powder

Table 9: Contamination found in commercial SiC powder as described by the manufacturer

Contaminant	Max wt%
O	2.5
Fe	0.05
Ca	0.01
Al	0.04

Table 10: Carbon contents of commercial SiC powder after various heat treatments.

Condition	C wt%
As-Received	30.2 ± 0.4
Post-TGA	28.6 ± 0.1
Post Hot Pressing	31.2 ± 0.9

4.4.1 Phenolic Resin

A Durez 28391BF phenolic resin (Sumitomo Bakelite, Japan) was used to add carbon to samples, either as a sintering additive or reactant. It was important to understand the reactions that occur with temperature, as well as the carbon content of the phenolic resin. TGA-DTA analysis, as seen in Figure 35, shows a significant mass loss occurring at between 350 °C and 750 °C. This is followed by a slow mass loss up to 1580 °C. The large mass loss was attributed to pyrolysis of the phenolic resin in the inert Ar atmosphere. The various gradients of this mass loss indicate reactions of several parts of the molecule to carbon. A significant quantity of oxygen, hydrogen and carbon is lost as CO, CO₂ and steam. The final mass after holding at 1580 °C was 36.8% of the initial mass. When comparing the carbon content before and after TGA-DTA, as seen in Table 11, an increase in the carbon content is observed. This is due to the loss of oxygen and hydrogen species during the pyrolysis. These values can be used to predict compositions of composites made using phenolic.

Table 11: Carbon content of commercial phenolic resin after various heat treatments

Condition	C wt%
As-Received	81.9 ± 1.2
Post-TGA	95.0 ± 0.1
Post Hot Pressing	-

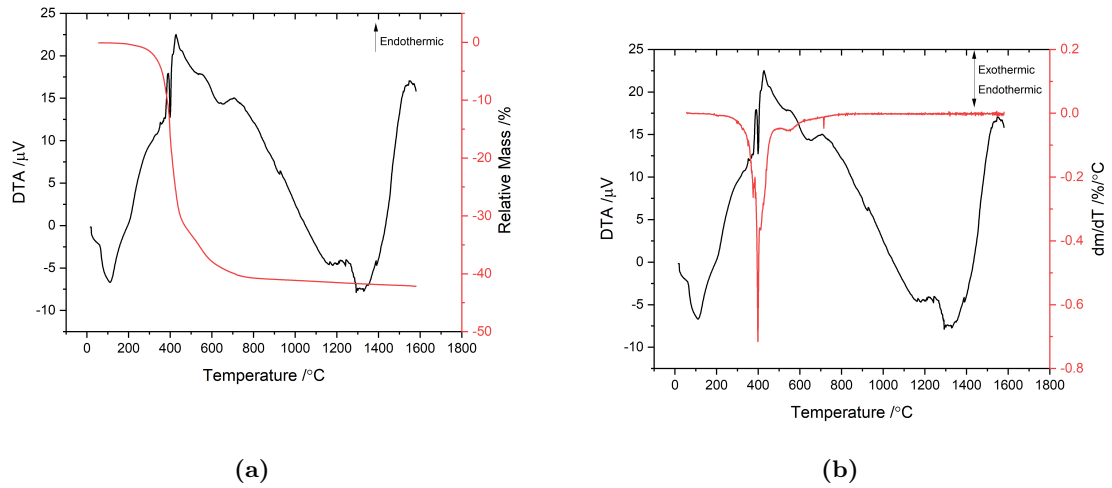


Figure 35: a) Graph showing the TGA-DTA response for the phenolic powder. b) DTA-DTG signal showing the change in the derivative of mass signal and DTA signal with temperature.

5 Production of Nanoparticle Based Ceramic Precursors

The use of nanoparticle based ceramic precursors is a key component in the production of a composite with a range of microstructures. The intimate mixing of precursors for SiC and B₄C gives the opportunity for unique composite microstructures to be created and then tailored for specific uses. When considering the SiC phase, a microemulsion SiO₂ based precursor provides an obvious avenue of work. Production of SiO₂ nanoparticles using a microemulsion is explored in the literature and can lead to nanometric particles with a range of morphologies [84–86, 155]. The use of nanoparticles allows flexibility, with smaller particles likely producing smaller SiC grains. SiO₂ particles could then be grown or agglomerated to alter the final SiC microstructure.

To achieve this it is essential to have robust manufacturing methods that reliably produce nanoparticles at a range of sizes. The microemulsion method described by Bagwe [84] and Zhao [155] has been selected for this work due to the demonstration of reliable nanoparticle production. Criteria can be defined which the particles must meet to be used in composite production:

1. SiO₂ nanoparticles must have a scalable production pathway, with the final particles being insensitive to changes in total reactant volume.
2. These particles must remain stable over a prolonged period of time with limited irreversible changes such as particle growth.
3. The particles must have flexibility to be tailored to a range of particle sizes by changing reactant ratios and conditions.
4. Once added to a carbon source, the production of SiC powders must be possible, with good understanding of the reactions occurring during this process.

In order to understand how microemulsion SiO₂ can be tailored to meet these criteria, four key studies were conducted in order to:

- Determine the effect of scaling up the microemulsion reaction on the particle size distribution.
- Understand how best to store nanoparticles and consider their subsequent dispersion.
- Confirm hypotheses on how different reactant ratios can tailor the size of nanoparticles.
- Investigate the SiO₂ to SiC reaction using both in-house and commercial SiO₂.

5.1 General Methodology

The nanoparticle production method is fully explained in Chapter 4 of this thesis. This was used to produce a range of microemulsion solutions, which were used in the above studies. These are classified by a reactant ratio set, as described in Table 12. These can be further classified by a total volume, as

seen in Table 13. Ratio set A was defined as the standard ratio set, with 184.6 ml being the standard total volume. Together, these give the standard SiO₂ batch, which was used throughout this work as a reference point for analysis. Ratio Set A uses the same ratios as the literature and hence was used as a reference point when variables were altered. This total volume was selected as it yielded enough SiO₂ to complete multiple analysis experiments.

Table 12: Definition of Ratio Set A, B, C and D from Ratios R, S, O, E. These are defined in Chapter 4.

Ratio Set	Ratios				Change vs Standard Ratio Set
	R	S	O	E	
A	0.25	0.15	22.8	4.43	Standard Ratio Set
B	0.50	0.15	22.8	4.43	TEOS x2
C	0.25	0.3	22.8	4.43	NH ₄ OH x2
D	0.13	0.08	11.4	4.43	NH ₄ OH x3

Table 13: Explanation of the experiments conducted during nanoparticle production. This defines the total volume used and the volume of each component used.

Ratio Set	Total Volume /ml	Mass /g	Volume /ml				
		Triton X-100	Cyclohexane	Hexanol	DI Water	TEOS	NH ₄ OH
A	11.5	1.77	7.50	1.60	0.40	0.10	0.06
A	23.1	3.54	15.0	3.20	0.80	0.20	0.12
A	46.1	7.08	30.0	6.40	1.60	0.40	0.24
A	92.3	14.2	60.0	12.8	3.20	0.80	0.48
A	184.6	28.3	120	25.6	6.40	1.60	0.96
A	369.2	56.6	240.0	51.2	12.8	3.2	1.9
B	11.6	1.77	7.50	1.60	0.40	0.20	0.06
B	23.3	3.54	15.0	3.20	0.80	0.40	0.12
B	46.5	7.08	30.0	6.40	1.60	0.80	0.24
B	93.1	14.2	60.0	12.8	3.20	1.60	0.48
B	184.6	28.3	120	25.6	6.40	3.20	0.96
C	23.2	1.77	7.5	1.60	0.40	0.10	0.24
D	46.1	7.08	30.0	6.40	1.60	0.40	0.72

This chapter will continue by considering each study in turn followed by drawing conclusions on the extent to which this method, and the resulting particles, meet the criteria laid out above.

5.2 The standard Ratio Set, A

In order to facilitate these investigations, the characteristics of the standard Ratio Set A must be understood. A typical particle size distribution can be seen in Figure 36. This shows the particles have a μ value of around 100 nm with a σ of around 40 nm. Figure 37 shows the particles when observed under an SEM and TEM. It can be seen that the particles are spherical and all appear to be less than 100 nm in size. The discrepancy between the observed particle sizes could be due to the nature of DLS, which reports a hydrodynamic diameter rather than an actual particle size. SEM

and TEM on the other hand only observe a small portion of the particles. It is therefore important to consider both observations hollistically, such that an accurate understanding of particle size and morphology across the sample can be achieved.

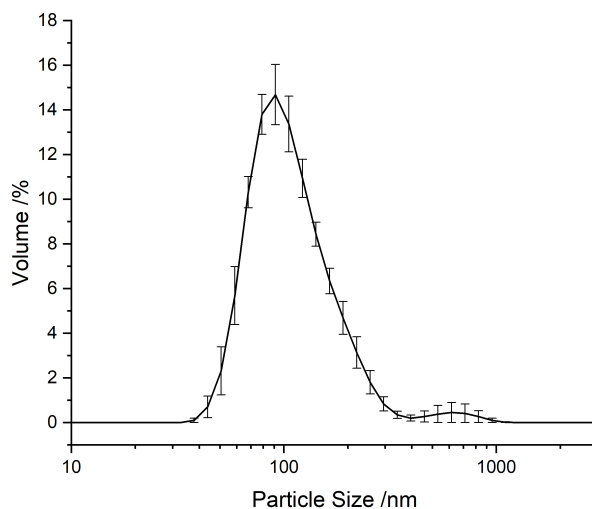


Figure 36: Particle size distribution of particles made using the standard Ratio Set, A at a total volume of 184.6 ml.

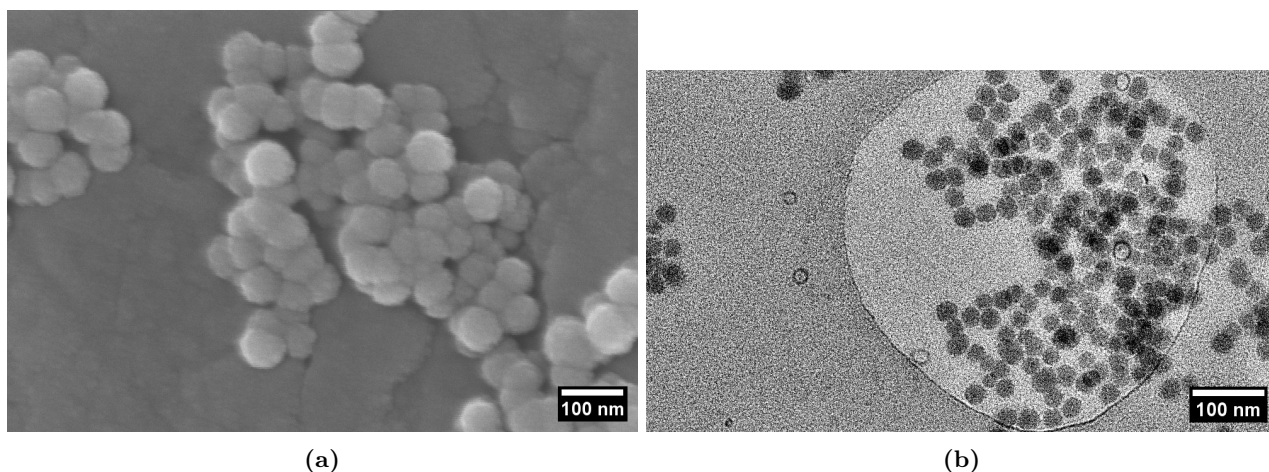


Figure 37: Micrographs obtained using a) SEM and b) TEM for particles made using Ratio Set A.

The standard Ratio Set, A, shows successful production of SiO_2 nanoparticles. When comparing to the original literature, the particles produced here appear smaller with a μ of 65 nm compared to 77 nm at a total volume of 11.5 ml. The particles are spherical in shape, similar to that of Bagwe *et al.* The particle shape [86] and size [84] is known to be affected by the shape of the water micelle, which in turn is linked to the surfactant itself as well as the surfactant:water ratio. As the particles are spherical it can be said that, in this configuration, the Triton X-100 produces a spherical micelle, a fact supported by literature [156].

5.3 Determining scalability of the reaction

As discussed in the literature, it is possible to produce SiO₂ nanoparticles at a small scale [84, 155] using the microemulsion process. Whilst useful scales for specific analysis, the potential yield from such experiments is significantly below that required to produce enough SiO₂ for use in composites. This work is based on a published procedure by Bagwe *et al* [84] whose primary reaction would produce around 20 mg of SiO₂. It is expected that at least 300 mg would be needed for composite production. It is necessary to verify if scaling up the experiment to larger volumes allows nanoparticles to still be reliably produced.

A key component to this work is to make an integrated production process, where primary SiO₂ particles are well dispersed throughout a ceramic precursor. It was theorised that this may mean dispersing particles in a carbon source immediately after production. This provides an alternative to drying, grinding and mixing. However, this method does not provide an easy way to measure the mass of particles produced. It was therefore important to conduct yield experiments, such that the yield from each experiment could be approximated without drying and weighing.

5.3.1 Methodologies for understanding the scalability of reaction

The effect of scaling up the volume of the reaction from around 10 ml to 186 ml on the particle size distribution was investigated using Ratio Set A. The total volume was increased as seen in Table 14 with experiments repeated at least 2 times at each volume. μ and σ , as defined in the methods section of this thesis, were reported and compared to determine the effect of scaling up the reaction on the particle size distribution.

Table 14: Experiments used to determine scalability. These consist of Ratio Set A at a range of total volumes. Ratio Set A is defined in Chapter 4 of this thesis

Ratio Set	Approx Total Volume /ml
A	11.5
A	23.1
A	46.1
A	92.3
A	184.6
A	369.2

5.3.2 Results

On observing Figure 38 it can be seen that, for Ratio Set A, there is a steady increase in both μ and σ up to 140 nm and 70 nm respectively when the reaction volume is increased from 11.5 ml to 100 ml. This trend then changes to a constant of 150 nm and 70 nm above 100 ml.

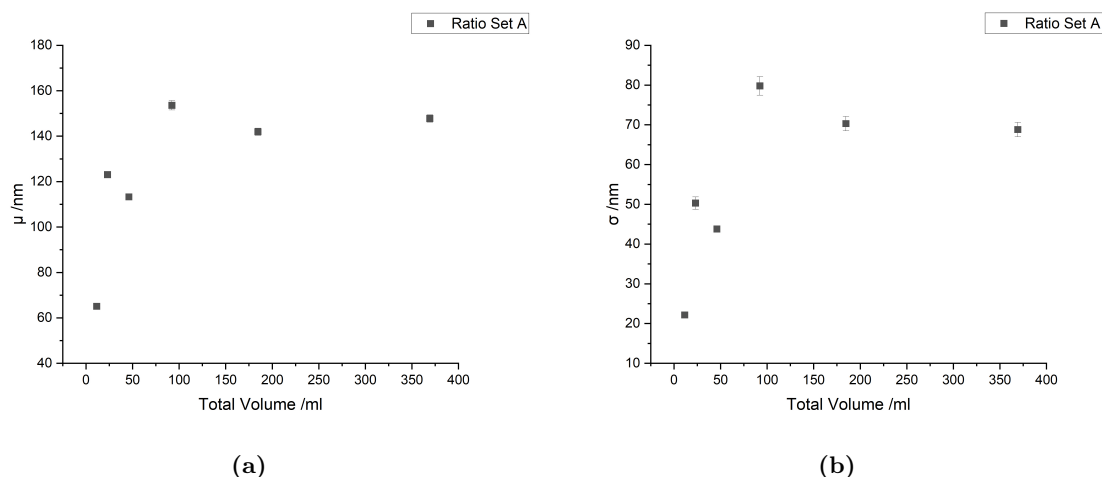


Figure 38: Graph showing the change in a) μ and b) σ with the scale, or total volume, of microemulsion reaction. Error bars are calculated as the standard error of the mean from several repeats at each scale. Ratio Set A is defined in the methods section of this thesis.

5.3.3 Discussion

There is no specific reasoning as to why the reaction to form SiO_2 , completed using the same reactant ratio set, would vary with the total volume. As the reaction requires the TEOS to contact, and then react with, the H_2O droplet, mixing can be crucial. The source of the trend is likely to do with H_2O micelle interactions. Bagwe *et al* noted in their original work that micelle rigidity affects particle size [84]. A micelle must contain a critical number of SiO_4 monomers to nucleate a particle. The more rigid a micelle, the less likely they are to coalesce or exchange monomers. This reduces the chance that all micelles have enough monomers to nucleate a particle. As there is less nucleation and more inhomogeneity, the particle sizes are larger with a broader σ . In this work, the micelles should have the same rigidity, as the surfactant to water ratio remains constant. Despite this, an increase in μ and σ is seen. It can be theorised that poorer mixing would also lead to fewer micelle interactions and hence less monomer exchange. Additionally, the variability in mixing, and hence micelle interaction, across the microemulsion would increase inhomogeneity and σ further as is observed here. This demonstrates that as the total volume, and hence reaction vessel size, is increased, poorer mixing will occur.

5.3.4 Conclusion

An increase in μ and σ of the particle size distribution is seen as the scale of the microemulsion used to produce SiO_2 increases. This is seen across two different reaction Ratio Sets. This observation can be attributed to a reduction in micelle interaction which occurs as mixing efficiency decreases with the size of reaction vessel. This work demonstrates the need to tailor mixing parameters, such as stirring RPM, to the scale being used. This, along with monitoring of μ and σ will allow desired particle size distributions to be maintained as industrial scales are reached.

5.4 Determining the stability of nanoparticles

The industrial context in this work adds a necessity to determine whether SiO_2 particles can be stored for long periods of time without an evolution of the particle size distribution. Whilst some literature expects SiO_2 to show good stability in neutral ethanol, with an isoelectric point of around pH 2 [157], others note the importance of investigating stability when considering engineering applications [158, 159]. This is especially important as, whilst many studies use commercial Ludox (Du Pont, USA) SiO_2 , this work considers lab-processed SiO_2 . Additionally, the process to produce Ludox is not defined by the manufacturer hence it is essential to carry out a study on the SiO_2 produced in this work.

When standard batch SiO_2 was stored statically, it showed a large degree of sedimentation. These formed an opaque deposit which could not be redispersed using manual shaking. An example of this is seen in Figure 39. It was therefore not possible to test this sample using DLS. The analysis of the solution would not provide a fair representation of the particle size as it would not include those in the sediment. This demonstrated the need for a storage method which could keep or regain the particle size distribution by preventing or breaking up agglomerates that form.

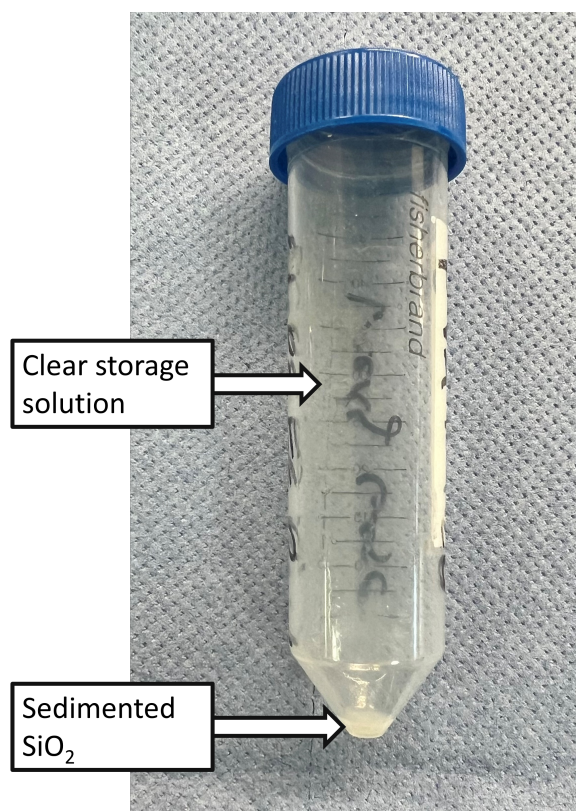


Figure 39: Image showing sedimentation in a standard batch of SiO_2 left for 7 days. These particles are considered un-washed and could not be redispersed without high energy sonication. This constitutes Sample 1.

Storage of particles can be affected by a range of factors, most notably the time they spend unagitated and how clean they are before storage. Agitated particles are unlikely to sediment and hence do not have significant interactions during storage. This prevents them from forming agglomerates or flocks. Particle cleaning is commonly used to remove adsorbed species such as excess reactants from particles.

These can alter the surface chemistry of the particle leading to agglomeration. The cleaning process however requires a large quantity of a cleaning solvent and an increased processing time. Ultimately, the final storage method must be as simple as possible whilst maintaining the original particle size distribution. This should balance the energy need of the agitation mechanism with other factors such as quantity of extra chemicals needed or additional processing time. To investigate how these factors can be optimised, whilst maintaining the particle size distribution, two aims were defined:

- Investigate how medium energy mechanical shakers and high energy sonication can be used to store and redisperse particles.
- Determine if washing of SiO₂ nanoparticles allows low energy manual shaking to be used.

5.4.1 Methodologies for recovering the particle size distribution

Before beginning this work, it was necessary to define several particle agitation methods. Since this work calls for a reliable and efficient processing method, the lowest energy, and hence simplest, system possible was aimed for. For example, identical particles that could be dispersed with a manual shake would meet this criteria more than those which required sonication. These methods are seen in Table 15.

Table 15: Definition of the energy used in each redispersion method. An ideal nanoparticle suspension will require as little energy as possible to redisperse the sedimented particles.

Energy	Agitation Method
None	No agitation
Low	Manual shaking with up and down being 1 count
Medium	Mechanical shaking at 250 RPM
High	Sonication in 1-second on-off segments at 120 W

This study began by considering the use of medium energy mechanical shaking and high energy sonication. Four standard SiO₂ batches were used in this study. A summary of the samples used in this work can be found in Table 16. All samples were produced and then dispersed in ethanol using high energy sonication for 20 minutes with a UP200s sonicator (Hielscher, Germany). Sample 1, seen above, and Sample 2 were then stored statically in a centrifuge tube. Unlike Sample 1, Sample 2 underwent high energy sonication before analysis. Sample 3 & 4 were stored using a constant medium energy mechanical shaker (Heathrow Scientific, UK). Sample 3 was analysed directly whilst Sample 4 underwent high energy sonication before analysis. These samples allowed the effects of the medium and high energy methods to be evaluated.

It was theorised that the cleaning of particles could prevent agglomeration and hence allow low energy dispersion mechanisms to be used. A standard batch is normally centrifuged out of the residual reactants and redispersed in ethanol; it is therefore considered un-washed. A washed sample was

produced by dispersing the product in acetone. Standard batch SiO₂ was dispersed in acetone using high energy sonication for 20 minutes and centrifuged out for 20 minutes at 7000 RPM. This process was repeated 3 times before redispersing half the sample in ethanol and the remainder in H₂O using high energy sonication for 20 minutes. A DLS instrument was used to test the samples periodically. All the samples were redispersed before every single analysis using 5 low energy manual shakes. To test stability over a longer time, these were also left for 3 weeks and then tested.

Table 16: The experiments used to investigate the optimal storage method for the nanoparticles.

Sample	Solution	Cleaning	Storage	Pre-testing treatment
1	Ethanol	Unclean	Static	-
2	Ethanol	Unclean	Static	Sonication (20 mins)
3	Ethanol	Unclean	Mechanical Shaker	-
4	Ethanol	Unclean	Mechanical Shaker	Sonication (20 mins)
5	Ethanol or H ₂ O	Clean	Static	Manual Shaking (5x)
6	Ethanol or H ₂ O	Unclean	Static	Manual Shaking (5x)

5.4.2 Results

From DLS results, seen in Figure 40a, it is possible to examine the effect of time on μ and σ for Sample 2, 3 & 4. It is shown that, initially, all samples have a $\mu > 100$ nm with variation likely being due to agglomeration during the centrifuging step that is not effectively broken up by sonication. As time proceeds there is a noticeable decrease in particle size for samples that undergo high energy sonication before analysis. There is initially a steep decrease in μ until 28 days after which both mechanically shaken and static samples become constant. Addition of a horizontal line of best fit reveals these values to be 81 nm and 77 nm, respectively. A similar trend is seen in σ with constant values of 23 nm and 27 nm achieved after 20 days. Samples stored on the mechanical shaker without high energy sonication before analysis show a different behaviour. A constant value is reached for both μ and σ at 0 days with no significant change with time. This is seen to be 119 nm and 33 nm, respectively.

Additional observations can be drawn from Figures 40a & 40b. A significant gap in testing between 75 days and 110 days occurred due to equipment unavailability. This separates the graphs into two distinct regions; the differences between these can be used to draw further conclusions on stability. It can be seen that there is no significant difference between the μ and σ before and after the analysis pause for all samples.

The effect of cleaning the SiO₂ particles is summarised in Figure 41. It can be seen that there is no significant change in particle size distribution with time when cleaned particles are dispersed in H₂O. This result is especially encouraging as, after the testing pause at 28 days, there is no significant change at 55 days. A similar observation is initially seen when SiO₂ is dispersed in ethanol. However, an increase in μ and σ is seen after the testing pause. It was noted that, despite this result, there was

no sedimentation in the sample after redispersion.

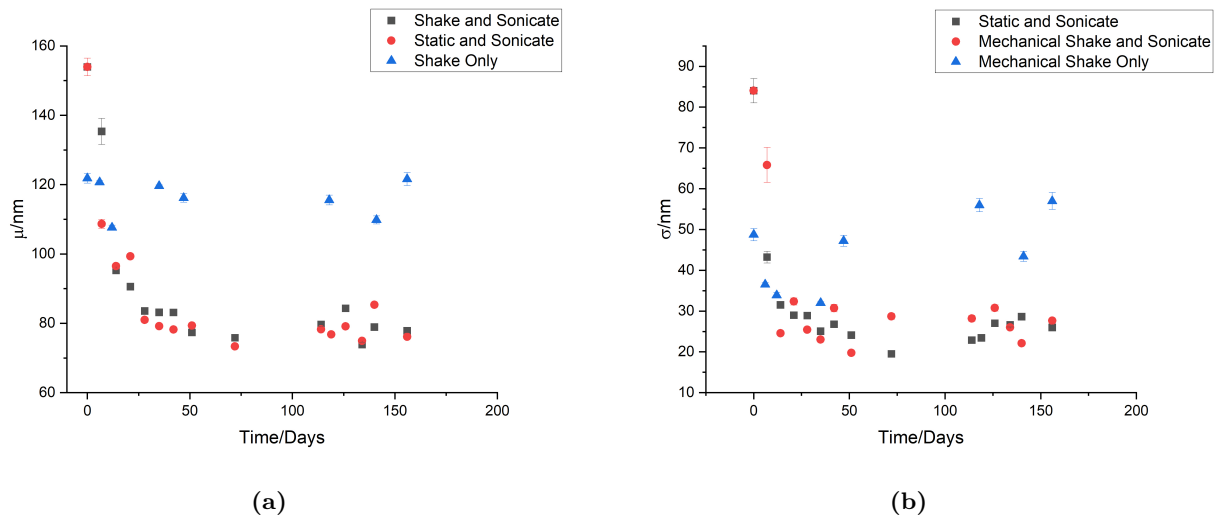


Figure 40: Effect of time on a) μ and b) σ on three standard samples stored stationary and sonicated before analysis (Sample 2), stored on a mechanical shaker and sonicated before analysis (Sample 3) and stored on a mechanical shaker and not sonicated before analysis (Sample 4). Error bars indicate the standard error of the mean, taken from multiple DLS spectra.

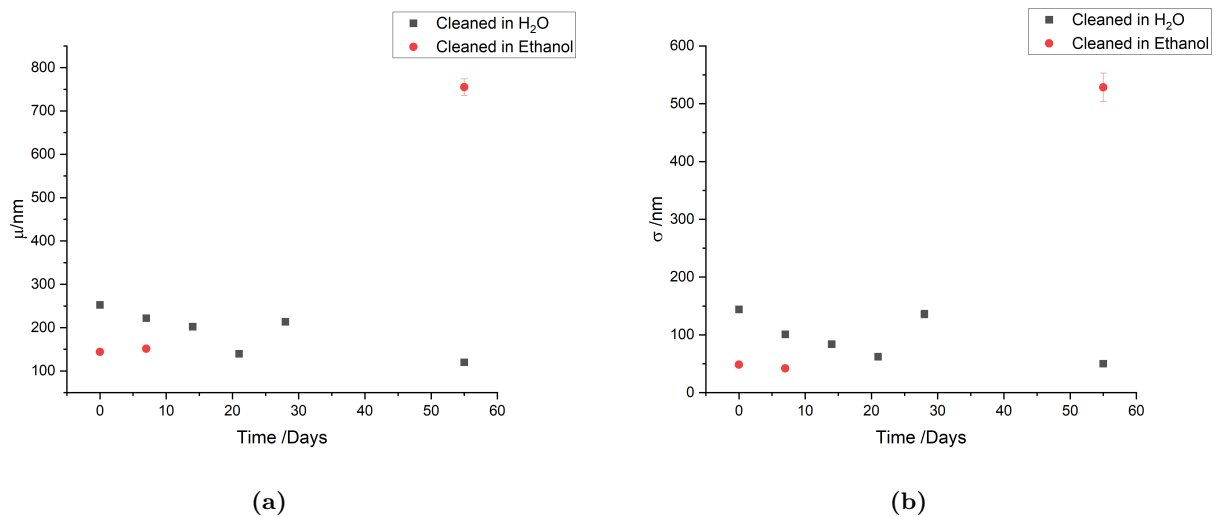


Figure 41: Graph showing the effect of time on the a) μ and b) σ for cleaned samples stored in ethanol and H_2O . These are redispersed using a low energy manual shake before each analysis.

5.4.3 Discussion

During the microemulsion process it is highly likely that agglomeration will occur. This is unlikely to be during the reaction itself, since contact between particles would lead to bond formation and a larger particle forming. During the subsequent microemulsion break and centrifuge steps, agglomeration can easily occur and is in fact favourable. Agglomeration reduces the loss of SiO_2 when transferred between flasks hence increasing yield. The formation of the SiO_2 sediment over a short time shows that agglomeration occurs within the sample. The fact that low energy manual shaking is unable to break up these in a standard batch poses a severe challenge. The initial sonication step serves to break up agglomerates and regain primary particles with sizes around 100 nm. The variation of initial μ

values shows that the effectiveness of this step varies; although the samples are sonicated at the same amplitude for the same amount of time, slight differences in probe positioning could make a difference. Beyond this point, significant differences are seen between samples stored on a mechanical shaker only and those sonicated regularly.

Samples that undergo high energy sonication before analysis show a decrease of μ and σ over time to a constant. This appears independent to their storage conditions. The effect of time cannot be clearly linked to this decrease in μ instead the results can be linked to a number of sequential sonications. The decrease of μ with sonications indicates that hard agglomerates are being broken up over time until primary particles remain. It is noted that resedimentation does still occur when the sample is stored statically, suggesting that agglomerates reform. Beyond 28 days, only one sonication is needed to break these up, indicating that the agglomerates are softer than those broken up over the first 28 days. The stability of the particles over the 35 day analysis gap verifies these hypotheses. It could therefore be said that 5 sonications are needed to break up some hard agglomerates after which softer agglomerates reform. These are considered softer as they only require 1 sonication to redisperse regardless of the gap between such sonications.

Sedimentation does not occur when a mechanical shaker is used, demonstrating that the mechanical shaker alone is enough to prevent reagglomeration. However, it does not reduce the size of the particles that are present. When a mechanical shaker is used alone, μ and σ are maintained at a greater value than when regular sonication is used. This demonstrates that the hard agglomerates that are initially present cannot be broken up by this medium energy technique. This confirms that only a high energy technique can break up the initial hard agglomerates.

When clean particles are used, a low energy manual shake is able to redisperse any sedimented particles effectively. This indicates that agglomerates that form are soft in nature and the sizes of these do not change significantly over time. This also shows that, whilst the particles are not completely stable in H_2O , they do not form any new hard agglomerates. Similar stability is seen when ethanol is used but μ does grow when the particles are left undisturbed. Harder agglomerates may be forming that can not be dispersed by low energy methods. The dispersion mechanism is hence not as effective in ethanol and at least some agitation is required, albeit only occasionally. Both these observations show that left over reactants and microemulsion components lead to sediments which contain harder agglomerates than those in sediments of clean particles. It is noted that in ethanol the μ value never achieves the smaller value of 80 nm seen when high energy sonication is regularly used. The SiO_2 only undergoes 3 sonications during cleaning which may not be enough to break up initial hard agglomerates. In this case, the clean particles can effectively replace the medium energy mechanical shaking, with smaller particle sizes achievable if 5 sonications are initially used.

In the literature, nanoparticles are often ‘cleaned’ after a reaction to remove excess reactants by sequentially dispersing particles in a solvent, centrifuging and repeating a predetermined number of times. The actual effect of cleaning on the surface of the nanoparticles is not well investigated in the literature and it is likely completed as a precaution to avoid any potential issues that may result from a change in surface chemistry. Work by Spina *et al* shows that, in the case of gold nanoparticles, a significant difference in surface chemistry occurs when particles are not ‘cleaned’ [160]. Two potential effects could be affecting unclean particles in this work. Excess reagents or solvent could adsorb onto the SiO₂ and affect its surface charge. SiO₂ particles will have OH groups on the surface when in contact with H₂O. These can dissociate to form O⁻ species; this leads to repulsion but may be affected by adsorbed species or pH. Alternatively, the left over reactants or microemulsion components could reduce repulsion between SiO₂ by bridging. Various components of the microemulsion, such as Triton X-100 and hexanol, have polar and non polar groups. These could interact with both with the surface and adsorbed species on other particles, forming a bridge. Determining this mechanism is complex due to the number of potential species involved and is hence beyond the purview of this work.

5.4.4 Conclusion

The storage of SiO₂ poses some challenges. It is noted that initially the process results in hard agglomerates that require sequential, high energy sonication to break up. However, once this is done, only limited sonication is needed to redisperse agglomerates that reform. Mechanical shaking, used alongside sonication, could be employed to achieve this, although it cannot break up hard agglomerates alone. The cleaning of particles provides a path to stability, with only a low energy, manual shake needed to redisperse the resulting particles.

From this, two potential storage solutions could be proposed. The particles could be sequentially sonicated until a plateau of μ is reached, after which they would be stored on a mechanical shaker to prevent reagglomeration. Alternatively, the particles could be cleaned and stored in H₂O or ethanol, with a low energy manual shake needed before use. Whilst the former uses higher energy methods, the latter requires an additional cleaning solvent. These methods are therefore equal in their reliability of particle size, with the exact method used depending on external factors such as chemical availability. In this work, the former method was selected.

5.5 Investigating ways to tailor particle size

To achieve a range of composite microstructures, the precursor powders must be tailored to include a range of particle sizes. As reported in the literature review (Chapter 2), the concentration of base, ratio of oil:water, type of surfactant and co-surfactant and concentration of TEOS is known to have an effect on the particle size distribution of the produced SiO₂. An increase in the concentration of base

is seen to decrease particle size by increasing the hydrolysis of TEOS to SiO_4 , which in turn forms SiO_2 particles [84]. This increases particle nucleation due to increased initial monomer concentrations. The selection of surfactant and co-surfactant was crucial as identified in the literature and can be used to both increase and decrease particle size by changing micelle number and rigidity [84, 86, 94]. The ratio of oil:water was also seen to cause the same effect[161]. The concentration of TEOS however did not cause significant size changes [84]. In this work it was key to design experiments that could determine the effect of changing reactant ratios on the particles and how these changes could be used to produce a range of SiO_2 ceramic precursors. To do this, two aims were identified:

- Determine if changing the concentration of TEOS affects particle size distribution.
- Examine the extent to which changing the concentration of the catalyst, ammonia solution, affects the particle size distribution.

5.5.1 Methodologies for tailoring particle size

To investigate how the SiO_2 particle size distribution is affected by changing the concentration of reactants, several experiments were conducted using the ratios outlined previously. A full list of experiments are found in Table 17. To complete full analysis of these results, several comparisons have been made. First, the effect of doubling the amount of TEOS compared to the standard will be analysed. Hence Ratio Set A will be compared to Ratio Set B across several volumes. Next, the effect of increasing the amount of catalyst will be analysed. The effect of doubling the volume of NH_4OH added will be considered and hence ratio A will be compared to ratio C. The effect of tripling the amount of NH_4OH added will also be considered, hence Ratio Set A will be compared to ratio D.

Table 17: Description of the experiments used to understand how the particle size distribution can be tailored using different reactant ratios. Ratio Set A, B, C and D are defined in Chapter 4 of this thesis.

Ratio Set	Approx Total Volume /ml
A	11.5
A	23.1
A	46.1
A	92.3
A	184.6
B	11.6
B	23.3
B	46.5
B	93.1
B	184.6
C	23.2
D	46.1

5.5.2 Results

This section considers the effect of varying chemical ratios on μ and σ . For the most part it is appropriate to do this using the DLS technique during which the particles' Brownian motion are used to determine key values. However, as stated earlier in this thesis, there is a limitation to this technique of approximately 10 μm . Particle sizes larger than this will trigger an alert from the device with fluctuations in the correlation function being used to determine their presence. Where this has presented, or is suspected based on a hypothesis for the experiment, SEM analysis will be used alongside DLS to identify larger primary particles. In the event that several repeats of an experiment show significantly different results, these will be reported individually.

Increasing the concentration of TEOS

Analysis of Table 18 shows the effect of increasing the concentration of TEOS ([TEOS]) on μ and σ . It can be seen that doubling the [TEOS] across various scales leads to limited change in particle size. In the majority of cases, it can be said that there is likely no significant difference between μ and σ , although ones do exist at total volumes of 92.3 ml and 23.1 ml with the former showing a decrease with [TEOS] and the other the opposite.

Table 18: Analysis of μ and σ values for samples where the relative concentration of TEOS ([TEOS]) increases from 1 to 2. Ratio Set A and B are defined in Chapter 4 of this thesis

Approx Total Volume/ml	Relative [TEOS]			
	1 (A)		2 (B)	
	μ /nm	sigma /nm	μ /nm	sigma /nm
11.5	65.1 $\pm$ 0.34	22.2 $\pm$ 0.4	63.3 $\pm$ 0.3	20.5 $\pm$ 0.3
23.1	123.1 $\pm$ 1.4	50.3 $\pm$ 1.6	95.1 $\pm$ 0.6	28.2 $\pm$ 0.6
46.1	113.3 $\pm$ 0.8	43.8 $\pm$ 0.8	111.6 $\pm$ 1.8	41.5 $\pm$ 2.0
92.3	153.6 $\pm$ 2.0	79.8 $\pm$ 2.3	224.3 $\pm$ 2.3	71.2 $\pm$ 2.4
184.6	142.0 $\pm$ 1.6	70.3 $\pm$ 1.8	157.2 $\pm$ 1.6	68.2 $\pm$ 1.8

Increasing the concentration of catalyst

Before completing a comparison between Ratio Sets A, C and D, it is first necessary to consider the data produced from Ratio Set C. Figure 42 shows the change in μ and σ when $[\text{NH}_4\text{OH}]$ is varied. The data is presented as individual DLS runs, with the colour indicating the height of the peak at μ . If multiple peaks are present, each peak is analysed individually and μ is the mean of that peak. This is indicated by an asterisk.

Ratio Set C shows increases in μ and σ compared to Ratio Set A. The data shown here indicates an individual DLS run, of which 3 are completed per experimental repeat. The run-to-run variation further verifies that significant changes in μ and σ have occurred. It is crucial to discuss each run individually here as their differences may indicate inhomogeneity in the sample. Additionally, there are several instances of multi-peak distributions which are indicated by an asterisk. For Ratio Set C,

additional peaks that are similar in height to the main peak occur at around 2000 nm. Due to this observation, SEM analyses of the samples were also conducted and these can be seen in Figures 43a 43b. Figure 43a shows a series of interconnected particles, this is where primary particles form necks to other particles hence increasing their sizes. The series of interconnected particles are around 2 μm across, significantly larger than those seen in Ratio Set A. This is supported by Figure 43b which shows particles of around 1 μm in size. It is noted that singular primary particles of around 100 nm can be seen in both samples in isolated areas. This supports the results seen from DLS data, which reports some particles with similar sizes to Ratio Set A.

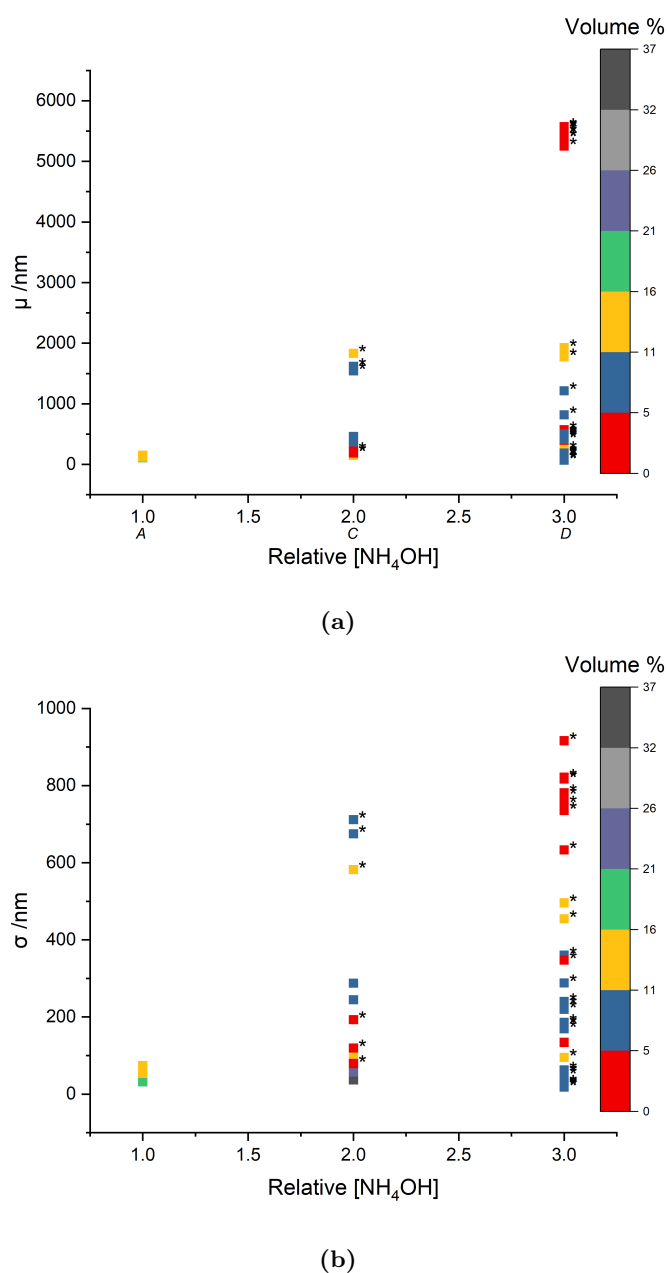


Figure 42: Graphs showing the variation of a) μ and b) σ for a range of $[\text{NH}_4\text{OH}]$. Each point indicates an individual DLS run. An asterisk indicates a peak resulting from a run with multiple peaks. Here, each peak is reported and the μ value becomes the mean of that peak.

Similar to Ratio Set C, Ratio Set D's results first need to be analysed individually before comparing

to those from Ratio Set A. Figure 42 shows the multi-peak nature of the particle size distribution when Ratio Set D is used. The graph can be roughly split into three regions. The low particle size region has peaks with a μ value of around 100 nm, a volume % at μ of 5-12% and a narrow σ of around 50 nm, as would be expected by Ratio A. Moving up from this there is an increase in μ to between 800 nm and 2 μ m, a volume % of 5-14% and σ of between 100 nm and 500 nm. The final region shows significantly larger particles with μ of 5-6 μ m and an increased σ of between 600 nm and 900 nm. However, the volume % at μ is reduced to <2%. It is noted that the majority of runs have a multi-peak distribution.

Ratio Set D shows that the majority of peaks with the largest volume % occur at higher μ than those in Ratio Set C. There is a corresponding increase in the range of σ for these peaks as the concentration of catalyst is increased. In both cases, a single value is not noted and instead the data is seen as a range. Additionally, Ratio D shows μ values greater than 4000 nm, a fact not seen in Ratio Set C. Ratio Set D was also investigated using SEM to gain a visual representation of the particle size distribution. Figure 43c & 43d show similar results to Ratio Set C. A range of larger particles is observed with a significant amount of necking between smaller particles. Alongside the larger particles, smaller particles below 400 nm remain.

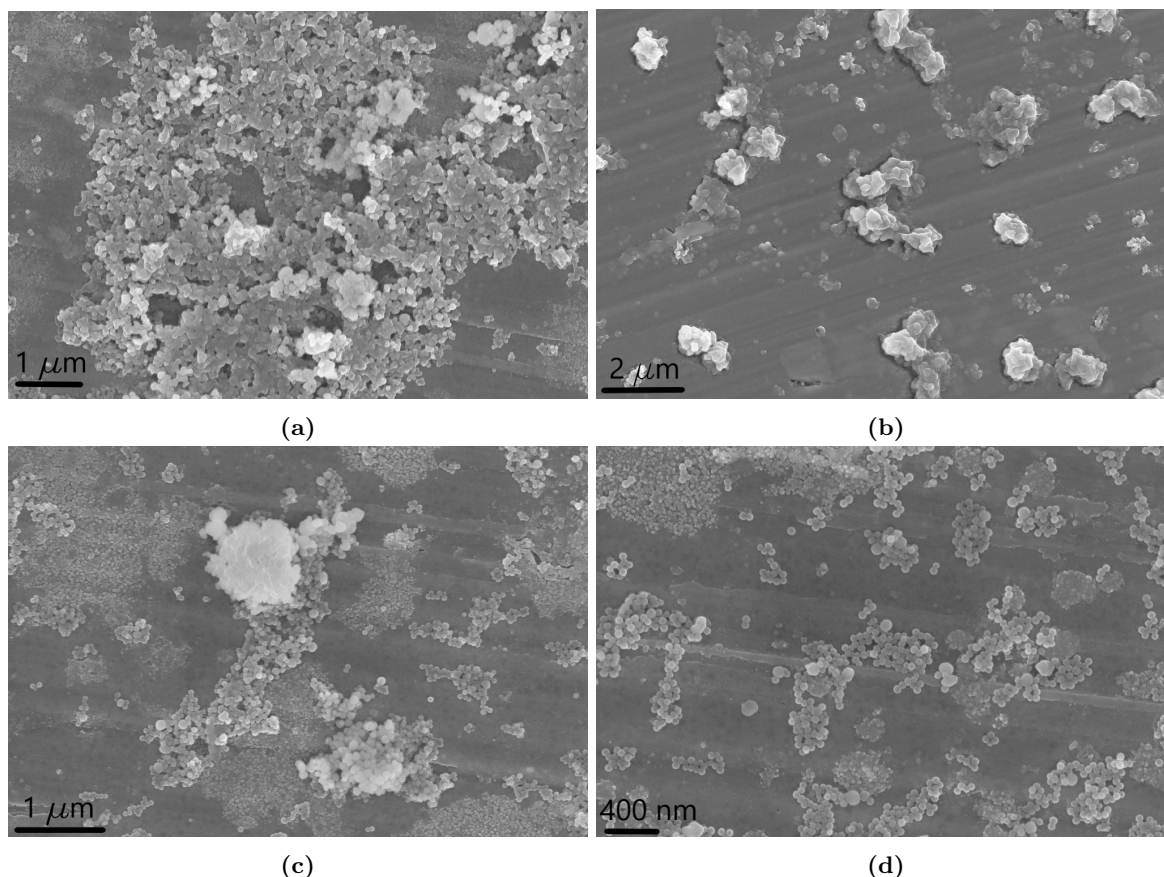


Figure 43: SEM micrographs showing the particles for a & b) Ratio C and c & d) Ratio D.

5.5.3 Discussion

Increasing the [TEOS] could have an effect on the particle size distribution, when compared to Ratio Set A. The TEOS is the limiting reagent in the SiO_2 reaction, as can be shown by molar calculations. An increase in the [TEOS] by a factor of 2 does not push it into excess. Therefore, the greater availability of TEOS should lead to more SiO_4 monomer formation, which will react to form SiO_2 . This could lead to an increase in μ by growing all the particles equally, or increase the number of nuclei hence leading to more and smaller particles. These effects could also occur together to change the σ . Arrigada *et al* agree with these hypotheses and observe the effects in a microemulsion using a nonylphenyl ether surfactant (NP5) [93]. However, neither of these two effects are seen to occur in this work or that by Bagwe *et al* [84]. This indicates that there is a limit to the amount of TEOS that can partition to the surface of the micelles, react with SiO_4 , absorb into the water phase and react to form SiO_2 . Whilst the TEOS is not in excess from a molar ratio standpoint, if it is unable to react then it will not affect the particle size distribution.

There is a clear link between increasing the concentration of the catalyst ($[\text{NH}_4\text{OH}]$) and the increases in μ and σ . The catalyst controls the rate of TEOS hydrolysis in the reaction and hence can affect the particle size distribution. The increase in μ demonstrates that faster hydrolysis leads to greater particle growth. The run-to-run variation suggests that this occurs inhomogeneously with some particles growing to micron sizes whilst others remain below 400 nm. The increased variability in σ would support this theory. However, as there is faster hydrolysis within the microemulsion, it would be expected that water droplets will rapidly react when TEOS contacts the surface. This would lead to a greater number of droplets containing significant SiO_4 monomers to produce an SiO_2 nuclei. The result is a larger number of smaller particles. This is seen in the literature when the amount of catalyst is varied from 0.5 wt%-2 wt% when Triton X-100 is used. A similar observation was seen when NP5 was used, however it was noted that there was an increase in particle size above a threshold concentration of catalyst [93].

One explanation could be the depolymerisation of SiO_2 in alkali conditions. The SiO_2 breaks down, either forming SiO^- groups or reforming SiO_4 [162]. If this is occurring it could affect the particle size. The local depolymerisation would produce a more reactive particle surface which could re-react to form Si-O-Si bonds with other particles. This would lead to necking between particles as was seen here. The rate of depolymerisation varies with concentration of alkali, hence the critical catalyst concentration to increase particle size could be linked to a critical rate of depolymerisation. The observations in this work indicate that the alkali concentrations used here are exceeding this value. However, the kinetic of such reactions in the conditions of a microemulsion is complex and further study would be needed to verify this hypothesis.

5.5.4 Conclusion

The standard Ratio Set A is able to produce a robust set of nanoparticles with a μ of around 100 nm. It would be expected that the particle size distribution could be affected by a change in [TEOS]. This is not seen to be the case and is linked to a local excess of TEOS. This effect may be controlled by alterations to the surfactant or surfactant:water ratio. An increase in the $[\text{NH}_4\text{OH}]$ is known to have a varying effect on the particle size distribution. In this work, it is seen to increase the μ and σ values significantly suggesting that $[\text{NH}_4\text{OH}]$ is above a critical concentration. This was explained as a balance between increased nucleation, which decreases μ , and depolymerisation, which could increase μ . In this case, the latter is more prevalent. It is unclear what the exact critical concentration is. From this, it can be said that only changes in $[\text{NH}_4\text{OH}]$ can be used to tailor SiO_2 particle size and hence the size of SiC in a resulting ceramic powder.

5.6 Investigating the SiO_2 to SiC reaction

Conversion of SiO_2 to SiC is a key component of this work. The use of ceramic precursors was considered to give a greater flexibility to the composite production process by providing size and morphology tailoring. It was therefore important to understand how the SiO_2 produced would react with a standard carbon source. A wide variety of carbon sources are available such as tartaric acid, carbon black and various resins. Here, phenolic resin was used as a carbon source. This has a number of advantages: it is dispersed in MEK before use and hence can be well dispersed amongst precursor particles; it has a high carbon yield, does not foam and can be cured before pyrolysis to produce a green body. This work focused on using phenolic resin for its dispersion and yield properties as shaping of pre-ceramic parts was not investigated. The literature has provided some insight into the reactions that occur between the SiO_2 and carbon. SiO_2 exists as an oxide layer on commercial SiC and this has been the motivation for investigation. However, limited work has looked at turning SiO_2 , produced by a microemulsion method, into a SiC powder.

Alongside investigating the reactions that occur with SiO_2 , it was also important to determine how carbon additions affect the final composition. It has been shown that graphite at grain boundaries and boron doping can affect the extent of B_4C amorphisation. Both of these can be a result when too much or too little carbon is present respectively. Factors such as gas flow and sample volume can also affect how the reaction occurs. Therefore, additional experiments were designed to determine how the final composition and crystallography are affected by carbon composition and reaction conditions. These effects led to the following objectives:

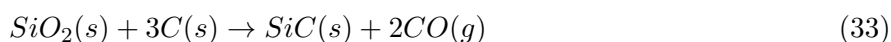
- Determine the crystallography and composition of powder produced by reacting microemulsion SiO_2 with a carbon source.

- Examine if the amount of carbon mixed with microemulsion SiO_2 changes the final composition and crystallography of the powder after heat treatment.
- Determine if commercial and microemulsion SiO_2 undergo similar reactions during heat treatment and how these affect the final crystallography and composition of the powder.
- Determine if the amount of B_4C added to the composite powder affects reactions between SiO_2 and SiC .
- Investigate if using a tube furnace to undertake the reaction affects the final composition and crystallography of the powder.

5.6.1 Methodologies for understanding the SiO_2 to SiC reaction

Commercial SiO_2 powder was used alongside in-house produced, standard batch SiO_2 . In-house SiO_2 nanoparticles were centrifuged from their storage solution and then immediately dispersed in MEK using high energy sonication. Commercial dry SiO_2 was dispersed in MEK in a similar manner. Where necessary, phenolic resin was then added to MEK along with commercial B_4C powder and ball milled for 12 hours using SiN milling media. In this work, a molar $\text{C}:\text{SiO}_2$ ratio was defined for each powder. Alongside this, an additional 2 wt% carbon was added as a sintering aid, which would be needed in a final composite powder. Only Method I (found in section 4.1) for determining the yield of microemulsion SiO_2 was available during this work.

Initially, a $\text{SiO}_2\text{-C}$ powder was prepared to determine the nature of the reactions and the final crystallography that results when no B_4C is present. This was labelled Sample 1 and is summarised in Table 19. The yield of SiO_2 was determined using Method I as Method II was developed later. The quantity of phenolic resin to be added was calculated using its TGA and carbon content characteristics. Enough carbon is provided for the reaction to complete at the desired $\text{C}:\text{SiO}_2$ ratio. For this sample it was assumed that the reaction between SiO_2 and C proceeds as per Equation 33 with a $\text{C}:\text{SiO}_2$ of 3:1. This ratio excludes the carbon which is added as a sintering aid. A composite powder was also prepared using this ratio (Sample 2).



To understand how the quantity of carbon used affects the final composition, Sample 3 was prepared. The ratio of $\text{C}:\text{SiO}_2$ was reduced to 2:1. It is expected, in a carbon rich environment, that the reaction would still complete, producing the target composition. This could either occur by using the additional C added as a sintering aid, or by gaining C from B_4C . The results of Sample 2 & 3 could then be compared.

Table 19: Definition of Samples 1-7 used to understand the formation of SiC from SiO_2 based nanopowders.

Sample	Target Composition ($\text{B}_4\text{C}:\text{SiC}:\text{C}$)	Silica source	Molar Ratio $\text{C}:\text{SiO}_2$	Heat treatment
1	00:98:02	Microemulsion	3:1	TGA
2	88:10:02	Microemulsion	3:1	TGA
3	88:10:02	Microemulsion	2:1	TGA
4	88:10:02	Commercial	2:1	TGA and Furnace
5	93:5:02	Commercial	2:1	TGA
6	88:10:02	Commercial	2:1	TGA
7	83:15:02	Commercial	2:1	TGA

Commercial and microemulsion SiO_2 have similar particle sizes and morphologies. However, the former exists as a dry powder whilst the latter can be dispersed directly from a storage solution. These differences could affect the homogeneity of the powder, and hence its final composition and crystallography. Therefore, commercial and microemulsion SiO_2 composites were produced using a 2:1 ($\text{C}:\text{SiO}_2$) ratio. From this Samples 3 & 4 were compared.

B_4C is a key component of the composite powder. Alongside the phenolic resin, it can also act as a carbon source but is larger in size and is harder to disperse. Samples 4-6 were prepared to determine if the $\text{B}_4\text{C}:\text{SiC}$ target composition affects the final carbon content and crystallography of the powder.

The atmosphere and gas flow within a reaction vessel can affect the extent and types of reactions SiO_2 undertakes. The TGA environment, using an alumina furnace, is oxygen rich in nature resulting in an oxidising atmosphere with a high gas flow. To predict how the powders might react in a hot press, Sample 4 was also reacted in a tube furnace under argon gas. An alumina crucible lined with graphite paper was used to simulate the carbon fixtures, which provide a reducing atmosphere in the hot press.

5.6.2 Results

Investigating the production of SiC from SiO_2 and carbon

When Sample 1 was heat treated in a TGA environment, it can be seen from Figure 44 that a crystalline phase forms from a fully amorphous one. The crystalline phase in question can be indexed as $\beta\text{-SiC}$ (ICDD 01-074-2307) with an additional shoulder peak indicating the presence of some stacking faults [163]. Figure 45 shows that, during the heat treatment, 3 mass losses occur at 100°C-200 °C, 400 °C- 1600 °C . The first derivative of the relative mass loss, dm/dt , provides further insight as seen in Figure 45b. The mass losses are accompanied by an exothermic process at 100 °C-200 °C a small exothermic process at 400 °C followed by an exothermic process above 1400 °C. Additionally there is another exothermic process at 700 °C, a large exothermic process between 1000 °C and 1250 °C which do not initiate a mass loss. The initial mass of the sample was 0.076 g and the final mass of the sample was 0.019 g.

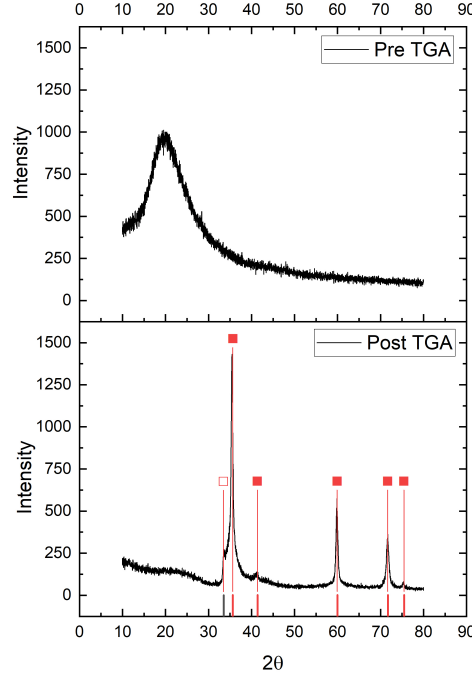


Figure 44: XRD pattern showing the change in crystallography with heat treatment for Sample 1. A red ■ denotes the peaks for β -SiC and red □ a slight peak caused by stacking faults in the (111) plane.

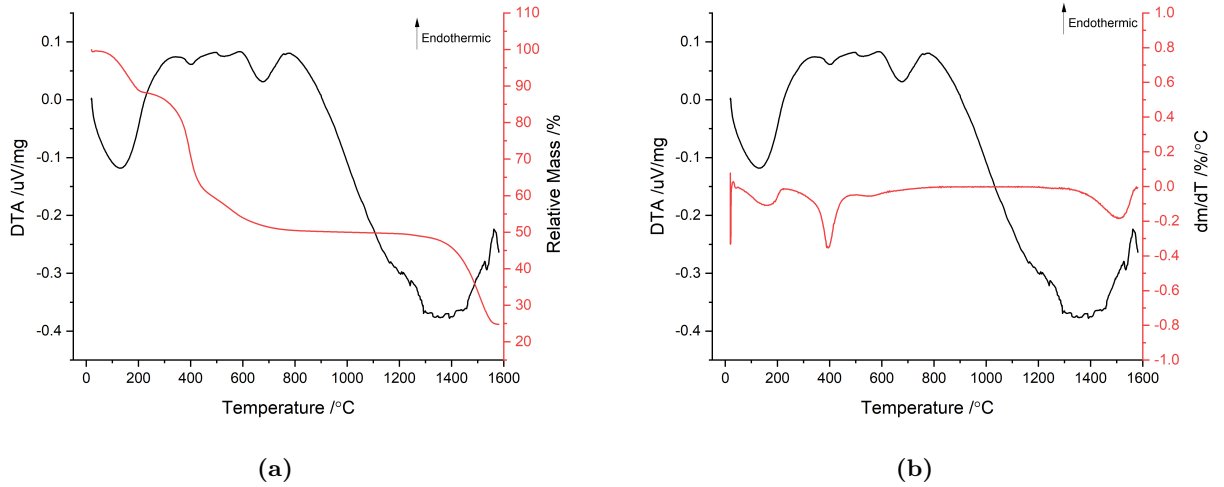


Figure 45: DTA-TGA data for Sample 1. a) Graph showing the variation in DTA and mass with temperature. b) Graph showing the variation in DTA and dm/dT with temperature. It is noted that an upward peak in the DTA is endothermic whilst a downward peak is exothermic.

Investigating the effect of C:SiO₂ ratio

By comparing Sample 2 & 3 it is possible to deduce how changing the carbon content of the sample will affect the final composite. Figure 46 shows the change in crystal structure within the samples. In both cases the sample initially contains crystalline B_4C along with amorphous SiO_2 and carbon. After heat treatment, β -SiC is formed with both samples showing some stacking faults. Sample 2 also contains some free carbon. The DTA-TGA data found in Figure 47 can provide insight into the reaction process. Sample 2 and 3 show similar DTA response to Sample 1; a small exothermic peak

is seen at 400 °C with larger descent from 800 °C and 1410 °C. Sample 2 does differ by having an additional exothermic peak at 100 °C. This is accompanied by a small mass loss. Sample 3 on the other hand has an additional exothermic process between 1490 °C and 1580 °C. The mass loss above 1400 °C is greater in Sample 3 than Sample 2.

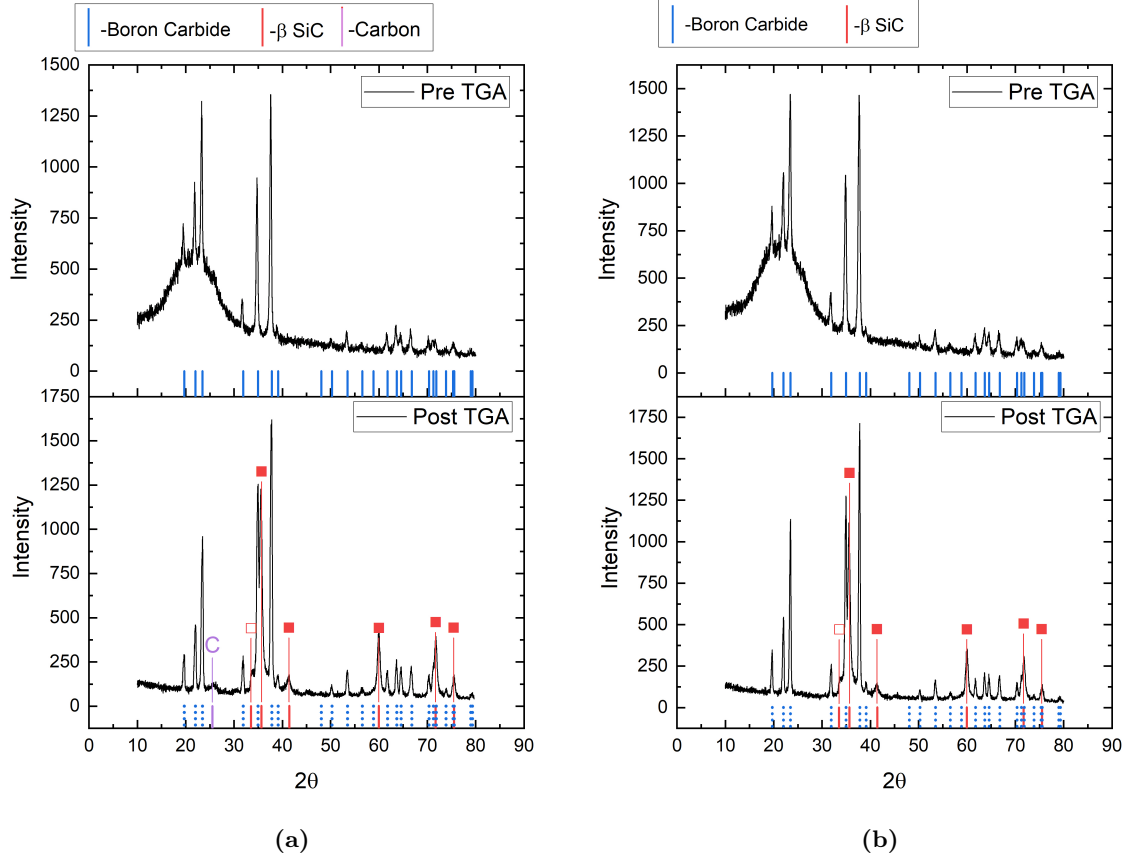


Figure 46: XRD patterns showing the changes in crystallography with heat treatment for a) Sample 2 and b) Sample 3. Sample 2 uses a 3:1 carbon: SiO_2 ratio whilst Sample 3 uses a 2:1 ratio. A ■ denotes the peaks for β -SiC and □ a slight peak caused by stacking faults in the (111) plane

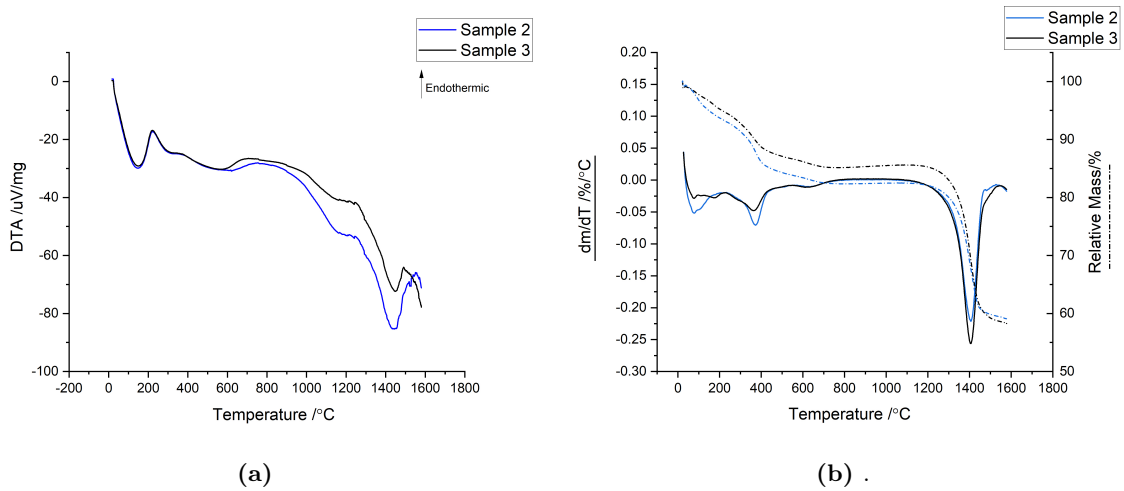


Figure 47: DTA-TGA data for Sample 2 and 3. Sample 2 uses a 3:1 carbon: SiO_2 ratio whilst Sample 3 uses a 2:1 ratio. a) Graph showing the variation in DTA with temperature. b) Graph showing the variation in dm/dt and relative mass with temperature. It is noted that an upward peak in the DTA is endothermic whilst a downward peak is exothermic.

Carbon analysis can provide information on the composition of the sample as seen in Table 20. The difference between initial and target carbon contents for both samples indicates that there is more SiO_2 present in the sample than expected, as the amounts of carbon in B_4C and phenolic resin are well understood. As the SiO_2 does not contain carbon, it reduces the wt% of carbon. This further verifies the difficulty in using Method I to determine the yield of SiO_2 . Despite this, the samples are still different enough to provide useful analysis. It can be seen that Sample 2 has a final carbon content similar to what would be expected whilst Sample 3 is greater than what would be expected.

There are a few points of contradiction within the data seen in Figure 47. The exothermic peak which begins at 800 °C is greater in Sample 2. This is linked to the crystallisation in SiO_2 and verifies that Sample 2 contains more SiO_2 than Sample 3. However, Sample 2 shows a similar mass loss during SiO_2 reduction when compared to Sample 3. Sample 2 has excess carbon at the end of the reaction which confirms that carbon did not limit the reaction; there is also no evidence of SiO_2 in the sample after heat treatment. It can therefore be said that the SiO_2 is fully reduced in Sample 2.

Table 20: Comparison of the carbon contents in Samples 2 and 3 both before and after heat treatment. A target carbon content, based on the target composition, is also reported. Sample 2 uses a 3:1 C: SiO_2 ratio whereas Sample 3 uses a 2:1 C: SiO_2

Sample	Target Composition $\text{B}_4\text{C}:\text{SiC}:\text{C}$	Before C /wt%		After C /wt%	
		Target	Observed	Target	Observed
2	88:10:02	35.8	31.3 ± 0.3	22.3	21.8
3	88:10:02	32.6	30.5 ± 0.2	19.7	20.8

Investigating the use of commercial and microemulsion SiO_2

By comparing Sample 3 and 4 it is possible to determine the effect of using commercial SiO_2 on the final composite powder. Figure 48 shows the formation of crystalline SiC within Sample 4 with a similar structure to Sample 3. This indicates that the source of the SiO_2 does not affect the final powder crystallography. By comparing the intensity of the (111) β - SiC peak located at 35.65 °, and the (104) B_4C peak located at 34.95 ° it can be noted that less SiC has been produced when commercial SiO_2 is used. This is in-line with the assessment that more SiO_2 than expected had been added to Sample 3. This hypothesis is supported by TGA evidence in Figure 49 which shows a much greater mass loss at 1400 °C, when microemulsion SiO_2 is used.

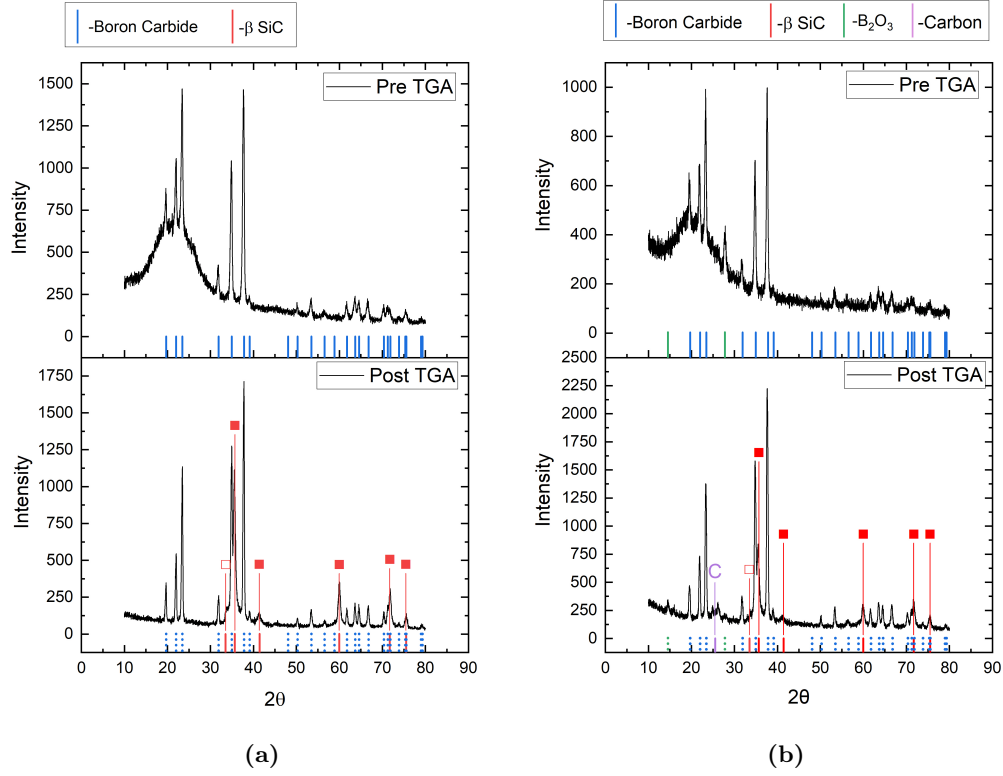


Figure 48: XRD patterns showing the changes in crystallography with heat treatment for a) Sample 3 and b) Sample 4. Sample 3 contains microemulsion SiO_2 whilst Sample 4 uses commercial SiO_2 . A ■ denotes the peaks for β -SiC and □ a slight peak caused by stacking faults in the (111) plane

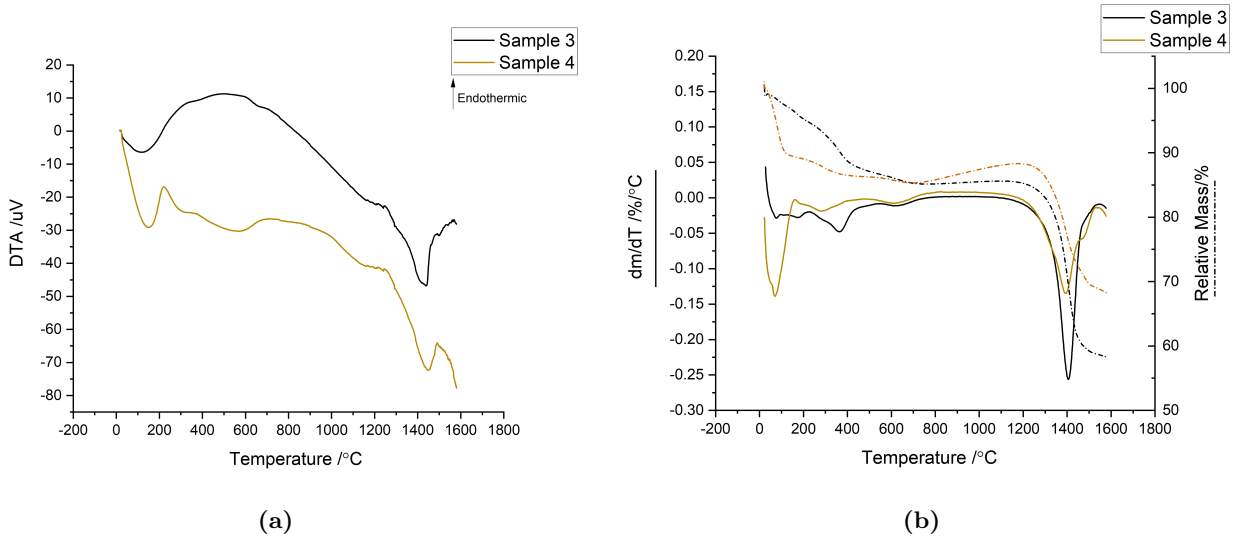


Figure 49: DTA-TGA data for Sample 3 and 4. Sample 3 contains microemulsion SiO_2 whilst Sample 4 uses commercial SiO_2 . a) Graph showing the variation in DTA with temperature. b) Graph showing the variation in dm/dt and relative mass with temperature. It is noted that a upward peak in the DTA is endothermic whilst a downward peak is exothermic.

Investigating the effect of adding B_4C

Changing the composition of the sample has a clear effect on the ratio of phases after heat treatment as seen in Figure 50. When comparing the SiC and B_4C peaks it is noted that their relative ratio decreases as the amount of SiC in the sample increases. All samples show a small presence of carbon

and Sample 6 shows a small indication of B_2O_3 . All three samples show the presence of an additional peak as indicated by the black arrow. Alongside this, a decrease in the (200) β -SiC peak (red arrow) is observed.

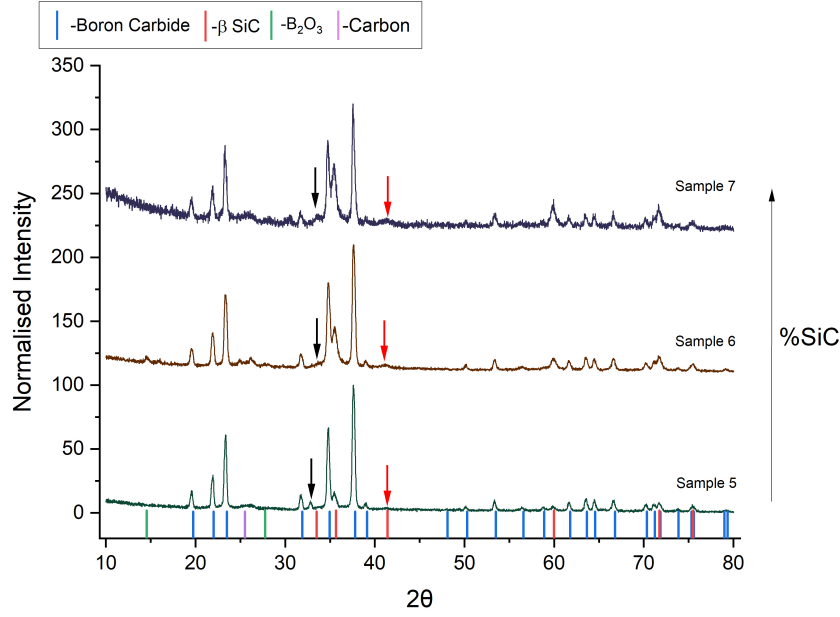


Figure 50: XRD patterns showing the changes in crystallography with heat treatment for Sample 5,6 & 7. These compositions are defined in Table 19 with the quantity of B_4C decreasing from Sample 5 to 7. The black arrow indicates an additional, unidentified peak. The red arrow indicates a change in the (200) peak associated with β -SiC

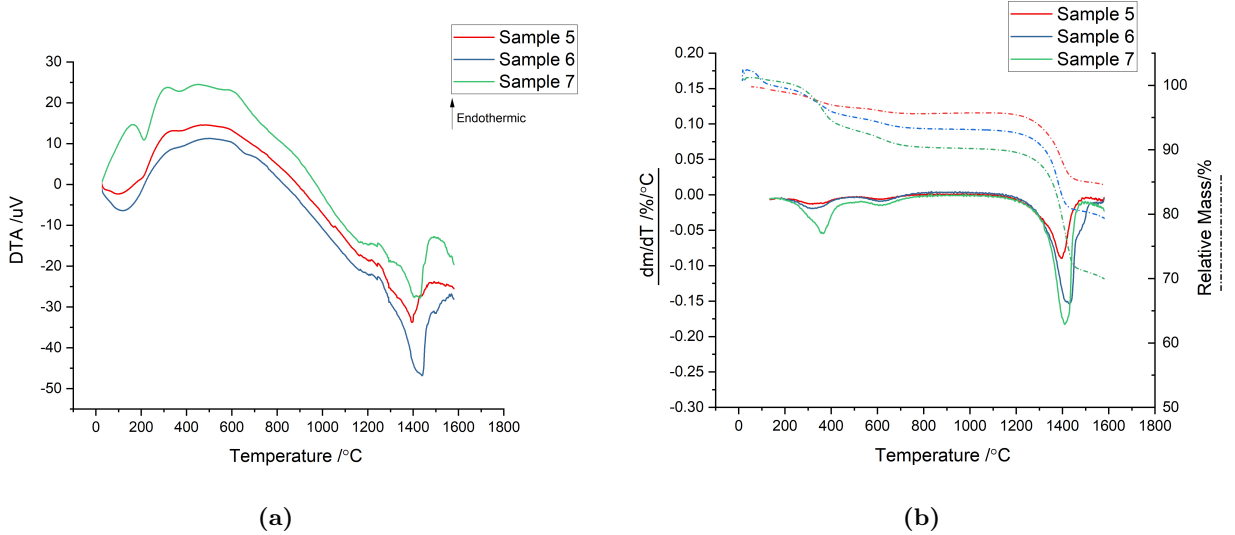


Figure 51: DTA-TGA data for Sample 5,6 & 7. These compositions are defined in Table 19 with the quantity of B_4C decreasing from Sample 5 to 7. a) Graph showing the variation in DTA with temperature. b) Graph showing the variation in dm/dT and relative mass with temperature. It is noted that an upward peak in the DTA is endothermic whilst a downward peak is exothermic.

The TGA data seen in Figure 51b shows increasing mass loss for Sample 5-7 at 400 °C. A similar trend is seen at 1400 °C as would be expected from the increasing amount of SiC produced. Carbon analysis, seen in Table 22, showed that all samples have initial carbon contents similar to those expected by target calculations.

Table 21: Comparison of the observed mass loss during the SiO_2 to SiC reaction for Samples 5,6 and 7. The amount of SiO_2 in the original powder increases from Sample 5 to 7.

Sample	Observed mass loss at 1400 °C /%
5	11.0
6	20.0
7	19.0

Table 22: Comparison of the observed change in carbon content during the SiO_2 to SiC reaction for Samples 5,6 and 7. The amount of SiO_2 in the original powder increases from Sample 5 to 7.

Sample	Before C /wt%		After C /wt%	
	Target	Observed	Target	Observed
5	30.0	29.0±0.4	19.4	24.0±0.9
6	33.1	34.2±0.8	19.6	22.8±2.7
7	35.6	35.5±1.1	19.9	24.3

Investigating the effect of reaction environment

The TGA environment does not accurately represent the environment of a hot press; the use of alumina crucibles and high gas flow are the main source of the differences. This effect is illustrated in Figure 52. A significant amount of free carbon is present in the sample when the sample is processed in the furnace environment. Alongside the (111) plane of graphite at 26.3 °, it is observed that another peak is present at around 42°. It is noted that graphite can have a peak in this region, depending on the exact stacking of the crystal [164]. It was observed that the graphite paper did become flakey during processing and was difficult to fully remove hence introducing carbon contamination. The increase in free carbon is also noted in the carbon analysis data as seen in Table 23.

Table 23: Carbon contents observed after tube furnace and TGA treatment of Sample 4. These can be compared to the carbon content expected from the target composition

Sample	Target Composition $\text{B}_4\text{C}:\text{SiC}:\text{C}$	Before C /wt%		After C /wt%	
		Target	Observed	Target	Observed
4 TGA	88:10:02	32.1	31.1±0.3	19.0	18.8
4 Furnace	88:10:02	32.1	31.1±0.3	19.0	25.7 ± 0.6

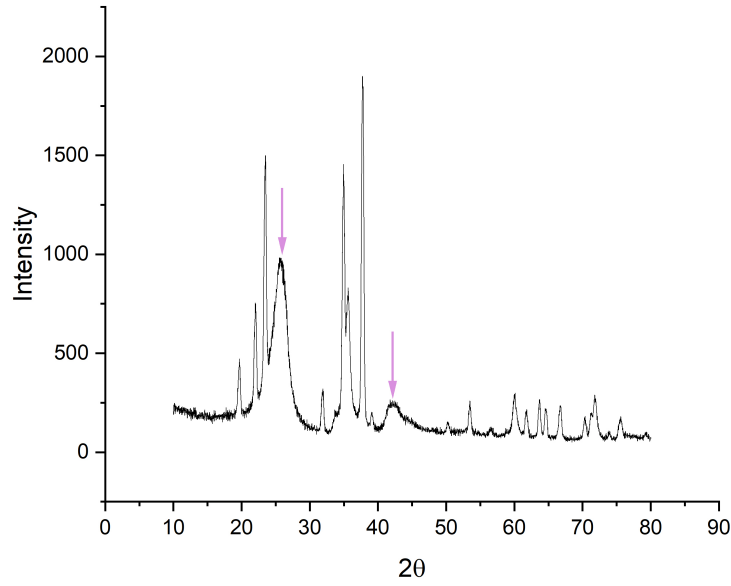


Figure 52: XRD pattern showing the effect of the use of a furnace on the final microstructure. It can be seen that significant extra carbon is included in the sample after processing (pink arrows)

5.6.3 Discussion

Investigating the production of SiC from SiO_2 and carbon

When examining the DTA-TGA data, some mass loss occurs at around 100 °C likely due to loss of residual MEK, which has a boiling point of 85 °C, from the sample. The mass loss at 400 °C can be linked to the pyrolysis of phenolic resin. The exothermic reactions at 700 °C and again at 1000 °C, are linked to the crystallisation of SiO_2 to quartz and cristoballite as seen in commercial SiO_2 [151, 152].

The mass loss, starting at 1330 °C can be linked to the formation of SiC from SiO_2 . This is a broad peak with a maximum mass loss at 1510 °C which is similar to the values suggested in the literature [80, 82, 95]. This temperature range aligns well with the carbothermal reduction of the SiO_2 surface layer on commercial SiC . This experiences two mass losses at 1400 °C and beyond 1470 °C. However, unlike commercial SiC , the carbothermal reduction in this sample is completed by 1580 °C. The dispersion of the SiO_2 throughout the carbon environment means the reaction can happen more efficiently, without the delay that carbon diffusion from within the SiC could introduce. This reduces the temperature and hold time needed to generate sufficient carbon diffusion. For a similar reason, it is noted that, unlike in literature [80, 82], temperatures of above 1600 °C were not needed to form SiC .

The formation of β - SiC from these processes is to be expected from the phase diagram [165]; the lack of pressure or significantly high temperature leads to cubic (β) SiC formation rather than hexago-

nal/rhombohedral (α) SiC formation. Stacking faults are common in SiC and can occur in a variety of forms [163]. The presence of an additional peak, appearing as a shoulder, demonstrates that stacking faults are occurring in the (111) plane. Simulations by Pujar *et al* demonstrated that these are not randomly distributed throughout the sample in this case. A broadening of the (200) plane found at 41.2° is to also be expected. Monitoring the presence of these faults may allow better prediction of their presence in a final sintered composite.

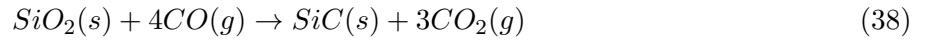
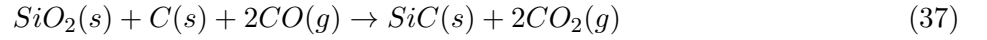
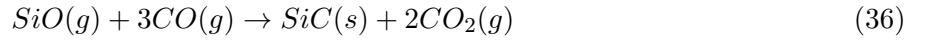
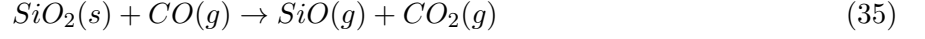
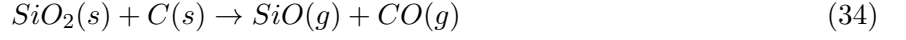
Investigating the effect of $\text{C}:\text{SiO}_2$ ratio

It is important to understand the quantity of free carbon in a final sample. Carbon may increase amorphisation resistance through inclusions at the grain boundaries [22] whilst a loss of carbon, resulting in a boron rich B_4C phase, has a similar effect [24]. Therefore, the carbon content must be well understood, such that its effect on amorphisation can be decoupled from any effect the SiC may have. The comparison of samples containing microemulsion SiO_2 does not appear straight forward. This is hampered by the inaccuracies of Method I for determining yield. It can be theorised that there is more SiO_2 present than was initially expected in Sample 2 (3:1); this explains the drop in initial carbon content as a wt% of the overall sample. Despite there being more SiO_2 than expected, it can be seen that there is no significant effect on the final samples. Free carbon is observed when a 3:1 carbon ratio was used, but this is very small in quantity. It is important to note that the XRD pattern, which is known to shift to the left as boron content increases [149], was not seen to change in this work when compared to the commercial B_4C powder. A shift of greater than 0.25° for the (012) plane would be expected for small degrees of B_4C doping [24]. This suggests that the SiO_2 is not receiving C from the B_4C and hence changing the stoichiometry. These observations confirm that the additional 2 wt% carbon added as a sintering aid is being used to produce SiC .

When considering the DTA-TGA and XRD data, it is clear that different reactions occur when a 2:1 molar ratio is used. There are three main processes that lead to mass loss in this region: CO formation during the formation of SiC (Equation 33), CO formation when surface B_2O_3 is reduced in B_4C and SiO loss during the SiC process. SiO loss is hard to predict as it forms as an intermediate in the SiC reaction. It could be said that, when a 2:1 ratio is used, SiO_2 is being lost as gaseous SiO, which is heavier than CO. Normally, 2 moles of CO are lost during the two step carbothermal reduction, in this case 1 mole of CO and SiO are lost. This results in a similar mass losses despite the 2:1 ratio sample containing less SiO_2 . This could be due to the lower quantity of carbon in the sample; if the likelihood of SiO contacting C and reacting is reduced, it is more likely to be lost.

Alternatively, it is noted that SiO_2 can undergo a range of other reactions. It is widely noted that a disconnect appears between what is thermodynamically possible and what actually occurs within the samples. An example is the production of CO and CO_2 , occurring as per Equation 34 or 35 followed

by 36. This would result in an overall reaction of 37 and 38 respectively. It is noted that Equation 37 & 38 are less thermodynamically favourable than Equation 33 due to the unfavourable reaction between SiO and CO_2 in the gaseous state [166, 167].



Equation 37 & 38 both produce CO_2 through reactions involving gaseous CO . These reactions are complex and depend heavily on solid carbon availability and partial pressures of CO and CO_2 . This could result in species being lost before SiC forms.

Both hypotheses indicate that the quantity of carbon required cannot simply be linked to the molar ratio required for reaction. The homogeneity of its dispersion and hence its availability to react, may also have an effect.

Investigating the use of commercial and microemulsion SiO_2

It is important to identify any differences in crystallography when different SiO_2 sources are used. This work provides strong evidence that cubic (β) SiC , as would be expected by the phase diagram, is formed when both commercial and microemulsion SiO_2 are reacted with a carbon source.

Investigating the effect of adding B_4C

Addition of B_4C to the composite powder provides an additional carbon source. The B_4C may also become boron rich if SiO_2 takes carbon from its structure, resulting in a potential change in stoichiometry. This effect will alter the crystallography of the final powder when the composition is changed. Additionally, a difference in final powder composition may affect the formation of SiC . This work suggests that, as the amounts of carbon and B_4C are changed to achieve the desired composition, there would be significant changes in the crystal structure.

It is noted that there is a change in the SiC stacking fault peak identified previously. In the 5 wt% SiC , the peak appears at 32.8° whereas in the samples containing 10 wt% and 15 wt% it appears as a small and significant shoulder, at 33.4° . The shifting to the left of the peak was shown by Pujar *et al.*, to indicate a decrease in n , in the stacking formula $(\text{ABC})_n\text{AB}$. Further to this, the decrease in the (200) peak can be attributed to a change in stacking faults. Pujar notes this observation to be linked to the probability that the stacking faults appear as twins. It is however difficult to determine if this effect is being seen, or is instead a product of the decreasing peak intensities, as a result of the reduction of SiC content. It is noted that the peak in the 5 wt% sample is similar to that of the 2H SiC polytype. However, this is usually accompanied by another peak at 38° which is not seen in this sample.

It would be expected that, as the quantity of SiC in the sample increases, so would the mass loss during pyrolysis. This was seen to be true and occurs because of the increase in phenolic resin needing to be added as a carbon source for the SiC production. This trend was also observed in the mass loss at 1400°C , where the SiO_2 and carbon react to form SiC . The carbon content is however greater than expected, despite these trends. This could be due to a number of factors, such as a variability in the quantity of free carbon or stoichiometry of the stock boron carbide powder. Additionally, the presence of a carbon containing phase could alter the SiC formation reaction, due to an increase in the availability of carbon. It is complex to deconvolute these effects; however the lack of significant quantities of free carbon as seen from XRD analysis, remains encouraging.

Investigating the effect of reaction environment

The TGA environment is significantly different to that of a hot press. The elements and crucibles are made of oxide materials rather than graphite and there is a higher gas flow due to the small chamber. The use of a furnace to simulate a hot press can give insight on how the samples may react in a carbon rich environment. XRD and carbon analysis data shows the presence of significant amounts of graphite within the sample. This could come from three sources: the poor removal of residual graphite paper, the loss of SiO over CO , or the incomplete reaction of SiO_2 . The breakdown of the graphite paper, which results in its difficulty to remove, indicates that SiO is lost from the sample, contacts the graphite paper and reacts to SiC . This would lead to incorporation of excess graphite into the sample. Alternatively, the loss of SiO would result in more free carbon in the final sample. However, the lower gas flow and tighter packing of powder within the tube furnace crucible likely results in less SiO loss, as the chance of SiO contacting carbon is much higher. It is therefore likely that the extra carbon is a result of extra graphite from the carbon paper. This indicates a need to carefully control the reaction environment, and account for any changes in carbon content that it might cause.

5.6.4 Conclusion

Both microemulsion and commercial SiO_2 are able to successfully produce β - SiC containing a number of stacking faults. A number of factors do affect the powder composition. The availability of carbon can alter which reactions occur within the powder. This can give unpredictable final powder compositions. The dispersion and quantity of carbon must be carefully controlled, such that the target composition of a final composite is achieved. Commercial SiO_2 provides benefits in this area. The use of a powder that can be weighed before use gives greater control over powder composition. The use of Method I to predict yield, when microemulsion SiO_2 is used, was seen as unreliable and hence Method II was developed for use in Chapter 6 & 7. Another variable is added when the reaction environment is changed. It was seen that a carbon rich environment may alter the reactions occurring within the sample, or provide contamination. This must be carefully monitored as it was seen to alter the carbon content of the final powder.

5.7 Conclusion on using SiO_2 to produce SiC powders

To determine if microemulsion SiO_2 can be used to produce SiC in this project, it is important to consider the particle use criteria. Microemulsion SiO_2 production can be scaled with only small changes in the particle size distribution. This is linked to changes in the quality of mixing which could be controlled reliably with appropriate apparatus. The particles can also be kept stable over a prolonged period of time if sedimentation can be mitigated. If the particles are not clean then this can be achieved with regular high energy sonications or continuous medium energy mechanical shaking. Particles could also be cleaned, in which case a low energy manual shake can be used. These methods provide flexibility, with machine and chemical availability determining which is used.

Particles can be grown to larger sizes with an increase in the concentration of catalyst. This would allow a range of SiO_2 , and hence SiC , powders to be produced. However, the multi size nature of these particles must be carefully controlled, such that the final powder is well defined. These powders can be successfully converted to β - SiC with the use of phenolic resin as a carbon source. Care needs to be taken to control the dispersion of carbon, which may alter the final powder composition. However, by considering this alongside the reaction environment, it is possible to predict the final powder composition successfully.

Microemulsion SiO_2 , mixed with phenolic resin, was able to meet the criteria for a SiC ceramic precursor powder. This allowed their use in subsequent composite production. These composites aim to investigate how the SiC phase affects the amorphous breakdown within the B_4C .

6 Characterisation of Composites

6.1 Introduction

In order to understand how SiC affects the amorphous breakdown of B₄C, composites containing these materials must be produced. Microemulsion SiO₂, investigated in the preceding chapter, demonstrated a robust SiC production method. Their use could allow the microstructure to be tailored to reduce amorphisation. To determine the feasibility of this, composites containing commercial SiC, commercial SiO₂ and microemulsion SiO₂ were compared to understand the benefits and drawbacks of each.

The preparation of composites directly from microemulsion SiO₂ has not been well studied. The work conducted previously in this thesis provides insight into the composition of starting powders and what reactions might be expected during heat treatment. This work will aim to determine which SiC source and production method produces the most suitable composite. Composition, density, homogeneity and crystallography were used to define a good quality composite criteria:

1. The composition must closely match that targeted during the experiment. This indicates good reliability of the production method.
2. The sample must have a homogeneous dispersion of SiC, with a high relative density. This assures that the performance of the composite does not differ across the sample.
3. A high relative density with low amounts of free carbon must be achieved. This ensures that amorphisation or fracture behaviour is not affected by defects such as pores.
4. The B₄C phase must be crystallographically unaltered compared to the starting commercial powder. Boron doping of the B₄C phase can affect the amorphisation resistance [24] and could occur if carbon is removed from the structure by SiO₂.

Once the composites were produced, experiments were designed to probe if SiC can be used to prevent or alter the amorphous breakdown in B₄C based composites. It was therefore necessary to consider hardness of the composites. The hardness of a ceramic gives an indication of its resistance to plastic deformation. Ceramics often undergo cracking during indentation, due to their high strength and low toughness. Additionally, in B₄C, it is known that an amorphous breakdown will occur during indentation if a high enough pressure is applied. The hardness and extent of cracking can be analysed to understand the extent of amorphous breakdown. Amorphous bands can initiate additional cracking and are likely softer than bulk B₄C. This makes the trends in the quantitative data complex to analyse. However, in this work, the comparison of samples to the commercial B₄C can demonstrate how the microstructure is affecting the material's response to load. For example, an increase in hardness may indicate an increase in resistance to amorphous breakdown.

Two clear aims were identified from these considerations:

- Conduct experiments that determine how closely the composites match the criteria for a good composite.
- Consider the hardness of the composites in order to hypothesise on their amorphisation resistance.

6.2 Methods for synthesising and characterising composites

The composites produced enabled consideration both the change in SiC source alongside changes in production techniques. The samples produced are summarised in Table 24. Initially, three composites were produced using commercial B₄C and either commercial SiC (1), commercial SiO₂ (2) or microemulsion SiO₂ (3) at a 88:10:02 (B₄C:SiC:C) composition. These were processed using Methods X, Y and Z, as defined in the Chapter 4 of this thesis. Sample 1X was considered the 'standard' sample and was produced once, using commercial B₄C, SiC and phenolic resin following Method X. This served as a reference point when determining the effect of using different SiC sources. Sample 2Y and 3Y were produced using commercial and microemulsion SiO₂ respectively. These used Method Y which followed a general mixing procedure similar to Method X. Here all components were mixed together at once, followed by further processing to help with homogeneity. These composites were then produced again using Method Z to form Samples 2Z and 3Z. Method Z focused on intimately mixing SiO₂ and carbon together followed by drying and mixing with B₄C. It was theorised that adhering the carbon source to the SiO₂ first could increase reaction efficiency and reduce gaseous reactions which lead to SiO loss.

Table 24: Composites produced using a range of powder sources and methods. Method X, Y and Z are defined in Chapter 4 of this thesis.

Sample	Target Composition (B ₄ C:SiC:C)	SiC Source	Production Method
B ₄ C	100:00:00	-	X
1	88:10:02	Commercial SiC	X
2	88:10:02	Commercial SiO ₂ and Phenolic Resin	Y&Z
3	88:10:02	Microemulsion SiO ₂ and Phenolic Resin	Y&Z

A range of analytical techniques, which are summarised in Figure 53, were used to investigate the quality of the composites. To determine composition, image analysis using the homogeneity method (found in section 4.3.2) was conducted on SEM micrographs. This could determine the quantity of SiC in the sample using image thresholding. The mean % SiC can be combined with the observed final carbon content to calculate an observed composition. This assumes that the homogeneity analysis method only identifies SiC, which, due to the difference in atomic numbers between SiC, B₄C and carbon is highly likely. Additionally, it can be assumed that the area percentage of SiC is a close equivalent to the volume of an SiC grain. Using these assumptions, the amount of B₄C and carbon

in the sample can be calculated, using Equations 39 & 40.

$$m\%_{SiC} = A_{SiC} \rho_{SiC} \quad (39)$$

where $m\%$ is the mass percentage of SiC, A_{SiC} is the area percentage of the SiC, determined as the mean value of the homogeneity measurement and ρ_{SiC} is the density of SiC. This assumes that the area identified using SEM analysis is similar to the volume of an SiC grain and that the boron carbide phase has a B_4C stoichiometry.

$$m\%_{B_4C} = mr_{B_4C} \frac{mr_C(M_{CT} - M_{SiC}) + (m_{SiC} - m_T)}{(mr_C - mr_{B_4C})m_T} \times 100 \quad (40)$$

where $m\%$ is the mass percentage of the component, mr is the molar mass, M is the number of moles, M_{CT} is the total moles of carbon in the sample and m_T is the total mass. This value could then be compared to the target composition. This is the composition that is expected if the mass losses and reactions within the composite match those of the individual components.

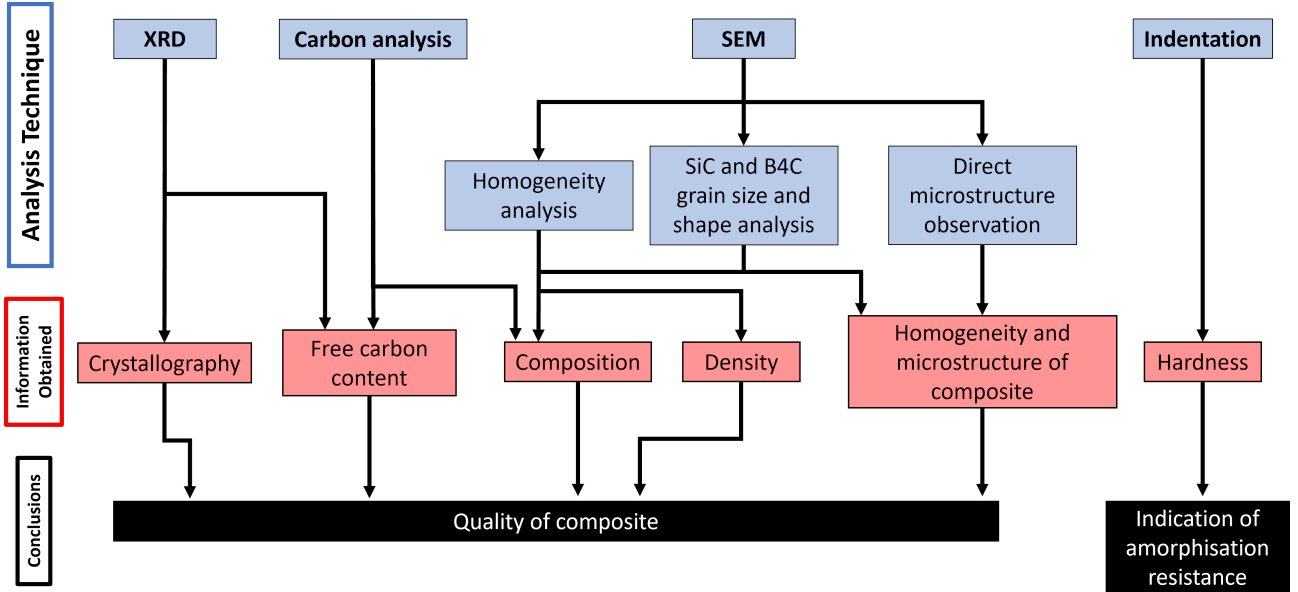


Figure 53: Flowchart showing the analysis route for the composites.

Density was measured using the Archimedes method and hence relative densities were calculated using the theoretical maximum density of the composite. SEM analysis was also used to report on homogeneity and SiC grain shape and size. These were conducted using the homogeneity and micrograph analysis methods respectively. This was compared between samples, alongside B_4C grain data collected using Argus imaging. XRD was then used to verify the crystallographic structure. By holistically considering these results, conclusions can be drawn on the quality of the sample when compared to the ideal criteria laid out above.

Hardness measurements were taken for all samples in the range of 500 mN to 2000 mN, using the

method outlined in section 4 of this thesis. These measurements could be compared to the standard sample, 1X, as well as commercial B_4C , such to determine any changes in hardness. Conclusions were then drawn on the possible reasons for variation in hardness and how this might indicate a variation in the amorphisation resistance. Samples of interest were selected to undergo analysis of the amorphous region.

6.3 Characterising the composites

Composition

SEM is an ideal technique for determining the observed composition of the sample. BSE imaging provides a good starting point, due to the significant difference in atomic numbers between SiC and B_4C . Figure 54 shows SEM micrographs for Samples 1-3. Sample composition can be determined using the homogeneity method, discussed in Chapter 4 of this thesis. This produces a mean SiC area % and a standard deviation value. The mean SiC area % gives a good estimate of the amount of SiC within the sample. It is necessary to assume that the area percentage of SiC, found using this method, is closely equivalent to the volume percentage of SiC. From this, a mean wt% SiC can be calculated. These are observed in Figure 55.

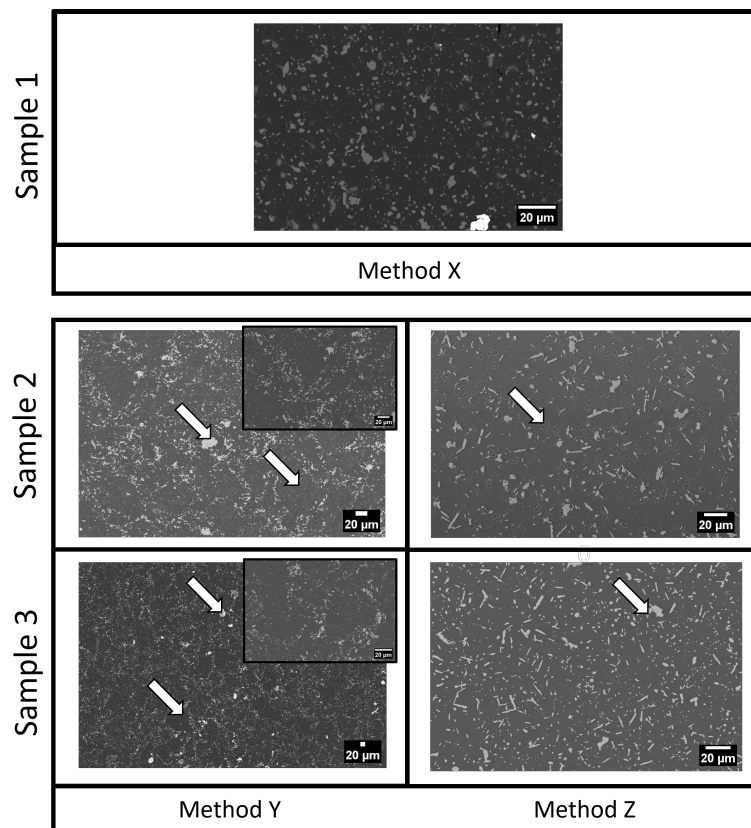


Figure 54: SEM micrographs, collected using BSE imaging, for Samples 1-3 and production Methods X, Y and Z. White arrows indicate observations about sample quality, such as inhomogeneity, SiC agglomeration and poor sintering. Samples 1, 2 and 3 indicate the use of commercial SiC, commercial SiO_2 and microemulsion SiO_2 , respectively. Methods X, Y and Z can be found in Chapter 4 of this thesis. The crucial difference is Method Z included intimate mixing of the SiO_2 and carbon source.

The mean can be compared to the target composition, to give an indication of the reliability of the processing method. Sample 1X, despite using commercial powder, shows a higher amount of SiC than expected at 16.3%. Sample 2 has a large difference in SiC content between Methods Y and Z, 13.0% and 7.6%, respectively. This could indicate that Method Z provides more opportunities for the loss of SiO₂ during processing. Sample 3 however shows values close to the target value of 10% with Method Y being 1.2% closer than Method Z. This result suggests that the microemulsion SiO₂ provides a more consistent SiC content which is not heavily affected by the processing method.

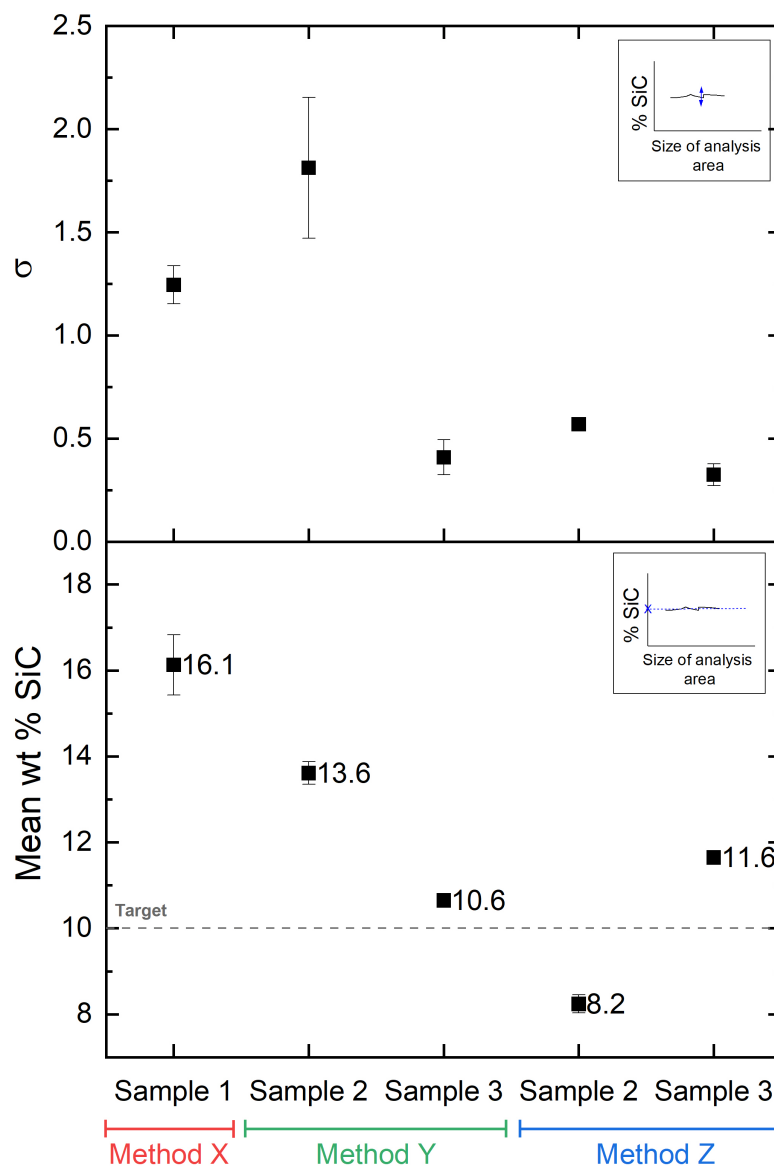


Figure 55: Graph showing the standard deviation and mean SiC % values for Samples 1, 2 & 3. These are determined using the homogeneity measurement defined in Chapter 4 of this thesis. The error bars are calculated as the standard error of the mean. For the mean wt% SiC, a grey line is used to indicate the expected SiC percentage, 10% in this case. Samples 1,2 and 3 indicate the use of commercial SiC, commercial SiO₂ and microemulsion SiO₂ respectively. Methods X, Y and Z can be found in Chapter 4 of this thesis. The crucial difference is Method Z included intimate mixing of the SiO₂ and carbon source.

Once the amount of SiC was determined, the percentage of other components could be calculated. As seen in Figure 56, all samples show a greater amount of free carbon than the target composition. This is smallest when commercial powders are used in Sample 1X at 3.2 wt%. This slight increase over the target value of 2 wt% may indicate extra graphite is being included from the hot press environment. It is unlikely that this addition varies significantly between samples, hence a carbon percentage above the target amount can be expected. Sample 2 & 3 show no particular correlation between method used and the amount of free carbon, suggesting that the amount of free carbon is linked to how the SiO₂ reaction occurs. Microemulsion SiO₂, found in Sample 3Z, provides the smallest amount of free carbon at 4.2%.

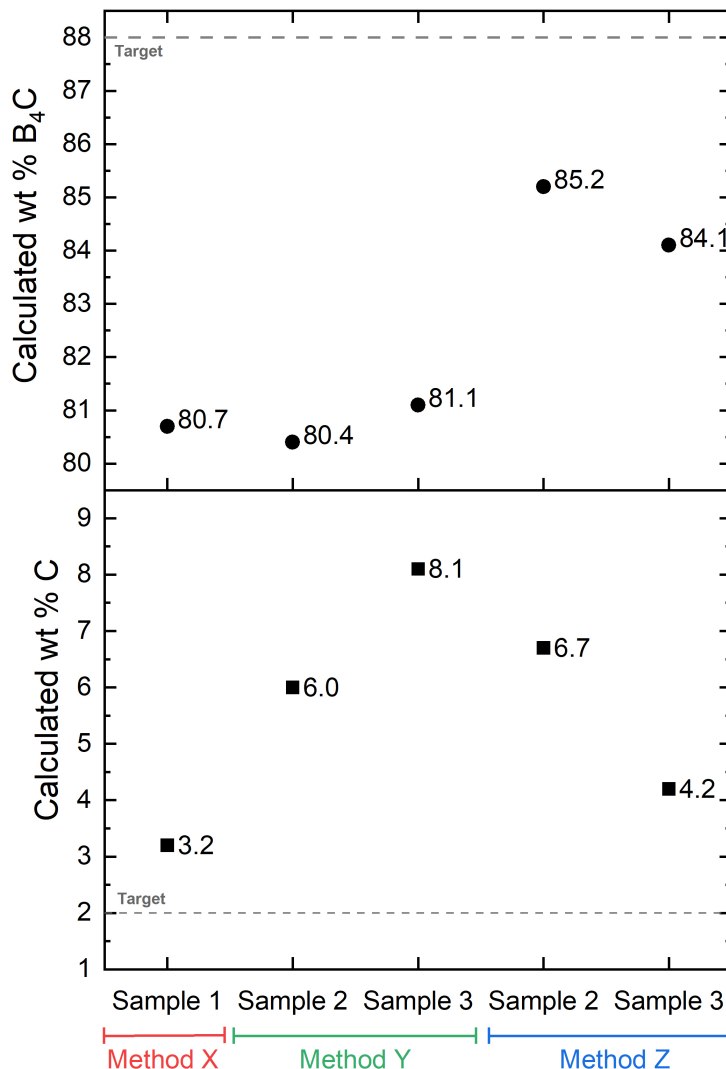


Figure 56: Graph showing calculated B₄C and carbon % values for Samples 1, 2 & 3. A grey line is used to indicate the target B₄C and carbon percentages. Samples 1, 2 and 3 indicate the use of commercial SiC, commercial SiO₂ and microemulsion SiO₂ respectively. Methods X, Y and Z can be found in Chapter 4 of this thesis. The crucial difference is Method Z included intimate mixing of the SiO₂ and carbon source.

When considering these results it should be noted that BSE has a lower resolution than SEI, due to

the lower signal return and increased interaction volume. Therefore any free carbon inclusions, found within a poorly sintered SiC grain for example, may be included in the SiC ellipse fitting. This can be difficult to deconvolute and may artificially inflate the SiC content of the sample. Additionally, it is important to observe the largest area possible during SEM analysis, whilst also identifying SiC of all sizes. It could therefore be possible that smaller SiC grains, not visible at this magnification, are not being counted. This artificially decreases the SiC content. A balance of these needs is necessary and these limitations must be considered when using this method.

Sample 1X shows less B₄C than the target composition at 80.5 wt%. Sample 2 also has less B₄C than expected with 80.9 wt% and 81.6 wt% for Methods Y and Z respectively. Similar to SiC percentage, Sample 3 shows B₄C values much closer to the target value, with 85.6 wt% and 84.4 wt% for Methods Y and Z respectively.

The densities of the samples provide insight into the quality of the sintering. Sample 1X provides a baseline of 97% relative density, as seen in Table 25, when the observed composition is used. This is similar to the density determined when Method Z is used for both Samples 2, at 98.3% and 3 at 97.7%. Method Y shows a 4% and 1% decrease in density compared to Method Z for Sample 2 and 3 respectively. This data must be considered holistically with composition information in order to determine if the composite meets the criteria discussed above.

Table 25: Relative density of Samples 1, 2 and 3, produced from powders containing commercial SiC, commercial SiO₂ and microemulsion SiO₂ respectively. Methods X, Y and Z are defined in Chapter 4 of this thesis. Method Y involves general mixing whilst Method Z involves intimate mixing of the SiO₂ and phenolic components.

Sample	Observed total C /wt%	Relative Density/%	
		using Target composition	using Observed composition
1X	25.5±0.1	98.8	97.2
2Y	27.6±1.0	95.3	94.3
3Y	29.0±1.3	98.7	96.4
2Z	27.7±0.2	97.8	98.1
3Z	26.0±1.4	98.1	97.6

Homogeneity

Homogeneity analysis also produces a standard deviation (σ) which shows how the amount of SiC varies as the area analysed is reduced. Samples 2 and 3 show some issues of homogeneity. White arrows have been used in Figure 54 to indicate areas of SiC agglomeration, areas with few SiC grains and locations of pores. These are likely related to sample composition and the homogeneity of the SiC phase. A homogeneous sample will have a very small σ . Figure 55 shows how the σ changes for different samples. Sample 1X provides a baseline with a σ close to 1. Sample 2 shows the largest change between the two processing methods. Sample 2Y shows a greater σ than Sample 2Z, indicating that Method Y produces a less homogeneous sample. This was expected when examining the SEM micrographs. A

similar, although less extreme change is seen for Sample 3. Sample 3Y shows a slightly larger σ than Sample 3Z, further verifying that Method Z produces more homogeneous samples. Sample 3Y, 2Z and 3Z have smaller σ than that of Sample 1X, indicating that better homogeneity is achieved through the use of SiO_2 , when an appropriate processing method is used. The similarity in values between Samples 3Y and 3Z indicates that microemulsion SiO_2 is less sensitive to the processing method, from a homogeneity perspective, than Sample 2.

Analysing the microstructure

SiC component

Analysis of the micrographs can also provide insight into the SiC particles' shape, size and quality of sintering. As the effect of microstructure on amorphisation is to be determined from this work, it is crucial to fully quantify the SiC particle characteristics. Micrograph analysis (found in section 4.3.2), which identifies and measures SiC grains using thresholding and ellipse fitting, was used to identify grain size and shape. In this case, two parameters can be determined: the aspect ratio and the area. Histograms for each of these parameters can be found in Figure 57 & 58.

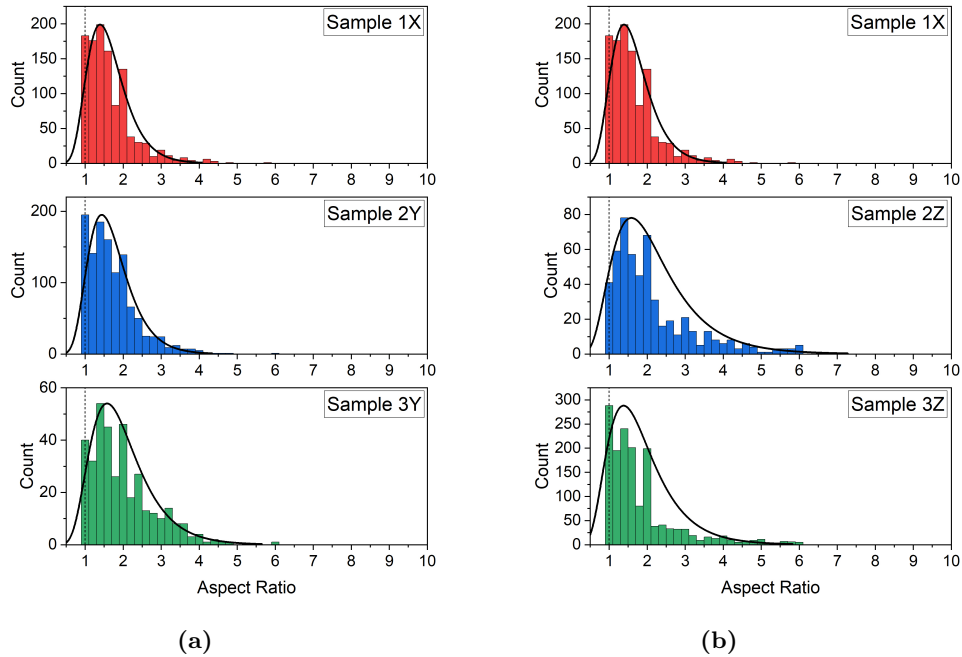


Figure 57: Histograms displaying the values of the aspect ratio of the fitted ellipse for a) Samples 1X, 2Y & 3Y and b) Samples 1X, 2Z & 3Z. The black line shows a lognormal distribution fit, scaled to the maximum count value, for the histogram. A dotted line indicates an aspect ratio of 1 which would indicate a spherical particle. Samples 1,2 and 3 indicate the use of commercial SiC, commercial SiO_2 and microemulsion SiO_2 respectively. Methods X, Y and Z can be found in Chapter 4 of this thesis. The crucial difference is Method Z included intimate mixing of the SiO_2 and carbon source.

The aspect ratio (AR) of the ellipse, fitted to the SiC particles, gives an indication of particle shape. The further this value moves from 1, the more elongated the particle is. It can be seen from Figure 57 that Samples 1X, 2Y and 3Y do not differ greatly but do however have peaks in the distribution

at values greater than 1. In these cases a value of between 1.5 and 1.7 is found. Samples 2Y and 3Y do show a wider range of AR values, suggesting there are some elongated particles. This difference is marginal when compared to Method Z. Method Z shows a wider range of AR, with sample 2Z having the largest values. In this case, number of particles with an AR greater than 4 increases in Sample 2Z compared to 2Y. For Sample 3Z, the opposite is seen where the number of particles with an AR greater than 2 decreases when compared to Sample 3Y. This leads to a decrease in the mean of the distribution peak to 1.4. The difference between Samples 2Z and 3Z suggests that the presence of carbon near the SiO₂ affects the final SiC differently, with the changes instead being linked to the SiO₂ source or final composition.

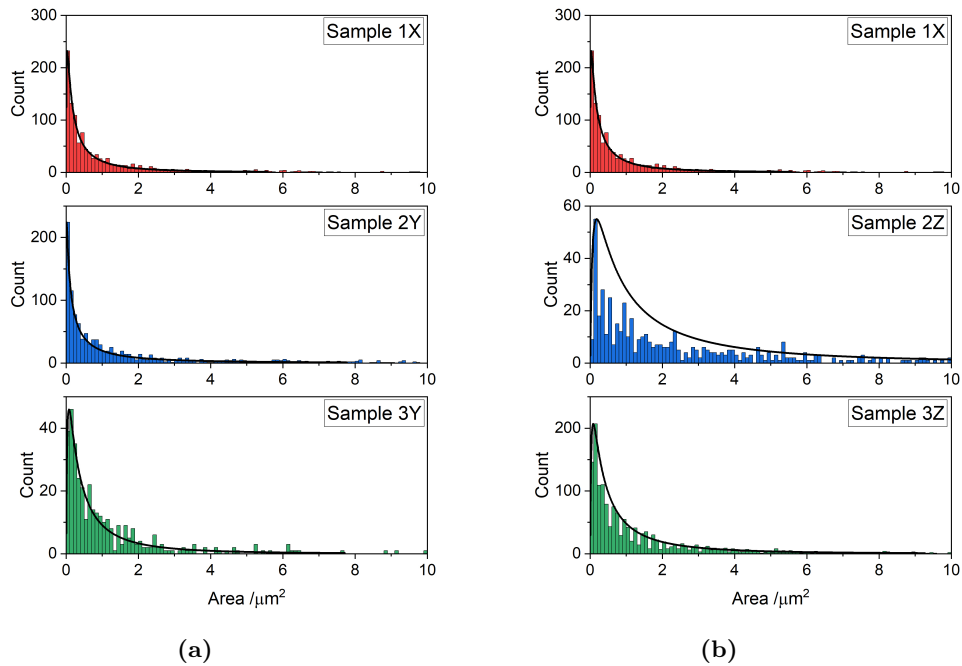


Figure 58: Histograms displaying the values of the area of the fitted ellipse for a) Samples 1X, 2Y & 3Y and b) Samples 1X, 2Z & 3Z. The black line shows a lognormal distribution fit, scaled to the maximum count value, for the histogram. Samples 1, 2 and 3 indicate the use of commercial SiC, commercial SiO₂ and microemulsion SiO₂ respectively. Methods X, Y and Z can be found in Chapter 4 of this thesis. The crucial difference is Method Z included intimate mixing of the SiO₂ and carbon source.

The area that a SiC particle occupies gives the closest practical estimate to the size of the particles. Figure 58 shows that Samples 2Y and 3Y both have a number of particles greater than 4 μm², when compared to Sample 1X. This suggests that some SiO₂ agglomeration is occurring, leading to larger SiC particles. Samples 2Y and 1X have a peak in the distribution at 0.05 μm² whilst 3Y has a peak at 0.15 μm². This suggests that Samples 1X and 2Y have smaller particles, on average, than sample 3Y. Sample 2Z shows a wider distribution than 2Y with a much greater number of particles larger than 2 μm². This also leads to an increase in the distribution peak to 0.15 μm². This suggests that there is more growth of the SiC particles occurring when Method Z is used. Additionally, this increase may be due to SiO₂ agglomeration before SiC conversion. Sample 3Z shows an opposite trend; the peak in

the distribution decreases to $0.1 \mu\text{m}^2$ when compared to Sample 3Y. The number of particles greater than $2 \mu\text{m}^2$ is also seen to decrease. This suggests that the size of the particles may not be directly linked to the processing method, and instead the source of the SiO_2 and final composition must be considered. It is unsurprising that this conclusion is similar to that of AR as the area will be affected by this factor. These quantitative results provide an insight into the particle characteristics that can be considered alongside the final composition and homogeneity to determine which composite is most suitable for amorphisation analysis.

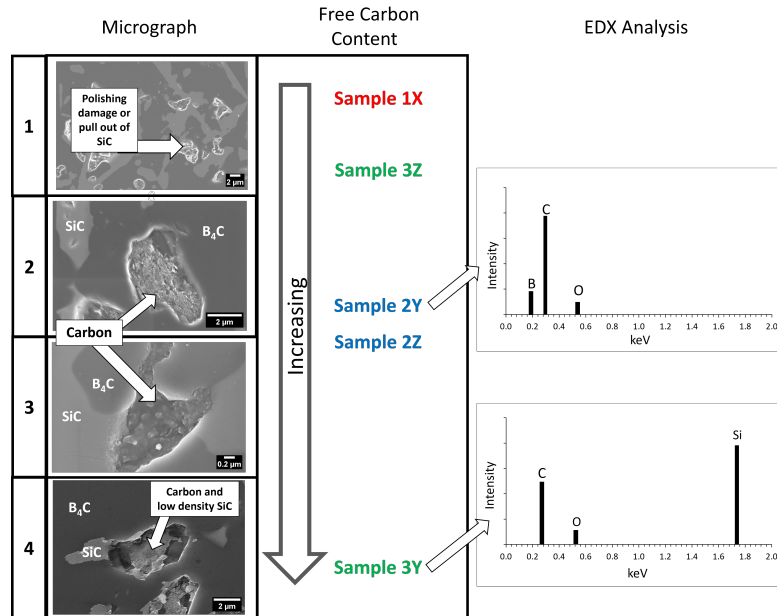


Figure 59: SEM micrographs of damaged and high carbon content regions. These occur in the samples displayed on the right, with their order closely related to the free carbon content. Method 1, 2 and 3 indicate the use of commercial SiC , commercial SiO_2 and microemulsion SiO_2 respectively. Method X, Y and Z can be found in Chapter 4 of this thesis. The crucial difference is Method Z included intimate mixing of the SiO_2 and carbon source.

Whilst the micrograph analysis method is able to indicate some changes in the SiC , relating to the use of different precursors or processing methods, inspection of the microstructure is still necessary to identify any defects in the sample. Figure 59 shows some defects found in various samples. It can be seen that micrographs 2, 3 and 4 showed higher than expected levels of carbon, when analysed using EDX. EDX does have a larger interaction volume than BSE imaging. However, it allows the identification of atoms within the structure. The presence of a large amount of carbon was seen alongside boron and silicon, as would be expected in B_4C and SiC . These were however weak in signal. It is possible to compare the micrographs to the carbon content of the sample. Graphite has a low hardness so the robust grinding and polishing techniques needed for B_4C based samples will preferentially grind these areas. Micrograph 2 and 3 show clear areas of graphite, with the majority of graphite still present in the former. This indicates that in these samples, the graphite is not homogeneously distributed and is instead found in 2-5 μm particles. Micrograph 4 shows a similar region, located near an SiC grain. It is likely that this region has a combination of low density, poorly

sintered, SiC and graphite. If excess carbon is present as SiC is forming, a structure of SiC and graphite will form. This will be softer and weaker than a SiC grain. This would explain why free carbon and large areas of damage are found near SiC in these micrographs. Micrograph 1, correlated to low free carbon samples, does also show damage around SiC grains. This is likely due to the preferential polishing of SiC, due to its softer nature. This could also indicate that the interface between SiC and B₄C is weaker in some areas, leading to grain pullout. Instances such as graphite along the grain boundary could cause this, although the detection of a thin layer is not possible due to the large interaction volume of the EDX.

B₄C component

Analysis of the B₄C phase of the composite is crucial in determining how the composite has formed, and give an indication of the holistic structure. Figure 60 shows micrographs, collected using the Argus method. Each colour indicates a different diffraction condition and hence a grain. It is noted that the majority of samples have some element of twinning within the grains. These appear as stripes in the micrograph and are common in B₄C, usually occurring as the grains grow. Holes in the surface, which can be caused by polishing, grain pull out or porosity, reduce the amount of diffracted electrons which reach the detector. This results in a low signal black spot. It can be seen that, on visual inspection, the amount of dark area is much less in Sample 1X and 3Z when compared to Sample 3Y, 2Y and 2Z. This correlates well to the amount of free carbon in these samples and is likely linked to defects in the microstructure discussed previously.

Investigating the shape and size of the B₄C grains, and how these might change with production method and powder sources, can further characterise the composite. Initially, Figure 61 shows that the addition of SiO₂, when Methods Y and Z are used, leads to little difference in the AR. The mean distribution value is around 1.5 for these samples 1X, 2Y and 3Y, which is similar to pure commercial B₄C. The FWHM is also similar with Sample 3Y having a marginally narrower distribution. A similar trend is seen when Method Z is used. This indicates that the addition of SiO₂ does not affect the shape of the B₄C grains, although it is noted that all samples, including commercial B₄C have some elongation to the grains.

The area can provide a representation of the particle size. Figure 62 shows how samples 2Y and 3Y have a smaller mean grain size of 100 μm^2 when compared to B₄C and Sample 1X, which have a grain size of 180 μm^2 . Additionally, there is not a significant number of particles larger than 1000 μm^2 in these samples. A further reduction in grain size is seen when Method Z is used. Sample 2Z shows a reduction in mean grain size to 20 μm^2 whilst Sample 3Z shows a smaller decrease to 70 μm^2 .

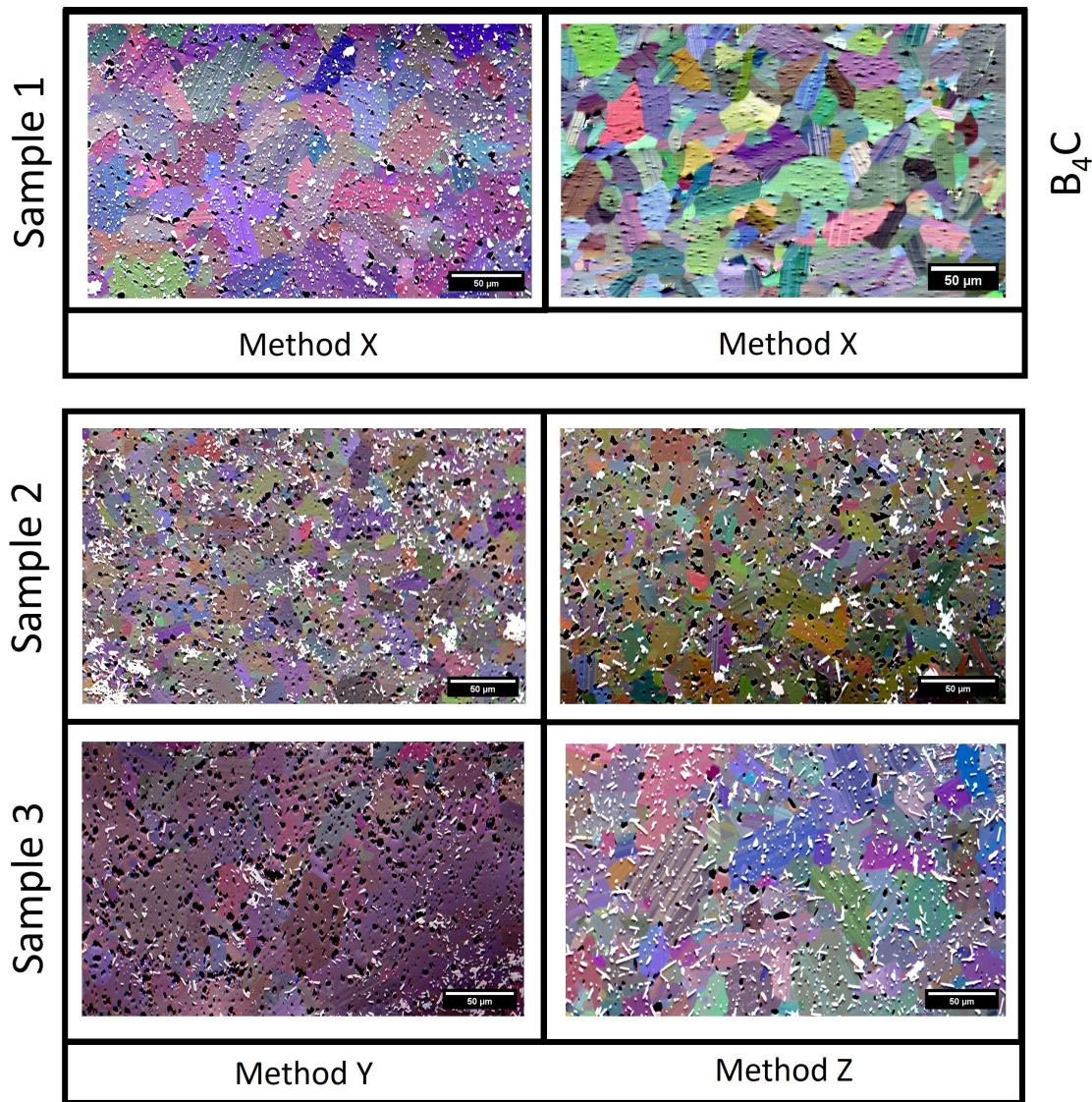


Figure 60: SEM micrographs, collected using the Argus method, showing the grain structure of the B_4C phase for commercial B_4C and Samples 1-3. The bright white phase is the SiC, whilst dark black areas are pores or polishing defects. Sample 1, 2 and 3 indicate the use of commercial SiC, commercial SiO_2 and microemulsion SiO_2 respectively. Method X, Y and Z can be found in Chapter 4 of this thesis. The crucial difference is Method Z included intimate mixing of the SiO_2 and carbon source.

Closer analysis of the B_4C grain sizes, using Argus imaging, can provide further information about the composite. It was noted that, in Sample 2 & 3 there were areas of significantly smaller grain sizes than those surrounding them. Figure 63 shows a higher magnification micrograph, highlighting one of these regions in each of the samples, accompanied by a quantitative measurement of the grain size in this region. These regions are most prevalent in samples produced using Method Z, with the grain size in these regions having a mean value of $5 \mu m^2$, smaller than the average size seen at lower magnifications of $20 \mu m^2$ to $70 \mu m^2$. It is noted that small SiC particles are observed in this region with an ellipse major of less than 500 nm. These particles are likely pinning the B_4C grains, preventing them from growing. Consideration of these regions is crucial for amorphisation work, which is known to be affected by grain size.

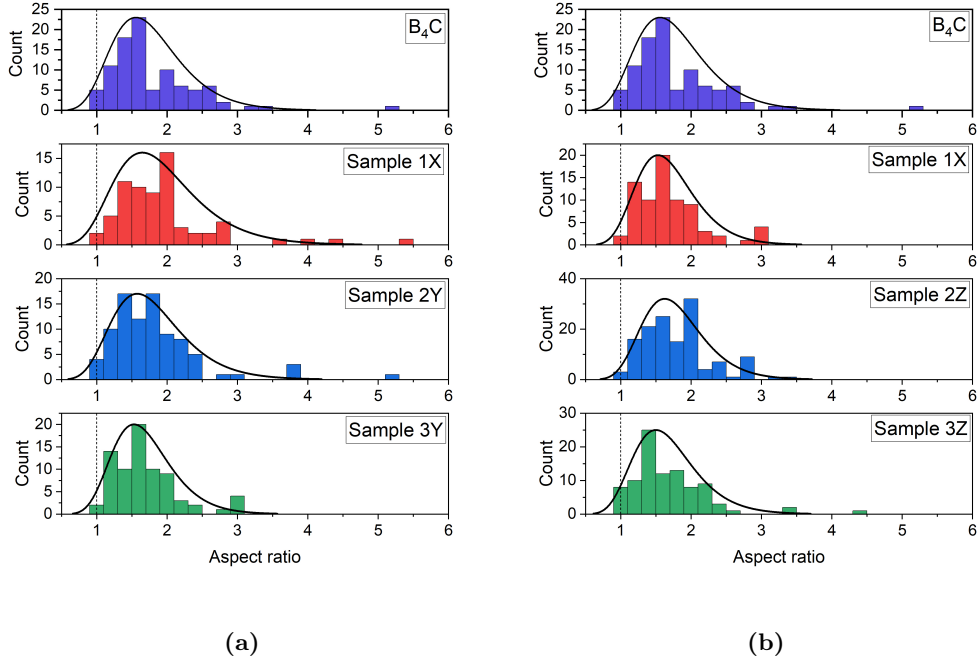


Figure 61: Histograms displaying the value of the aspect ratio of the fitted ellipse for a) Samples 1X, 2Y & 3Y and b) Samples 1X, 2Z & 3Z. The black line shows a lognormal distribution fit, scaled to the maximum count value, for the histogram. A dotted line indicates an aspect ratio of 1 which would indicate a spherical particle. Method 1, 2 and 3 indicate the use of commercial SiC, commercial SiO₂ and microemulsion SiO₂ respectively. Method X, Y and Z can be found in Chapter 4 of this thesis. The crucial difference is Method Z included intimate mixing of the SiO₂ and carbon source.

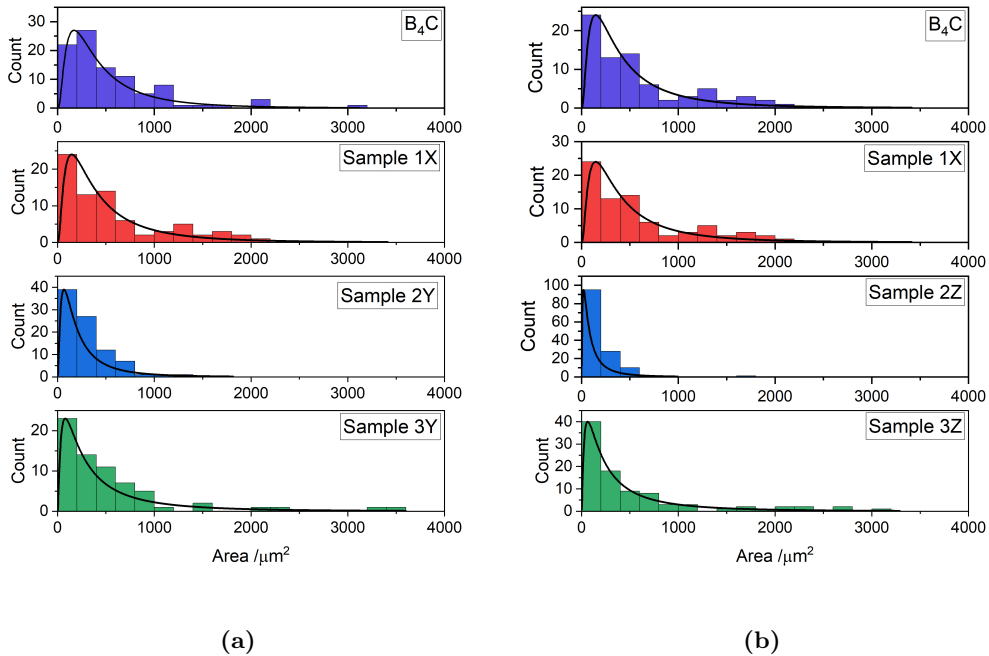


Figure 62: Histograms displaying the value of the area of the fitted ellipse for a) Samples 1X, 2Y & 3Y and b) Samples 1X, 2Z & 3Z. The black line shows a lognormal distribution fit, scaled to the maximum count value, for the histogram. Method 1, 2 and 3 indicate the use of commercial SiC, commercial SiO₂ and microemulsion SiO₂ respectively. Method X, Y and Z can be found in Chapter 4 of this thesis. The crucial difference is Method Z included intimate mixing of the SiO₂ and carbon source.

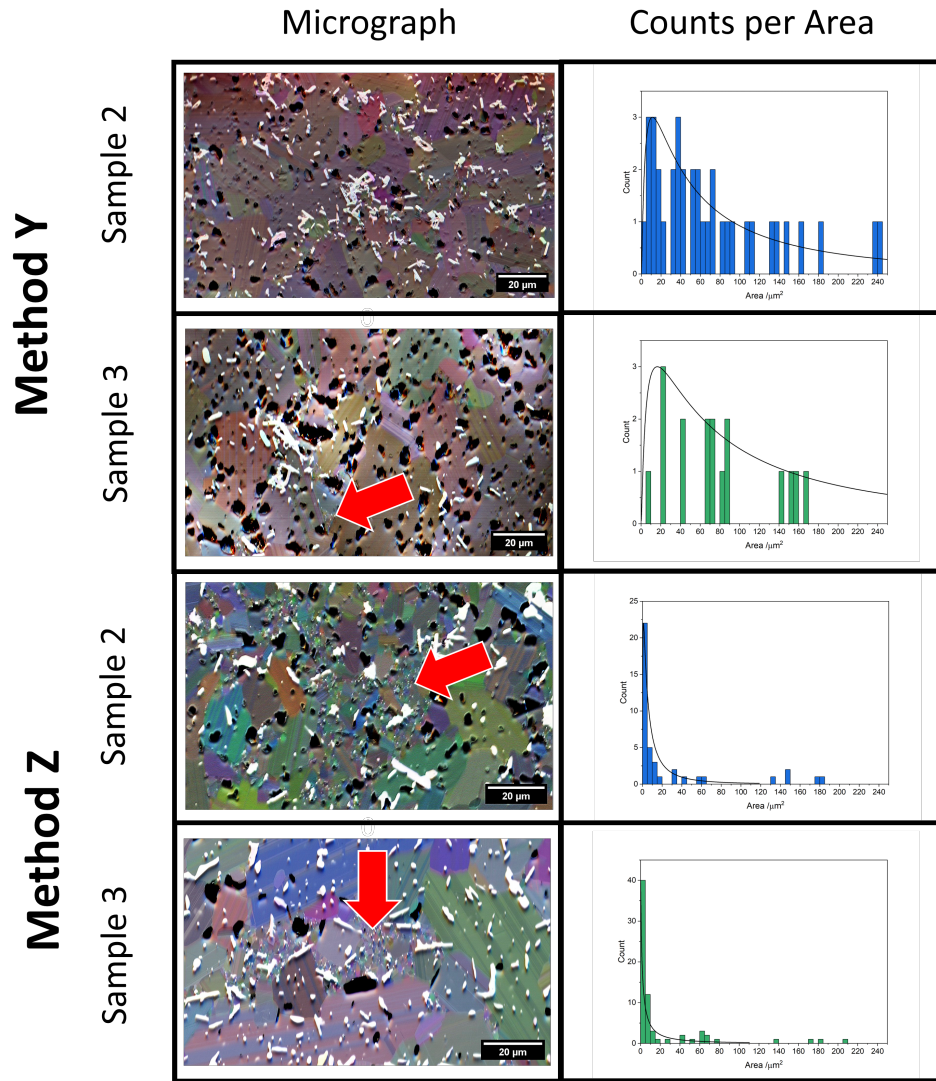


Figure 63: Micrographs showing how, at higher magnifications, regions with significantly smaller B_4C grains are seen. Red arrows highlight these regions. Quantitative analysis, shown in the histograms, using ellipse fitting shows how the area of B_4C grains in these regions vary across the samples. Sample 1,2 and 3 indicate the use of commercial SiC, commercial SiO_2 and microemulsion SiO_2 respectively. Method X, Y and Z can be found in Chapter 4 of this thesis. The crucial difference is Method Z included intimate mixing of the SiO_2 and carbon source.

Determining the crystallography of B_4C and SiC components

XRD analysis can be used to compare the differences in samples made using commercial and microemulsion SiO_2 . It can be seen in Figure 64 & 65 that Samples 2Y, 3Y, 2Z and 3Z show similar structures to 1X. The B_4C phase closely resembles that of the commercial B_4C (blue dotted line) and matches ICDD-00-035-0798. It is therefore unlikely that boron doping, which would result in a peak shift [168], is occurring within the sample.

Figure 64 compares the crystallography of Samples 1X, 2Y and 2Z. The patterns show the clear formation of α -SiC alongside the expected B_4C and graphite peaks. Free carbon in the form of graphite readily occurs within these samples. For commercial SiO_2 (Sample 2), the graphite peak

increases in intensity when Method Z is used. When comparing it to the nearest B_4C peak, this relative intensity is greater in Sample 2Z than 2Y, and greater than 1X. This would indicate that the free carbon content is greatest in Sample 2Z. Table 26 shows how this affects the crystallite size (D) and inter planar distance (d), as calculated using the Scherrer equation [169], for the (002) plane of carbon (pink arrow in Figure 65). Sample 2Y and 2Z have similar crystallite sizes which are 5 nm larger than those in Sample 1X and 8 nm or 13 nm larger than 3Y and 3Z respectively.

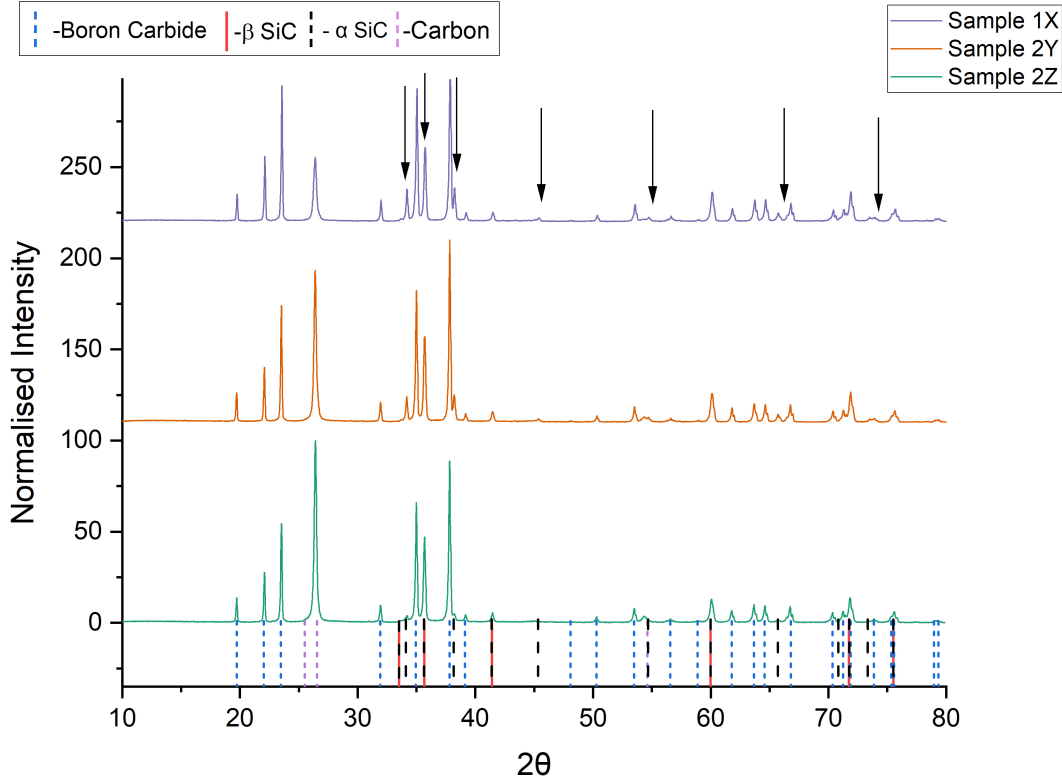


Figure 64: XRD patterns showing the variation in crystallography for Samples 1X, 2Y and 2Z. A red arrow highlights the change in a peak associated with graphite whilst black arrows indicates peaks of note associated with α -SiC. Sample 1,2 and 3 indicate the use of commercial SiC, commercial SiO_2 and microemulsion SiO_2 respectively. Method X, Y and Z can be found in Chapter 4 of this thesis. The crucial difference is Method Z included intimate mixing of the SiO_2 and carbon source.

Table 26: Crystallographic measurements of crystallite size (D) and interplane spacing (d) of the (002) plane of carbon for Samples 1 2 and 3, produced from powders containing commercial SiC, commercial SiO_2 and microemulsion SiO_2 respectively. These are calculated using the Scherrer equation [169]. Methods X, Y and Z are defined in Chapter 4 of this thesis. Method Y involves general mixing whilst Method Z involves intimate mixing of the SiO_2 and phenolic components.

Sample	D/nm	$d(002)/\text{\AA}$
Sample 1X	25.81	3.37
Sample 2Y	31.33	3.37
Sample 2Z	31.88	3.37
Sample 3Y	23.05	3.38
Sample 3Z	18.28	3.41

For Sample 3, seen in Figure 65, there is a significant reduction in free carbon peak intensity when Method Z is used. A broader peak also occurs which is shifted to lower angles. The crystallite size is smaller in Sample 3 than Sample 1, with 3Z showing a smaller size than 3Y. This is combined with an increase in $d(002)$ of 0.01-0.03Å for Sample 3Y and 3Z respectively, associated with the shift of the peak to the left. Whilst D is not a direct measurement of grain size, the decrease in size could suggest that the carbon is dispersed throughout the sample as smaller grains in Sample 3Z. Alongside this, the increase in $d(002)$ has been shown to indicate increased disorder in the graphite structure [170]. As Samples 2Z and 3Z share different intensity, and locations, of the graphite peak, it can be said that the prevalence and size of graphite in Method Z is likely a factor of final composition or SiO_2 source rather than processing method.

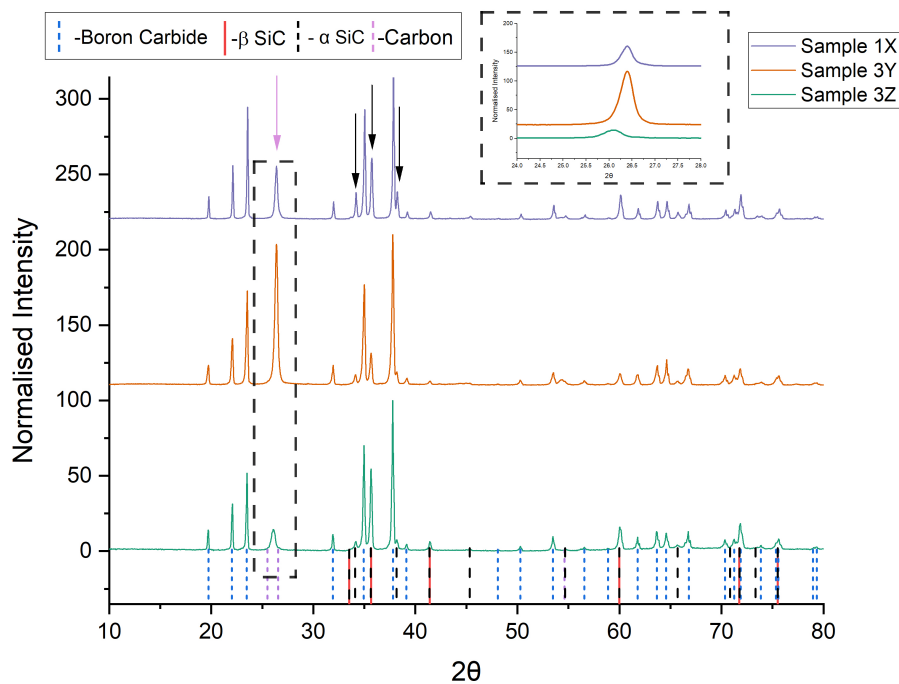


Figure 65: XRD patterns showing the variation in crystallography for Samples 1X, 3Y and 3Z. A red arrow highlights the change in a peak associated with graphite whilst a black arrow indicates peaks associated with α -SiC. A grey dashed pop out graph indicates the change in the graphite peak between the samples. Sample 1,2 and 3 indicate the use of commercial SiC, commercial SiO_2 and microemulsion SiO_2 respectively. Method X, Y and Z can be found in Chapter 4 of this thesis. The crucial difference is Method Z included intimate mixing of the SiO_2 and carbon source.

There are also some differences in the structure of SiC. TGA samples, from earlier work, showed the formation of 3C β -SiC (red indicator in XRD data) whereas here, the formation of 6H α -SiC can be seen (black arrows and dotted indicator lines). It is noted however that the ratios of the SiC peaks do change between the samples. This can be caused by a number of factors such as texturing or a change in the quantity of a polytype. It is unlikely that samples which undergo the same sintering load and direction would experience different amounts of texturing. An alternative explanation would be the presence of different SiC polytypes. Whilst the patterns closely match that of 6H SiC found in commercial SiC, the polytypes 4H and 15R share very similar diffraction patterns. These three

polytypes are closely related, with the difference between them related to the stacking sequence. It can be seen that whilst the peak locations are similar, the relative ratios of these peaks differ. Comparison between peak P1, at 38.25° , and P2 at 35.74° , is shown in Table 27a. The same ratio was acquired for commercial SiC and Sample 1X to 3Z, as seen in Table 27b. The values for Sample 1X and 3Y are similar to that of the 6H and 15R polytypes, whilst commercial SiC and 2Y are slightly less. It is difficult to differentiate between these two polytypes as smaller 15R peaks are often hidden by B_4C peaks. The difference in value likely indicates the presence of some 3C polytype. 6H or 15R α -SiC and 3C β -SiC both share P2, whilst 3C lacks P1. Therefore, any increase in 3C will increase P2, reducing P1/P2. This could also be the cause of the significantly smaller values for Sample 3Z and 2Z, indicating the Method Z reduces 6H formation.

Table 27: a) expected intensity ratios calculated from Ruska *et al*'s work on polytype differentiation using XRD [171–174] b) the observed intensity ratios in these samples.

Polytype	P1/P2	Sample	P1/P2
		Commercial SiC	0.31
6H	0.41 ± 0.07	1X	0.45
4H	1.20 ± 0.09	2Y	0.32
15R	0.45 ± 0.06	2Z	0.11
3C	N/A	3Y	0.42
		3Z	0.14

(a)
(b)

There is good parity between the compositional data seen here and that qualitatively found within the XRD. The quantity of carbon, and its correlation to the intensity of the associated peak in the XRD is most relevant. Most samples' carbon content links well to the XRD pattern, with the peak in 3Y being larger than the peak in 1X for example. This is untrue for Sample 3Z, which shows a very small carbon peak despite containing more graphite than Sample 1X. However, as the peak is broader than in 1X, a reduced intensity can be expected. This agreement provides a robust basis for determining the quality of the composites, and hence their usability in amorphisation studies.

Investigating how hardness is affected by composite properties

The hardness of a ceramic gives an indication of its resistance to plastic deformation. Ceramics often undergo cracking during indentation, due to their high strength and low toughness. In B_4C it is known that a phase transformation, in the form of an amorphous breakdown, will occur during indentation at an appropriate load. This means that a hardness value, in a cracked indent, does not simply demonstrate the material's resistance to plastic deformation; it will instead incorporate the resistance to plastic deformation, a factor determined by the difficulty of the phase transformation, and a factor related to the difficulty of crack growth. This makes the trends in the quantitative data complex

to analyse. However, in this work, the comparison of samples to the commercial B_4C can give an indication of effects on the microstructure on hardness. For example, an increase in hardness could indicate an increase resistance to amorphous breakdown.

Figure 66 shows how the hardness is affected by the maximum load, for each sample. All samples show a decrease in hardness with load, as would be expected. The larger the area indented, under higher load, the greater the chance a defect is present or that fracture occurs. The ceramic will hence have a lower resistance to deformation and the hardness will therefore decrease. It would be expected that the softer SiC, present throughout the sample, would reduce the hardness. Additionally, the free carbon, in the form of graphite, is significantly softer than both carbides, hence also decreasing hardness. This expectation is met by Sample 1X which shows a consistently lower hardness than B_4C in a range of 35-28 GPa as seen in Figure 66. Sample 3Y also shows a lower hardness than B_4C ranging from 31-25 GPa. This could be explained by the increased amount of graphite within this sample. It is noted however that the hardness at 2000 mN is similar to that of Sample 1X and 2Y. Sample 2Y shows lower hardness values than Sample 1X, similar to Sample 3Y. It however appears to have an increase in hardness up to 1000 mN, followed by a similar decrease to Sample 1X. However, much like Sample 3Y, when errors are considered, it can be said that Sample 2Y has a decrease in hardness from 750 mN, with an outlier at 500 mN. These samples contain more free carbon than Sample 1X and have lower density, likely decreasing their hardness. Sample 2Z has a largest amount of free carbon but does have a high density and high B_4C content. This likely allows it to perform similarly to sample 1X as is seen here with hardness values of 33-31.5 GPa. Sample 3Z shows a hardness very similar to B_4C at around 40 GPa with a slight decrease in hardness with load. The sample has a low free carbon content, high density and a high B_4C content.

Observation of the cracking around the indent of Sample 3Z could provide insight into its response to load under the indenter. As discussed previously, the hardness will be contributed to by the resistance to plastic deformation or amorphous breakdown and to crack propagation. Transverse cracking along the direction of load occurs during indentation, and decreases hardness by increasing indenter penetration. A sample with a small plastic zone and sizable transverse cracking is likely to have a similar hardness to a sample with a large plastic zone and limited transverse cracking. In this case the indentation is similar in size, but the way the sample deals with the load is different. Radial and lateral cracks, perpendicular to the loading direction, occur during unloading as the material undergoes relaxation elastically. These cracks are a measure of the elastic response of the material or the resistance of the new plastic zone to the elastic relaxation. Figure 67 shows the cracking occurring in commercial B_4C and Sample 3Z. It can be seen that both samples have similar lengths and location of cracks. As both samples have been ion milled, it is important to consider the location and length of the cracks as milling can increase their thickness.

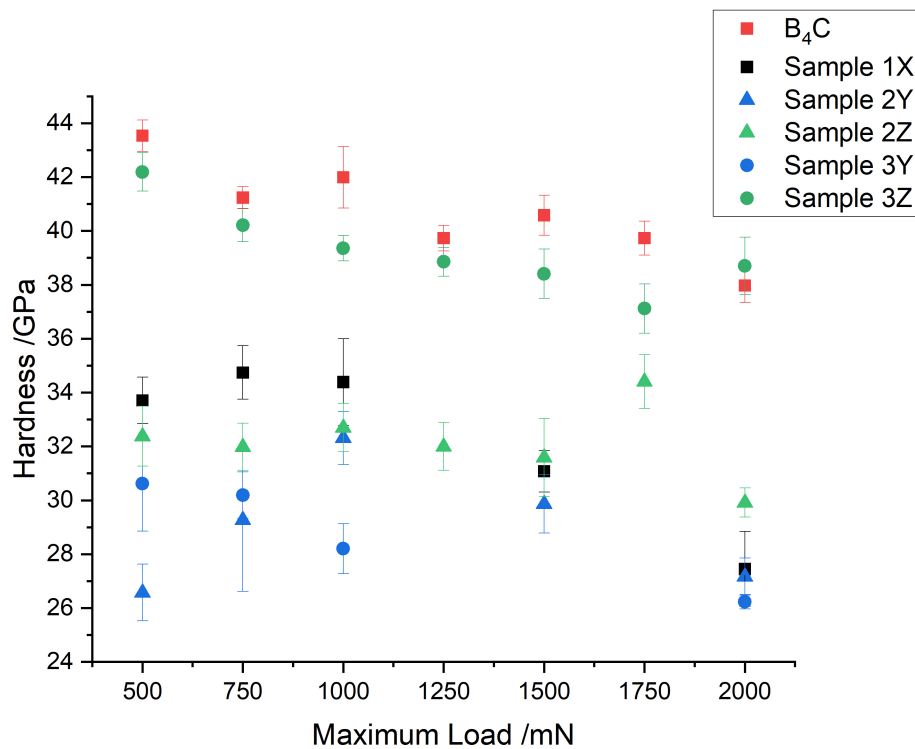


Figure 66: Graph showing how the hardness is affected by applied load for Samples 1-3 and commercial B₄C. The error bars are calculated as the standard error of the mean. Method 1, 2 and 3 indicate the use of commercial SiC, commercial SiO₂ and microemulsion SiO₂ respectively. Method X, Y and Z can be found in Chapter 4 of this thesis. The crucial difference is Method Z included intimate mixing of the SiO₂ and carbon source.

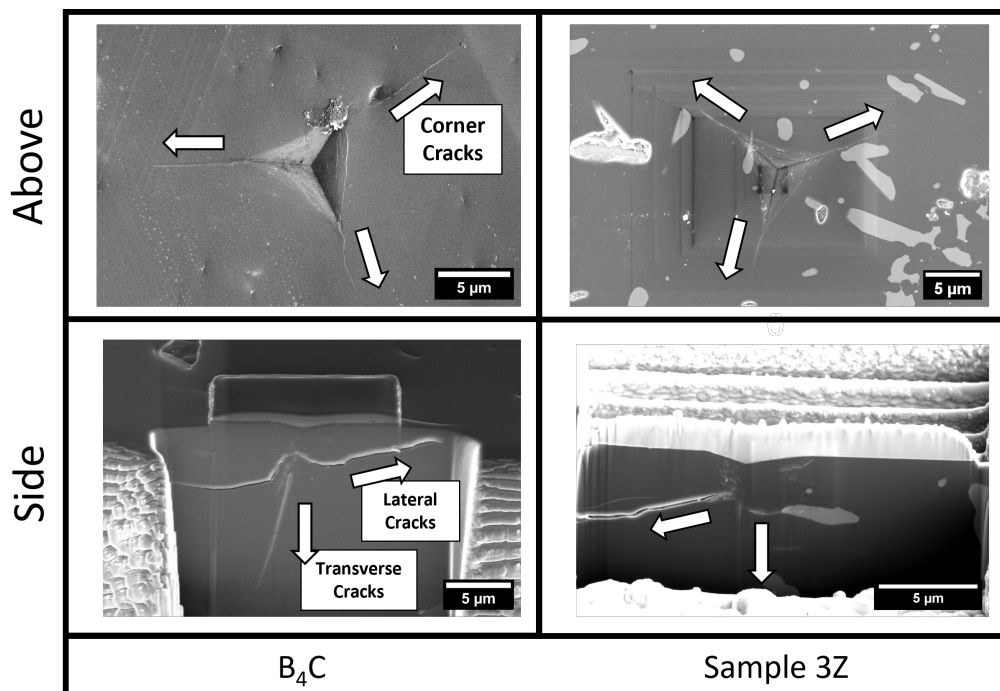


Figure 67: Graph showing the cracking around and below the indent for commercial B₄C and Sample 3Z. Method 1, 2 and 3 indicate the use of commercial SiC, commercial SiO₂ and microemulsion SiO₂ respectively. Method X, Y and Z can be found in Chapter 4 of this thesis. The crucial difference is Method Z included intimate mixing of the SiO₂ and carbon source.

6.4 Discussion

For a sample to be considered of good quality, it must have: a composition closely matching the target composition, a homogeneous dispersion of SiC, a high relative density and a B₄C phase which does not undergo boron doping. Alongside these, the grain structure and crystallography of each phase must be well understood, such that their effect on amorphous breakdown can be evaluated in a later study. It is clear that boron doping within these samples is not occurring as this would result in a shift in the XRD pattern [168]. The addition of extra carbon was designed to prevent this as the need for SiO₂ to take carbon from the B₄C structure is reduced if excess free carbon is available.

The compositional analysis shows a great degree of variation across the samples. From previous work it can be seen that the B₄C does not undergo any significant reactions, other than limited reduction of surface B₂O₃. It is therefore likely that variation in the composition is partly resulting from changes to the SiO₂ to SiC reaction. It has been seen previously that changes in the availability of carbon can alter the reactions occurring within the sample. When carbon becomes unavailable, the SiO₂ must react with CO in the gaseous form as SiO. This results in greater loss of SiO and hence more free carbon remaining within the sample. The intimate dispersion of SiO₂ and carbon (Method Z) clearly shows a reduction in free carbon, compared to non intimate mixing, when microemulsion SiO₂ is used. Additionally, it is likely that less SiO is lost. This results in a composition close to what is expected. The intimate mixing of carbon and silicon source is clearly needed to achieve the target composition.

The loss of B₄C during processing is likely due to its interactions with phenolic resin. The loss of B₄C during processing is reduced when intimate mixing (Method Z) is used. During drying, phenolic resin forms a thick gel that can adhere to glassware. As the B₄C does not interact with the phenolic resin significantly during this method, it is likely less becomes stuck to glassware during processing. Therefore, less is lost. As there is more B₄C than SiO₂, it is more likely that B₄C will be lost in this way. This artificially inflates the ratio of SiC:B₄C in the final sample. SiO₂ losses are occurring, as seen by the relative differences in the amount of free carbon. However, as the SiC:B₄C ratio is greater than expected, it is still possible to have a final SiC content greater than what is expected. This demonstrates further the benefits of intimate mixing of SiO₂ and a carbon source, as well as the need to fully characterise composites during this study.

The SiC phase produced from SiO₂ appears to vary between samples. It is clear that when intimate mixing of SiO₂ and carbon source is used, the sample is more homogeneous. This is likely due to the dispersion of SiO₂ and its subsequent reactions. If the SiO gas can immediately react with solid carbon it does not have to progress through the structure to a carbon source. This would result in inhomogeneity and porosity. This demonstrates the benefit intimate mixing can bring to both commercial and microemulsion SiO₂ based composites.

When considering crystallography, an increase in preferential growth or greater prevalence of the 3C SiC polytype is seen when intimate mixing is used. It is unclear why samples would have different degrees of texturing when they undergo the same sintering regime. Instead it could be hypothesised that a difference in the polytype ratio is present. The high temperatures, combined with a medium length hold time, as used here, would normally encourage the 3C-6H transition. This is likely what is seen when normal mixing is used (Samples 2Y and 3Y). It could be theorised that the better mixing of SiO₂ and carbon, which occurs in Method Z, results in a suppression of the transition. This could be caused by greater carbon availability although this has not previously been seen in the literature. Vlaskina *et al* do note that stacking faults in the 3C structure act as the seed for 6H formation as they allow the atomic movement needed for the cubic to hexagonal transformation. It could be theorised that, when the SiO₂ and carbon are intimately mixed, fewer stacking faults occur in the 3C structure and less 6H is formed [175, 176].

Similar conclusions can be drawn when analysing the microstructure. Intimately mixed samples of commercial and microemulsion SiO₂ (Sample 2Z and 3Z) both experience abnormal grain growth which is often attributed to the 3C to 6H, 4H or 15R transition [131, 177]. This reduces in Sample 3Z compared to other samples suggesting that less transformation does occur, matching crystallographic observations. The opposite trend is seen in Sample 2Z. This is especially surprising as the large amount of free carbon in 2Z was seen by Yasar *et al* to reduce abnormal grain growth (AGG) [177]. These conflicting results could be due to the micrograph analysis method used (found in section 4.3.2). The micrograph analysis method is unlikely to be able to identify the smallest SiC particles which, from analysis of the small grain areas in Sample 2Z and 3Z, are spherical in nature. This comes from the need to use a representative image that covers a wide area but also includes all particle sizes. It could be theorised that the smallest particles remain as the 3C polytype during sintering but are not detected during aspect ratio analysis. It still remains a possibility that preferential growth could be occurring, although this is not reported in the literature independently of polytype transitions. These observations demonstrate the difficulty in developing a robust micrograph analysis method and the need for further work in this area.

Despite the initially small B₄C powder size, significant grain growth occurs in the B₄C phase of the microstructure. This indicates that the processing temperature is too high, or hold time too long, to allow a fine grain structure to be produced [116, 178]. This can provide benefits to this work; the reduction of B₄C grain size is known to decrease amorphisation, although the mechanism for this is not well understood [22]. Larger grain sizes allow the effect of SiC inclusions on amorphisation to be studied independently. Care must be taken to ensure amorphisation is not induced in B₄C grains that are a long distance from SiC.

Intimate mixing of SiO₂ and a carbon source results in some areas of pinned B₄C and SiC grains, as

well as a general reduction in B_4C grain size. It is likely that Zener pinning is occurring due to the small SiC grains which are also present in this region. These areas provide potential for amorphisation reduction through a decrease in B_4C grain size and the presence of SiC. It is important to note that, if amorphisation is proved to be reduced, further work will be needed to deconvolute the effect of grain size and SiC.

The free carbon within the samples has a similar structure to graphite, with the $d(002)$ spacing similar across all samples. There is however a marked decrease, of 8-12 nm, in the size of the crystallites when microemulsion SiO_2 is used. This suggests that the SiO_2 is better dispersed. When the SiO_2 is well dispersed it will react evenly across the structure with carbon. Any remaining carbon would be well dispersed and, if added in the correct amount, small in size. The literature shows that small carbon inclusions across the sample could aid in amorphisation resistance by increasing grain boundary sliding [22]. Therefore, the change in carbon crystallite size must be taken into account when considering the amorphous breakdown of these composites.

Analysis of hardness to determine amorphisation resistance is complex due to the number of deformation mechanisms occurring within the sample. When general mixing (Method Y) is used, samples produced using microemulsion SiO_2 and commercial SiO_2 likely have a lower hardness due to poorer densities. When intimate mixing is used (Method Z), the presence of SiC and free carbon, which are softer than B_4C , will decrease hardness. Additionally, the homogeneity of SiC and presence of pores can affect the hardness. It is therefore difficult to directly compare samples, with hardness differences resulting from a combination of all of these factors. This makes it difficult to determine what should be expected from each sample. This does verify samples made using intimate mixing alongside microemulsion SiO_2 (Sample 3Z) provide the gold standard. The hardness here is within 0.4-3 GPa of commercial B_4C whilst Sample 1X is within 8-12 GPa. The small grain areas, seen when intimate mixing is used, will likely have a higher hardness as B_4C is known to follow a Hall-Petch relationship [178]. These, combined with a high density and close to expected composition could explain the hardness value similar to B_4C . Deducing combined hardness is not straight forward, however it is expected that a composite containing SiC and free carbon would be softer than commercial B_4C . This is due to the difference in hardness between SiC and B_4C of 10 GPa - 15 GPa [179–182]. This difference varies with SiC polytype and the harder 3C SiC, found in samples made using intimate mixing, could be increasing the hardness here.

When considering the material response to load, the softer SiC and carbon phases found in the composites will undergo greater plastic deformation. The hardness of the composite will then result from a combination of the plastic and cracking responses. To achieve a similar hardness to B_4C , the microemulsion SiO_2 composite must undergo less plastic deformation, as the cracking appears similar. This could indicate that there has been a reduction in the amorphous breakdown in the material, or

that the interface between B_4C and SiC is capable of reducing plastic deformation. Further analysis is needed to verify if this observation is linked to a reduction in the amorphous breakdown.

6.5 Conclusion

This study has demonstrated that the intimate mixing of SiO_2 and a carbon source provides benefits over general mixing. This includes an increase in reliability of composition, increased homogeneity of the SiC phase and small grain areas with the potential for increased amorphisation resistance. It is however complex to determine the exact structure of the SiC in these composites, with a potential decrease in the polytype transition being demonstrated. The use of microemulsion SiO_2 stands out in this work due to it achieving a closer to desired composition than commercial powders made using the same method. Additionally, composites produced in this way show a potential to have decreased amorphous breakdown due to their higher than expected hardness. Whilst this hypothesis contains several assumptions on the deformation mechanism in these composites, it provides a good basis for amorphisation studies. It is also clear that a full characterisation of any composite is needed. This is so the various factors that affect amorphisation, such as boron doping, carbon content and B_4C grain size can be taken into account.

7 Investigating Amorphisation in B₄C-SiC Composites

7.1 Introduction

Analysis of amorphisation, specifically the zone size and location, is especially important in composites. The composites produced during this work consist of a homogeneous dispersion of SiC phase in a B₄C majority matrix. The SiC may affect the amorphous breakdown by altering the stress state in the B₄C. Understanding of this relationship will allow the development of microstructures, with the aim of reducing amorphous breakdown. It is therefore important to develop a robust method to analyse the amorphous zone, and correlate any changes to the presence of SiC.

In this work, it was deemed crucial that a large number of composites could be iterated through an analytical process in a timely manner. This would allow multiple microstructures to be tested to generate iterative improvements in amorphisation resistance. Traditional methods centre around TEM analysis of the amorphous band directly, or Raman spectroscopy surface mapping. Direct observation of the bands across a TEM specimen, containing an indent, is commonly used. Amorphous bands are usually around 200 nm in length and 5 nm wide [62], hence are difficult to identify at low magnification. The literature therefore focuses primarily upon the identification of the amorphous bands at high magnification, and considers their attributes such as crystallographic orientation. However, TEM has a limited field of view and can only take a slice through an indent.

Raman surface mapping can identify the amorphous zone from the presence of a peak associated with disordered (D) graphite. It can also map an entire indent but only from the surface. However to fully understand the effect of SiC, the amorphous zone must be mapped in three dimensions. This will allow the presence of SiC to be correlated to a change in the shape or size of the amorphous zone. The development of 3D Raman mapping has some precedent in the literature. Currently, 3D Raman characterisation requires iterative polishing and 2D scanning, using a reference indent to estimate the depth of each slice [15, 65]. These slices are then compiled into a volume intensity map, showing the amorphous region. This has some notable drawbacks. The method is destructive meaning additional analysis, such as TEM examination, is not possible. The process is also very slow and hence only limited sample numbers can be investigated. Additionally, polishing can induce amorphisation and introduce contamination. However, its ability to map the entire indent suggests Raman spectroscopy to be the best starting point for an analytical technique. A technique must be developed to allow 3D mapping, non-destructively, in a shorter time frame than more intensive TEM analysis.

Whilst a Raman-based method could provide fast, holistic and non-destructive analysis, confirmation using traditional TEM observation would be needed during development. The direct observation of the zone using TEM would give understanding of the limitations and accuracy of the new Raman method. HR-TEM is usually used to examine the amorphous band. However to examine the entire

region, such that it can be compared to the 3D map, a reduction in resolution is normally necessary. Whilst time intensive, HR-TEM used alongside montaging software can allow large scale maps of the amorphous region to be produced without reducing resolution. This can then give a high quality representation of the amorphous bands across the specimen.

Experiments need to be designed to allow the two techniques to be compared, with the aim of drawing a conclusion about usability and accuracy of the newly-developed 3D Raman method. This technique can then be used to examine indents in commercial B₄C and B₄C-SiC composites. Thus two clear aims emerge:

1. Develop a 3D non-destructive Raman-based method which can analyse amorphisation under indents in B₄C.
2. Analyse amorphisation around indents in B₄C-SiC composites to determine the effect of SiC on amorphisation.

7.2 Developing the Raman method

The novel Raman method was developed through iterative experiments, which examined best practices for investigating amorphisation. Traditional TEM micrographs from a range of B₄C indents were initially examined to determine how the amorphous zone changes with load and how the zone might look when Raman mapping is used. To develop the Raman method, it was necessary to first examine if it is possible to identify the amorphous zone beneath the indent. Once its feasibility was asserted, the experiments were repeated on a range of indentation loads to determine if the scans matched expected trends from the TEM micrographs. 2D maps at varying depths were then compiled to produce a 3D map of the amorphous zone. This method was used on both B₄C and B₄C-SiC composites to understand if SiC is able to reduce the extent of amorphous breakdown. Building from this, analysis of amorphisation in an SiC rich environment was conducted to understand if constraining the B₄C in SiC would change the amorphous breakdown. Throughout this work the standard Raman setup, as defined in Chapter 4 of this thesis, was used.

Traditional TEM analysis

Before considering the Raman method, it is necessary to understand how the amorphous zone develops under an indent using traditional TEM analysis. Figure 68 shows an amorphous band seen within the sample, alongside a band viewed with objective over focus. Figure 69 shows TEM micrographs, produced using HR-montaging, for 3 indent loads. These micrographs have a Sobel filter applied along with objective over-focus. The over-focus of the objective lens allows regions of different phases to be identified, due to a phase shift resulting in Fresnel fringes. In this case the amorphous bands appear white. A Sobel filter, which highlights edges between light and dark areas by enhancing local contrast,

is then applied. This, combined with montaging, allows the amorphous bands to be viewed across the entire indent, rather than just in specific areas.

It can be seen that the amorphous bands follow the general direction of the yellow arrows, which can give an indication of the stress state across the indent. These directions are similar for each load. The size of the region containing amorphous bands is seen to increase with load as would be expected. Additionally, cracking (red arrows) becomes more prevalent at higher loads. It can be difficult to determine which features are amorphous bands and which are cracks. However, in this case, careful analysis of the individual montage image, alongside comparison to literature, allows their general direction to be identified.

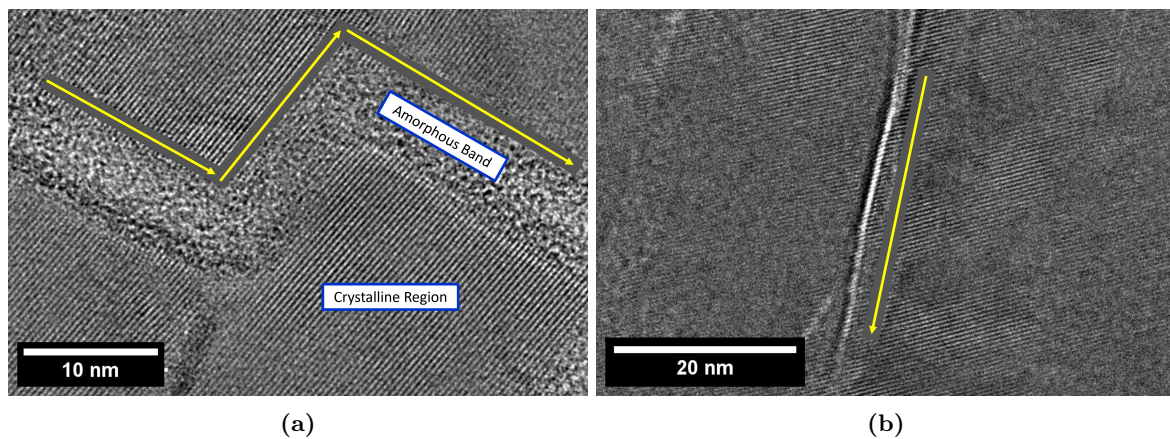


Figure 68: a) TEM micrograph showing amorphous bands interacting and hence forming a non linear path. b) An amorphous band viewed when objective overfocus is applied. The yellow arrows indicate the direction of the amorphous band.

The amorphous bands are parallel to the sample surface across the long side (L) of the indent. A similar observation is seen on the short side (S), although these bands appear shorter in nature. Under the centre of the indent, when moving from S to L, the amorphous bands begin at the surface of S before crossing under the indent centre and progressing deeper into the material at an approx 135° angle. Determining the crystallographic direction of the amorphous bands is not straight forward. Warping of the sample during preparation, alongside indentation induced cracking, inhibits diffraction based work by limiting how thin the sample can be made before it becomes unstable. Additionally, the sample's polycrystalline nature makes orientation prediction complex. As no grain boundaries are seen, it is likely each indent is within a single grain.

As noted in the literature review, there is range of hypotheses as to the origin of amorphous bands. Additionally, even where the formation mechanism is not investigated, the bands are oriented along a range of directions depending on which single crystal is used. These directions are activated by shear that exceeds that required for amorphisation [17–19]. These micrographs therefore provided an indication of the shear direction across the indent and yielded an understanding of the shape and size of the amorphous region. It is noted by Ge *et al* that a similar shear structure is seen in indents of

100 mN and 200 mN, with the direction of the bands varying across the indent. Their study provides good agreement with this work [18].

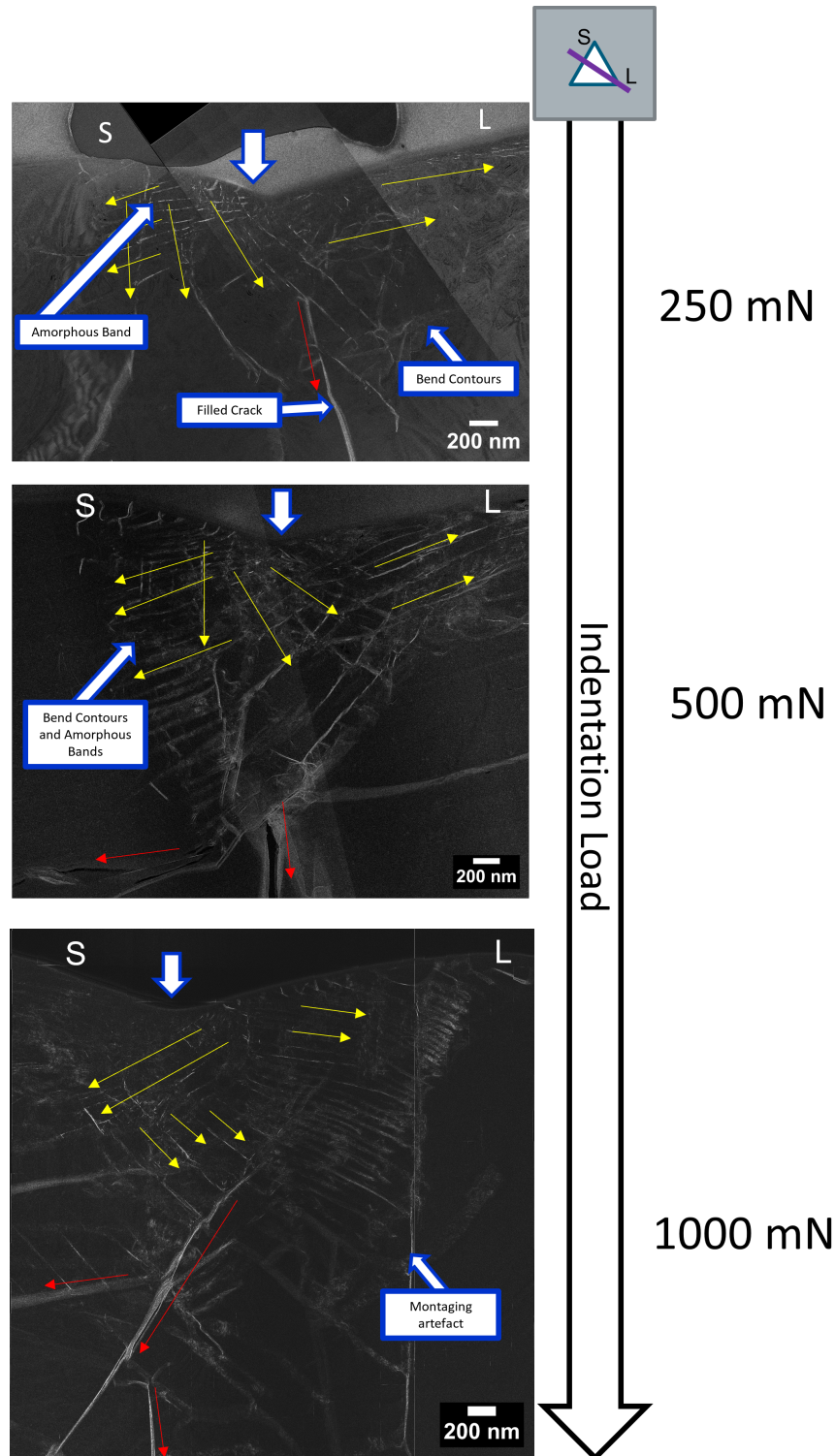


Figure 69: TEM micrographs of various load indents in B_4C . HR-TEM montaging allows the amorphous bands and nanocracks they cause to be identified. The general direction of these is shown with the yellow arrows. The centre of the indent is identified by the white arrow and the median (transverse) and lateral cracks are identified by the red arrows.

The micrographs indicate that cracking increases when higher loads are used. It is noted by An *et al* that amorphous bands, formed by twin coalescence, can act a nucleation points for cracks [23,

69]. It is therefore likely that smaller cracks may have amorphous material at their edges or ends. This means that some amorphous bands may have progressed to the crack stage but still contain amorphous material. Unfortunately, warping of the sample near cracks made this difficult to verify. This observation must be considered when analysing the amorphous zone; cracking could change the location or concentration of the amorphous bands hence altering the amorphous region shape or size.

This TEM analysis provides a good understanding of the location of amorphous bands in the samples, and sheds light on the potential appearance of the amorphous volume under 3D Raman mapping. The Raman method can be compared to the TEM analysis to verify the shape of the observed zones.

1D depth point scans using Raman

Whilst TEM analysis can clearly identify amorphous bands, it is destructive and time consuming. Raman analysis, with an approximate spot size of 700 nm, cannot identify individual amorphous bands. Therefore, it will detect an amorphous zone, in which a number of amorphous bands, as well as virgin material, will be found. The amorphous region is clearly identifiable by a D peak at 1340 cm^{-1} when a 2D surface scan is conducted (found in Figure 27). To investigate the viability of depth scanning, the scans of this zone were initially reduced to 1 point at the centre of the indent as described in Figure 70a. These experiments aim to identify the bulk B_4C , situated under the amorphous zone. Detecting the bulk would give an indication that the method could see below the surface and hence map the edge of the amorphous zone.

Scans were conducted at $0.1\text{ }\mu\text{m}$ z intervals using the Raman setup discussed previously. Here, the z interval is the amount incrementally moved towards the apertures by the stage. This results in a movement of the focal plane downwards into the sample. The scan depth, D_s , can be defined as the distance between the surface of the sample and the focal plane. Indents with a maximum load of 100 mN, 150 mN and 250 mN were studied. A relative ratio was established that compared the intensity of a non-amorphous B_4C peak (I_{B_4C}), located at 1080 cm^{-1} , to the amorphous, D, peak (I_D) at 1340 cm^{-1} . This is described in Equation 41. Plotting this ratio, B , against D_s provides insight on the depth of the amorphous zone. Figure 70b shows the resulting trend for a 100 mN indent. For each indent, 3 regions could be identified as described in Equation 42, 43 & 44.

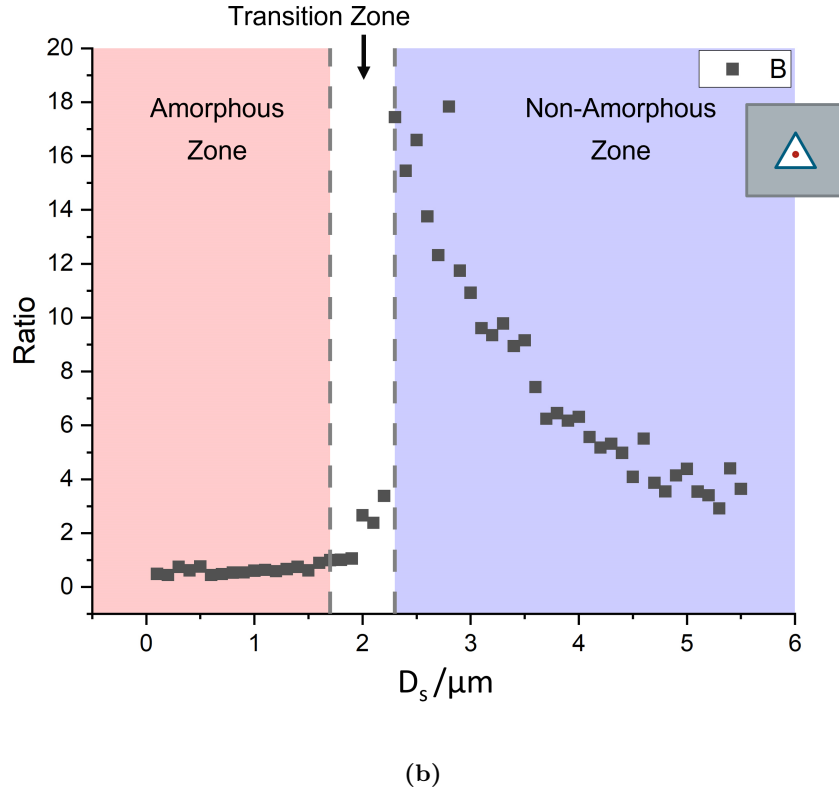
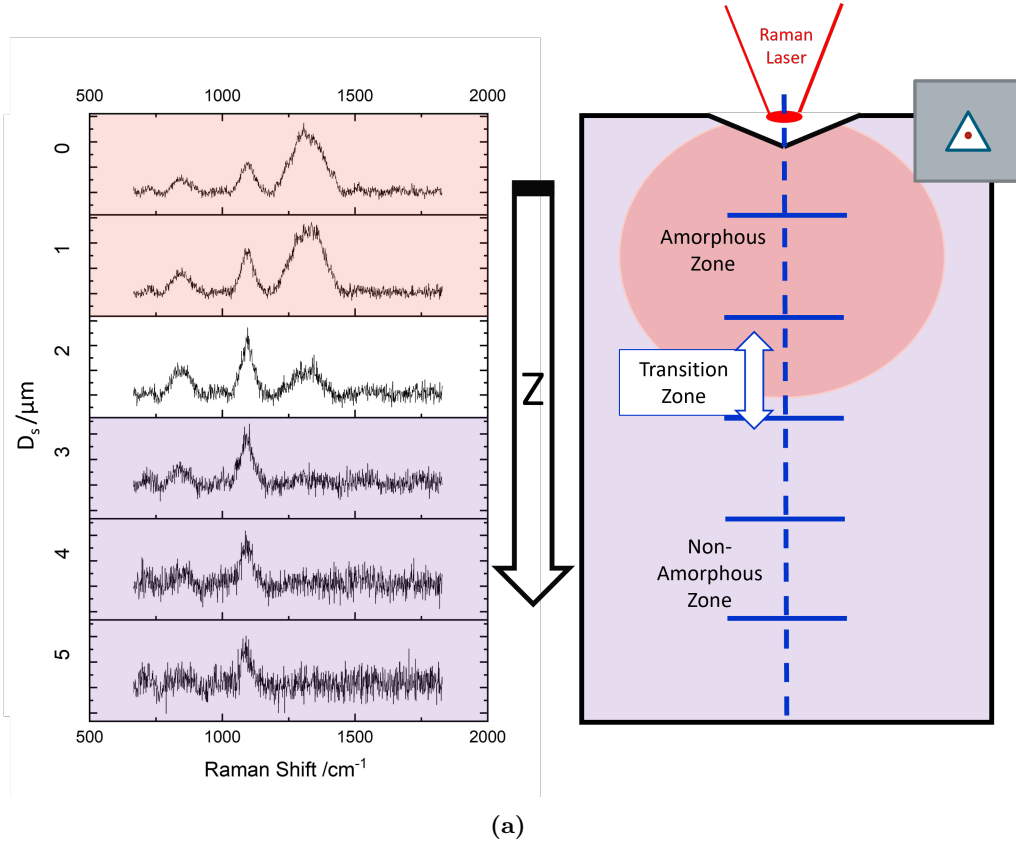


Figure 70: a) Diagram showing the location of the amorphous zone (pink), transition zone (white) and non-amorphous zone (purple) and the corresponding Raman spectra in these regions. b) Graph showing the variation of B with the scan depth. Three regions can be identified and are defined by Equation 42, 43 & 44.

$$B = \frac{I_{B_4C}}{I_D} \quad (41)$$

$$\text{Amorphous Zone : } B < 1 \quad \text{Red Zone} \quad (42)$$

$$\text{Transition Zone : } 1 \leq B < \text{Maximum} \quad \text{White Zone} \quad (43)$$

$$\text{Non-Amorphous Zone : } B < \text{Maximum} \quad \text{Blue Zone} \quad (44)$$

The transition zone indicates the amorphous zone is decreasing in size with depth and bulk B_4C signal is becoming more prevalent. At the interface between the transition zone and non-amorphous zone, it can be said that the amorphous region has ended. Here, it is assumed that the beam is now in a material not containing amorphous bands (bulk B_4C). The presence of this interface shows that the beam is able to penetrate sufficiently into the material to view the amorphous region, and the bulk below it.

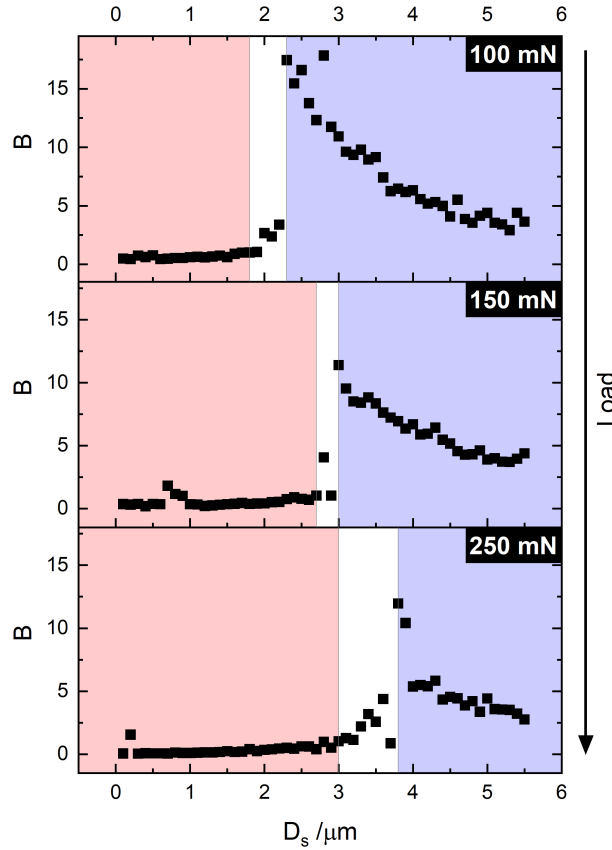


Figure 71: Graph showing the change B with scan depth for 100 mN, 150 mN and 250 mN indents. Here the amorphous zone (pink), transition zone (white) and non-amorphous zone (purple) are also labelled.

It is possible to verify this observation by comparing scans at multiple indent loads. The amorphous zone would be expected to increase in size with indentation load, as is seen from TEM analysis. Figure

71 shows the resulting plots of the B ratio for 100 mN, 150 mN and 250 mN. As is expected, a shift to higher depths occurs as the load increases, indicating that the amorphous zone occurs deeper into the material. This agreement with the expected trend demonstrates further that the method of depth scanning is capable of identifying the size of the amorphous zone within B_4C .

3D volumes from 2D surface maps

A point scan experiment can only identify the amorphous, transition and non-amorphous zone directly below the indent. A 2D scan can allow this transition to be identified across the indent. This proceeds by rastering the laser across the surface to produce a map, with each point having it's own Raman spectra. These maps were processed using a Python script, included in the appendix section 11.2, developed for the task. The fundamental steps of this are described in Figure 72. This allows the virgin and amorphous B_4C peaks to be quickly identified and mapped for comparison. It was noted that the transition zone often occurred where the D-peak intensity was in the 20th percentile of intensity across the map. It was hence assumed that the 20th percentile of intensity, mapped in orange, is analogous to the transition zone.

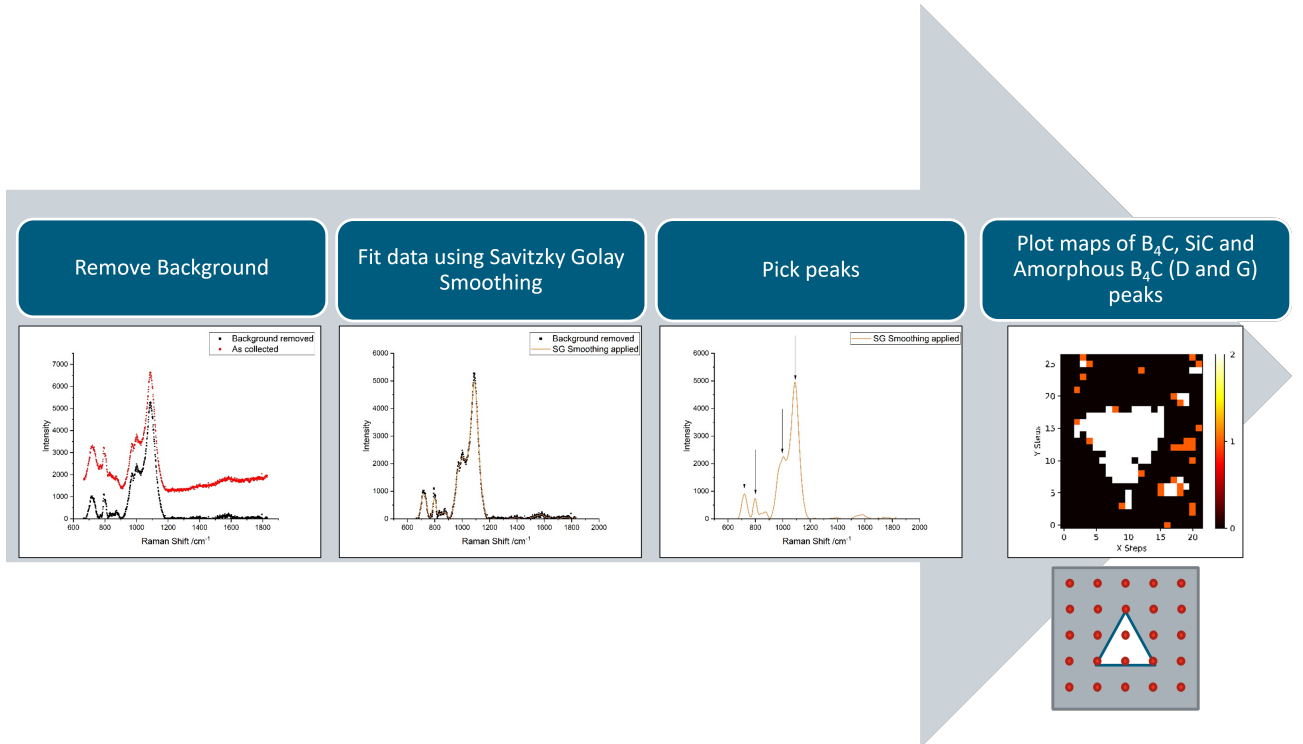


Figure 72: Diagram explaining the standard Raman processing method conducted for a 2D map. The final plots, found on the right, have the strong signal (white, 2) plotted alongside the weak (orange, 1) signal. The weak was defined as below the 20th percentile of the maximum map intensity. This region is analogous to the transition zone described in Figure 70 .

To produce a 3D map, a 2D map is conducted at each depth interval. In this case, D_s was varied between 0 μm (surface) and 5 μm in 1 μm intervals. To produce a 3D volume, the 2D peak intensity maps were turned into a stack, with a layer height of 1 μm using Image J. These were then modelled

as a 3D volume from which a volume of amorphisation (V_{amorp}) could be obtained. This was termed the 3D non-destructive method and is described in Figure 73b.

To understand the accuracy of the 3D Raman method, the Raman cross section was also determined destructively. TEM cross sections cannot undergo Raman analysis due to poor signal return. Here, a FIB-SEM was used to cross-section the indent, exposing its depth profile. A 2D scan of the face could then be conducted and processed. The difference in these two methods can be seen in Figure 73. 1000 mN, 1500 mN and 2000 mN indents were examined using the non-destructive method, followed by the destructive method. This produced both a 3D non-destructive map and a 2D destructive depth profile.

It was possible to extract a slice (purple dotted line) from the 3D map and compare it to the 2D profile as seen in Figure 74 in order to directly compare between the two methods. Features that appeared in both maps provide insight into the 3D depth mapping method; for instance, when the features highlighted in blue are compared, the slice appears stretched in the z direction. This suggests that the layer height is less than the 1 μm set during the Raman mapping. In addition, areas of no amorphous signal (highlighted in red) were not detected by 3D Raman mapping when surrounded by the amorphous zone (white), which may indicate that the signal becomes smeared during scanning.

Reducing stretching through layer height correction

In order to reduce the stretching effect along the z -axis, it was necessary to determine the physical layer height. A major benefit of the non-destructive method is that a cross section or a TEM specimen can be produced from the indent that was mapped. From this the layer height could be calibrated as demonstrated in Figure 75. Here, the TEM micrographs, produced using the montaging method described in Chapter 4, could indicate where the concentration of fine, amorphous bands began to decrease. This could be compared to the location of the transition zone observed in a 3D slice and a correction factor calculated as per Equation 45. This approach was used on a 250 mN indent bearing both a detectable transition zone and sufficient stability to produce a TEM specimen.

$$L_R = L_E \frac{Z_R}{Z_E} \quad (45)$$

Where L_R is the corrected layer height, L_E is the experimental layer height, Z_R is the location where the concentration of fine amorphous bands is seen in the TEM micrograph to decrease and Z_E is the location of the depth at which the amorphous Raman signal reduces to 0 in the 3D Raman slice.

An assumption has to be made on the exact position of zone interfaces in the TEM micrograph. The process is hindered somewhat by the difference in resolution between Raman and the TEM: the Raman laser spatial accuracy is around 700 nm whilst an amorphous band may be 5 nm wide and 20 nm

long. This means the exact number of amorphous bands in the transition zone cannot be determined. Given this fact, an assumption was made that the transition zone ended where no amorphous bands were seen. Under this axiom, the amorphous-non-amorphous interface was estimated across the TEM specimen and compared to the Raman slice. Using the calibration method, the corrected layer height factor was calculated to be $0.41\ \mu\text{m}$ as seen in Table 28. Whilst the standard error on this value is small, the interface identification is down to operator judgement. It is important to consider this assumption when examining the Raman maps.

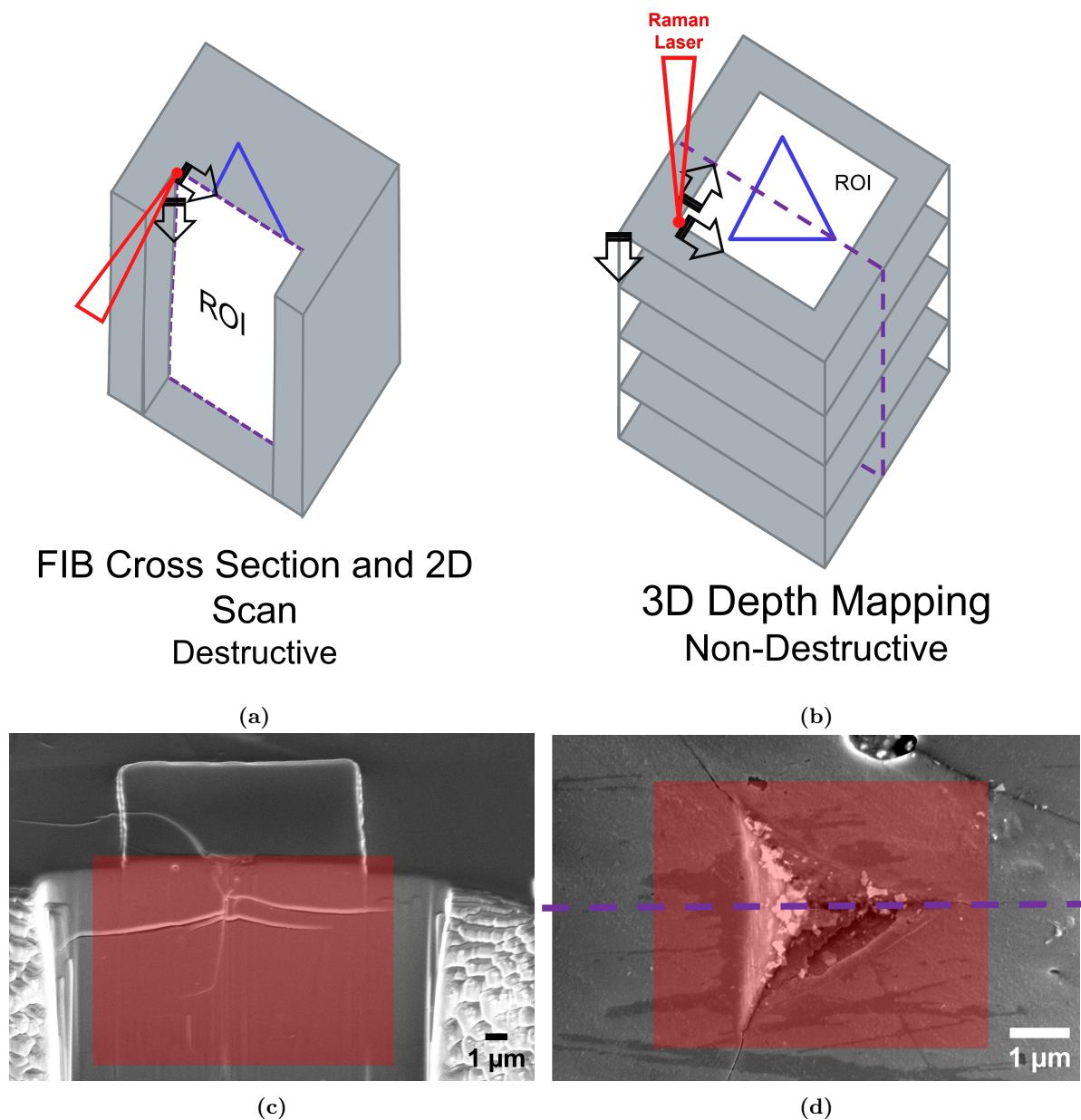


Figure 73: a) Diagram showing how a destructive scan of the amorphous zone could be conducted. The region of interest (ROI) is shown in white. This method produces a 2D map of the amorphous zone through depth. The indent is indicated in blue. b) Diagram showing how a non-destructive 3D mapping could be conducted. This method produces 2D slices that can be combined into 3D volumes. From this, a 2D slice could be taken along the purple dashed line. This slice is then comparable to the scan produced using the destructive method. c) SEM micrograph showing the indent cross section post-FIB milling. d) SEM micrograph showing the indent before milling. The ROI is shown in red and the slice direction is shown in purple.

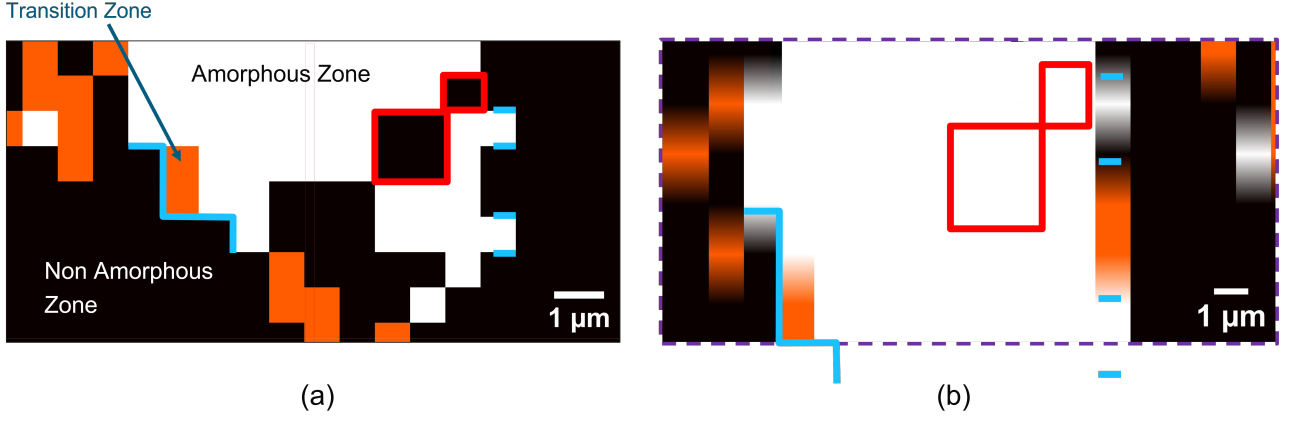


Figure 74: a) A map of the amorphous (D) peak taken for a depth profile produced using the FIB cross section method. Here the strong signal (white) was plotted alongside the weak (orange) signal. The weak signal was defined as below the 20th percentile of the maximum map intensity. This region is analogous to the transition zone. b) A slice taken from the 3D volume of the same indent showing the amorphous (D) peak. A 2000 mN indent was used for this comparison with a 1 µm layer height. Features common to both maps are edge highlighted in blue. Selected features only found in (a) are highlighted in red.

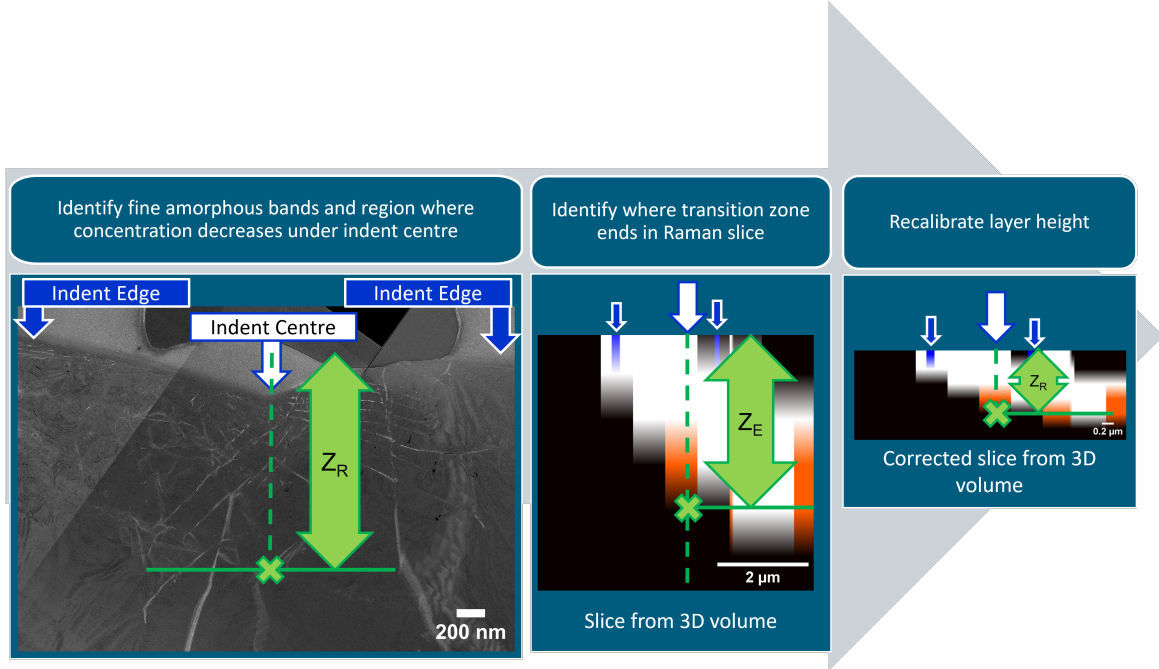


Figure 75: Diagram showing the method for calibrating the layer height. Here, a TEM micrograph is observed and fine amorphous bands are identified to a depth (Z_R) below the surface. The location corresponding to this depth is identified in the Raman slice at a height, Z_E . These two are compared to produce a correction factor, with the new layer height being calculated using Equation 45. A 250 mN indent was used for this calibration.

Comparing the map and slice in Figure 76 shows the effect of using the calibrated layer height. It can be seen that the blue lines occur at similar depths, unlike in Figure 74. Greater parity between the two is evident but not perfect and is controlled by the assumption that has been used. It is noted that the red areas become more similar in size, although adjusting the layer height has not reduced the smearing effect. The corrected layer height was used throughout the rest of this work. Using the same layer height allows comparison between Raman maps as each contain the same assumption and

error associated with this.

Table 28: Table showing the corrected layer height calculation. A horizontal location is defined with 0 being the indent centre and right of indent being positive. A final value for the correction factor was determined as 0.41.

Horizontal location / μm	$Z_E/\mu\text{m}$	Interface type	$Z_R/\mu\text{m}$	Z_R/Z_E
0.80	4.00	Amorphous to Non Amorphous	1.50	0.38
1.50	4.50	Amorphous to Non Amorphous	2.00	0.44
0.00	4.00	Amorphous to Transition zone	1.50	0.38
0.00	2.00	Amorphous to Non Amorphous	0.80	0.40
-0.60	3.00	Amorphous to Non Amorphous	1.45	0.48
-0.90	1.50	Amorphous to Non Amorphous	0.58	0.39
			Mean	0.41 ± 0.02

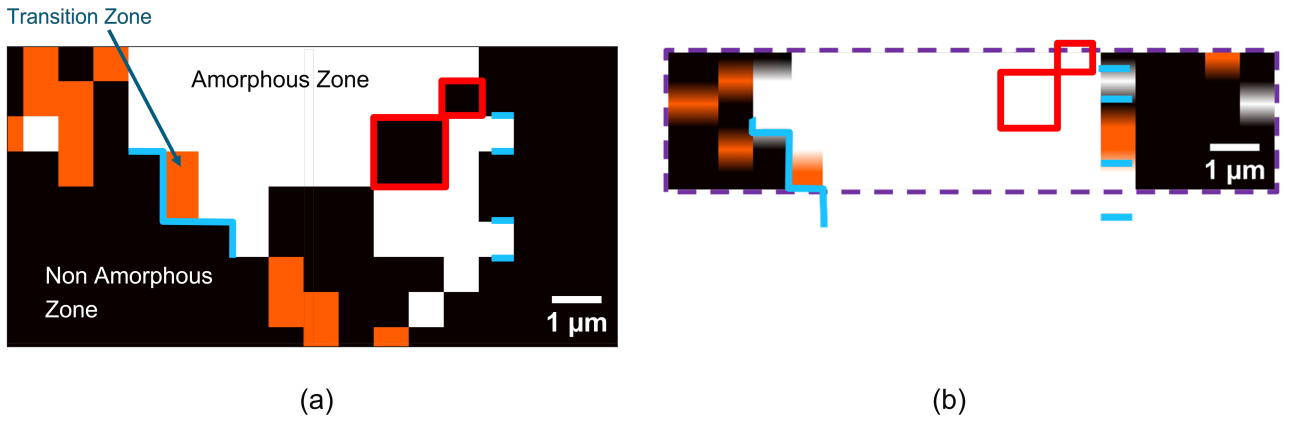


Figure 76: a) A map of the amorphous (D) peak taken for a depth profile produced using the FIB cross section method. Here the strong signal (white) was plotted alongside the weak (orange) signal. The weak signal was defined as below the 20th percentile of the maximum map intensity. This region is analogous to the transition zone. b) A slice taken from the 3D volume of the same indent showing the amorphous (D) peak with a corrected layer height of 0.41 μm . A 2000 mN indent was used for this comparison. Features common to both maps are edge highlighted in blue. Selected features only found in (a) are highlighted in red.

Investigating interaction volume to reduce smearing

Calibration of the layer height is unable to completely mitigate the smearing effect seen in the slice taken from the 3D mapping method. The smearing effect itself likely comes from the difference in refractive index across the sample, which can be linked to the various constituents (B_4C , amorphous B_4C and SiC grains) and geometric features such as cracking. This results in a loss of resolution and hence non-amorphous areas may appear amorphous. Thus, to gain an understanding of how to reduce the smearing, an investigation into the relationship between resolution and depth was necessitated.

Baldwin and Batchelder provide a method for analysing the depth resolution of a confocal microscope, operating in a fluorescence setup, using an axial Probe Response Function (PRF) [183]. This method seeks to characterise the subsurface diffraction of the beam, yielding a correlation between the focal plane location and interaction volume. To provide further insight, an interaction volume (IV) experiment was conducted to determine a PRF in B_4C . Here, a wedge of B_4C was produced with a

thickness ranging from 0.44 μm to 4.5 μm as seen in Figure 77a. Scans were completed across 6 points on the wedge. The surface was brought into focus, before moving the laser focal plane 8 μm above the surface. The focal plane was then moved downwards in 0.1 μm increments to a maximum of 16 μm . A scan was taken at each increment, capturing information between 8 μm above and below the surface. The PRF plots the normalised intensity of a peak against the movement in focal plane (Δz). The PRFs are plotted in Figure 77b, with the wedge surface being at 0 μm . The intensity of the B_4C peak at 1080 cm^{-1} is used here. It should be noted that the location of maximum intensity can move about 0 μm due to the inherent difficulty in focusing the Raman laser on the surface.

Lipkin and Clarke advanced general understanding of the PRF by using a Lorentzian function as part of the fitting process [184]. Guo *et al* noted that, when alumina based composites were used, the function seen in Equation 46 fitted well to the data [185]. However, it was noted that the function failed to accurately fit the tails of the datapoints. They conducted experiments to determine the optimum PRF for a nanocomposite, modifying the original formula to account for the extra diffraction by grain boundaries and pores often found in imperfect polycrystalline samples. This can be seen in Equation 48. By using initial values taken from a single crystal of sapphire (alumina), a curve fitting could be conducted and physical meaning attributed to the values. This work has some similarities to the present studies and hence will be used as a basis of data fitting herein. Figure 77c demonstrates the benefits of using the method proposed by Guo *et al*.

$$I(z_0) \approx \int_0^t \frac{p}{(z - z_0)^2 + p^2} dz \quad (46)$$

$$z_o = n\Delta z \quad (47)$$

where I is the intensity of a peak, n is the refractive index, Δz is the incremental movement of the stage (focal plane), t is the thickness of the sample and p is the probe half length (half the FWHM of the PRF).

$$I(\Delta z) = \int_0^t e^{-2k_9 z} \left[k_{11} \frac{k_2}{k_2^2 + [z - k_1(\Delta z - k_7)]^2} + k_{12} \frac{k_{10}}{k_{10}^2 + [z - k_1(\Delta z - k_7)]^2} \right] dz \quad (48)$$

where k_1 corresponds to the effective refractive index, k_2 the axial resolution at the surface, k_7 the focus offset and k_9 is closely related to the absorption coefficient.

Guo *et al* determined k_1 and k_2 using a single crystal of sapphire, an alumina polymorph. However, a single crystal of B_4C was not available for this work. In our fitting, k_1 will be fixed at the refractive index of 3.25 as predicted by Laruquert *et al* [186]. It is not possible to determine an equivalent k_2 value, hence it was not fixed. The value of k_9 is closely related to the absorption coefficient. It was noted that its value for pure alumina in the work of Guo *et al* was 100 times greater than that

predicted in the literature. Therefore, the fitting value for the absorption coefficient was fixed at $0.114 \mu\text{m}^{-1}$, two orders of magnitude smaller than the predictions of Laruquert *et al* for B_4C . Table 28 shows the fitted parameters. Besides these two, it was not possible to fix other coefficients without further experimentation.

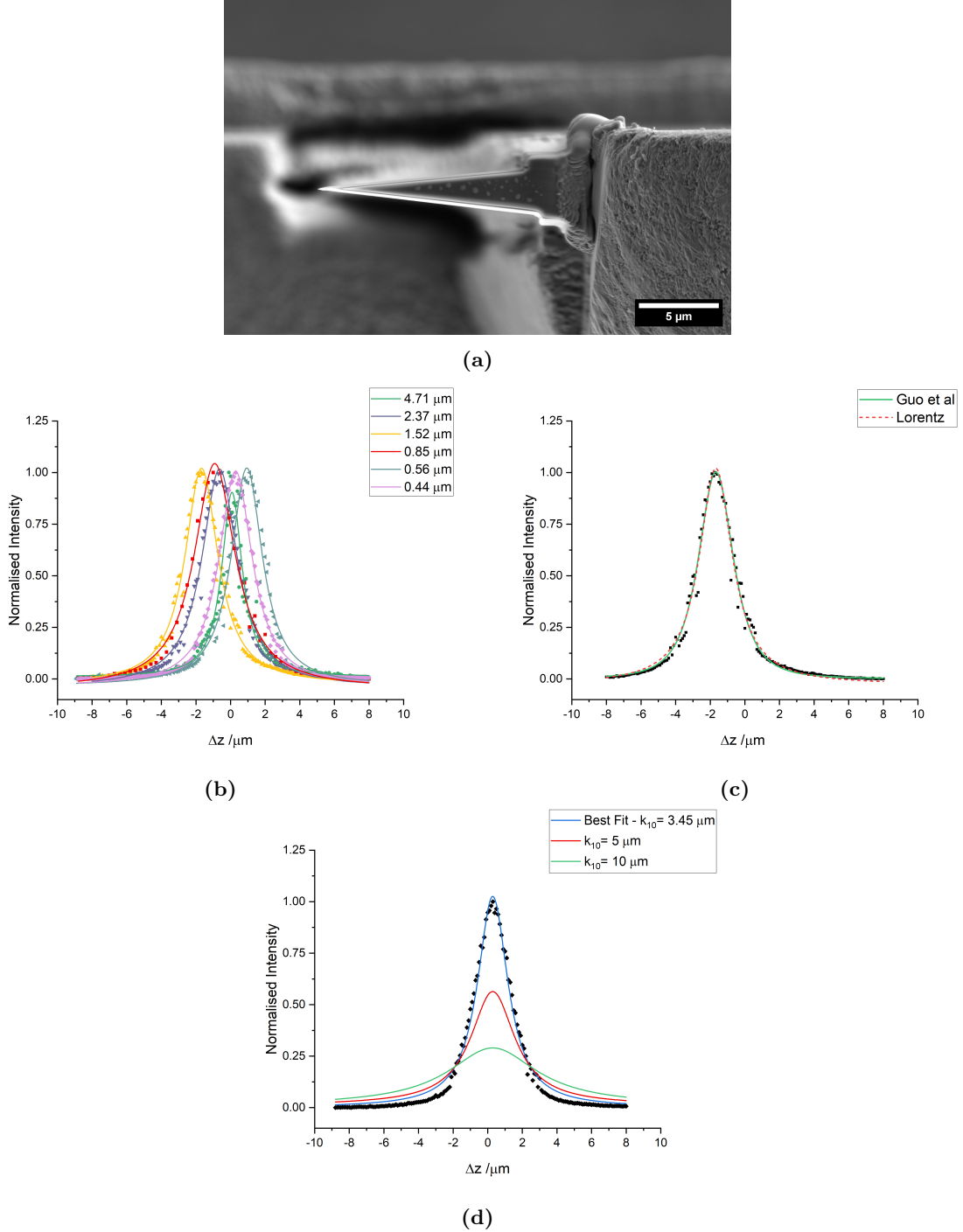


Figure 77: a) SEM micrograph showing the B_4C wedge used during this work to investigate the interaction volume of the Raman laser. b) PRF functions produced when a wedge of B_4C is scanned through depth using Raman spectroscopy. The intensity shown is the normalised intensity of the main B_4C peak at 1080 cm^{-1} .

These are fitted with a basic Lorentz function. c) Graph showing the PRF of the $1.52 \mu\text{m}$ part of the wedge. d) The PRF for the $0.44 \mu\text{m}$ wedge thickness with a range of k_{10} (axial resolution) values

The values obtained from this fitting are found in Table 29. A test of the fit can be conducted by

noting how close k_7 is to the offset of the maximum intensity from 0 μm . In our case these were seen to be similar, providing some confidence in the accuracy of other values.

Table 29: The values of coefficients obtained when the function, proposed by Guo *et al* [185], is used to fit the PRF function obtained for B_4C .

Wedge Thickness/ μm	k_1	$k_2/\mu\text{m}$	$k_7/\mu\text{m}$	$k_9/\mu\text{m}^{-1}$	$k_{10}/\mu\text{m}$	k_{11}	k_{12}	k_{12}/k_{11}
0.44	3.23	3.45	0.22	0.11	3.45	1.93	6.54	3.39
0.56	3.23	3.28	0.86	0.11	3.28	4640.00	11805.00	2.54
0.85	3.23	2.66	-1.05	0.11	2.69	-254.70	260.30	-1.02
1.52	3.23	9.67	-1.90	0.11	4.30	-1.61	4.11	-2.56
2.37	3.23	2.08	-0.96	0.11	2.11	-55.45	57.42	-1.04
4.71	3.23	1.97	-0.47	0.11	1.96	-6.30	7.03	-1.12

Figure 77d demonstrates the high sensitivity of the fit to changes in k_{10} . Since the necessary resources to facilitate the experimental determination of coefficients such as k_2 were unavailable for this study, extra degrees of freedom (*i.e.*, model parameters) were introduced into the model fitting process in comparison with Guo *et al*. This increases the probability of model overfitting and introduces uncertainty into the fitted coefficients of interest, namely k_{10} . However, the high sensitivity of the fit to this coefficient suggests the value reported is accurate. k_{10} can be interpreted as the maximum depth that can be analysed; it varies in value, averaging 2.97 μm . This is similar to the maximum depth of mapping seen in the Raman 3D method after layer height correction, which was 2.1 μm . In contrast, Guo *et al* determined k_{10} values of 16.1 μm and 71.6 μm for a 90:10 (alumina:SiC) composite and pure alumina respectively. This suggests that the depth that can be investigated for B_4C is significantly smaller than in alumina based nanocomposites.

Following further data analysis and experimentation, Guo *et al* were able to assign a percentage accuracy to the signal at each depth, demonstrating that the accuracy for composites with a lower k_{10} is greater. For example, the spectra in pure alumina ($k_{10} = 71.6 \mu\text{m}$) at 2.5 μm deep contained only 70% signal from the focal plane. All remaining signal resulted from scattering around the focal plane that is not removed by the confocal Raman setup. In contrast, the spectra of 90:10 (alumina:SiC) composite ($k_{10} = 16.1 \mu\text{m}$) contained 98% signal from this depth. These findings make it clear that whilst greater penetration can be achieved with alumina, mapping accuracy at shallow depths is significantly poorer than for the composite. For a 90:10 (alumina:SiC) composite the maximum depth of accuracy (accuracy drops below 50%) was 4 μm .

Comparison to Guo *et al* suggests that maps in B_4C ($k_{10} = 2.97 \mu\text{m}$), will be more accurate near the surface than alumina based composites. However, this accuracy will rapidly decrease with depth and hence only a small depth can be analysed. This analysis provides some confidence that the 3D Raman method is able to examine below the surface of B_4C . Further work is needed to determine how the accuracy of the signal changes with depth. Understanding of this could allow the smearing effect seen in the scans to be reduced or accounted for.

7.3 Understanding the effect of SiC on amorphisation

To understand the effect of SiC on amorphisation, it is necessary to first consider how the Raman 3D method reports amorphisation in B₄C. In order to determine a quantitative value, the volume of amorphisation is calculated, a process which presumes that each point of the sample is a $700 \times 700 \times Z$ nm rectangle based on the spot size of the Raman setup. The height of each slice (Z) was determined from TEM calibration as 0.41 μm . Hence, the volume of the 3D map which contains an amorphous signal could be calculated. This includes both the amorphous and transition zones.

Once the size of the amorphous zone was determined, it was compared those obtained in B₄C:SiC composites. Additionally, specific microstructures were developed to understand how the B₄C and SiC interact under load.

Amorphous zone in B₄C

The 3D Raman method was used to determine the volume of amorphisation for 100 mN to 250 mN indents. The 1D point scans and PRF measurements demonstrated that bulk B₄C could be detected under the amorphous zone in these indents. It can therefore be asserted with some confidence that the whole amorphous zone is characterised in these scans. Figure 78a shows the variation in amorphous volume with load. Similar to previous observations, the amorphous zone increases with load, as does sample deformation. This trend provides confidence that the 3D Raman method can determine the volume of amorphisation and highlight associated trends.

Further work in this area should focus on correlating the amorphous volume to the stress condition under the indent. Whilst difficult to accurately determine, linking the volume of material that is loaded above the force needed for amorphisation to the amorphous volume seen here could provide useful understanding of the methodological accuracy.

Small indents, such as those below 500 mN, are difficult to find and measure in an optical setup. Additionally, in composites, it is more likely that an indent will be localised to a B₄C or SiC grain. This is especially true due to the large B₄C grain size. The effect of the SiC on amorphisation was therefore challenging to determine. To somewhat mitigate these hurdles, indents with loads of 500 mN to 2000 mN were used; however, as the bottom of the amorphous zone is not seen in these indents when the 3D method is used (*e.g.* figure 76b), comparison between loads is not possible. This is because each load will be ‘missing’ a different proportion of its amorphous zone.

Figure 78b shows the amorphous volume relationship. Although trends cannot be quantified, the amorphous volume generally increases with load as is expected. The trend represents a fairly consistent increase, although at lower loads the amorphous volume increases to a plateau. The whole zone trend seen at lower loads is likely more accurate, with the part zone trend being an artefact of its incomplete

nature. These indents can be compared to those in composites to determine if the SiC has an effect on the amorphous region.

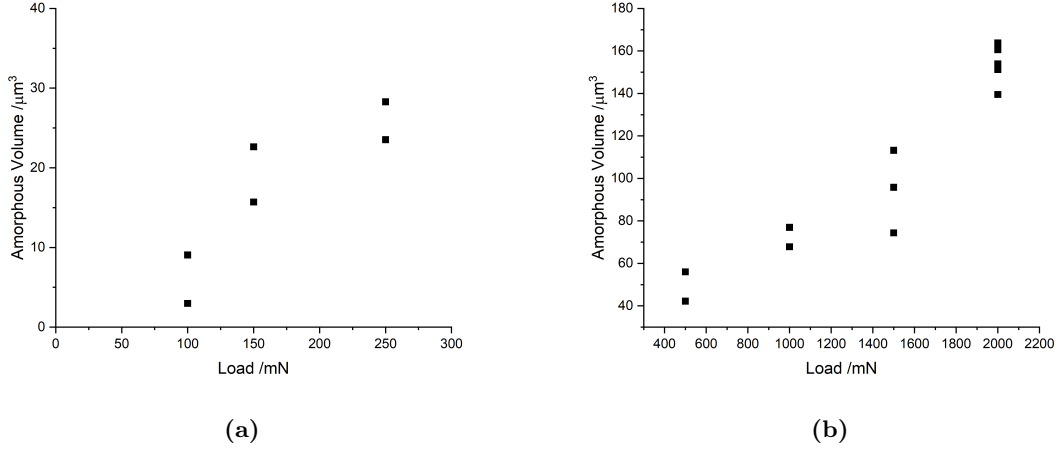


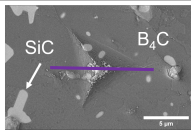
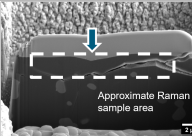
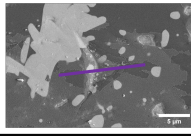
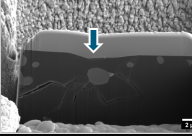
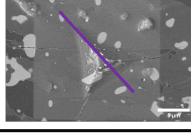
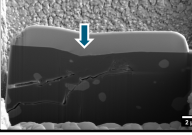
Figure 78: a) Graph showing the volume of amorphisation plotted against maximum indentation load up to 250 mN. These are considered full zones, as the whole amorphous zone is visible in the scan. b) Graph showing the volume of amorphisation up to 2000 mN. These are considered incomplete zones as the whole amorphous zone is not visible during the scan.

Amorphous zone in B₄C-SiC composites

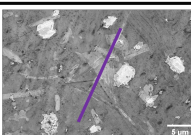
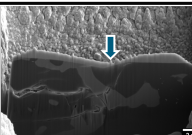
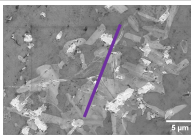
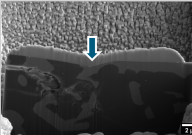
Before considering the amorphous volume found using the 3D Raman method, it is first necessary to inspect the indent location. Composites made using microemulsion SiO₂ using Method Z had a good level of homogeneity. Nevertheless it is still feasible that SiC is scarce in the region which can be interrogated by 3D Raman mapping. Indents were therefore cross sectioned using FIB-SEM to understand the subsurface SiC location. Figure 79 shows a range of indents in Sample 1X (commercial SiC), Sample 2Y (commercial SiO₂) and Sample 3Z (microemulsion SiO₂). Sample 3Z showed a similar hardness to B₄C, despite predictions it would be softer, and is hence of interest here. A prediction can be made of the potential change in the amorphous zone around the indent based on the amount of SiC that is present. SiC could reduce amorphisation by altering the stress state in the B₄C, hence the critical stress for amorphisation is not reached. Alternatively, SiC is not known to undergo an amorphous breakdown, thus the amorphous volume measured is less when SiC is present. It is key to differentiate which of these effects is occurring.

The amorphous volume calculated using the 3D Raman method, is shown in Figure 80. Sample 1X shows amorphisation values similar to B₄C for both 1000 mN and 2000 mN indents. This is to be expected, due to the limited amount of SiC under or near the indent. At 1500 mN a greater amount of amorphisation is seen, despite the presence of SiC both under the centre of the indent and near the edge.

Sample 1X

Load /mN	Indent	Cross Section	Comments and Predictions
1000			- Limited amount of SiC near indent. - Expect little change in amorphous signal compared to B₄C.
1500			- SiC directly under indent. - Reduction in amorphous signal may be present.
2000			- Limited amount of SiC near indent. - Expect little change in amorphous signal compared to B₄C.

Sample 2Y

Load /mN	Indent	Cross Section	Comments
2000-A			- Large amount of SiC directly under indent. - Reduction in amorphous signal highly likely.
2000-B			- Large amount of SiC directly under indent. - Reduction in amorphous signal highly likely.

Sample 3Z

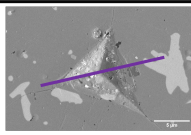
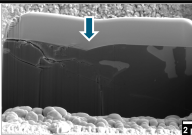
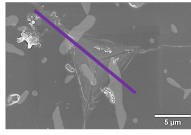
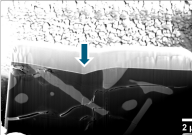
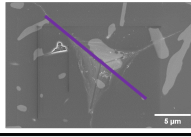
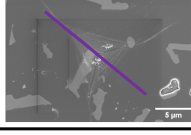
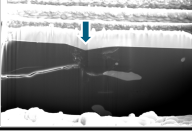
Load /mN	Indent	Cross Section	Comments
2000-A			- Limited amount of SiC near indent. - Expect little change in amorphous signal compared to B₄C.
2000-B			- SiC directly under indent. - Reduction in amorphous signal may be present.
1500-A			- SiC directly under indent. - Reduction in amorphous signal may be present.
1500-B			- Limited amount of SiC near indent. - Expect little change in amorphous signal compared to B₄C.

Figure 79: SEM micrographs of indents from Sample 1X (Commercial SiC), 2Y (Commercial SiO₂) and 3Z (Microemulsion SiO₂). The micrograph from above can be seen with the cut direction (purple). This cut results in a cross section, with a blue arrow showing the location of the indent.

There is significant variability in the amorphous volume seen in commercial B₄C, likely due to changes in grain orientation or local defects such as twins. The increase in amorphisation in Sample 1X could be as a result of a very amorphous B₄C grain, or it could indicate that in some configurations, SiC

may actually increase amorphous breakdown. Sample 2Y does not support this hypothesis however. Both indents at 2000 mN show a significant quantity of SiC both under and around the indent. This is reflected in the amorphous volume, which is consistently less than B₄C. This signposts the ability of the 3D Raman method to identify reductions in amorphous volume due to SiC, despite smearing in the scan. From these results, it is still unclear if the B₄C matrix undergoes less amorphous breakdown in the presence of SiC, or if the amorphisation signal is less simply because SiC, which does not break down, is present.

Sample 3Z is of particular interest. It demonstrated a hardness similar to that of B₄C, despite the softer SiC phase present in the composite, which could be linked to a reduction in amorphous breakdown as previously discussed. Furthermore, the indents for this sample provide a range of SiC environments. At 1500 mN, limited quantities of SiC are present near the indents, as demonstrated by the similarity between the amorphisation volumes of the sample and B₄C. Indent 1500B does show marginally less SiC than 1500A, which is reflected as a larger amorphous volume. This further highlights the capacity of the method to identify the predicted change in amorphisation. A similar observation is seen at 2000 mN. 2000B shows a significant amount of SiC around the indent, whilst 2000A does not. This is seen in the amorphous volume as a 20 μm^3 reduction in amorphisation between the two indents. It must be noted that both values are in the range of those seen in B₄C.

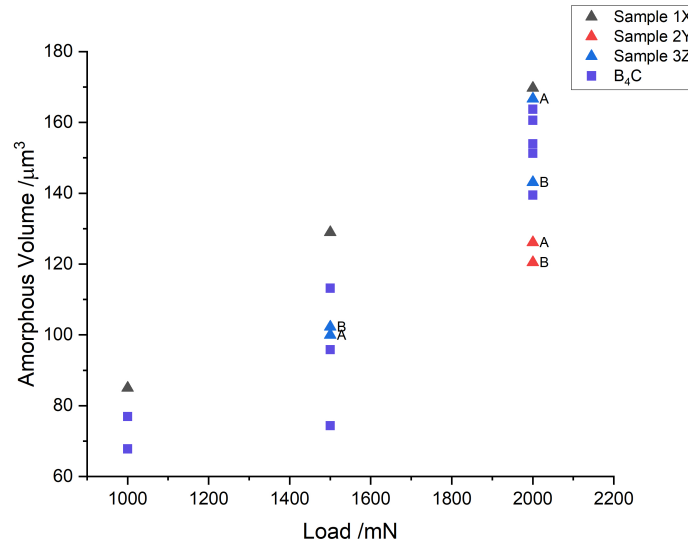


Figure 80: Graph showing the change in amorphous volume with load for B₄C, Sample 1X (Commercial SiC), 2Y (Commercial SiO₂) and 3Z (Microemulsion SiO₂). Where there are two of the same samples at the same force, a letter label is provided. Comparison between forces is not possible, as the scans do not detect the entire amorphous volume at these forces, hence comparison between samples at the same force is most appropriate.

Considering these observations, it is clear that the 3D Raman method is able to detect changes in amorphous volume due to the presence of SiC. Reduction in amorphous volume is seen in both Sample 2Y and 3Z when SiC is present, despite their difference in hardness. This suggests that the difference in

hardness is not linked to the amorphous breakdown and is instead defined by other material characteristics, such as microstructure. SiC could reduce amorphous volume either by reducing amorphisation in B₄C, or its inherent resistance to breakdown. Amorphisation is not prevented in any indent, despite the presence of SiC throughout the composite. This work suggests that, in the microstructure used here, SiC cannot prevent amorphisation.

Amorphisation in SiC rich composites

An alternative method for reducing amorphisation is to replace the B₄C phase with SiC. However, for this to be successful, the SiC should also reduce the amorphisation in the B₄C, such that all components of the composite maintain mechanical properties under load. In order to understand if this is a viable solution, indentation experiments were conducted on a 10:88:02 (B₄C:SiC:C) composite. In this environment the individual B₄C grains are surrounded by SiC. This constrains the B₄C and hence the amorphous breakdown cannot spread beyond that grain. The aim of this work was to understand if SiC reduces amorphisation in the B₄C phase and if there exists a particular B₄C grain size or morphology that is less prone to amorphisation. As the 3D Raman method has only been fully investigated in B₄C rich composites, a line scan method was used here. 100 mN indentations were conducted on or near B₄C grains of varying sizes and morphologies. Raman surface spectra were then taken monodirectionally across the B₄C grain, to identify any amorphous signals within. Figure 81 shows the location of amorphous signals across the B₄C grain.

Due to the accuracy of the nanoindenter device, some indents are not specifically in the B₄C grain. This does, however, provide insight on the ease of amorphisation in B₄C grains: if an indent is far away from a grain, but amorphisation is still observed, it can be concluded that the SiC matrix does not help prevent amorphisation.

All indents within this study show some indication of amorphisation (green dot). The B₄C grain size is seen to vary between 0.6 µm and 3 µm. This suggests that the grain size itself does not directly correlate with resistance to amorphisation. Figures 81 e,f and h demonstrate how the amorphous region can exist inside the B₄C phase even away from the indent. Figures 81 e and h show the indent to predominantly be in the SiC phase. Despite indentation in the softer SiC, which can absorb more energy through plastic deformation, sufficient pressure is localised to the B₄C phase that amorphous breakdown is triggered. An initially obvious solution to reduce amorphous breakdown is to enrich the composite in SiC; however, this work demonstrates that the B₄C will still undergo amorphous breakdown even in this constrained environment. The failure of one phase will in turn have a detrimental effect on the performance of the composite. This work would also indicate that the presence of SiC, even at high mass fractions, is not enough to prevent amorphisation. This effectively rules out a core (B₄C)-shell (SiC) microstructure.

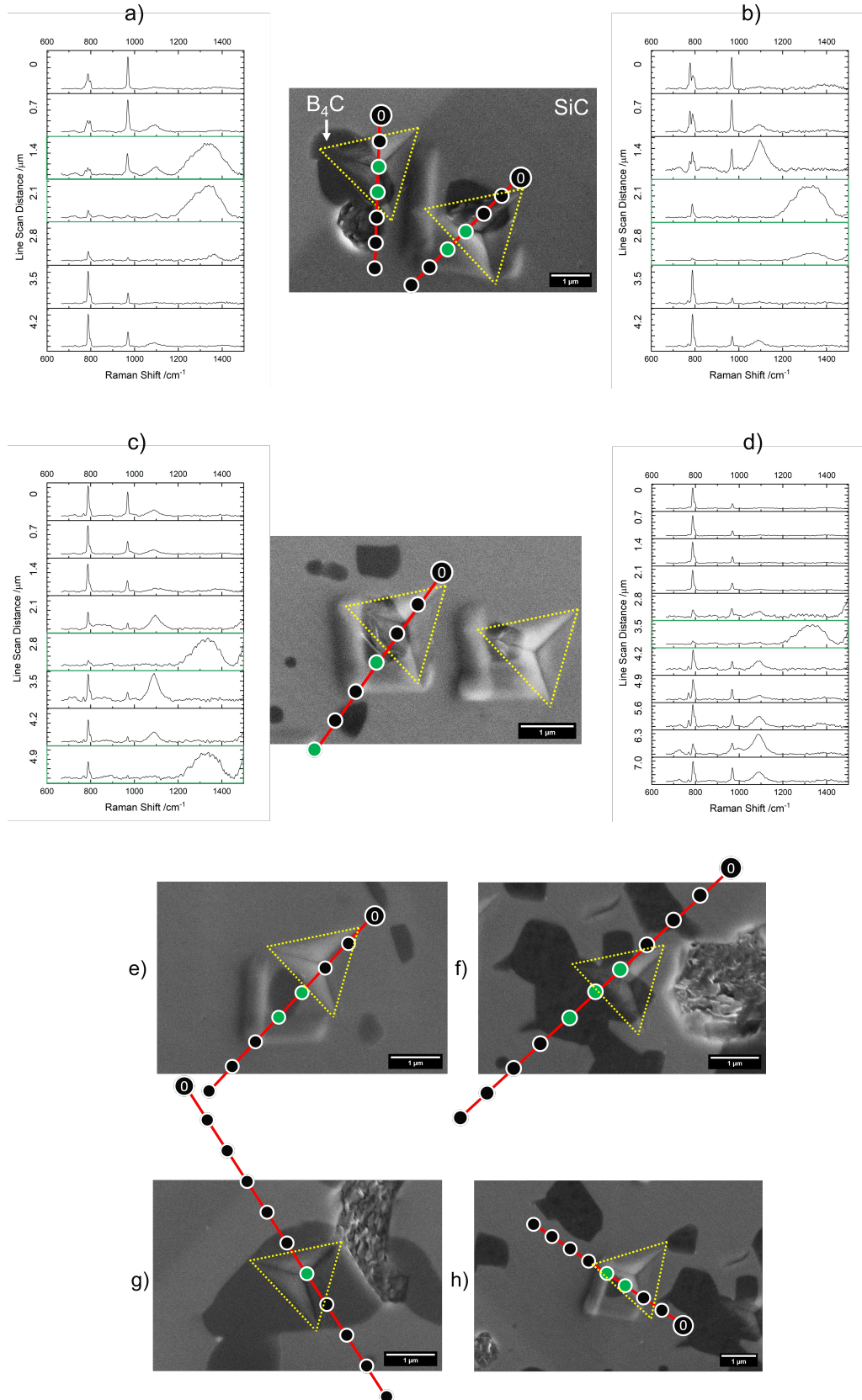


Figure 81: Diagrams showing the location of amorphous signal (green dot) when a line scan (red line) is taken across an indent in a SiC-B₄C composite. a-d demonstrates the amorphous signal alongside Raman spectra. e-h demonstrate the amorphous signal without spectra. The light areas of the image are SiC, whilst dark are B₄C. Yellow lines indicate the sides of the indents whilst black dots show the location where Raman spectra were taken. 0 μm indicates the origin, and corresponds to 0 line scan distance.

7.4 Conclusion

A novel 3D Raman method has been developed as part of this work. Initially, a simplified 1D setup was utilised to identify the edge of the amorphous zone in indents in B_4C . It was then shown, when appropriate corrections are made using TEM analysis, that the 3D method can non-destructively map amorphous zones under indents. The TEM analysis serves to calibrate the layer height to partially mitigate the stretching observed in the maps. However, the smearing effect cannot be removed by layer height corrections. PRF measurements demonstrate that the depth of penetration is small in this configuration and that the amorphous volume detected is most accurate near the surface. It is however unclear from this work as to the specific effect of this limitation on the analysis of amorphous zones. The accuracy of the method is reaffirmed by its agreement with traditional TEM micrographs, which show an increase in amorphous zone size with indent load. Additionally, in B_4C -SiC composites, those indents containing SiC reported a lower amorphous volume.

A reduction in amorphous volume was observed in the B_4C -rich microstructures when SiC was present near the indent. These experiments link this result to the innate stability of SiC and not a reduction in breakdown of the B_4C phase. This was supported by observations of a microstructure containing B_4C constrained by SiC: even when the SiC was indented, local B_4C grains still underwent amorphous breakdown. SiC-rich composites may pose a solution to the amorphisation problem by replacing the B_4C ; however, this evidence would suggest that SiC cannot prevent amorphous breakdown in the remaining B_4C phase and hence the mechanical properties will likely be impacted. These microstructural studies imply that SiC is having a limited effect on the amorphous breakdown in these cases. It remains unclear if this observation can be presumed for other microstructures containing B_4C and SiC.

8 Conclusion

A microemulsion SiO_2 production method was developed which could be scaled and tailored to a range of particle sizes. Additionally, understanding was developed on particle storage and and SiC conversion. The production process was scalable, and alterations to the concentration of catalyst could be used to change particle size. Following from this, clean particles, or those regularly undergoing high energy dispersion, could be stored for over 50 days. The conversion of SiO_2 to SiC was seen to be unpredictable, with a range of different reactions occurring. β -SiC was seen to form, with carbon content needing to be carefully controlled to prevent contamination.

A series of composite production methods were developed to include the use of SiC precursors. The composites produced from these powders were seen to have improved homogeneity and density when the carbon source was intimately mixed with the SiO_2 . This effect was particularly prevalent in microemulsion SiO_2 , which showed a higher density and closer to target composition than commercial SiO_2 . The composites produced in this fashion also showed higher than expected hardness, with a hypothesis that this may indicate an increase in amorphisation resistance.

To develop understanding of the amorphisation resistance of B_4C -SiC composites, a 3D non-destructive Raman method was developed. This built on initial observations which showed the amorphous to non-amorphous material interface could be detected in basic 1D depth scans. TEM was used to calibrate the 3D method layer height, which resulted in a similar analytical depth to those predicted by the probe response function. The method was able to detect a reduction in amorphous volume when SiC was present in B_4C -SiC composites produced in this work. However this was linked to the inability of SiC to breakdown, rather than prevention of amorphisation in B_4C . Further experiments showed that, in a SiC majority composite, B_4C still undergoes an amorphous breakdown.

The evidence presented here suggests SiC does not prevent amorphisation in B_4C when these microstructures are used. However, this work cannot confirm that the same conclusion can be drawn for all potential microstructural and compositional combinations.

9 Further Work

This work has demonstrated a reliable production method for B_4C -SiC composites, alongside the development of a novel 3D non-destructive Raman analysis technique. The composite production process appears well understood, with increases in homogeneity and density resulting from the intimate mixing of standard batch microemulsion SiO_2 and a carbon source. This work has shown that current microstructures do not appear to decrease amorphisation in B_4C . These composites, whilst produced using a variety of methods and SiC sources, are very similar in terms of grain size and morphology. Identifying how these methods could be used to further alter the composite microstructure provides an obvious avenue of work.

The literature indicates that the use of nanograin B_4C could reduce amorphisation [22]. Additionally, nanograin areas in Samples 2Z and 3Z are theorised to result in a higher than expected hardness in these composites. A series of microstructures with a range of grain sizes could be produced for pure B_4C . Investigation of their amorphous zone could give an indication of the extent to which grain size affects the amorphous breakdown. The effect that SiC has on this response could then be investigated by producing and analysing a composite with a fixed grain size and composition.

To investigate these microstructures, optimisation of the processing method will be needed. Despite standard batch SiO_2 and commercial B_4C having carefully controlled particle size distributions, nanograins of SiC or B_4C are not widely seen. To produce a nanograin microstructure will require a comprehensive sintering study which should optimise the temperature and pressures used. Additionally, the same study should aim to understand why the target composition is not always reached, and what the source of free carbon is. Whilst the reactions that likely cause this are understood in this thesis, they cannot be predicted reliably. The use of DSC-TGA with a graphite furnace, as well as analysis of the gas stream, could identify which reactions are occurring. Mass losses in a hot press environment would then be better understood, and hence starting powders could be altered to reliably reach the target composition and grain size.

The amorphisation analytical method has demonstrated sensitivity to changes in the volume of amorphisation caused by the presence of SiC. Verification of the accuracy of this method will require a significantly larger data set involving a range of compositions and microstructures. These should be produced, analysed, and compared to B_4C to determine their amorphous volume. The experiment should then be repeated using traditional measurement techniques, such as sequential polishing or TEM observation. By completing this on a range of samples, optimisations to the Raman method can be suggested and its usage range defined. Full confidence can then be expressed in the method, leading to its adoption by the community. Additional experiments, following the example of Guo *et al* [185], can be conducted to define the accuracy at varying depths, and hence propose changes to the analytical

process which takes best advantage of this.

The composites produced in this work do not show increased amorphisation resistance in the B_4C phase. However, the optimal sample, 3Z, does show a higher than expected hardness which is a positive ballistic property. Indentation is a simple and effective method of inducing amorphisation, however it does not simulate a ballistic impact. Ballistic testing, such as plate impact or depth of penetration experiments, could be conducted to understand the effectiveness of the material. The results of these can be used to inform whether the current microstructure has any advantages over other ceramic armours.

10 References

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11 Appendix

11.1 Code for homogeneity image analysis method

```
import numpy as np
import scipy
from scipy import interpolate
import pandas as pd
from scipy.interpolate import RegularGridInterpolator
from scipy import signal
from scipy import stats
from PIL import Image
import matplotlib.pyplot as plt

# Set the final file names

file='file '
filename='filename '

# Open an image

image=Image.open('file.png')

# Turn image into an array and find it's size

A1= np.array(image)
S=A1.shape
Xnum=S[1]-1
Ynum=S[0]-1

# Setup results array

Percentagearray=np.empty(shape=(1,3))

# Get length of shortest side (Y)

X=np.arange(0,Ynum)
Y=np.arange(0,Ynum)
Xs=X.size

# Intiate SiC percentage variable

percentageSiC=1

# Calculate micron per pixel(px)

size=len(X)*len(Y)
Micronsize=187

# Add size in microns of smallest edge (frome image data)

micronperpix=Micronsize/len(X)

# Set image size limits

while Xs>5 and percentageSiC>0:
    pixcount=0

    # Count bright px (SiC) in square inside image
```

```
for county, y in enumerate(Y):
    for countx, x in enumerate(X):
        I=A1[y,x]
        if I>0 :
            pixcount+=1

# Calculate amount of SiC and add to result file

percentageSiC=pixcount/pow(Xs,2)
sizeinmicron=len(X)*micronperpix
toadd=np.array([percentageSiC, len(X), sizeinmicron])
Percentagearray=np.r_[Percentagearray, [toadd]]

# Decrease array size by 1 in X and Y and repeat until limit reached

X=X[1:-1]
Y=Y[1:-1]
Xs=X.size
np.savetxt(filename+"1"+" .csv", Percentagearray, delimiter=";")

# Empty file array

Percentagearray=np.empty(shape=(1,3))

# Repeat above for each 4 corners

A2=np.flip(A1,1)
X=np.arange(0, Ynum)
Y=np.arange(0, Ynum)
Xs=X.size
etc .....
# Rerun code with A2
```

11.2 Code for identifying and mapping Raman peak intensities at a range of scan depths

```
import numpy as np
import scipy
from scipy import interpolate
import pandas as pd
from scipy.interpolate import RegularGridInterpolator
from scipy import signal
from scipy import stats
import matplotlib.pyplot as plt
from mpl_toolkits.mplot3d import Axes3D

###

# Aim: Automatic generation of a base array, with each point being a coordinate
from the map

p=1085

# Set a peak
```

```
P=1085 # Set a peak
Step=0.7 #Set X,Y map stepsize
Res=30 # Set a distance between ideal peak and peak found

# Set position of centre and corners of indent relative to Raman map
(found in Raman device). Convert from real coordinates to array coordinates

centrex=8.4 # Insert
centrex=centrex/Step
centrex=int(centrex)
centrey=7.0 # Insert
centrey=centrey/Step
centrey=int(centrey)

C1x=10.5 # Insert
C1x=C1x/Step
C1x=int(C1x)
C1y=9.1 # Insert
C1y=C1y/Step
C1y=int(C1y)

C2x=3.5 # Insert
C2x=C2x/Step
C2x=int(C2x)
C2y=7.0 # Insert
C2y=C2y/Step
C2y=int(C2y)

C3x=9.1 # Insert
C3x=C3x/Step
C3x=int(C3x)
C3y=3.5 # Insert
C3y=C3y/Step
C3y=int(C3y)

# Turn data into long array

T=np.loadtxt("A_Name.txt")
T=np.around(T,4)

# Find index where difference between wavelength and the peak selected in
minimised

min_index_D = np.argmin(abs(T[:,2]-P))

# Find wavelength at that point

Pi=T[min_index_D,2]

#Find intensity at location

L=T[np.where(T[:,2]==Pi)]

# Each spectra will give a value, find max and min of map X and Y values

LX=len(L)
X=L[:,0]
X=X-min(X)
X=X/Step
X=np.around(X,0)
X=X.astype(int)
```

```
A=max(X)

Y=L[:,1]
Y=Y-min(Y)
Y=abs(Y)
Y=Y/Step
Y=np.around(Y,0)
Y=Y.astype(int)
B=max(Y)

# Use above to generate an array

D=np.zeros((A+1,B+1))
Prm=np.zeros((max(X)+1,max(Y)+1))
Pri=np.zeros((max(X)+1,max(Y)+1))

###

# Aim: Set which peaks to pick out and which maps to plot

Dpth=np.array([0,10,20,30,40,50]) # Set name of each depth map file
V=np.array([1340,1810,1085,1580]) # Set peak positions
Vm=["D", "Amorph", "B4C", "G"] # Set peak names

###

# Aim: Find peak and intensity, determine if peak has high or low intensity, give
it a value of 2 (high), 1 (below 20th percentile) and 0 (low or no intensity),
Repeat for each peak and depth map

# Load file
for count, df in enumerate(Dpth): # Repeat for each depth
    print(count, df)
    dep=df
    print(dep)
    T=np.loadtxt("depthscan.txt")
    T=np.around(T,0)

# Plot a test spectra to check Savgol Filter and peak picker are working
effectively

    Q= np.where((T[:,0]==dep/10))
    R=T[Q[0]]
    W=R[:,1]
    I=R[:,2]
    I=np.around(I,1)
    s=scipy.signal.savgol_filter(I,23,1,mode='nearest')
    fig=plt.figure()
    plt.plot(W,I)
    plt.plot(W,s)
    peaks=scipy.signal.find_peaks(s, prominence=10,width=30) # Pick values
    prom=scipy.signal.peak_prominences(s, peaks[0])
    plt.xlabel("Raman Shift (cm-1)")#print
    plt.ylabel("Intensity (Counts)")

    T=np.loadtxt('A_Name.txt' % (dep))
    T=np.around(T,4)
```

```
Datname='A_Name.txt' % (dep)
counts1=str(count)

for count, Pval in enumerate(V): # Repeat for each peak
    D=np.zeros((A+1,B+1))
    Pm=Vm[count]
    K=str(Pval)
    print(Pval,Pm)
    counts=str(count)
```

```
# Identify all the coordinates that have spectra
```

```
X3=L[:,0]
Y3=L[:,1]
num2=(min(X3)-max(X3))/0.7)
num2=abs(num2)
num2=int(num2)+1

X1=np.linspace(min(X3),max(X3),num=num2)
X1=np.around(X1,4)

num1=(min(Y3)-max(Y3))/0.7)
num1=abs(num1)
num1=int(num1)+1

Y1=np.linspace(min(Y3),max(Y3),num=num1)
Y1=np.around(Y1,4)
```

```
# Turn into whole numbers for array and set top left as 0,0 in array
```

```
X2=X1
X2=X2-min(X2)
X2=X2/Step
X2=np.around(X2,0)
X2=X2.astype(int)
Y2=Y1
Y2=Y2-min(Y2)
Y2=Y2/Step
Y2=np.around(Y2,0)
Y2=Y2.astype(int)
```

```
# Find the spectrum at a coordinate and analyse, repeat for all coordinates
with a spectra
```

```
for county, y in enumerate(Y1):
    for countx, x in enumerate(X1):

        Q= np.where((T[:,0]==x) & (T[:,1]==y))
        R= T[Q[0]]

        W=R[:,2]
        I=R[:,3]
        I=np.around(I,1)

        x1=X2[countx]
        y1=Y2[county]
```

```

# Remove noise
s=scipy.signal.savgol_filter(I,23,1,mode='nearest')
# Pick peaks
peaks=scipy.signal.find_peaks(s,prominence=50,width=30)
# Get peak prominence
prom=scipy.signal.peak_prominences(s,peaks[0])
proml=prom[0]
Dat=peaks[0]
P=np.zeros(len(Dat))
M=np.zeros(len(Dat))

# Turn indexes of peaks into a wavelength and intensity

for countL, xa in enumerate(Dat):

    P[countL]=W[xa] #peak wavelengths
    M[countL]=I[xa]
    S=P-Pval

# Check if found peaks are close to what we are analysing using 'Res' value

for item in S:
    if -Res<item<Res :

        D[x1,y1]=1

        index=np.where(S==item)
        In=index[0][0]
        prom2=proml[In] #collect peak promienece
        Prm[x1,y1]=prom2
        Pri[x1,y1]=prom2

# If low intensity is low give 0 on array at this coordinate, if in 20th
percentile give 1 and if in range give 2

tvarray=Prm
tvarraynozero=tvarray[tvarray!=0]
tenthval=np.nanpercentile(tvarraynozero, 20)
Prm[(0<Prm)&(Prm<=tenthval)]=1
Prm[(tenthval<Prm)]=2
D=D.T
Prm=Prm.T
Pri=Pri.T

# Plot heatmap of array, other arrays can be plotted e.g a pure intensity heatmap

interp="bilinear"
bounDpth=[0,1,2]
fig=plt.figure()
plt.axis('on')
map=plt.imshow(Prm[:,:], vmin=0,vmax=2, cmap='hot', )
plt.colorbar(ticks=bounDpth)
plt.xlabel("X_Steps")#print
plt.ylabel("Y_Steps")
ax=plt.gca()
plt.savefig(Datname+K+Pm+counts+'prom_graph'+'.PNG',dpi=2500)

# Coordinates of centre and corners of indent can be added at this stage

D=np.zeros((max(X)+1,max(Y)+1))
Prm=np.zeros((max(X)+1,max(Y)+1))

```

```
Pri=np.zeros((max(X)+1,max(Y)+1))
```


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2	Fig. 8. Surface (top) and sub-surface indentation damage (bottom) beneath a 19.6 N Vickers indentation in B ₄ C moving from the edge to the mid-point of the indentation. Surface images are off-set to correspond to their positions relative to the original indent size highlighted in red. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)	The correlation of indentation behaviour with ballistic performance for spark plasma sintered armour ceramics	Crown copyright © 2015 Published by Elsevier Ltd.	N/A	Yes	This is an open access article distributed under the terms of the Creative Commons CC-BY license, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.
3	Fig. 9. Surface (top) and sub-surface indentation damage (bottom) beneath a 19.6 N Vickers indentation in SiC–5 wt.% B ₄ C moving from the edge to the mid-point of the indentation. Surface images are off-set to correspond to their positions relative to the original indent size highlighted in red. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)	The correlation of indentation behaviour with ballistic performance for spark plasma sintered armour ceramics	Crown copyright © 2015 Published by Elsevier Ltd.	N/A	Yes	This is an open access article distributed under the terms of the Creative Commons CC-BY license, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.
4	Fig. 10. (a) A SE SEM micrograph of the indentation-induced damage beneath a 19.62 N Vickers indentation in B ₄ C showing the large dominant median and lateral cracks and (b) the extensive fragmentation present in the hemi-spherical compressively damaged zone. (c) A reflected light micrograph showing a direct comparison of the sub-surface indentation-induced damage beneath the mid-point of Vickers indentations at 19.62 N in SiC–AlN–C and B ₄ C.	The correlation of indentation behaviour with ballistic performance for spark plasma sintered armour ceramics	Crown copyright © 2015 Published by Elsevier Ltd.	N/A	Yes	This is an open access article distributed under the terms of the Creative Commons CC-BY license, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.
5	Figure 3. (a, b) Structures of boron carbide in the rhombohedral crystal lattice and hexagonal crystal lattice. (c) The main compositions for the chain [53, 55], with boron atoms in blue and carbon atoms in orange. The structures were plotted using VESTA [56] with slight modification of the cif file from Clark et al. [54].	Silicon doped boron carbide for armour	Author	N/A	Yes	'The copyright of this thesis rests with the author and is made available under a Creative Commons Attribution Non-Commercial No Derivatives licence. Researchers are free to copy, distribute or transmit the thesis on the condition that they attribute it, that they do not use it for commercial purposes and that they do not alter, transform or build upon it. For any reuse or redistribution, researchers must make clear to others the licence terms of this work.'
6	Figure 2 B-C Phase Diagram	Ullmann's Encyclopedia of Industrial Chemistry	Copyright © 2002 by Wiley-VCH Verlag GmbH & Co. KGaA. All rights reserved.	04/11/23	Yes	CCC Rights Link Permission
7	Fig. 2. Raman spectra from the virgin surface and from subsurface regions at various depths beneath a static indent at a load of 0.98 N (100 g). The plots reveal that the intensity of amorphization is high just beneath the surface and decreases with increasing depth into the subsurface region of the indentation.	Characterization of the 3-D amorphized zone beneath a Vickers indentation in boron carbide using Raman spectroscopy	Copyright © 2013 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.	04/11/23	Yes	CCC Rights Link Permission
8	Fig. 5. Spatial distribution of the amorphized zone beneath an indentation in two different orientations. This zone was created by stacking 26 areal maps of the D peak on each polished surface at the appropriate depth. The outer hemisphere is the calculated plastic zone size. (a) Contour plot revealing a higher intensity along the center of the indentation and a lower intensity along the periphery. (b) Another orientation of the amorphized zone in a single color, which also reveals the indentation imprint. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)	Characterization of the 3-D amorphized zone beneath a Vickers indentation in boron carbide using Raman spectroscopy	Copyright © 2013 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.	04/11/23	Yes	CCC Rights Link Permission
9a	Figure 11. Schematic diagram of the formation of a-C and a-B12 from rhombohedra crystal structure of boron carbide B11C(CBC) (reproduced from [86] and plotted using VESTA [56]).	Silicon doped boron carbide for armour	Author	N/A	Yes	'The copyright of this thesis rests with the author and is made available under a Creative Commons Attribution Non-Commercial No Derivatives licence. Researchers are free to copy, distribute or transmit the thesis on the condition that they attribute it, that they do not use it for commercial purposes and that they do not alter, transform or build upon it. For any reuse or redistribution, researchers must make clear to others the licence terms of this work.'
9b	Figure 10. Schematic diagram of the formation of B12(CCC) from B11Ceq(CBC), with eq for equatorial and p for polar (reproduced from [22, 23] and plotted with VESTA [56]).	Silicon doped boron carbide for armour	Author	N/A	Yes	'The copyright of this thesis rests with the author and is made available under a Creative Commons Attribution Non-Commercial No Derivatives licence. Researchers are free to copy, distribute or transmit the thesis on the condition that they attribute it, that they do not use it for commercial purposes and that they do not alter, transform or build upon it. For any reuse or redistribution, researchers must make clear to others the licence terms of this work.'
10 a&b	Fig. 2 Microstructural characterization of (214) single crystal after nanoindentation testing.(C) The cross-sectioned TEM image displaying a shear band with the length of ~300 nm and width of ~1 to 4 nm. (D) A magnified TEM image of shear band confirming amorphous structure along the (122) plane. Fast Fourier transform (FFT) pattern taken from the band shows the amorphous diffuse halo ring pattern (inset b). The inserted FFT pattern acquired from the lattice image corresponds to the direction of rhombohedral B ₄ C (inset a).	Dislocation-mediated shear amorphization in boron carbide	Copyright © 2021 The Authors, some rights reserved; exclusive licensee American Association for the Advancement of Science. No claim to original U.S. Government Works. Distributed under a Creative Commons Attribution NonCommercial License 4.0 (CC BY-NC).	N/A	Yes	This is an open-access article distributed under the terms of the Creative Commons Attribution: NonCommercial license , which permits use, distribution, and reproduction in any medium, so long as the resultant use is not for commercial advantage and provided the original work is properly cited.
11	Fig. 4 Schematic illustration shows the dislocation-mediated amorphization in B ₄ C. (A) Perfect crystal before deformation. (B) Shear deformation distorting the lattice. (C) Dislocation kink formation under shear deformation. (D) Amorphization under shear deformation, initiating from dislocation.	Dislocation-mediated shear amorphization in boron carbide	Copyright © 2021 The Authors, some rights reserved; exclusive licensee American Association for the Advancement of Science. No claim to original U.S. Government Works. Distributed under a Creative Commons Attribution NonCommercial License 4.0 (CC BY-NC).	N/A	Yes	This is an open-access article distributed under the terms of the Creative Commons Attribution: NonCommercial license , which permits use, distribution, and reproduction in any medium, so long as the resultant use is not for commercial advantage and provided the original work is properly cited.
14	Figure 3 Ellingham diagram showing relative thermodynamic stability of composite constituents toward oxidation. The diamond on the B ₂ O ₃ lines indicate the melting point of boria, whereas the dots on the SiO ₂ lines indicate phase transformations from α-quartz to β-quartz, β-quartz to tridymite, and tridymite to cristobalite. The dashed vertical line is at the test temperature of 1000°C	High-temperature Na2SO4 deposit-assisted corrosion of silicon carbide—II: Effects of B, C, and Si	© 2016 The American Ceramic Society	04/11/23	Yes	CCC Rights Link Permission
15a	FIGURE 6 - influence of pressure on specimen final density	CERAMICS INTERNATIONAL, Vol. IO. n. 2.1983 49 Hot-Pressing of Boron Carbide	Copyright © 1984 Published by Elsevier Ltd.	03/02/23	Yes	CCC Rights Link Permission
15b	FIGURE 7 - Influence of heating rate on specimen final density	CERAMICS INTERNATIONAL, Vol. IO. n. 2.1983 49 Hot-Pressing of Boron Carbide	Copyright © 1984 Published by Elsevier Ltd.	03/02/23	Yes	CCC Rights Link Permission