The Effect of CNTs on the Sintering Behaviour and Properties of Structural Ceramic Composites

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A thesis submitted for the Degree of Doctor of Philosophy

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April 2013
Abstract

This research provides a comprehensive investigation into the effects of carbon nanotubes (CNTs) on the sintering behaviour, grain growth and properties of ceramics. Contradictory results reported in the literature on the effect of CNTs on sintering behaviour indicated the need for a systematic investigation under reproducible, controllable conditions. The sintering studies were performed using instrumented spark plasma sintering (SPS). It is a rapid sintering process that allows sintering to be studied in real time under isothermal conditions, enabling accurate calculation of time exponents and activation energies.

A study into the effects of CNTs on the sintering behaviour of PSZ and B₄C has shown that the presence of CNT content above the percolation threshold significantly reduces the sintering activation energies by 62 and 38% respectively. In both systems, the CNTS were also found to enhance the grain boundary diffusion mechanism of consolidation. Below the percolation threshold there was no significant effect on the activation energy.

As well as the sintering behaviour, the grain growth of the PSZ and PSZ CNT composites was investigated. This research found that the CNTs acted as a grain growth inhibitor through a solute drag like mechanism both below and above the percolation threshold although with a high CNT content the solute drag effect was enhanced further with no significant change to the activation energy.

The degradation of the CNTs was examined to determine whether they maintain their structural integrity during sintering. It was found that in both matrices with increasing temperature the CNTs were degraded to a greater extent. In the case of the PSZ-CNT composite the degradation was measured with respect to time at a series of temperatures to investigate the mechanism of degradation.
Abstract

The thermal properties of the ceramic CNT composites and porous ceramics were examined to determine the effect of CNTs on the transport properties of the matrix. It was found that the inclusion of CNTs in a PSZ matrix could enhance the thermal diffusivity and the residual porosity caused by burning them out causes a reduction.
I would like to express my sincere appreciation to Professor Mike Reece for giving me the opportunity to study in his research group, his support and guidance throughout my PhD has been crucial in my completion of this thesis. He has encouraged me in my work as well as providing numerous collaborative research projects for me to work on to help broaden both my technical and theoretical knowledge base.

I would also like to thank everyone in our research group for their assistance and friendship throughout my time at Queen Mary, in particular, Dr Guiseppe Viola and Dr Zhipeng Gao for their help and advice regarding this research. The staff at Queen Mary University of London (QMUL), Nanovision and Nanoforce have been extremely generous in the provision of both equipment time and support.

Thank you to my friends and family for their support, in particular my partner Jessica for her patience and reassurance with my prolonged studies. I would also like to give a special thank you to my parents Bernadette and Paul who has supported me throughout my studies, not just my PhD, I can never repay you for the opportunities you have given me and will be eternally grateful.

Finally I would like to acknowledge the Engineering and Physical Science Research Council (EPSRC) and the centre for advanced structural ceramics (CASC) for their provision of funding for this research project.
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1. Introduction

1.1 Introduction

Ceramics have been widely used for their structural properties with applications as diverse as antiballistic armour, sand and water jet nozzles, cutting and grinding tools and biomedical applications such as joint and tooth replacements [12]. A key area of research has been to incorporate CNTs into ceramics to improve various properties. Initial research focussed on the mechanical properties because it was believed that the high modulus and toughness of the CNTs would reinforce intrinsically brittle matrices. The anticipated improvement in mechanical properties has not always been realised and there are extensive contradictions in the literature. These can be attributed to the sintering technique, dispersion process and method of characterisation used in each case, as well as a lack of understanding regarding the role CNTs play on the sintering process itself [7, 13-22].

This research provides a comprehensive investigation into the effects of CNTs on ceramics and examines the reasons for the contrasting results presented in the literature such as the type and quality of the CNTs, as well as the dispersion methods used during processing. The ceramics in this research were sintered using spark plasma sintering (SPS), which is a rapid sintering process that minimises any potential damage to the CNTs. The SPS is instrumented with high resolution displacement and multi point temperature systems which enabled accurate in situ measurement of shrinkage during sintering. The main aim of the current research was to impart greater understanding of the role of CNTs during the consolidation of ceramic powders. The ceramics investigated during this research were zirconium dioxide (ZrO$_2$) and boron carbide (B$_4$C). Both materials are widely used structural ceramics but have significantly different sintering temperatures, structures, and electrical and thermal properties.
Chapter 1. Introduction

The study of the sintering behaviour focussed on the effect of varying concentrations of CNTs on grain growth and densification. By studying rates of densification and grain growth, the mechanism and associated activation energies associated with these processes were estimated. It is generally accepted that the presence of CNTs in a ceramic will retard grain growth at a comparable temperature to the monolithic ceramic, and has been demonstrated in several matrices [5, 23-25]. The effect on the sinterability is not clear however with contrasting reports showing they enhance or retard densification at a comparable temperature to the monolithic material. [5, 7, 19, 23-24, 26-29]

A key area of ceramic CNT research is that of the high temperature degradation of CNTs. This is important for determining potential sintering processes for CNT composites. There are several instances reported in the literature of hot pressing consolidation of ceramic CNT composites with long dwell times [30-33]. This research has analysed the degradation between 1500 and 1800°C and with a 0 to 20 minute dwell time and found that degradation occurs in all cases with a higher level of amorphisation and defective graphite present in samples prepared at higher sintering temperatures and dwell times.

The thermal diffusivity of several ceramic and ceramic CNT composites was measured from room temperature up to 1000°C to determine the effect of CNTs on the thermal diffusivity. The effect of the addition of CNTs to a ceramic matrix on electrical and thermal properties has been less well documented than for mechanical properties but fortunately is less unclear. CNTs do enhance the electrical and thermal conductivity of the matrix although the values obtained vary significantly between different groups [7, 34-36]. This work reinforces these findings with an increase in thermal diffusivity with increasing CNT content of ZrO₂. As well as investigating the effect of CNTs, the nanostructured porosity that forms when they are burnt out was also investigated. The results indicate that the presence of porosity did reduce the thermal diffusivity although the porosity left by burning out the CNTs closes at a significantly lower temperature (≈350°C) than is necessary to facilitate sintering.
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Chapter 2. Review

2.1 Sintering of Ceramics

Ceramic Sintering is not a new process, there is evidence that the first ceramic components being formed and fired over 25000 years ago [12]. Until the turn of the 20th century, however, the main advances in the consolidation of ceramic focused on the temperature the furnaces could achieve. Over the course of the 20th century the mechanisms of the sintering process were investigated to improve the sinterability of materials. The preparation of powders for sintering was one area where significant developments were made, with the use of grinding aids, sintering aids and binding agents becoming widespread. Two key mechanisms to reduce the sintering temperature were identified, the application of pressure during the sintering and decreasing the particle size [12, 37-38]

There have been several novel field assisted processes for the consolidation of ceramics that are still being investigated, namely spark plasma sintering (SPS), flash sintering and microwave sintering. The most developed of these is SPS, the initial patent was filed in 1906 by A.G. Bloxam but it wasn’t until more recently in the 1990s that the equipment became commercially available and extensive research into the process began [39]. The technique involves the application of a pulsed DC current to a conductive die to heat the sample and in turn the green body within. This allows a rapid heating rate of hundreds of degrees a minute to be attained combined with the application of a uniaxial pressure. Several key findings demonstrated by work on SPS thus far include the fact that materials can be sintered at considerably lower temperatures than are required with hot pressing and with shorter dwell times [40-41]. Novel materials can be sintered by the rapid processing of the samples possible, such as the sintering of a metastable Al₂TiO₅ powder by R.G Zhan, et al. [42].

A recent progression of the SPS process has led to a technique called flash sintering. There are similarities between SPS and Flash sintering in that an electric current is used to heat a material,
however, there are significant differences. Primarily the applied voltage in the case of flash sintering is in the order of 100 V/cm compared to ≈20 V/cm for SPS [43]. There is no die assembly used in flash sintering, instead, a green body is produced in a ‘dogbone’ configuration which then has the current passed directly across it which heats the samples to 850°C in under a second and can sinter a ZrO\textsubscript{2} green body to near full density in 5 seconds [43]. The flash sintering technique has several disadvantages compared to SPS, the sample can only be prepared in the dogbone shape and it is currently not possible to apply pressure during sintering which lead to residual porosity, particularly if any large defects are in the green body before sintering. Also, it is limited to materials that are electrically conductive at high temperatures.

Another technique that is being research for ceramic sintering is that of microwave sintering. It is a technique that heats the material directly as is the case in flash sintering but instead of a DC current the heat is induced in the green body by microwave radiation. The heating rates used in microwave sintering are typically 20 – 50 °C/min with dwell times of 10 - 60 minutes [41, 44-45]. This technique can only be applied to materials that are not transparent to microwaves; structural ceramics such as ZrO\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3}, B\textsubscript{4}C and SiC are all either insulators or wide bandgap semiconductors which allow dielectric heating. Metallic powders can also be sintered by microwave sintering because they do not reflect microwaves in powder form in the same way they do as a bulk material [41, 44, 46].

Ceramic research is a rapidly evolving area with diverse applications from highly accurate piezoelectric sensors and thermoelectric power generators to heat resistant tiling for space craft and body armour. Despite this there are still many limitations observed within the field of ceramic research from their intrinsically low fracture toughness and the expensive and/or toxic nature of many raw materials used in the development of functional ceramics. The area of ceramic research will continue to evolve in both
industrial and academic settings due to this high demand for materials and the desire to overcome the limitations currently presented.
2.2 Ceramic used in this Research

2.2.1 Comparison of Materials

The ceramic matrices used in this research are zirconium dioxide (ZrO₂), and boron carbide (B₄C). Both of these materials are widely used structural ceramics with a diverse range of applications, however, their properties are very different, allowing this work to be a comprehensive study of ceramic CNT composites. ZrO₂ had a relatively high fracture toughness of 5.3 MPa m¹/² compared to 1.2 MPa m¹/² for B₄C [17, 24, 47]. B₄C is the harder of the materials with a Vickers hardness value of up to 38 GPa compared to 12 - 14 GPa for ZrO₂ [24, 29, 36, 48]. In terms of their electrical properties B₄C is a wideband gap semiconductor and ZrO₂ has a very high electrical resistivity and can be considered an insulator although doped ZrO₂ is an ionic conductor.[49-50]. The thermal conductivity of B₄C is 30 - 42 W/mK whilst for ZrO₂ is 1.8 - 2.2 W/mK. Finally the processing temperatures vary considerably with ZrO₂ sintering at temperatures around 1200 °C whilst B₄C sinters at >1800 °C [24, 29, 48].

2.2.2 Zirconium Dioxide

ZrO₂ has many applications from solid oxide fuel cells to biomedical implants [51-53]. It has three possible crystal structures, monolithic, tetragonal and cubic (fluorite). The three structures are shown schematically in figure 2.2.1. The transition from monolithic to tetragonal occurs at 1170°C and from tetragonal to cubic at 2370°C [2]. The cubic structure and the tertragonal have a similar hardness value, typically 12-14 GPa, whilst the tetragonal has the highest fracture toughness (∼6 MPa m¹/²) as shown in figure 2.2.2 [2, 36]. For this reason ZrO₂ is often sintered in a stabilised or partially stabilised form by adding other oxide material such as yttria (Y₂O₃), calcium oxide (CaO) or magnesia (MgO). This lowers the transition temperature; in the case of fully stabilised ZrO₂ (with around 9 vol% Y₂O₃) the cubic phase
remains metastable down to room temperature. For partially stabilised ZrO₂ it is the tetragonal form that is stable to room temperature. It is frequently used in solid oxide fuel cells due to high ionic conductivity value of 0.18 S/cm⁻¹ at 1000°C for oxygen ions in Y₂O₃ (8.5 vol %) stabilised ZrO₂ as well as its high temperature stability up to 2200°C [54]. A fundamental requirement of the solid electrolyte component of a solid oxide fuel cell is that electronic conductivity must be prohibited whilst ionic conductivity is maximised. ZrO₂ meets this requirement as it has a large band gap of ≈5eV with variations depending on the crystal structure [50].

![Schematic representation of possible crystal structures of ZrO₂](image)

**Figure 2.2.1:** Schematic representation of possible crystal structures of ZrO₂ a) monoclinic, b) tetragonal and c) cubic [1]

As one of the most widely studied structural ceramic systems the number of composites that have been synthesised is exhaustive. Many commercially available ZrO₂ powders now come either partially or fully stabilised with either MgO or Y₂O₃. The primary reason for the addition of the stabiliser is to inhibit the phase transformation from tetragonal or cubic to monoclinic that occurs upon cooling after sintering.

Initial work on the stabilisation of ZrO₂ was carried out in 1929 by Ruff et al. who stabilised the cubic phase after sintering using calcium oxide (CaO) [55]. Following this, several other solid solutions were examined to determine the stabilisation effect on ZrO₂ including CeO₂, MgO and Y₂O₃, with Y₂O₃ being...
the most successful at producing a fine grained partially or fully stabilised composite and in turn is the commonly used stabiliser.

The addition of $\text{Y}_2\text{O}_3$ to partially stabilise the $\text{ZrO}_2$ also increases the fracture toughness of the material through a method known as transformation toughening. This phenomenon is caused by a 3-4 vol% expansion of the unit cell volume when the structure changes from tetragonal to monoclinic [2, 56]. This transformation can be stress induced by a fracture tip or abrasive action. The result is that energy is dissipated through a structural change and the corresponding volume increase exerts a closure force on the crack tip that increases its resistance to fracture [2]. This transformation does not always enhance physical properties as can be seen in surface effects. The unconstrained surface grains can exhibit a volume increase during cutting and polishing, which leads to micro cracking and surface ejection of the grains. This can lead to surface roughening and, in turn, a catastrophic failure of a component such as a hip joints [56].

As the $\text{Y}_2\text{O}_3$ content is increased further above the 2 mol% necessary to stabilise the tetragonal phase, the fracture toughness of the ceramic decreases as shown in figure 2.2.2. This phenomenon is due to the increased stability of the tetragonal phase and formation of the cubic phase leading to less monolithic phase transformation at the crack tip. The result is that for many applications partially stabilised $\text{ZrO}_2$ is used as it is a good compromise of high fracture toughness and hardness [2].
The ZrO$_2$-Y$_2$O$_3$ material in both the partially and fully stabilised state is now commonly used in both research and industrial applications.

2.2.3 Boron Carbide

Rhombohedral B$_4$C is a well established structural ceramic that has found many applications due to its excellent physical properties. As well as being extremely hard 25 - 32GPa, it is also very lightweight with a density of only 2.52g/cm$^3$ [49, 57]. This makes it ideal for applications such as lightweight armour and
sand blasting nozzles [49]. The powder is commercially prepared by reacting boron trioxide (B$_2$O$_3$) with carbon at >2000K. It also has a very high neutron absorption coefficient and can be used as control rods as well as protective shielding in nuclear reactors [12, 58]. Other applications include water nozzles as well as various tribological components [12, 59]. B$_4$C is a very inert material even at high temperatures, in particular it is very resistant to oxidation, more so than diamond making it very effective at cutting ferrous materials [49]. The model of the Rhombohedral B$_4$C unit cell is shown in figure 2.2.3 and has eight 12 atom icosahedral clusters linked by a 3 atom chain [49, 60].

![Atoms in Unit Cell](image)

Figure 2.2.3: boron carbide unit cell [47]

The most widely accepted stable polytype is a C-B-C chain and B$_{11}$C icosahedral structure, although there is an ongoing debate due to the interchangeability of boron and carbon atoms within the structure, and other polytypes have been observed [61]. This phase exists when there is between 8.8 and 20 at% carbon, giving a formula of B$_{10.3}$C to B$_4$C showing just how readily the carbon and boron atoms can be substituted. At concentrations of carbon below and above these values boron and carbon are formed respectively as a second phase within the structure. The preferred composition is reached
with a carbon content of 20 at % as this gives a reduced cell volume shown in Figure 2.2.4. This reduced volume is a result of a smaller atomic radii of the carbon atom compared to the boron [49].

Figure 2.2.4: Change in B₄C unit cell volume with increasing C content [47]

Due to the large amount of interest in B₄C it has been extensively studied and a wide range of manufacturing processes have been implemented to meet the ever growing demand from industry. It can be readily made through a hot pressing procedure to form a variety of structures at a temperature of 2200°C and pressure of 30 – 40 MPa [49]. It is also possible to fabricate components by pressureless sintering and sputtering, which can be used to give high quality coatings of B₄C on various materials to improve wear resistance[62].

The major disadvantage of B₄C for structural applications is its intrinsically low fracture toughness. This is a major obstacle and research has been done to try to improve upon this property [24, 63]. There is also an obstacle to be overcome to utilise B₄C in heavy duty body armour, which is linked to the material response to impacts at very high velocities. B₄C exhibits post Hugoniot elastic limit softening, which
severely restricts the materials antiballistic properties due to the formation of bands of graphite and boron upon impact [64-66]. The Hugoniot elastic limit can be defined as the maximum stress that can sustained by a supersonic impact without causing permanent damage to the material, so whilst some damage is expected the amorphorisation seen in the case of B₄C is unusual and has a greater effect on subsequent impacts.
2.3 Carbon Nanotubes

Carbon can exist in several different allotropes, primarily diamond and graphite. The difference between the two is simply the bonding between carbon atoms. In diamond the bonding is sp$^3$ with each carbon atom being bonded to 4 others, in graphite the bonding is sp$^2$ and each carbon atom is bonded to 3 others. This difference has a profound effect on the relating crystal structure. In an sp$^3$ bond the most stable bond angle is 109° giving a 3D lattice. In an sp$^2$ bonded structure the highest achievable bond angle is 120°. This means the carbon atoms arrange in a planar orientation and form two dimensional sheets. The bonding in the plane is exceptionally strong but the bonding between planes is governed by weaker van der waals forces. The result is that the physical properties of graphite are significantly poorer than diamond and it can be used as a solid state lubricant [67]. There are several iterations of graphitic carbon which are rarely found in nature but can be synthesised. The most simple of these is graphene; this is a single layer of graphite. It has a 2D structure with excellent physical properties. If we imagine rolling up a sheet of graphene it is possible to create a single walled carbon nanotube (SWCNT). It is also possible to create the ball structure of fullerenes which are spherical single layer sp$^2$ organised carbon structures.

Carbon nanotubes can exist in several forms, single, double and multi walled, as the names suggest double walled CNTs (DWCNTs) are one graphene sheet rolled up inside the other, the two layers are bonded by the same weak interlayer forces in graphite. Multi walled CNTs (MWCNTs) consist of more than two sheets of graphene and can have 10s of layers inside each other. The weak bonding of the layers does not result in a complete loss of mechanical properties of the CNTs because they often have imperfections along the nanotube during their synthesis. These imperfections can take the form of kinks or twists and can be a significant source of friction between the layers which in turn improves the
mechanical properties of the nanotubes. It is possible to roll the graphene layer that forms the CNT in several ways, armchair, zigzag or chiral. These different structures are illustrated in figure 2.3.1.

These different carbon nanotubes have different electrical properties. In general Armchair CNTs are metallic as are zigzag or chiral CNTs when equation (2.3.1) is satisfied [68].
All other carbon nanotubes are semiconductors. The band gap of the semiconducting nanotubes is determined by their diameter with larger CNTs having smaller bandgaps [68]. During synthesis a combination of metallic and semiconducting CNTs are produced. Recently methods have been developed to grow CNTs with a specific chirality and thus control their electrical properties [3]. Carbon nanotubes can be synthesised in several ways. Primarily these are arc discharge, laser ablation and chemical vapour deposition [3, 69-70].

Arc discharge is a high temperature process that involves using a high DC voltage to generate a discharge between two graphite electrodes. This method produces CNTs with a low defect content [3]. If no catalyst is used MWCNTs are formed, however, by using transition metal catalysts and modifying the environmental conditions it is possible to obtain single or double walled CNTs. The yield obtained also depends on environmental conditions, the use of an organic atmosphere such as ethanol enhances CNT production due to the decomposition into carbon atoms which are then used in the CNT production [69].

Laser ablation is another high temperature method for the production of CNTs which involves focussing a laser on a graphite target containing nickel or cobalt catalyst particles. SWCNTs with a high purity and low defect concentrations are produced [70]. The process allows a degree of control in that by altering the energy of the laser it is possible to alter the diameter of the CNT.

The most widely used method for CNT production is now chemical vapour deposition (CVD) [3]. There are many variants on this theme but the general method involves the initial deposition of catalyst particles on a substrate followed by a catalytic reaction of hydrocarbons on the surface that liberates gases such as H$_2$. The hydrocarbon ions can either be generated thermally or through plasma ionisation.
The carbon is then deposited on the catalyst particles. A combination of top down and bottom up growth has been reported for CNTs. The length and format of the CNT is determined by the conditions in which they are formed [3]. For example SWCNTs are formed in a configuration where methane is passed through a furnace at 900°C in an argon environment with an iron/molybdenum intermetallic catalyst. If these conditions are changed to 680°C and a nickel oxide/silica catalyst is used, MWCNTs are produced with a diameter of 40-60nm [71].

One of the biggest challenges associated with CNT synthesis is the purification that is needed post production. There is often significant amounts of amorphous carbon and as well as metal catalyst present in the CNTs. Typically an acid wash is used to remove the metal catalyst particles, although this can damage the CNTs [3].
2.4. Ceramic CNT Composites

2.4.1 Motivation for Ceramic CNT Research

Initial work on incorporating CNTs into a matrix material were carried out in polymers due to the low processing temperatures and forming routes used. They have been successfully incorporated into a variety of polymer matrices. The polymer composite exhibited improved mechanical properties as well as electrically conductive polymers at a low volume content of CNTs (<0.25 vol%) [72-74]. Following this success, work on the formation of ceramic CNT composites was initially reported by Zhan, et al. Who found an improvement in fracture toughness of Al₂O₃ from 3.3 to 9.7 MPam¹/² with the addition of 10 vol % SWCNTs [14]. This initial report led to a rapid rise in the number of groups working in the area. The later publications that followed presented very mixed results [17, 28, 32, 75-76]. Several key issues have been identified including how CNTs should be dispersed in a ceramic matrix, what is the effect of the CNTs on the sintering of ceramics and also the effect of the sintering process on the stability of the CNTs. It is also important to establish how the material properties of the composites can be measured.

2.4.2 Preparation of Composite Materials

The dispersion method used for the production of composites materials is essential because the CNTs have a very high surface energy and rapidly agglomerate forming dense bundles or birds nest structures as shown in figure 2.4.1.
The wide range of dispersion methods used has led to conflicting results on the effect of CNTs on the sintering behaviour of ceramics. It has been reported in several cases that CNTs reduce the grain size of Al₂O₃ ceramics whilst increasing their density under comparable sintering conditions [7, 23, 77]. The methods used to disperse the CNTs by these groups varied, but in all cases the processing focused on the deagglomeration of the CNTs. Inam et al used dimethyl formamide (DMF) utilising its high polarity to disperse the CNTs [4]. Balani et al and Lee et al used plasma and ultrasonic atomisation spray drying techniques respectively [7, 77]. Both of these techniques exert large forces on the CNT agglomerates which improve their dispersion. The rapid drying of the powders also reduces the amount of reagglomeration that can occur compared to traditional drying techniques [7].

Research by Woodman et al found that dry ball milling of B₄C was not an effective dispersion method for CNTs [28]. It was found that the addition of even 1 wt% CNTs reduced the density from ~100% to 93% under the same sintering regime. CNT agglomerates of up to 100 μm were found in the microstructure, comparable to the initial agglomerate size of the CNT powder. This decrease in density is very significant in B₄C because carbon has previously been shown to act as a sintering aid [78]. Work by Hirota et al on B₄C - carbon nanofiber (CNF) composites found that the addition of up to 15 vol% CNFs increased
density and reduced grain size when compared to monolithic B₄C [24]. The dispersion process used was ultrasonication of the CNFs in the polar solvent 2-propanol before the addition of the matrix powders.

Other research with inefficient dispersion routes have resulted in the CNTs retarding sintering, for example a study by Duszova et al on ZrO₂-CNT composites found that the addition of 1.07 wt% CNTs resulted in a reduction of density for both hot pressed and spark plasma sintered ZrO₂ [19]. The reason for the reduction in density can be attributed to the dispersion method; an aqueous solution was placed in an ultrasonic bath and resulted in large aggregates of CNTs within the samples.

Ethanol is frequently used for the suspension of CNTs for composite preparation. A study comparing the stability of CNT dispersions found that a suspension in ethanol begins to sediment after only 15 minutes of being removed from an ultrasonic bath. A DMF suspension is highly stable for over 10 weeks as shown in figure 2.4.2 [4]. This suggests that ethanol is not a suitable medium for dispersing CNTs and will result in the formation of large agglomerates of CNTs within the sintered sample.

![Figure 2.4.2: The dispersion of CNTs in DMF remained stable for over 10 weeks whilst the suspension in ethanol becomes unstable after 15 minutes [4]](image-url)
Another technique that has been shown to improve the dispersion of CNTs is to incorporate functional groups onto the CNTs. This method was reported by Bakshi, et al who used CNTs with COOH functional groups attached [27]. The problem with this technique, however, is that a lot of the proposed benefits of the incorporation of CNTs are influenced by the presence of functional groups. It is the strength of the SP$^2$ carbon bonding that gives the CNTs their excellent mechanical properties and also their high electrical and thermal conductivity, therefore, if it is possible to incorporate unfunctionalised CNTs into ceramic matrices this should be the preferred route.

2.4.3 Sintering and Grain Growth

One development that has allowed the incorporation of CNTs into ceramic composites is the use of SPS to densify them. As described in detail in section 2.5, this process involves very rapid sintering and as the integrity of the CNTs is maintained at high temperatures as has been shown in publications by Inam, et al and Estili et al [79-80]. This was achieved by comparing the intensities of the D and G peaks obtained via Raman spectroscopy for a series of samples with varying sintering temperatures and dwell times. These two Raman peaks gave an indication of the extent of amorphisation and defect concentration within the CNTs. The G band is a peak at $\approx 1590\text{cm}^{-1}$ and is a result of the tangential stretching of the SP$^2$ carbon lattice. The D band at 1330 cm$^{-1}$ is a double resonance mode caused by both amorphous carbon and also defective graphitic structures [79, 81-82].

Some of the initial work reported on ceramic CNT composites used the traditional sintering routes of conventional sintering and hot pressing, which are slow processes compared to SPS and do not necessarily maintain the structural integrity of the CNTs [30-33]. Some groups continue to use hot pressing such as Blugan et al, who found that after the hot pressing at 1450-1650 $^\circ\text{C}$ of $\text{Al}_2\text{O}_3$ composites there was only limited degradation of CNFs. CNFs, however, do not have the same structure as CNTs so
measuring the degradation is not possible using Raman spectroscopy. Instead they used mass loss during TGA is used to give an indication of the mass of carbon lost [83]. The degradation that occurs in hot pressing of CNTs may not directly lead to a mass loss but instead an amorphorisation of the carbon. One study by Inam et al found that with CNTs were stable up to 1600°C with limited degradation, whereas severe damage was produced at 1800°C in both Al₂O₃ and B₄C [79]. Another study by Zhang et al looked at the effect of spark plasma sintering various forms of carbon and found that for pure CNT samples sintered at 1500°C with a 20 minute dwell time, the CNTs underwent a partial transformation to a cubic diamond phase although a large proportion of the CNTs maintained their graphitic structure [82].

There are contradictory reports on whether the CNTs act as a sintering aid or inhibit sintering. Research by Garmendia using conventional sintering has shown that the CNTs reduce the relative density of the composite even when they have a hydrothermally deposited ZrO₂ layer on the surface of the CNTs [51]. Other work on ceramic oxides, however, has shown that the presence of CNTs can significantly lower the sintering temperature [5]. Research on tantalum carbide composites has also shown that the incorporation of CNTs increased densification and reduced grain size [27].

Silicon carbide (SiC) – CNT composites have been investigated by several groups with mixed results. A group from the Max-Planck institute in 2004 showed that spray pyrolysis of a SiC-CNT composite powder produced a high quality dispersion of CNTs [75]. Several groups followed this research with in situ formation of SiC around a CNT mesh [47, 84]. CNTs were dispersed in a polymer suspension that was then catalytically cross linked and pyrolysed to create a network of CNTs encased in an amorphous carbon preform. Silicon can be introduced in two ways, either by high temperature infiltration of molten silicon or the inclusion of silicon in the polymer matrix [47, 84]. Densities achieved by Katsuda et al after sintering showed a slight increase from 2.15 g/cm³ to a maximum of 2.21 g/cm³ for a 2 wt % composite
Thostenson however reported a reduction in the density for high temperature silicon infiltration from 3.04 to 2.75 g/cm$^3$ for a 2.1 vol% composite. The reduction in density in this case may have been due to the incomplete infiltration of molten silicon through the preform.

Unlike the contradictions surrounding the effect of CNTs on sintering, there is general consensus that the grain size is decreased with the addition of CNTs to a ceramic matrix. Grain growth refinement in ZrO$_2$ was observed by Duszova et al with the addition of CNTs they saw a reduction in grain size from 190 – 144nm [19]. It was also noticed by Mazaheri et al although as well as decreasing grain growth they also found an increase in sintering temperature required to obtain full density [29]. Other work that has investigated the effect of CNTs include a detailed study by Inam et al on the effects of carbon on the grain growth behaviour of Al$_2$O$_3$ [5]. Figure 2.4.3 (a) shows how the grain size was retarded by the addition of CNTs, particularly at high temperatures when the grain growth rate accelerates rapidly in the monolithic ceramic. The contrast in behaviour is shown in figure 2.4.3 (b) where a cosintered Al$_2$O$_3$/Al$_2$O$_3$-5 wt% CNTs sample exhibits an abrupt transition at the interface. The reduction in grain size may be much more pronounced than in the work by Duszova due to a better quality of dispersion of the CNTs but also the choice of matrix is much more susceptible to grain growth in the case of Al$_2$O$_3$.

Figure 2.4.3: The impact of CNTs on the grain growth of Al$_2$O$_3$ can be seen by: a) in relation to temperature, and b) the interface of a cosintered Al$_2$O$_3$/Al$_2$O$_3$-5 wt% CNTs [5]
Despite this information on the effect of CNTs on the grain growth, there has been no systematic attempt to quantify the impact of CNTs on the mechanism by which grain growth it takes place and the associated activation energy.

2.4.4 Mechanical Properties

The effect of CNTs on the mechanical properties is a very contentious one. One of the initial publications on ceramic CNT composites by Zhang et al reported a dramatic improvement in the fracture toughness, following research has not been able to replicate this work. One potential reason for this is due to the testing method used for the composites [14, 17]. The fracture toughness of a ceramic CNT composite measured using Vickers indentation crack length overestimates fracture toughness compared to using more appropriate 3 or 4 point bending testing.

A study into the properties of SiC-CNT composites showed that the addition of 2.1 vol% CNTs caused the flexural strength of SiC to drop from 140 to 50 MPa and the elastic modulus to reduce from 376 GPa to 278 GPa [84]. A paper published in 2007 concluded that indentation fracture toughness measurements are not an appropriate method for determining the fracture toughness of ceramic CNT composites and gives an artificially high value [22]. This could be due to the CNTs enhancing the elastic behaviour under point loading or allowing the ceramic to plastically deform by acting as a lubricant, so whilst CNTs do improve a ceramics response to point loading it is not indicative of the intrinsic fracture toughness. Even following the publication of this research, however there have been many publications still claiming increased fracture toughness based solely on the indentation fracture toughness, which has only added to the discrepancies over the true effects of CNTs [24, 26-27, 29, 85].
Some of the greatest improvements in mechanical properties have been found in the area of glass CNT composites. One significant benefit of using a glass matrix is that the CNTs can be dispersed uniformly throughout the sample whilst in the case of a polycrystalline material the CNTs have very poor wetability with the ceramic grains and form networks at the grain boundaries. The result is weakened bonding between ceramic grains and in many cases a loss of mechanical performance. A study on the mechanical properties of silicon dioxide (SiO$_2$) reinforced with MWCNTs showed an improvement in bending strength from 50 to 80 MPa with 5 vol% CNTs [6]. Higher CNT contents cause the bending strength to reduce as shown in figure 2.4.4. The fracture toughness was measured by the indentation method and the values recorded may not be accurate and the number of samples tested by the researchers was not indicated, however it does show similar behaviour to the bending strength.

![Figure 2.4.4: Effect of CNT content on bending strength and indentation fracture toughness of SiO$_2$ [6]](image)

Another study on the effect of CNTs on a glass matrix was performed by Boccaccini, et al. They found that the fracture strength was reduced from 106 to 63 MPa with the addition of 10 wt % CNTs [86].
Large CNT agglomerates were found in the structures which were attributed to poor quality dispersion, this coupled with the high CNT content may be responsible for the reduction in fracture strength.

One area of research that has generated significant interest in the past 10 years is that of ZrO$_2$-CNT composites. Some of the initial work was carried out by Sun et al using both single and multiwalled CNTs [17]. It was found that the hardness of ZrO$_2$ composites decreased with increasing CNT content although the addition of 0.1 wt% had no significant effect on the hardness. The fracture toughness of the ZrO$_2$ increased marginally from 5.2 to 5.5 MPa$\cdot$m$^{1/2}$ with the addition of 0.5 wt% CNTs and then decreased significantly upon the addition of 1 wt%. They also found no significant difference when comparing single and multiwalled CNTs at the same loading.

It is often highlighted in research of ZrO$_2$-CNT systems that there is a lack of a chemical bond between the ZrO$_2$ and the CNTs. It is due to this that the expected increase in fracture toughness from their incorporation is not observed [36]. To try to enhance the bonding between the two phases a group at the Max Planck institute tried to coat the CNTs with ZrO$_2$ via a hydrothermal crystallisation route. They found that ZrO$_2$ crystals can be grown on CNTs but there is no significant chemical bonding between the two phases [31].

More recent work on ZrO$_2$ has been contradictory with some research showing an increase in fracture toughness and even hardness through the incorporation of high CNT contents whereas others have shown that the fracture toughness is reduced slightly and the hardness significantly [29, 87-88]. In research by Duszova, et al, on ZrO$_2$ – CNF composites they found a reduction in both hardness and fracture toughness from 1395 to 830 kg/mm$^2$ and 6.2 to 5.6 MPa $m^{1/2}$ respectively [19]. This loss can be attributed to low density caused by large aggregates of CNFs in the sample. Several publications in 2010 showed improved mechanical properties for ZrO$_2$ – CNT composites based on indentation fracture.
toughness testing [29, 58, 87]. The study by Datye, et al however also compared the three point bending strength of composites and found a trend of increasing strength from 240 to 312MPa with increasing CNT content from 0 to 4.25 wt % [87].

B$_4$C- CNT composites are of interest due to the inherent low fracture toughness of the ceramic matrix. Carbon has previously been shown to be a sintering aid for the consolidation of B$_4$C [89]; however, considering the potential benefits there has been relatively little published work on this system. One early paper studied the use of dry ball milling as a processing technique for B$_4$C-CNT composites [28]. It was found to be an ineffective dispersion method with significant agglomeration of the CNTs, which resulted in a decrease in density as well as a reduction of Vickers hardness, fracture toughness and young’s modulus. More recent work by Wei et al has shown that incorporation of low loadings of 1 wt% CNT’s can improve both the flexural strength and fracture toughness of the resulting composite [20]. In this case the dispersion was created using ethanol with a dispersant of polyvinylpyrrolidone (PVP).

A paper published in 2009 studied the effect of CNTs on the mechanical properties of B$_4$C and found increases in both hardness and fracture toughness. The hardness however, increased from 26 to 30 GPa with the addition of 1 wt % CNTs, the value for the monolithic B$_4$C is particularly low suggesting that their samples were not fully dense. The improvement in hardness of the composites may be attributed to an increased density, unfortunately sintering data was not supplied in the paper [90].

One mechanical property that appears to show an improvement with the addition of CNTs is that of wear properties. Research by Hvizdos, et al found that the addition of 1.07 wt % CNFs significantly improved the tribological properties of ZrO$_2$ [91]. The friction coefficient reduced from ≈0.5 to 0.25 for a load between 1 and 6 N and the wear rate was reduced by around 50%. A study on the tribological behaviour of aligned CNT - Al$_2$O$_3$ composites also found that the coefficient of friction is reduced with
CNT addition, they also studied the effect of CNT diameter. It was reported that 12nm wall CNTs significantly outperformed 5nm wall CNTs in a pin on disk tribology study, however, both CNT composites showed no improvement over the monolithic Al₂O₃ in a diamond stylus scratch test [92]. A second study on Al₂O₃ CNT composites found that with increasing CNT content the friction coefficient decreases but wear rate increased [32]. This is in contradiction to the previously mentioned study on ZrO₂. The two main differences between the studies were the load applied during wear testing and consolidation technique used in each case. The load for the Al₂O₃ study was fixed at 25N whilst for the ZrO₂ it was considerably lower at 1 to 6N, The Al₂O₃ study used hot pressing whilst the ZrO₂ study used SPS. The difference in results may be due to the degradation of the CNTs during hot pressing or a change in tribological behaviour with increasing applied load.

Work by Thostenson studying SiC – CNT composites found a trend of decreasing elastic modulus with the addition of CNTs, from 376 GPa for the monolithic SiC to 278 GPa for a 2.1 vol% CNT composite. They also found a reduction in the flexural strength for the 2.1 vol% composite but interestingly not for the lower CNT content samples.[84]. A later study showed chemical vapour infiltration of aligned carbon nanotubes gave a 56% increase in the Young’s modulus, however they found the monolithic SiC had a modulus of 150GPa which is considerably lower than the 376GPa found by Thostenson [59] This difference could be due to the sample not being fully sintered, density values for the SiC and composite samples were not provided. Wang, et al studied SiC composites with low CNT content (<0.5 wt %) and found a trend of increasing tensile strength and modulus with increasing CNT content [93]. Further work is needed, therefore, to determine the reasons for the discrepancies in the literature with a focus on measuring mechanical properties of samples prepared with good dispersion and measured via a three or four point bending technique.
2.4.5 Electrical and Thermal Transport Properties

The high aspect ratio of CNTs means there is a very low electrical percolation threshold, typically around 1 vol%, although this is influenced by the grain size and also the type of CNT. An early study on the electrical properties of Al₂O₃ CNT composites in 2003 reported increased electrical conductivity. Electrical conductivities of 1050, 1510 and 3345 S/m were reported for 5.7, 10 and 15 vol % CNT composites respectively [14]. A study in 2006 on the electrical percolation behaviour of MWCNTs in an alumina matrix found a percolation threshold of around 0.8 vol % as shown in figure 2.4.5 (a) [8]. A paper published in 2011 by Lee, et al showed an exceptionally low electrical percolation threshold for a ZrO₂– MWCNT composite of 0.18 % as shown in figure 2.4.5 (b). This low percolation threshold is due to the high quality dispersion achieved by initially dispersing the CNTs in an aqueous metal salt suspension before being ultrasonically atomized. The spray coating at 800°C causes rapid drying and allows insufficient time for CNT reagglomeration [7].

![Figure 2.4.5: Percolation threshold of a) Al₂O₃ - MWCNT composite and b) ZrO₂ – MWCNT composite][7][8]

As well as improving the electrical conductivity of ceramics, CNTs also have an impact on the thermal conductivity. A study on the effect of CNTs on Al₂O₃ found that the addition of CNTs to Al₂O₃ significantly
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reduced the thermal conductivity from 27 W/mK for the monolithic ceramic to 7.3 W/mK for a 15 vol% CNT composite [25, 94]. This is a surprising result due to the exceptionally high thermal conductivity of CNTs, with reported values of over 6000 W/mK [95]. Other research has shown that the addition of CNTs to a ceramic matrix does increase the thermal conductivity. A more recent study on Al₂O₃ composites found that the thermal conductivity increased with the addition of 7.4 wt% CNTs from 20 W/mK to 64 W/mK at 300°C [96]. They also found an overall increase in the thermal conductivity with a higher CNT content of 19 wt% although in this case it was from 23 to 37 W/mK at 250°C. The reduction in thermal conductivity when the CNT content increased can be attributed to the low densities achieved <60% for the 19 wt% composite compared to >80% for the 7.4 wt% sample.

Work by Jiang et al. has shown that the addition of CNTs to titanium nitride (TiN) increases the thermal conductivity. The addition of 5 wt% CNTs has increased the thermal conductivity by 11% at room temperature and 97% at 430°C as shown in figure 2.4.6 [9].

![Figure 2.4.6: shows the increase in thermal conductivity of TiN with increasing CNT content at 375 – 705 K [9].](image)

It is not only the 5 wt% sample that showed an increase in the thermal conductivity. The sample containing 1 wt % shows a significant increase over the TiN. The increase in thermal conductivity with
such a low CNT content means the functional properties of the ceramic can be significantly affected without having a large detrimental effect on the mechanical properties.

The thermal conduction process within materials can be influenced by several factors, the mean free path of phonons within the material, the specific heat and the sound velocity. The thermal conduction of a crystalline material is strongly influenced by defects within the structure as well as grain boundaries as these all cause scattering of phonons [141]. Phonons travel through solid materials as vibrational modes which can be classed as either acoustic or optical. The key difference between the two is that in an acoustic mode the atoms of a unit cell all vibrate in the same direction whilst in an optical mode the atoms within the unit cell vibrate in different directions due to variations in properties such as mass and charge. Due to the covalent nature of the CNTs the phonon modes are primarily acoustic with optical modes being generated at high temperatures and when structural damage is caused to the CNT such as a kink. In PSZ there is both acoustic and optical modes and both play an important role in the conduction process [142].

A phonon scattering process called the Umklapp process becomes the dominant scattering mechanism at high temperatures, above the Debye temperature[141]. This phenomenon involves phonon-phonon scattering rather than defect scattering and is responsible for the high temperature plateau that is observed for the thermal conductivity of PSZ. The Debye temperature can be thought of as the temperature at which the highest vibrational mode in a solid material is activated. The influence of CNTs on the thermal properties of ZrO$_2$ has not previously been investigated, however CNTs have a very high Debye temperature (>1000°C) compared to PSZ (350°C) and can therefore continue to activate higher phonon modes above the plateau observed for ZrO$_2$, in turn having a significant effect on the thermal properties.
2.5 Spark Plasma Sintering

The process of producing a dense ceramic material by passing an electric current through a conductive die assembly, whilst applying a high uniaxial pressure has become known by several names, the most common of which are Spark Plasma Sintering (SPS), Field Assisted Sintering (FAST), pulsed electric current sintering (PECS) and plasma activated sintering (PAS), and will be referred to as SPS from here onward [57, 89, 97-98]. The complication over the name is generated by the uncertainty of the mechanism by which this process densifies materials. Several potential mechanisms have been proposed to explain the densification process in a SPS furnace. The most established mechanism is joule heating of the sample powder due to the electrical resistance of the powder, punch and die. Localised melting at the grain boundaries may also occur in some systems, but is more likely in metallic consolidation than ceramic due to the lower melting and sublimation points found in most cases [98]. Other mechanisms that have been proposed include the idea that an electrical spark passes from one particle to the next heating them as it passes and also creating a plasma which enhances densification and cleans the particle surface of residual oxides. This removes trace oxides and contaminants thus allowing the particles to sinter more readily. These more exotic mechanisms have no experimental evidence and are entirely theoretical in nature [97-98].

Figure 2.5.1 is a schematic of a typical SPS system. The powder to be sintered is first placed in a graphite die between two punches to allow pressure to be applied. A layer of graphite wool is then wrapped around the die to reduce the thermal gradient across the die and sample. A graphite piece called a stepper is placed on the end of both punches to allow the pressure from the pistons to be applied to the narrower punches in a uniaxial manner. A disk of carbon paper is inserted between the stepper and the piston to ensure a good contact is present to allow for the electric flow between the two components. The chamber is then evacuated to avoid oxidation of the graphite dies and the sample. Pressure is
applied from the top piston whilst the bottom remains fixed. Due to the extreme temperatures achieved by this machine of over 2000°C the metal pistons and chamber need to be constantly cooled with inbuilt coolant channels. As previously mentioned the heat is applied to the sample by passing a pulsed DC current through the assembly.

Figure 2.5.1: Schematic of SPS
In the setup used throughout this research the temperature is measured by a pyrometer above the top piston. It measures the temperature of the punch as near to the sample as is possible to obtain an accurate sample temperature. To do this there is a hollow centre in the top piston which lines up with a similar hole in the carbon paper, the stepper and the punch. The pyrometer is then focussed down this channel and records the temperature very close to the powder surface. There is a second pyrometer focussed on the outer surface of the die which is useful for observing temperature gradients but is separated from the sample by a thicker layer of graphite and therefore does not give an accurate sample temperature although it can be used as the control pyrometer.

One of the biggest advantages of SPS over other sintering techniques is the extremely rapid heating and cooling rate >1000°C/min for conventional dies. A comparative study was carried out on β-Si₃N₄ using SPS and hot pressing sintering routes [99]. The hot pressed sample was heated at a rate of 15°C a minute and the SPS sample was heated at 100°C a minute with a maximum temperature of 1700 and 1500°C respectively. Both processes produced samples with a density >90%. This means that it is possible to densify materials using SPS in a fraction of the time that can be achieved via other methods, which in turn allows the synthesis of novel materials and material properties. It is possible to densify metastable ceramic phases through rapid controlled heating and cooling leaving the material insufficient time to undergo the phase transformation it would experience in other sintering processes [100]. This benefit is extended to materials that are degraded at high temperatures such as composites of ceramic-CNTs which can be sintered to full density with little or no degradation of the CNTs. It is also possible to produce nanostructured ceramics meaning the polycrystalline material consists of grains with dimensions in the nanometre range [23, 51, 101]. This can only be achieved through very rapid sintering techniques such as SPS because the grain size of the polycrystalline ceramic is directly linked to the time the material is held at high temperatures due to grain growth mechanisms.
2.6. Summary

The development of ceramic - CNT composites has been a widely studied area for the past decade and has yielded mixed results. The percolation threshold to produce electrically conductive samples has been significantly reduced with improved dispersion techniques. There has been publication of evidence of unsuitable techniques; this however has not stopped the bad practice of techniques, such as dry ball milling for dispersion. There are examples of improvements to mechanical properties of ceramic matrices with the inclusion of CNTs, although the vast majority of these are based on inappropriate testing methods such as obtaining the fracture toughness using the indentation method. There are several exceptions to this, with evidence suggesting that the wear properties of ceramic materials can be improved with the addition of CNTs, and several examples of improved bending strength. It is now widely accepted that CNTs reduce grain growth in ceramics, although the mechanism by which this occurs is not understood. Whilst the effect of CNTs on the densification is still being debated, it does appear that poor densification correlates with poor dispersion.
# 3. Experimental

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3.1 Powder preparation

The first stage in the preparation of ceramic CNT composites used in this study was to disperse the CNT’s in a suitable medium. As discussed in section 2.4, the use of DMF is a very effective solvent for this purpose. It is highly polar which helps the CNTs deagglomerate from the birds nest structure they are in after fabrication. The Concentration of the CNTs in the dispersant is also a factor affecting the quality of composite powder obtained. The concentration for all composites in this work was <1 g/l. This value was chosen because it does not lead to heavily agglomerated powders but is a high enough concentration to be practical for the processing of composites. The suspension was then placed in an ultrasonic bath for two hours to reduce the agglomeration of the CNTs in the resulting ceramic-CNT composite. The CNT’s used were NC7000 (MWCNT), formed by a catalytic chemical vapour deposition (CVD) technique by Nanocyl S.A. Belgium. They have an outer diameter of around 10nm, a length of around 1.5μm and a density of 1.35g/cm³. Anhydrous dimethyl formamide (DMF) of 99.8% purity was supplied by Sigma-Aldrich UK and used to disperse the CNTs.

The ceramic matrices used throughout this study were all commercially available powders. The ZrO₂ powder (TZ-3YSB-E), partially stabilised with 3mol% Y₂O₃ (TZ-3YSB-E), was supplied by TOSOH, Japan and will be referred to as PSZ from this point onward. The powder was spray dried with a mean particle size of 36nm and a soft agglomerate size of around 80μm and a theoretical density of 6.12g/cm³. This particular PSZ powder was chosen due to its high flowability and its smaller particle size and narrow particle size distribution giving a well defined sintering peak. The as received powder was calcined at 850°C for 30 min with a 5°C/min heating rate and a natural cooling rate to remove the organic binder phase. The B₄C powder (HD20) was supplied by H.C. Stark; average particle size was 500nm and theoretical density was 2.52 g/cm³. It was used as supplied.
After the CNT suspension was formed the ceramic powder was added to the slurry and the mixture placed in a planetary ball mill for 4 hours at a speed of 350rpm with a ZrO$_2$ ball to powder ratio of 20:1. This served only to disperse the CNTs in the ceramic powder and to break up any agglomeration in the ceramic powder. It was not used to significantly reduce the particle size of the ceramic. Nylon milling pots were used with ZrO$_2$ balls of 6, 8 and 10mm diameter to ensure the samples were well dispersed. The mass of ZrO$_2$ balls was measured both before and after ball milling to ensure no catastrophic failure of the balls had occurred, this coupled with the low ball milling speed ensured minimal contamination of the powder during preparation. The powders were all dried at 80-100°C on a hot plate for 24 hours to evaporate the DMF. This was done in a fume cupboard to avoid the dangers of inhalation of the DMF which was known to be harmful. Once dry the powder was sieved though a coarse sieve with 2mm pores and a fine sieve with 250μm pores.
3.2 Spark Plasma Sintering (SPS)

All the sintering carried out in this work was done using an FCT Systeme HPD 25/1 furnace with the temperature controlled by the top pyrometer of the SPS. The samples sintered were all 20mm in diameter and the same die design was used throughout the study. The dies and punches used are all manufactured from graphite supplied by Erodex (ISO 63). Unfortunately the same punch and die sets could not be used throughout as breakages occurred under loading in the SPS or the dies became unusable though ceramic deposits on the inner face of the die. As shown in figure 3.2.1, the dies used had a height of 48mm and a 9.65mm wall thickness.

Figure 3.2.1: Schematic of die used for sintering (units in mm)

The chamber in the die was 20.7 mm in diameter; this was to accommodate 20 mm punches as well as a single layer of graphite foil (0.35mm thick). The graphite foil was used to protect the die from
contamination, make removing the sintered sample from the assembly easier and provide good contact 
between the punch and die to allow higher electrical conductivity though the assembly. This in turn 
resulted in more efficient heating and lower temperature gradients. The graphite foil was supplied by 
SGL (Sigmaplex TH Foil). The punches were 20mm in diameter and 35mm in height. There was a 10mm 
diameter hole drilled in the top that extended to within 5mm of the powder face as shown in figure 
3.2.2.

Figure 3.2.2: schematic of punch used for sintering (units in mm)

The punch and die assembly was placed between two steppers which allowed the pressure to be 
applied uniformly and uniaxially to the punches and in turn the sample. They also allowed the current to 
be channelled into the punches. The schematic of the steppers used throughout the study is shown in 
figure 3.2.3. They are 45mm high and have a diameter of 80mm at the large end, which was the same 
diameter as the rams used in the SPS, this tapers to 33.81mm. There was a 20 mm hole recessed 3mm 
into the surface of the stepper that the punch fits into tightly to allow good electrical contact. As with
the punch there was a hole through the centre of the stepper through which the pyrometer focuses. It is important to note that although there was no bottom pyrometer, the bottom punch still had the hole through its centre to ensure the entire graphite assembly was as symmetrical as possible to reduce any conductivity difference and in turn any thermal gradients that may have arisen.

![Figure 3.2.3: schematic of stepper used in sintering (units in mm)](image)

The whole assembly was then wrapped in 2 layers of 8mm graphite wool supplied by SGL (Sigmatherm GFA5). This was used to reduce the thermal gradient across the sample and also to avoid damaging the eyesight of anyone accidentally looking through the observation window during the sintering run, particularly at temperatures >2000 °C.
Before loading the powder to be sintered into the die, it was cleaned using polymer wool to remove any contamination from previous runs. A layer of graphite paper was then placed inside the die, this had to be a very tight fit to reduce the amount of ceramic powder that will come into contact with the die because it can weld itself to the graphite and result in damage to both the sample and die upon its removal. The lower punch was inserted into the die carefully to ensure that the graphite paper was not torn. Two 20mm disks of the 0.35mm graphite paper were pushed into the die from the upper edge until they were in good contact with the lower punch, they had to be flat on the surface or the resulting sample would not have had a flat surface but will instead appear chipped. The powder was then poured into the assembly. Samples of typically 1-5mm thickness were prepared, which gave a sufficiently large sample to work with but did not lead to a significant thermal gradient and consequently a non uniform microstructure during sintering. Two more disks of graphite paper were placed over the powder, and it was gently pressed with a polymer punch. It was important that the powder did not spill over the top of the graphite disks or they would have been sintered into the sample. The upper graphite punch was then cold pressed into the die to a pressure of 32MPa. For the majority of samples the cold pressing was carried out in a hydraulic press, however, for the sintering studies where reproducibility was essential, the cold pressing was performed in the SPS. As will be described in section 4.1, the sintering studies were all performed with a lower pressure than that applied during cold pressing making this step critical. All other samples had a higher pressure applied for sintering than cold pressing making this step less vital to the overall process.

The programmes used to sinter the samples differed depending on the experiment being carried out. The details will be given in the relevant sections of this thesis. The programmes all started with a step that evacuated the chamber followed by the application of the minimum force of 5KN (equivalent to a pressure of 16MPa for a sample with a 20mm radius) that is necessary to ensure good electrical contact
between the rams and the graphite assembly. Following this there was a heating phase up to 450°C. The pyrometer is not capable of measuring temperatures below 400°C, so instead the power the machine can apply to heat the sample is limited and the samples were heated until the upper pyrometer reached 450°C. It was at this stage different programmes were used depending on the aim of the sintering run.

Several aspects of the sintering process had to be optimised to produce reproducible, and reliable data for the sintering analysis. There were two key adjustments to the experimental work which required significant time to identify and modify. Initial work was carried out using a uniaxial press to apply pressure to the green body. This method is widely used before sintering but the results obtained for the sintering study were not reproducible and showed no clear trend. By running a separate programme on the SPS it was possible to obtain reproducible green body densities which are essential for the determination of the activation energy as the measurements are dependent on the shrinkage of the compact during sintering. Another aspect of the sintering process that had to be modified was the use of multiple die sets for sample preparation. Initially three punch and die assemblies were used to sinter samples, however, this created large errors in the resulting data. This was believed to be due to the change in contact resistance that occurs from one die to the next and in turn the pressure on the sample during sintering and cold pressing. The reason for this contact resistance difference is that over multiple uses the die is repeatedly cleaned, removing graphite from the inner face of the die and allowing the punches to move more freely. By using one punch and die set it was possible to mitigate the effect of changing die geometry.
3.3 Post Sintering Characterisation

The sintered samples had the graphite paper removed with a scalpel blade, the remaining graphite was removed and the sample flattened by a 120 grit diamond embedded metal disk on a Kemet Forcipol IV grinding machine. This process was done manually with the duration dependant only on the time needed to achieve a flat surface with no carbon paper remaining. For observation of a fracture surface no further polishing was required and the sample was shattered and the pieces observed. To observe the grain size and distribution it was necessary to polish the samples. They were initially mounted in an epoxy resin to allow them to be polished in a semi-automatic polishing machine (Struers Tegrapol 21). The samples were placed in a holder that applies a uniform pressure across a number of samples to give a flat high quality surface finish. Several diamond suspensions ranging from 9 to 3μm were used in conjunction with polymer disks before a final stage of colloidal silica on a neoprene disk to give a submicron surface finish.

The density of all samples was measured using the Archimedes method which involves using equation (3.3.1)

\[
\rho = \frac{\text{mass in air}}{(\text{mass in air} - \text{mass in water})}
\]  

(3.3.1)

To determine an accurate value for the mass in water the sample is initially measured in air, then in water. The samples surface was then blotted dry to remove any surface water and the mass in air was recorded again. Any increase in mass over the first measurement is due to water being absorbed into the open porosity of the sample. This difference can then be subtracted from the mass in water to obtain a second mass in water value which accounts for any open porosity on the sample. When this
value is used in equation (3.3.1) it gives a more accurate value for the samples density, particularly for lower density samples with extensive open porosity.

Thermal etching was used on the PSZ samples, between 1000-1200°C depending on the sintering temp. The heating cycle used was the same in all cases with the only difference being the ultimate temperature achieved. Initially a heating rate of 5°C/min was used to heat to 900°C, a dwell time of 1 hour at this temperature allowed the CNTs present in the composites to be burnt out without damaging the samples. The samples that were heated directly to the etching temperature showed surface damage, this could have been caused by the out gassing of CO\textsubscript{2}. It should be noted that when samples of PSZ and B\textsubscript{4}C were required with latent porosity, formed by burning out CNTs that were present during sintering, the previously mentioned heating regime was used. The process of etching the PSZ however, required a further heating ramp with a heating rate of 3°C/min to the etching temperature and a dwell time of 45 min was used for all samples. Cooling was allowed to occur naturally with the cooling rate of the furnace.

X-ray diffraction (XRD) was carried out on the ceramic powders to determine their initial phase as well as the sintered sample. The machine used was a Siemens D5000 diffractometer (Germany) at QMUL. Raman spectroscopy was used to measure the level of amorphorisation of the CNTs during sintering. It was possible to measure the relative intensity of the D and G peaks where the D peak is caused by amorphous carbon and by defects within a graphitic structure and the G band is produced by tangential stretching of the Sp\textsuperscript{2} lattice [10]. The spectroscopy was carried out on a Thermo Fisher Scientific, Nikolet Almega XR dispersive Raman imaging microscopy system (America) at QMUL. The laser frequency used for the Raman spectroscopy was 785 nm and the spot size 3.1 μm. The Raman shift was measured from 734 - 1787 cm\textsuperscript{-1}. For all samples 128 scans with a 0.5 second exposure time were used to obtain a
spectrum and 3 spectra were averaged before the D and G peaks were integrated and their ratio’s determined.

All high magnification imaging was carried out on a scanning electron microscope (SEM) FEI (USA) Inspect F model at QMUL (10-20KV accelerating voltage, 5-10 mm working distance). To prepare the samples for SEM it was necessary to first make a conductive pathway with carbon paste from the top surface of the sample to the metal stub upon which they were mounted, following this the samples were coated with a 5-10nm thin film of gold on an Agar Autosputter coating system to make the surface conductive.

The grain size was determined by the line intercept method which involves counting the number of grain boundaries intercepted by a line of known length drawn on an SEM image of the sample. In all cases 10 lines were used per image and typically 3-5 images were chosen to calculate the grain size from. The lines were drawn on the image at regular intervals in both the horizontal and vertical directions to ensure a consistent approach for all samples. The uniformity of the temperature during the sintering experiments was assessed by observing and comparing the microstructure in the exterior and interior regions of a cross section of each sample. Typically 400 grains were measured for each sample.
3.4 Thermal Diffusivity Measurements

The thermal diffusivity was measured on a Nietzsche (Germany) LFA 457 microflash system. The samples geometry in all cases was a disk with a 20mm diameter and a typical thickness of 1-1.2mm. The samples were ground flat on both faces as described in section 3.3 but were left unpolished to ensure the IR laser was not reflected off a polished surface. A graphite coating was sprayed onto both faces off the sample before it was tested using a hand held aerosol canister (graphite 33) supplied by kontakt chemie (Germany). Thermal diffusivity measurements were carried out at room temperature, 100°C and then at 100°C intervals up to 1000°C with three data points recorded at each temperature to give increased statistical significance. A heating rate of 5°C/min was used to get within 10°C of the testing temperature, after which a 1°C/min heating rate was used to reduce the temperature difference across the sample. The maximum temperature fluctuation during each test was set at 1°C/min.
4. Densification and Grain Growth Theory

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Chapter 4. Densification and Grain Growth Theory

4.1 Densification Theory

Different mechanisms of material transport have been identified during the densification of metallic and non-metallic powder, namely plastic or viscous flow, evaporation-condensation and diffusion mechanisms such as surface or grain boundary [102]. For all the materials used in this research significant shrinkage is observed throughout the densification process which suggests the mechanism cannot be evaporation or surface diffusion [38]. It is for this reason that a model based on the two-spheres shrinkage equation will be applied [103]. Figure 4.1.1 shows the potential densification mechanisms based on the approach of two sphere centres.[38]

<table>
<thead>
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<th>Related Parameters</th>
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<td>Neck</td>
<td>Lattice Diffusivity ($D_t$)</td>
</tr>
<tr>
<td>2. Grain Boundary Diffusion</td>
<td>Grain Boundary</td>
<td>Neck</td>
<td>Grain Boundary Diffusivity ($D_b$)</td>
</tr>
<tr>
<td>3. Viscous Flow</td>
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<tr>
<td>4. Surface Diffusion</td>
<td>Grain Surface</td>
<td>Neck</td>
<td>Surface Diffusivity ($D_s$)</td>
</tr>
<tr>
<td>5. Lattice Diffusion</td>
<td>Grain Surface</td>
<td>Neck</td>
<td>Lattice Diffusivity ($D_t$)</td>
</tr>
<tr>
<td>6. Evaporation / Condensation</td>
<td>Grain Surface</td>
<td>Neck</td>
<td>Vapour Pressure Difference ($\Delta p$)</td>
</tr>
<tr>
<td>7. Gas Diffusion</td>
<td>Grain Surface</td>
<td>Neck</td>
<td>Gas Diffusivity ($D_g$)</td>
</tr>
</tbody>
</table>

Figure 4.1.1: Two sphere shrinkage model showing various densification routes [36]
Chapter 4. Densification and Grain Growth Theory

The shrinkage model describes the shrinkage from the rate of approach of spherical particles, occurring through the diffusion of atoms into the neck region. The assumptions made by this model are that the grain size is constant and the sintering is carried out under isothermal conditions. To ensure minimal variation in grain size the all samples were sintered to below 90% density, above which the rate of grain growth increases rapidly. Using SPS allowed rapid heating of the sample and ensured minimal densification before the desired temperature was reached. However if the heating rate was too high temperature gradients would have developed. The optimal conditions were found to be a heating rate of 200 °C / min up to the sintering temperature followed by a period of 20 seconds for the temperature to equilibrate. The final assumption made by the model was that the sintering be performed via a pressureless route. This was not possible in the SPS due to the necessity of good electrical contact between components so the minimum possible pressure of 16MPa was applied throughout.

The equation of the shrinkage is given by [102]:

\[
\frac{\Delta L}{L_0} = \left( \frac{Ay_a^2D_0 \exp\left(\frac{-Q}{RT}\right)}{r^p k^T} \right)^m t^m
\]  \hspace{1cm} (4.1.1)

The term \(\Delta L\) represents the change in length of the compact during sintering, and it is normalized with the length \(L_0\) of the compact at the point at which analysis of the data was begun during isothermal sintering. The constants \(A\), \(m\) (sintering exponent) and \(p\) are dependent on the dominant sintering mechanisms and sample geometry. Equation (4.1.1) can be simplified to

\[
\frac{\Delta L}{L_0} = \left( \frac{Kt}{T} \right)^m
\]  \hspace{1cm} (4.1.2)

Where, \(t\) is the time, \(T\) the absolute temperature and

\[
K = \frac{Ay_a^2D_0 \exp\left(\frac{-Q}{RT}\right)}{r^p k^T} = B \exp\left(\frac{-Q}{RT}\right)
\]  \hspace{1cm} (4.1.3)
with

\[ B = \frac{Ay a^3 D_0}{r^p k} \]  

(4.1.4)

In these equations, \( K \) can be interpreted as a diffusion coefficient, which includes \( D_0 \) (self-diffusion constant), \( r \) (particle radius), \( a^3 \) (volume of diffusing atom), \( \gamma \) (surface tension), \( k \) (Boltzmann’s constant), \( R \) (the gas constant) and \( Q \) (activation energy for atomic diffusion). In this study, cylindrical dies were used for the SPS sintering, therefore the sintering shrinkage was constrained to occur in the direction of the uniaxially applied force and the material shrinkage along the radius direction is neglected. Therefore the previous equations change into:

\[ \frac{\Delta L}{L_0} = 3 \left( \frac{Ay a^3 D_0 \exp\left(-\frac{Q}{RT}\right)}{r^p kT} \right)^m t^m = 3 \left( \frac{Kt}{T} \right)^m \]  

(4.1.5)

According to Equation (4.1.5), the sintering exponent \( m \) may be estimated from the slope of the ln-ln plot of the normalized shrinkage \( \frac{\Delta L}{L_0} \) versus time at a constant temperature:

\[ \ln \left( \frac{\Delta L}{L_0} \right) = \ln \left[ 3 \left( \frac{K}{T} \right)^m \right] + m \ln t \]  

(4.1.6)

The slope of the plot \( \frac{\Delta L}{L_0} \) versus \( t^m \) at each temperature can be used to estimate \( K \) using Equation (4.1.2).

From Equation (4.1.3) it follows that:

\[ \ln K = \ln B - \frac{Q}{RT} \]  

(4.1.7)

The activation energy \( Q \) can be obtained from the slope of \( \ln K \) vs \( \frac{1}{T} \).
4.2 Grain Growth Theory

Grain growth in polycrystalline materials is driven to reduce surface energy and the relationship between grain growth rate and its radius of curvature can be expressed as [104-105]:

$$\frac{dD}{dt} = \frac{G}{D}$$  \hspace{1cm} (4.2.1)

Where $t$ is the time, $D$ is the average grain size and $G$ is a rate term that contains the activation energy, $E_g$, for atoms to pass across the grain boundaries as shown by:

$$G = G_0 \exp\left(-\frac{E_g}{RT}\right)$$  \hspace{1cm} (4.2.2)

The term $G_0$ is a preexponential term that contains the surface tension, frequency and entropy of atomic jumps as well as the volume of the process. The gas constant $R$ and temperature $T$ in Kelvin are both in the exponential term with the activation energy. It is possible to integrate equation 4.2.1 with respect to time and write the expression:

$$D^2 - D_0^2 = \left[2G_0 \exp\left(-\frac{E_g}{RT}\right)\right]t$$  \hspace{1cm} (4.2.3)

This equation is only valid for normal grain growth and is replaced by an empirical model for systems that deviate from normal grain growth:

$$D^n - D_0^n = \left[2G_0 \exp\left(-\frac{E_g}{RT}\right)\right]t$$  \hspace{1cm} (4.2.4)

It is possible to empirically deduce the grain growth exponent $n$ from the best fit for the plot of 4.2.4 which can be rewritten as:

$$D^n - D_0^n = K't$$  \hspace{1cm} (4.2.5)

Where:
This can be rewritten as:

\[ K' = B \exp \left( -\frac{E_g}{RT} \right) \]  \hspace{1cm} (4.2.7)

It is then possible to obtain the activation energy for a material using the \( K' \) values obtained across a range of temperatures and measuring the slope of \( \ln K' \) against \( \frac{1}{T} \) described by:

\[ \ln K' = \ln B - \frac{E_g}{RT} \]  \hspace{1cm} (4.2.8)
5. Densification Activation Energy

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5.1 Introduction

This chapter reports a systematic investigation of the effects of CNTs on the densification behaviour of PSZ and B₄C. The aim of the research was to address contradictions in the literature regarding the effect of CNTs on the densification behaviour of ceramics. The study involved composites with CNT contents of 0.5 and 2 vol%, below and above the percolation threshold respectively. The densification behaviour and associated activation energy were studied to gain insight into the mechanism by which CNTs enhance densification. Using an SPS furnace with rapid heating enabled the thermal activation energies of the rate limiting step during densification to be measured under isothermal conditions. Partially stabilised ZrO₂ was chosen as a model system for this study because it is a well studied structural ceramic oxide and commercial powders of high quality are readily available. B₄C was chosen because it is a widely used structural ceramic and also because it is a carbide and sinters at a significantly higher temperature than the PSZ. By using two distinct ceramics matrices, it was possible to identify whether any changes to the densification behaviour were simply dependant on the CNTs or additionally dependant on the ceramic matrix.
5.2 Experimental

The materials used and the setup of the sample and die for sintering to obtain the data used in this chapter are described in section 3.1. Once the sample reached 450°C they were sintered at a heating rate of 200°C/min and a cooling rate of 150°C/min. All the PSZ and PSZ-CNT samples were sintered between 1150-1400°C to achieve a wide spread of sintering rates and the B4C and B4C-CNT samples were sintered between 1600-1750°C. These sintering temperatures were chosen for the study based on a temperature scan of the materials to determine the onset of shrinkage as discussed further in sections 5.3 and 5.4. The dwell time at the sintering temperature was 8 minutes in all cases. To ensure that the sample temperature was equilibrated and any thermal gradient across the sample was minimised, the initial overheating period observed in the pyrometer data, which is around twenty seconds of the dwell time with a heating rate of 200°C/min, was discarded from the analysed data. All the samples had a uniaxial pressure of 16MPa applied during sintering, this was the minimum pressure required by the SPS to ensure good electrical contact between the rams and the die assembly. The density, grain size and microstructural uniformity were all measured as is described in section 3.3 whilst the sintering activation energy was calculated using Kingery’s model of particle sintering. The model, as well as all assumptions made is explained in detail in section 4.1.
5.3 Results

5.3.1 Zirconium Dioxide

The green body densities for PSZ, PSZ 0.5 vol% and PSZ 2vol % CNT samples were 48.5±2.8%, 52.2±0.9% and 53.4±1.5% respectively. This suggests that CNTs acted as a solid state lubricant allowing the PSZ particles to re-orientate themselves into a denser packed green body.

Figure 5.3.1 shows the shrinkage rate and sample density for a PSZ sample heated at a constant heating rate of 200°C/min and a constant pressure of 16MPa. The onset of densification for PSZ is at around 1050°C and sintering is complete by 1500°C under these conditions.

![Shrinkage versus temperature plot](image)

Figure 5.3.1: Shrinkage versus temperature plot for a PSZ sample with a heating rate of 200°C/min and pressure of 50MPa to determine the temperature of the sintering behaviour of the PSZ powder.

The shrinkage curve is a well defined single peak although it is over a narrow temperature range which limits the range the analysis can be performed in. The two vertical lines on figure 5.3.1 indicate the temperatures of 1150 and 1400°C, the region initially identified for the sintering analysis. The lower
temperature limit of 1150°C was chosen because it is just over the onset of sintering and the upper limit set because it is just after the peak sintering rate observed at 1325°C under these conditions which would give as wide a range of densities as possible for the analysis without initiating rapid grain growth >90% density.

Figure 5.3.2 shows the density of the PSZ and PSZ CNT composite samples sintered between 1150°C and 1450°C at a pressure of 16MPa for 8 minutes. For both the samples containing 0.5 and 2 vol% CNT’s there is an increase in density up to 1400°C compared to the monolithic PSZ. A further density increase was measured from 0.5 to 2vol% CNTs up to 1350°C, moving from below to above the percolation threshold for the composite.

![Figure 5.3.2](image)

Figure 5.3.2: Relative density of PSZ and PSZ-CNT composites across the temperature range 1150-1450°C sintered for 8 min with 16MPa uniaxial pressure and a heating rate of 200°C/min

The samples sintered at 1350°C and above had a density of over 90% and were not used to measure the densification activation energy. This is due to the large increase in grain size observed above 90% density as shown in figure 5.3.3 for the PSZ samples sintered above 1350°C. It also shows that all
samples used in the data analysis had a mean grain size of 121nm and a standard deviation of 17nm. Using the data of samples with a density >90% would mean adjusting equation 4.1.5 to account for the changing particle radius \( r \) in the constant \( B \), and would have complicated the estimation of the activation energy.

The exponent \( m \) was calculated for the PSZ and PSZ CNT composites from the plots of figure 5.3.4 (a-c) using equation 4.1.7. A value for \( \Delta L \) was obtained by using the ram displacement data recorded by the SPS at one second intervals. In all cases a period of at least twenty seconds after reaching the sintering temperature was allowed for the system to reach thermal equilibrium. This duration corresponded to the time required for the sample to stabilise at the sintering temperature. In all cases there was an initial temperature overshoot of between 7 and 15°C before the temperature stabilised. To accurately measure the activation energy it is important to analyse data from the samples with the same starting microstructure and density. To achieve these requirements, the starting densities for the analysis of the shrinkage data were chosen as 57.1%, 62.0% and 64.0% for the PSZ, 0.5 vol% and 2 vol% CNT
composites respectively. The PSZ sample sintered at 1150°C showed very little densification (41 to 44%) and was disregarded in the analysis. An average value for the exponent \( m \) value of 0.32 between 1200-1300°C was obtained for the data as shown in fig 5.3.4.(a) for the monolithic ceramics. This corresponds to a sintering mechanism dominated by grain boundary diffusion [103].

Figure 5.3.4 (b) shows the plot used to determine the exponent \( m \) value for PSZ 0.5 vol% CNT. The exponent value of 0.28 is similar to the value of 0.32 for the PSZ with no added CNTs. Also the data at 1300°C shows some deviation from the linear behaviour shown for the PSZ during the first minute of sintering. Figure 5.3.4 (c) shows the plot used to determine the \( m \) value for the 2 vol% CNT composites. The average exponent of 0.30 once again shows an unchanged sintering mechanism with a percolating network of CNTs. The linearity of the fit is also further reduced during the initial sintering for the samples at high temperature. The exponent values for the three systems give an average value of 0.30 which was used for the remaining data analysis [103].

Figures 5.3.5 (a-c) were plotted in accordance with equation 4.1.6 to determine a value for \( K \) at a series of temperatures for the materials. Figure 5.3.5 (a) shows the sample shrinkage as a function of time using the exponent determined from figure 5.3.4. There is a clear increase in gradient and therefore \( k \) value which can be used to calculate the sintering activation energy \( Q \) when plotted as described in equation 4.1.7. Figure 5.3.5 (b) shows the plot to determine \( k \) for the 0.5 vol% samples. As for the plot of \( \ln \Delta L/L_0 \) versus ln time (5.3.4) it is less linear than the data for the PSZ sample, particularly at 1300°C. Initially the rate of shrinkage was considerably higher with the CNTs before slowing to a linear shrinkage rate for the remaining dwell time. Figure 5.3.5 (c) shows the determination of the \( k \) value for the 2 vol% CNT samples. The departure from a linear plot is most pronounced for the 2 vol% CNT sample at 1300°C.
Figure 5.3.4: Plot used to calculate $m$ value for a) PSZ, b) PSZ 0.5 vol% CNT and c) PSZ 2 vol% CNT from 1200-1300°C, every 20th data point is shown. The start and finish densities for all samples are indicated on the plots.
Figure 5.3.5: Plot used to calculate $k$ value for: a) PSZ, b) PSZ 0.5 vol% CNT and c) PSZ 2 vol% CNT from 1200-1300°C, every 20th data point is shown.
The In of the gradients obtained was plotted against \(1/T\) as described in equation 4.1.7 to give a linear slope with a value \(Q/R\) as shown in figure 5.3.6 which was used to determine the activation energies of the three systems. The values for \(\ln K\) are similar for all three composites as 1250 and 1300°C whilst the PSZ 2 vol\% CNT sample sintered at the lowest temperature of 1200°C shows a markedly different \(\ln K\) value and gives significantly different activation energy.

![Figure 5.3.6: Plot to obtain a value for Q/R for PSZ, PSZ-0.5 vol\% CNT and PSZ-2 vol\% CNT](image)

The activation energies for the three materials are shown in Table 5.3.1. The value of the activation energy for PSZ and PSZ 0.5 vol\% are similar and within the errors. However, the value for the PSZ -2 vol\% CNT composite is significantly lower.
Table 5.3.1: activation energy calculated from figure 5.3.6

<table>
<thead>
<tr>
<th>Composition</th>
<th>Q (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSZ</td>
<td>456±65</td>
</tr>
<tr>
<td>PSZ-0.5 vol% CNT</td>
<td>432±84</td>
</tr>
<tr>
<td>PSZ-2 vol %CNT</td>
<td>172±16</td>
</tr>
</tbody>
</table>

Figure 5.3.20 shows the interface of a cosintered PSZ/PSZ 2 vol% CNT composite. There is an abrupt transition in the density at the boundary which reinforces the belief theory that the addition of CNTs increases the density achieved after sintering under comparable conditions.

Figure 5.3.20: Interface of a cosintered PSZ/PSZ 2 vol% CNT composite highlighting the increased density observed with the addition of CNTs.

5.3.2 Boron Carbide

The green body densities of the B₄C composites reinforce the idea that CNTs act as a solid state lubricant with green body density values of 47.8±1.7%, 50.2±1.1% and 51.3±1.4% for the 0, 0.5 and 2 vol% CNT.
composites respectively. Figure 5.3.7 shows the shrinkage rate for B₄C. It has an onset of sintering at 1550°C and is complete by 2150°C, giving a sample with a theoretical density >99%. The peak shape observed is much broader than that of the PSZ. The two vertical lines in figure 5.3.7 are at 1600°C and 1750°C and show the temperature range in which the analysis was performed. As with the PSZ, the lower temperature limit was chosen because it is just after the onset of shrinkage with the rate at 0.5 mm/min. The upper limit at 1750°C was chosen because it gave a wide range of temperatures to analyse the data over whilst having an overlap of densities to perform the analysis.

![Shrinkage rate versus temperature plot](image)

*Figure 5.3.7: Shrinkage versus temperature plot for a B₄C sample with a heating rate of 200°C/min and pressure of 50MPa to determine the temperature of the sintering behaviour of the B₄C powder.*

The densities of B₄C and B₂C CNT composites are shown in figure 5.3.8, there was an increase in density with increasing CNT content at 1750°C, however, at lower temperatures the densities are all within the margins of error.
Figure 5.3.8: Relative density of $B_4C$ and $B_4C$-CNT composites across the temperature range 1600-1750°C sintered for 8 min with 16MPa uniaxial pressure and a heating rate of 200°C/min.

The upper density attained for the $B_4C$ and $B_4C$ composites was 78%, which is below the 90% cut-off value determined in the case of PSZ for accelerated grain growth. During the initial scan of the $B_4C$ a partial loss of vacuum was noticed beginning at 1600°C and peaking at 2000°C as shown in figure 5.3.9. This is due to the outgassing of the $B_2O_3$ layer that forms on the surface of the $B_4C$ [106].
The vacuum level during sintering was monitored for all samples and shown figures 5.3.10 – 5.3.13 to determine whether any significant outgassing was occurring during the isothermal analysis. There is no loss of vacuum for the samples prepared at 1600°C and a marginal loss for all samples sintered at 1650 and 1700°C. Figure 5.3.13 shows a significant loss of vacuum for the B₄C 2 vol% CNT sample compared to the 0 and 0.5 vol% samples due to the evolution of B₂O₃ and COₓ from the oxide layer. In all cases the point at which the sintering temperature is reached is indicated by an arrow.
Figure 5.3.10: plot of vacuum level against temperature for $B_4C$ and $B_4C$ CNT composites sintered at 1600$^\circ$C

Figure 5.3.11: plot of vacuum level against temperature for $B_4C$ and $B_4C$ CNT composites sintered at 1650$^\circ$C
Chapter 5. Densification Activation Energy

Figure 5.3.12: plot of vacuum level against temperature for B₄C and B₄C CNT composites sintered at 1700˚C

Figure 5.3.13: plot of vacuum level against temperature for B₄C and B₄C CNT composites sintered at 1750˚C
The outgassing had an influence on the shrinkage rate of the samples as shown in figure 5.3.14. There was an increase in shrinkage rate during the dwell time after around two hundred seconds at 1750°C. This is believed to be due to the reaction of the oxide layer on the B₄C particles with the free carbon in the system. The shrinkage rate then returned to the value observed for the first three minutes of the dwell time. The shrinkage data of a B₄C and 2 vol% composites during the dwell time at 1750°C is compared in figure 5.3.14. The 2 vol% composite showed an increase in the shrinkage rate after 200 seconds which corresponds with the completion of the outgassing at around 700 seconds in figure 5.3.13.
Figures 5.3.15 (a-c) were used to calculate the sintering mechanism exponent \( m \) for \( \text{B}_4\text{C}, \text{B}_4\text{C} 0.5 \) and 2 vol\% CNTs respectively. Figure 5.3.15 (a) shows the plot used to determine the exponent \( m \) for \( \text{B}_4\text{C} \), the average value of 0.44 corresponds to a sintering mechanism by bulk diffusion. The average exponent value for the \( \text{B}_4\text{C} 0.5 \) vol\% CNT composites was found to be 0.40 from figure 5.3.15 (b) and therefore corresponds to the same sintering mechanism by bulk diffusion observed for the \( \text{B}_4\text{C} \). The average sintering exponent for the \( \text{B}_4\text{C} 2 \) vol\% CNT samples was found to be 0.36 from figure 5.3.15 (c). This value did not directly relate to one sintering mechanism but appears to show a combination of bulk diffusion and grain boundary diffusion suggesting a change in the sintering mechanism once a percolating network of CNTs is formed.

Figures 5.3.16-5.3.18 show the plots used to determine the \( k \) values for \( \text{B}_4\text{C}, \text{B}_4\text{C} 0.5 \) and 2 vol\% CNT samples respectively. In all cases up to 1700°C the plots show a high degree of linearity, however for the samples prepared at 1750°C the plots deviate from this linear behaviour. It is most strongly pronounced in the case of \( \text{B}_4\text{C} 2 \) vol\% CNTs although is also present for the 0 and 0.5 vol\% samples.

The \( k \) values obtained from figures 5.3.16 – 5.3.18 were then plotted against the inverse temperature as shown in figure 5.3.19. To obtain the activation energies, equation 4.1.7 was applied to the slopes in figure 5.3.19 and the results are shown in table 5.3.2.
Figure 5.3.15: Plots used to calculate m value for: a) B₄C, b) B₄C 0.5 vol% CNT and c) B₄C 2 vol% CNT from 1600-1750°C. Every 20th data point is shown. The start and finish densities for all samples are shown on the plots.
Figure 5.3.16: Plot used to calculate $k$ value for B$_4$C from 1600-1750°C. Every 20$^{th}$ data point is shown.

Figure 5.3.17: Plot used to calculate $k$ value for B$_4$C 0.5 vol% CNT from 1600-1750°C. Every 20$^{th}$ data point is shown.
Figure 5.3.18: Plot used to calculate $k$ value for B$_4$C 2 vol% CNT from 1600-1750°C. Every 20th data point is shown.

Figure 5.3.19: Plot used to calculate $Q$ for B$_4$C and B$_4$C CNT composites
Chapter 5. Densification Activation Energy

Table 5.3.2: Sintering activation energy for $\text{B}_4\text{C}$ and $\text{B}_4\text{C}$ CNT composites

<table>
<thead>
<tr>
<th>Composition</th>
<th>$Q$ (KJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{B}_4\text{C}$</td>
<td>647±62</td>
</tr>
<tr>
<td>$\text{B}_4\text{C}$ 0.5 vol% CNT</td>
<td>705±59</td>
</tr>
<tr>
<td>$\text{B}_4\text{C}$ 2 vol% CNT</td>
<td>400±73</td>
</tr>
</tbody>
</table>

The sintering activation energy followed a similar pattern to the PSZ and PSZ CNT composites with a significant reduction above the percolation threshold. The value for the 0.5 vol% composite, however, is higher than that of the monolithic ceramic although they are within the error bars.
5.4 Discussion

The exponent, $m$, value for PSZ and PSZ CNT composites was estimated in the current work to be around 0.3, which corresponds to a sintering mechanism dominated by grain boundary diffusion [103]. The fact that it is similar for the sintering of PSZ and PSZ CNT composites, both above and below the percolation threshold, suggests that the sintering mechanism is not changed by the presence of CNTs. Previous work on the sintering of PSZ has found the same sintering mechanism [107-109]. For work involving high pressure (≥100MPa), creep was found to be the dominant sintering mechanism [110-111].

For the B$_4$C and B$_4$C CNT composites the value obtained for $m$ and in turn the sintering mechanism was not constant, but instead decreased from 0.45 to 0.40 and 0.36 for the 0, 0.5 and 2 vol% CNT composites respectively. Both the B$_4$C and B$_4$C 0.5 vol% CNT composite had a sintering mechanism dominated by bulk diffusion whilst the B$_4$C 2 vol% CNT had an exponent value that does not correspond to one dominant sintering mechanism but may instead reflect a combination of bulk diffusion and grain boundary diffusion [103]. Previous work on the sintering of B$_4$C powders by Lee and Speyer found that the addition of free carbon to aid sintering reacted with the oxide layer that forms on the B$_4$C particles [106]. They found that the boiling point of the boron suboxide (B$_2$O$_3$) layer on the powder to be between 1600°C and 1910°C at atmospheric pressure. The addition of 3 wt% phenolic resin provided a source of free carbon that reacted with B$_2$O$_3$ layer at temperatures as low as 1350°C. In this research the density attained at 1750°C for the 2 vol% composite was 10% higher than the monolithic ceramic. The work by Lee and Speyer found ≈8% increase in density but used 6.6 vol% phenolic resin [106]. The change in sintering mechanism found in this work was caused by the same reaction of the surface oxide with the free carbon, in this case CNTs.
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The activation energy of PSZ has been measured in several previous papers giving a wide range of values from 100-935 KJ/mol as shown in table 5.4.1. The range of activation energies is very large due to several factors including different experimental conditions, different methods for calculating the activation energy and also different powders being used. The value obtained in this work of 456 KJ/mol for the partially stabilised PSZ is consistent with several of the studies [110, 112-114].

<table>
<thead>
<tr>
<th>Investigator</th>
<th>Starting Particle Size</th>
<th>Sintering Conditions</th>
<th>Temp Range (°C)</th>
<th>Mol% Y₂O₃</th>
<th>Activation Energy (KJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Theunissen</td>
<td>9nm</td>
<td>Non isothermal</td>
<td>650-900</td>
<td>5.8</td>
<td>100</td>
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<tr>
<td>Cruz</td>
<td>12nm</td>
<td>Non Isothermal</td>
<td>700-980</td>
<td>4</td>
<td>157</td>
</tr>
<tr>
<td>Suarez</td>
<td>530nm</td>
<td>Isothermal</td>
<td>1200-1400</td>
<td>8</td>
<td>170</td>
</tr>
<tr>
<td>Theunissen</td>
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<td>Non isothermal</td>
<td>900-1050</td>
<td>3</td>
<td>275</td>
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<tr>
<td>Chaim</td>
<td>34nm</td>
<td>Non Isothermal/ applied pressure</td>
<td>&lt;1400</td>
<td>3</td>
<td>280</td>
</tr>
<tr>
<td>Granger</td>
<td>&lt;100nm</td>
<td>Non isothermal</td>
<td>1650</td>
<td>3</td>
<td>310</td>
</tr>
<tr>
<td>Granger</td>
<td>60nm</td>
<td>Isothermal/ applied pressure</td>
<td>950-1050</td>
<td>3</td>
<td>450</td>
</tr>
<tr>
<td>Mazaheri</td>
<td>75nm</td>
<td>Non Isothermal</td>
<td>1050-1300</td>
<td>3</td>
<td>485</td>
</tr>
<tr>
<td>Chaim</td>
<td>34nm</td>
<td>Non Isothermal</td>
<td>&gt;1400</td>
<td>3</td>
<td>546</td>
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<tr>
<td>Matsui</td>
<td>65nm</td>
<td>Isothermal</td>
<td>950-1050</td>
<td>3</td>
<td>670</td>
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<tr>
<td>Cruz</td>
<td>&lt;1μm</td>
<td>Non Isothermal</td>
<td>1000-1200</td>
<td>8</td>
<td>762</td>
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<tr>
<td>Granger</td>
<td>&lt;100nm</td>
<td>Non Isothermal</td>
<td>900</td>
<td>3</td>
<td>935</td>
</tr>
</tbody>
</table>

The activation energy of the PSZ-CNT composites shows very interesting behaviour. The sample with a low CNT content (0.5%), below the percolation threshold, has a similar activation energy to the PSZ, within the errors. The sample with a higher content of CNTs (2 vol%), above the percolation threshold, shows a reduction in the activation energy of ≈63%. This coupled with the unchanged exponent, and thus sintering mechanism, suggests CNTs enhance grain boundary diffusion when they form a percolating network. It has also been shown that the rate limiting step in the grain boundary diffusion of PSZ is the diffusion of the Y³⁺ and Zr⁴⁺ cations [115-116]. It is proposed that the percolating network of CNTs provide an easier diffusion pathway for the metal ions at the grain boundary. There has been some
initial work on the use of CNTs as diffusion pathways, however no diffusion coefficient for zirconium or yttrium ions has been calculated which would help confirm this proposition [117-118]. The drop in activation energy is supported by figure 5.3.20 which clearly demonstrates an increase in density for the 2 vol% composite at the interface with a PSZ powder.

Due to the high processing temperatures there has been relatively little research into the sintering activation energy of B$_4$C and B$_4$C composites. A study by Skorohod and Krstic found that the sintering activation energy for B$_4$C was 717 kJ/mol [13]. They also studied the impact of TiB$_2$ additions and found that the activation energy decreased with increasing TiB$_2$ content. The sample containing 25 vol% showed a reduction of 63% to 266 kJ/mol. Previous research by Lange et al calculated the activation energy to be 162 kJ/mol which is significantly lower than the value reported in this research and that obtained by Skorohod and Krstic [119]. This value seems exceptionally low considering the sintering temperature of B$_4$C, and there may have been significant measurement errors as the samples were heated relatively slowly at 20 - 40 °C/min to the sintering temperature before having the displacement measured after set periods of time.

The activation energies measured for the B$_4$C and CNT composites reinforce the conclusions for the PSZ. The B$_4$C 2 vol% CNT composites showed a 43% reduction with a corresponding change in the sintering mechanism. The sintering activation energy for the 0.5 vol% CNT composite is similar to the PSZ with both values within their margins of error. This shows that below the percolation threshold there is very little effect of the CNTs on the activation energy. The reduction of the oxide layer on the B$_4$C is extensive when there is a percolating network of CNTs along the grain boundaries whereas in the 0.5 vol% composite there is insufficient coverage of the B$_4$C grains to reduce the B$_2$O$_3$ on the surface. The presence of the CNTs may also act as a percolating path for the escape of the gas produced from the reduction of the oxide layer.
5.5 Conclusion

The sintering mechanism and activation energy for PSZ, $B_4C$ and their respective CNT composites, both below and above the percolation threshold were studied under isothermal conditions using SPS. Kingery’s model of particle sintering was used to determine both the sintering mechanism and activation energies. The exponent value for the partially stabilised PSZ as well as the PSZ-CNT composites was found to be ≈0.3, which corresponds to a sintering mechanism dominated by grain boundary diffusion. An activation energy of 456±65 KJ/mol was calculated for the PSZ, a reduction to 432±84 KJ/mol and 172±16 KJ/mol was observed for the 0.5 and 2 vol% CNT composites respectively. For the $B_4C$, an activation energy of 647±62 KJ/mol was observed with a similar value of 705±59 KJ/mol for the 0.5 vol% CNT composite and a significant reduction to 400±73 KJ/mol for the 2 vol% composite. The sintering mechanism for $B_4C$ was found to be bulk diffusion which was unchanged for the sample with CNT content below the percolation threshold; however, with the addition of 2 vol% CNTs the sintering mechanism is changed to a combination of bulk diffusion and grain boundary diffusion. This shows that there is a significant reduction in the activation energy above the percolation threshold of the composite and that the presence of well dispersed CNTs in a ceramic powder are an effective sintering aid due to their reduction of the $B_2O_3$ layer on the surface of the $B_4C$ particles. Another possible effect of the CNTs is that they enhance cation diffusion along the interparticle neck regions during densification.
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6.1 Introduction

This aim of this chapter was to study the effect of CNTs on the grain growth behaviour of ceramics. As discussed in section 2.4.3 there is a general consensus in the literature that CNTs inhibit grain growth in ceramic materials [5, 7, 23, 26]. However, there has been no attempt to quantify this phenomenon. This work presents the results from a systematic investigation of composites with CNT contents both below and above the percolation threshold, (0.5 and 2 vol% respectively) as well as a commercially available partially stabilised PSZ powder. As with the sintering activation energy study described in chapter 5, this work was carried out in an SPS furnace to enable the experiment to be done under near isothermal conditions.
6.2 Experimental

The materials used and the experimental details for the sintering and grain growth are described in section 3.1 and 3.2 respectively. Once the sample reached 450°C they were heated at a rate of 200°C/min. All the PSZ and PSZ CNT samples were sintered between 1500 and 1800°C, to achieve a wide spread of temperatures to measure the grain growth rate at. Dwell times of 0, 5, 10, 15 and 20 minutes were used to give a comprehensive dataset for the grain growth rate. The samples were cooled at a rate of 150°C/min. The samples were thermally etched at 1150°C for 30 minutes using the heating and cooling cycles described in section 3.3. The microstructure of the samples was observed via SEM and the grain size determined using the line intercept method, described in detail in section 3.3.
6.3 Results

The grain size of the PSZ and PSZ CNT composites was determined for a range of temperature and dwell times. Figures 6.3.1 to 6.3.6 show the grain growth behaviour for both the PSZ and PSZ CNT composites (0.5 and 2 vol%), with the mean, standard deviation and range for all samples compiled in table 6.3.1. The grain size of the PSZ samples at 1500°C showed a small increase in grain size (≈25%) after 20 minutes. For the samples at 1600 and 1700°C the grain growth was more pronounced. As well as the increase in grain size there was also a wider grain size distribution, as evidenced by the wider error bars. The average standard deviation for the four dwell times was 53nm for the samples sintered at 1500°C, 93nm at 1600°C and 177nm at 1700°C.

![Figure 6.3.1: Grain size of PSZ at 1500, 1600 and 1700°C with dwell times between 5 and 20 minutes and 0 minutes at 1500°C](image-url)
Chapter 6. Grain Growth Activation Energy

Figure 6.3.2 shows the microstructure of the PSZ samples after 20 minutes at the different temperatures. Figure 6.3.2(c) illustrates the high grain size variation exhibited at 1700˚C compared to the lower temperatures.

![SEM images of the microstructure of PSZ sintered at: a) 1500˚C, b) 1600˚C and c) 1700˚C with a 20 minute dwell time.](image)

The Grain growth of the PSZ 0.5 vol% CNT samples, shown in figure 6.3.3, exhibited similar behaviour to that of monolithic ceramic with a small increase in grain size at 1500˚C and significant grain growth at higher temperatures. The grain size and distribution were also similar with an average standard deviation of 56, 109 and 174 nm at 1500, 1600 and 1700˚C respectively.
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The microstructure of the 0.5% CNT composite is shown in figure 6.3.4. The samples all attained a relative density of >98%, the small amount of porosity visible on the surface of the samples was caused by pull out of the surface grains during polishing and the oxidation of CNTs during the thermal etching process.

Figure 6.3.4: SEM images of the microstructure of PSZ 0.5 vol% CNTs sintered at: a) 1500°C, b) 1600°C and c) 1700°C with a 20 minute dwell time.
The grain growth behaviour of the 2 vol% CNT composites, shown in figure 6.3.5, exhibited a similar pattern of grain growth as was observed for the 0 and 0.5 vol% materials at both 1500 and 1600°C. However, at 1700°C there was a deviation after 15 minutes and rapid grain growth occurred within the sample. This grain growth is due to the high temperature reaction between the PSZ and CNTs and is discussed in greater detail later in this chapter. The standard deviation of the grain size was found to be 38nm, 53nm and 114nm at 1500, 1600 and 1700°C respectively. This was notably lower than the values obtained for both the 0 and 0.5 vol% CNT composites across the entire temperature range. The increase in grain size observed after a 20 minute dwell time at 1700°C was not associated with a significant increase in the grain size distribution. A standard deviation value of 136nm was recorded for the 20 minute dwell time, almost identical to the 138nm size distribution observed for a 15 minute dwell time.

Figure 6.3.5: Grain size of PSZ 2 vol% CNTs at 1500, 1600 and 1700°C with dwell times between 5 and 20 minutes and 0 min for 1500°C
The microstructure of the PSZ 2 vol% CNT composites is shown in figure 6.3.6. As was the case in the 0.5 vol% composite the samples all had a relative density of >98% and the observed porosity was caused either by grain pull out during the polishing process or, the oxidation of the CNTs during the thermal etching of the sample.

Figure 6.3.6: SEM images of the microstructure of PSZ 2 vol% CNTs sintered at: a) 1500˚C, b) 1600˚C and c) 1700˚C with a 20 minute dwell time.
Table 6.3.1: Mean, standard deviation and range for all samples used in the grain growth activation energy calculation. All measurements are in nm.

<table>
<thead>
<tr>
<th>Dwell time (min)</th>
<th>PSZ 0.5 vol% CNT</th>
<th>PSZ 2 vol% CNT</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temperature (°C)</td>
<td>Temperature (°C)</td>
</tr>
<tr>
<td></td>
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<td></td>
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<td>20</td>
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PSZ 0.5 vol% CNT

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<thead>
<tr>
<th>Dwell time (min)</th>
<th>Temperature (°C)</th>
<th>Temperature (°C)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1500</td>
<td>1600</td>
<td>1700</td>
</tr>
<tr>
<td></td>
<td>Mean</td>
<td>St Dev</td>
<td>range</td>
</tr>
<tr>
<td>0</td>
<td>189</td>
<td>25</td>
<td>88</td>
</tr>
<tr>
<td>5</td>
<td>266</td>
<td>34</td>
<td>133</td>
</tr>
<tr>
<td>10</td>
<td>291</td>
<td>34</td>
<td>158</td>
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<td>15</td>
<td>321</td>
<td>43</td>
<td>183</td>
</tr>
<tr>
<td>20</td>
<td>366</td>
<td>41</td>
<td>173</td>
</tr>
</tbody>
</table>

PSZ 2 vol% CNT
Figures 6.3.7 – 6.3.9 compare and contrast the grain size of the composites at 1500, 1600 and 1700°C. In all cases the samples containing 2 vol% CNTs appears to show a lower mean grain size than the corresponding PSZ and 0.5 vol% CNT composite. The results for the 0.5 vol% were broadly similar to those observed for the monolithic ceramic; however, there were examples of grain growth retardation in the 0.5 vol% composite at 1600°C as well as one of the samples at both 1500 and 1700°C.

For a dwell time of 20 minutes at 1700°C, the 2 vol% CNT composite showed abnormal grain growth, as shown in Figure 6.3.9 where there is a convergence of the grain size of the PSZ and PSZ CNT samples. The grain size was within the margins of error for the grain size of the 0 and 0.5 vol% CNT composites. For the shorter dwell times the grain size is notably lower for the 2 vol% composites than either of the other systems studied.

Figure 6.3.7: Comparison of grain growth for PSZ, PSZ 0.5 vol% CNTs and PSZ 2 vol% CNTs at: 1500°C with dwell times between 0 and 20 minutes.
Chapter 6. Grain Growth Activation Energy

Figure 6.3.8: Comparison of grain growth for PSZ, PSZ 0.5 vol% CNTs and PSZ 2 vol% CNTs at 1600°C with dwell times between 5 and 20 minutes

Figure 6.3.9: Comparison of grain growth for PSZ, PSZ 0.5 vol% CNTs and PSZ 2 vol% CNTs at 1700°C with dwell times between 5 and 20 minutes
To understand the rapid grain growth that was observed for the sample at 1700°C for 20 minutes a further batch of samples was prepared at 1800°C for all composites to examine whether the effect would be exasperated with more severe processing conditions. Figure 6.3.10 shows the material obtained immediately after thermal etching of a PSZ 2 vol% CNT sample that was sintered at 1800°C for 20 minutes. The sample has disintegrated to a powder in figure 6.3.10 (a) and has a particle size of ≈100µm. Figure 5.3.10 (b) shows a large aggregate from the same sample with extensive cracking on the surface.

Figure 6.3.10: SEM images of the microstructure of PSZ 2 vol% CNTs sample as: a) disintegrated powder and b) heavily cracked aggregate. The sample was sintered at: 1800°C with a 20 minute dwell time.

Figure 6.3.11 shows the vacuum level plot obtained for the PSZ 2 vol% CNT composites. The vacuum level for the samples sintered at 1700°C and below show a small decrease in the vacuum level during the temperature ramp. The sample sintered at 1800°C, however, shows a very large loss of vacuum peaking at the sintering temperature before gradually recovering over a period of several minutes. The reason
for this behaviour is the formation of ZrC which has previously been seen to occur at temperatures over 1650°C [120]. The reaction that occurred between the PSZ and the CNTs at 1800°C is believed to also occur in the sample prepared at 1700°C for 20 minutes. The vacuum loss observed at 1800°C is not observed at the lower temperature; however, the rapid grain growth associated with the transformation is exhibited in both cases. The SPS was run under vacuum and a sample expelling gas at a nominal rate may go undetected by the pressure sensor, as is believed to be the case in the sample prepared at 1700°C for 20 minutes. Because of the increase in particle size at 1700°C, coupled with the similar but more pronounced increase in particle size and sample disintegration at 1800°C, with all other conditions being constant, the sample sintered at 1700°C for 20 minutes was removed from further data analysis.

Before plotting determining the grain growth behaviour it was important to establish a value for $D_0$, the grain size at the start of the test for the materials across the temperature range. To do this the grain size at 1500 and 1800°C was measured and plotted as shown in figure 6.3.12. to ensure an accurate value
was used for $D_0$ the values obtained from figure 6.3.12 were compared with the extrapolated values derived from figure 6.3.1, 6.3.3 and 6.3.5. The values from the two methods are shown in table 6.3.2 along with the average value used in the determination of the grain growth activation energy of the PSZ and CNT composites. The values obtained do differ using the two methods, however, the values at 1600 °C show very little difference with the monolithic ceramic showing a grain size 60nm greater through the extrapolated technique. At 1700°C there is a larger discrepancy between the two techniques and again the monolithic materials has the largest difference of over 200nm for the two methods.

Table 6.3.2: comparison of $D_0$ values obtained from interpolating grain size at 0 minutes between 1500 and 1800°C and extrapolated a value for 0 minutes from the data between 5 and 20 minutes.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Interpolated from 6.3.12</th>
<th>Extrapolated from 6.3.1, 3 &amp; 5</th>
<th>Average value</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0 vol%</td>
<td>0.5 vol%</td>
<td>2 vol%</td>
</tr>
<tr>
<td>1600</td>
<td>440</td>
<td>397</td>
<td>370</td>
</tr>
<tr>
<td>1700</td>
<td>679</td>
<td>593</td>
<td>558</td>
</tr>
</tbody>
</table>

Figure 6.3.12: Plot of the grain size at 0 minutes, values were measured at 1500 and 1800°C and inferred for 1600 and 1700°C
The grain growth exponent was determined by plotting $D^2 - D_0^2$ against time in accordance with equation 4.2.5 in section 4.2. Figure 6.3.13 shows the plot for the PSZ samples including the additional samples made at 1800°C. These samples were included because the lack of carbon in the monolithic ceramic meant there was no reaction and therefore no abnormal grain growth. An exponent of 2 was estimated from the highest average $R^2$ value (0.988) for the three temperatures. This exponent corresponds to normal grain growth; intrinsic self diffusion under the model developed by Burke and Turnbull [105].

The exponent for the PSZ 0.5 vol% CNT composite was found to be 2.7 using the same method as for the PSZ samples. For both the 0.5 and 2 vol% composites the samples prepared at 1800°C were disregarded from the analysis due to the formation of ZrC. Figure 6.3.14 shows the fit obtained when this exponent value is used with an average $R^2$ value of 0.974. The exponent is associated with a sintering mechanism of solute drag. The change in mechanism can be attributed to the presence of CNTs at the grain boundary.

Figure 6.3.15 shows the plot obtained for the PSZ 2 vol% CNT composite with an exponent of 3.2 was used. This value gave the highest average $R^2$ value of 0.983 which as for the 0.5 vol% composite corresponds to a sintering mechanism of solute drag. This shows that the presence of CNTs is sufficient to affect the grain growth mechanism but the formation of a percolating network does not influence the mechanism of grain growth. The increase from the value obtained for the 0.5 vol% corresponds with an increase in the effect of solute drag on the grain growth.
Figure 6.3.13: Plot of $(D^n - D_0^n)$ against time for PSZ at 1500, 1600, 1700 and 1800°C with dwell times between 5 and 20 minutes. The best fit is obtained when $n = 2$.

Figure 6.3.14: Plot of $(D^n - D_0^n)$ against time for PSZ at 1500, 1600 and 1700°C with dwell times between 5 and 20 minutes. The best fit is obtained when $n = 2.7$. 
Figure 6.3.15: Plot of $(D^n - D_0^n)$ against time for PSZ 2 vol% CNTs at 1500, 1600 and 1700°C with dwell times between 5 and 20 minutes. The best fit is obtained when $n = 3.2$.

To determine the grain growth activation energy of the materials, $\ln K'$ was plotted against $1/T$ in accordance with equation 4.2.8 in section 4.2. Figure 6.3.13 shows the plot obtained for PSZ and the CNT composites.
The calculated activation energies are shown in table 6.3.3 there is a significant increase in the activation energy with the addition of 0.5 vol% CNTs and no significant change when the CNT content is increased further to 2 vol%.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Activation energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSZ</td>
<td>417 ±20KJmol</td>
</tr>
<tr>
<td>PSZ 0.5 vol% CNTs</td>
<td>509 ±41KJmol</td>
</tr>
<tr>
<td>ZrO₂ 2 vol% CNTs</td>
<td>497 ±17KJmol</td>
</tr>
</tbody>
</table>
6.4 Discussion

The addition of CNTs to a ZrO$_2$ matrix has been shown to reduce grain growth in ceramics. This is shown in figures 6.3.1, 6.3.3 and 6.3.5, in which a trend was observed across a range of temperatures and time points for the composite containing a 2 vol% CNTs. There was evidence of a reduction in grain growth for the composites containing 0.5 vol% CNTs network although the effect is not as pronounced as was the case for the 2 vol% CNT composites.

The samples sintered at 1800°C with 2 vol% CNTs showed rapid grain growth and then disintegrated during thermal etching/annealing. The samples containing 0 and 0.5 vol% CNTs also exhibited rapid grain growth but this did not cause the sample to disintegrate. The disintegration of the 2 vol% sample is due to the reaction of the CNTs with the PSZ at the grain boundaries. Previous work by Maitre and Lefort have shown that a carbothermal reduction of ZrO$_2$ to a zirconium oxycarbide, (ZrC$_{1-x}$O$_x$) and subsequently zirconium carbide (ZrC) occurs above 1650°C [120]. This is believed to have occurred for the samples of PSZ 2 vol% CNT sintered at 1800°C due to the drop in vacuum observed during sintering which is believed to be due to expelled CO$_x$ after the reduction of expelled oxygen from the ZrO$_2$ + C$_{CNT}$ reaction by the graphite die. During the thermal etching of the samples in air the ZrC on the surface of the PSZ grains would be oxidised to ZrC from 390°C although this rate rapidly increases at ≈600°C, thus allowing the sample to lose structural integrity and disintegrate, as was observed [121]. The result upon annealing the samples would not be as dramatic if a large percentage of the surface was not covered in ZrC. This explains why the 0.5 vol% CNT composite did not disintegrate in the same way as the 2 vol% composite. This PSZ 2 vol% CNT sample sintered at 1700°C for 20 minutes exhibited rapid grain growth associated with the formation of ZrC but did not disintegrate due to the incomplete reaction between PSZ and carbon.
Chapter 6. Grain Growth Activation Energy

The determination of the grain growth exponent from figures 6.3.10 – 6.3.12 show that there was a significant change in the grain growth mechanism with the addition of CNTs. A sintering mechanism of normal grain growth was observed for the samples containing 0 vol% CNTs, both the 0.5 and 2 vol% composites had a sintering mechanism dominated by CNT drag. The grain growth mechanism was not influenced by having a percolating network of CNTs in the same way that was observed during the sintering activation energy study in chapter 5. Instead, the increase in CNT content further enhances the CNT drag mechanism.

Previous work studying the grain growth of ZrO$_2$, both partially and fully stabilised with Y$_2$O$_3$, have found a sintering exponent of 3 using the same analytical model which relates to a solute drag mechanism (9-10). This has been attributed to the migration of Y$^{3+}$ ions to the grain boundary during sintering and the increasing concentration at the grain boundary during grain growth [122]. This behaviour was not observed in this research and there are several reasons this is believed to be the case. Previous studies have been carried out at lower temperatures than were used here; The isothermal grain growth experiments carried out by Boutz et al., were carried out below 1150°C and non-isothermal experiments below 1450°C whilst a study by Sagel-Ransijn et al. was performed below 1375°C [123-124]. Research by Matsui et al. was carried out at 1300 and 1500°C and found a higher concentration of Y$^{3+}$ at the grain boundary in both cases. The Y$^{3+}$ was found in a higher concentration across a smaller distance in the sample prepared at 1300C than 1500°C. This may suggest that at the higher temperatures the Y$^{3+}$ ions become more mobile and may be more soluble within the ZrO$_2$ grains and inhibit grain growth to a lesser extent [122]. In this study the higher temperatures of up to 1700°C may have been significant in that there is a greater driving force for grain growth which may overcome the drag mechanism usually observed for the matrix. A more significant factor is the heating rate and dwell time typically applied to the material. Heating rates of 2-100°C/min and dwell times of several hours were used by several
research groups which provide an extended period of time for the $Y^{3+}$ ions to migrate and build up higher concentrations at the grain boundary. The SPS processing used in this study has a total period of time above 450°C of only 30 minutes which does not allow the same time for $Y^{3+}$ migration as traditional processing [122-124].

The activation energies observed for the materials show an interesting pattern with a significant increase from 417 to 508 KJ/mol with the addition of 0.5 vol% CNTs and then a very similar value of 499 KJ/mol being observed for the 2 vol% CNT composites. This shows that the presence of CNTs increases the activation energy for grain growth, however, the final grain size of the composite is due to the volume content of CNTs within the system. The presence of a higher CNT content causes less contact between PSZ grains, and inhibits grain boundary movement to a greater extent. The reason CNTs have such a pronounced effect on the grain growth is due to their poor wetability with the ceramic matrix. The inhibition of grain growth observed in this research is also found in the literature, with research by Mazaheri et al. has showing that the grain size of $ZrO_2$ decreased steadily with an increasing CNT content from 0.5 - 5 wt% and no direct link to the percolation threshold [125].
6.5 Conclusion

The grain growth behaviour of PSZ partially stabilised with Y$_2$O$_3$, containing 0, 0.5 and 2 vol% CNTs was investigated and quantified though the Burke and Turnbull grain growth model. It was found that the addition of 2 vol% CNTs significantly reduces the grain size across a range of temperatures and dwell times and also reduces the grain size range within the sample. Composites containing 0.5 vol% CNTs showed some evidence of a grain size reduction although it was not as pronounced as in the 2 vol% composite. The grain size range for the 0.5 vol% composite was also broader than the 2 vol%. This was not surprising because the nature of a lower CNT composite means there was a significant proportion of the grains within the material not in contact with the CNTs. The grain growth mechanism observed for the partially stabilised ZrO$_2$ was normal intrinsic grain growth which is at odds with the mechanism of solute drag found by previous research. This is believed to be due to the higher temperatures and shorter processing time used in this research overcoming the solute drag of the Y$^{3+}$ ions. The samples containing both 0.5 and 2 vol% CNTs were found to have a grain growth mechanism of CNT drag which shows that the content of CNTs is not responsible for the grain growth mechanism. The grain growth activation energies were found to be 417, 509 and 497 KJ/mol for the 0, 0.5 and 2 vol% CNT composites respectively showing a large increase with the addition of CNTs, whilst there is very little change with the increase in CNT content from 0.5 vol% to 2 vol%.
7. Degradation of CNTs During SPS Processing

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Chapter 7. Degradation of CNTs During SPS

7.1 Introduction

The aim of this chapter was to investigate the degradation behaviour of CNTs during SPS sintering in a reducing atmosphere. This was achieved by comparing the intensities of the D and G peaks obtained via Raman spectroscopy for a series of samples with varying sintering temperatures and dwell times. These two Raman peaks gave an indication of the extent of amorphorisation and defect concentration within the CNTs. The G band is a peak at ≈1590 cm\(^{-1}\) and is a result of the tangential stretching of the \(SP^2\) carbon lattice. The D band at 1330 cm\(^{-1}\) is a double resonance mode caused by both amorphous carbon and also damaged CNTs [10]. A typical example of the origin of the D peak is shown in figure 7.1.1

![Schematic representation of the origin of the G and D Raman modes within CNTs](image)

Figure 7.1.1 Schematic representation of the origin of the: a) G and b) D Raman modes within CNTs [10-11]

This study used PSZ as a matrix with a 2 vol% CNT content, this concentration was chosen because it gave a strong Raman signal but also allowed for high quality dispersion in the matrix to ensure there was contact between the two phases. Ceramic CNT composites are often prepared by SPS due to the rapid processing and inert reducing atmosphere allowing the CNTs to retain their structural integrity [79, 126].
There is limited information, however, on the amorphourisation that occurs at high temperatures with some contradictory accounts in the literature. One study by Inam et al using SPS found that with CNTs were stable up to 1600°C with limited degradation in both Al₂O₃ and B₄C matrices [79]. However, at ≥1800°C they were severely damaged. Another study by Zhang et al looked at the effect of spark plasma sintering various forms of carbon and found that for pure CNT samples sintered at 1500°C with a 20 minute dwell time, the CNTs underwent a partial transformation to a cubic diamond phase although a large proportion of the CNTs maintained their graphitic structure [82]. Several other groups have reported using hot pressing to prepare composite samples but did not comment on the stability of the CNTs [21, 127-128]. Using this processing route, the CNTs would need to maintain their structural integrity they would have to be stable at high temperatures for several hours. This work was a systematic study of the effect of matrix and processing temperature on the degradation of CNTs.
Chapter 7. Degradation of CNTs During SPS

7.2 Experimental

The materials used and the setup of the sample and die for sintering are described in sections 3.1 and 3.2 respectively. Once the sample reached 450°C they were sintered at a heating rate of 200°C/min and a cooling rate of 150°C/min cooling rate with a constant pressure of 16MPa throughout the sintering cycle. All the PSZ and PSZ CNT powders were sintered between 1500 and 1800°C, for dwell times of 0, 5, 10, 15 and 20 minutes. A cross section of each sample was used for the Raman spectroscopy with each sample being ground flat on a 120 grit diamond disk. All samples were analysed by Raman spectroscopy as described in section 3.3 with the average of three spectra used to give an accurate measurement of the D and G peaks for each sample.
7.3 Results

The Raman spectroscopy for all samples was performed between 733 and 1787 cm\(^{-1}\) wave number. The first scan was performed on the as received CNTs and is shown in figure 7.3.1. The D:G ratio was found to be 1.6:1 which gave a baseline value to measure the processed CNT composites by. The D and G peaks are both well defined and show the D peak at 1310 - 1330 cm\(^{-1}\) and the G peak at 1590-1600 cm\(^{-1}\).

![Raman Spectra obtained for unprocessed Nanocyl N7000 MWCNTs.](image)

The spectra for PSZ 2 vol% CNT composites are shown in figures 7.3.2 - 7.3.5 for sintering temperatures of 1500, 1600, 1700 and 1800\(^{0}\)C respectively. In all cases there were well defined peaks for both the D and G vibrational modes with the exception of the sample sintered at 1800\(^{0}\)C for 20 minutes which shows neither a D or G peaks. This temperature range was chosen because it is significantly higher than the sintering temperature of the PSZ which ensured all samples were >98% theoretical density and also
enabled significant grain growth to occur. Figures 7.3.2 – 7.3.5 show the position of the D and G peak was not influenced by time or temperature. The D peak was found at $1330\ \text{cm}^{-1}$ and the G peak at $1590\ \text{cm}^{-1}$ for all samples.

![Raman plots of PSZ 2 vol% CNT composites sintered at 1500°C with dwell times 0 - 20 minutes. (Every 20th data point is shown)](image)

Figure 7.3.2: Raman plots of PSZ 2 vol% CNT composites sintered at 1500°C with dwell times 0 - 20 minutes. (Every 20th data point is shown)
Figure 7.3.3: Raman plots of PSZ 2 vol% CNT composites sintered at 1600°C with dwell times 5 - 20 minutes. (Every 20th data point is shown)

Figure 7.3.4: Raman plots of PSZ 2 vol% CNT composites sintered at 1700°C with dwell times 5 -20 minutes. (Every 20th data point is shown)
Chapter 7. Degradation of CNTs During SPS

Figure 7.3.5: Raman plots of PSZ 2 vol% CNT composites sintered at 1800°C with dwell times 5 - 20 minutes. (Every 20th data point is shown)

Figures 7.3.6 and 7.3.7 show a comparison of the Raman peaks with the same dwell time and varying temperatures to better compare the condition of the CNTs. In figure 7.3.6 the samples with a dwell time of 0 minutes at 1500 and 1800°C were compared. The intensity of both peaks is significantly reduced for the scan at 1800°C, the G peak is reduced to a greater extent resulting in a higher D:G ratio. In figure 7.3.7 the samples sintered for 20 minutes are compared. The most obvious feature is the sample sintered at 1800°C having no discernible carbon peaks indicating it was no longer present. The figure also shows a gradual increase in the D:G ratio from 1500 - 1700°C. It is important to note that the intensity of the peaks can be influenced by factors such as the surface finish and it is the ratio that provides information on the state of the CNTs.
Chapter 7. Degradation of CNTs During SPS

Figure 7.3.6: Smoothed Raman plots of PSZ 2 vol% CNT composites sintered with a dwell time of 0 minutes at 1500 and 1800°C. (Every 20th data point is shown)

Figure 7.3.7: Smoothed Raman plots of PSZ 2 vol% CNT composites sintered with a dwell time of 20 minutes with a sintering temperature between 1500 and 1800°C. (Every 20th data point is shown)
Figures 7.3.8 and 7.3.9 compare the D:G ratios for all samples and show an increasingly disordered carbon phase as the processing temperature increases. Figure 7.3.8 shows that the D:G ratio increases with time across all of the temperatures studied. Also there is a significant increase in the rate of damage for the samples with a 20 minute dwell time compared to the near constant rate exhibited across all temperatures with dwell times between 5 and 15 minutes. Figure 7.3.9 shows the damage as a function of temperature. The plots are linear with an average $R^2$ value of 0.993 ± 0.006. The slope for all time points is similar with an average value of $1.7 \times 10^{-3} \pm 2.3 \times 10^{-4}$.

![Figure 7.3.8: Plot of D:G ratio against dwell time for PSZ 2 vol% CNT composites sintered at 1500-1800°C](image)

Figure 7.3.8: Plot of D:G ratio against dwell time for PSZ 2 vol% CNT composites sintered at 1500-1800°C
Figure 7.3.9: Plot of D:G ratio against sintering temperature for PSZ 2 vol% CNT composites with dwell times between 0 and 20 minutes.
7.4 Discussion

The high temperature degradation of CNTs in a ceramic matrix during SPS has been examined in this work to expand on the limited studies currently reported in the literature [5, 82]. Figures 7.3.2 - 7.3.5 show that in all cases with the exception of the sample sintered at 1800°C for 20 minutes the CNTs have maintained the G peak representative of the tangential stretching mode of the SP2 carbon atoms. This fits with the research by Inam who found that CNTs in Al2O3 retain some structural integrity at temperatures up to 1700°C before showing complete degradation at 1900°C when sintered for 3 minutes [79]. This research also reported a time dependence of the degradation behaviour which was observed in this research although the time period differs. It was reported that for an Al2O3 sample sintered at 1600°C for 20 minutes there was a D:G ratio of ≈3.5 whereas in this work the D:G ratio for a PSZ 2 vol% CNT sample prepared under similar conditions had a D:G ratio of 2.5. Apart from the matrix the only differences in the experimental procedure are the higher heating rate and pressure (300°C/min, 100MPa) used by Inam compared to this research (200°C/min, 50MPa). The higher pressure used may induce mechanical damage to the CNTs during sintering which would account for the increased D:G ratio.

In Figures 7.3.2-7.3.5 the peak position of the D and G bands were constant at 1330 cm⁻¹ and 1590 cm⁻¹ respectively. This corresponds with work by Inam et al, Jorio et al and Osswald et al who found the D peak centred around 1330-1334cm⁻¹ for both undamaged and thermally degraded CNTs [10, 79, 81]. Other groups have reported slightly different values for the D band, Zhang et al and Liu et al both report the D band peak centre at 1344 cm⁻¹ whilst Babanejad et al report the D peak centre at 1350 cm⁻¹ [82, 129-130]. The Research by Zhang et al also found a shift in the D band with increasing temperature from 1344cm⁻¹ to 1333cm⁻¹ which they attributed to the formation of cubic diamond during SPS. No shift in the D peak centre was observed during this research or in other high temperature degradation
processing studies of CNTs [79, 81]. Whilst the cause of the shift noted by Zhang et al was not seen in this work, the exact position of the D band can be influenced by the type and radius of the CNTs being used as well as the presence of any impurities and it is likely that the high temperature peak observed at 1333\text{cm}^{-1} is a result from a defective graphitic structure [10].

Figure 7.3.6 and 7.3.7 show a clear trend of increasing damage with temperature at both 0 and 20 minutes of the dwell times. At zero minute the D:G ratio for the sample sintered at 1500°C is 1.85, when this was compared to the value of 1.6 obtained for the unprocessed CNTs from fig 7.3.1. This shows that the CNTs are damaged during heating, and at temperatures below what has been used by several research groups to prepare composites, via SPS and hot pressing [81-82, 126-128]. The increase in D:G ratio from 1.85 to 2.45 when the sintering temperature was raised from 1500 to 1800°C demonstrates a strong temperature dependence of the degradation. With increased dwell times the damage to the CNTs increases further with the samples sintered for 20 minutes showing a rapid increase in the damage to the CNTs.

The high temperature degradation of CNTs during SPS can be seen most clearly in figures 7.3.8 and 7.3.9. Figure 7.3.8 illustrates that across the temperature range 1500-1800°C the degradation rate of CNTs increased linearly. Figure 7.3.9 however shows that there was a sharp increase in the D:G ratio with a sintering time above 15 minutes. At 1800°C the CNTs carbothermally react with the PSZ to form ZrC. This has previously been documented by Sondhi et al. among others, who found the formation of ZrC from ZrO$_2$ pellets after a heat treatment at 1800°C [131]. This is the cause of the loss of Raman signal after 20 minutes rather than a sudden rapid increase in the degradation of the CNTs. Despite the early onset of CNT degradation it is important to note that at 1800°C with a dwell time of ten minutes there is still a strong G peak indicating a slow degradation of the CNTs with time as well as temperature. The level of degradation that is acceptable is entirely dependent on the reason for including the CNTs in the
composite. If they are being used to enhance electrical properties then very little degradation is acceptable as it will have a detrimental effect on the conductivity. If however, they are being used to impede grain growth it is not essential that they retain their ordered graphitic structure and they can be sintered at higher temperatures for longer dwell times.
7.5 Conclusion

This research has shown that CNTs are degraded during SPS in all samples sintered at or over 1500°C with dwell times from 0 to 20 minutes. Despite this however the CNTs are degraded at a near constant rate with increasing temperature suggesting it should be possible to predict the degradation behaviour of CNTs under a certain sintering regime. For PSZ CNT composites sintered at 1800°C, for 20 minutes there is no trace of the CNTs remaining. This is believed to be due to a reaction with the matrix rather than degradation of the CNTs because it was not only the G peak that was lost but also the D peak. This research demonstrates the importance of devising sintering regimes for ceramic CNT composites with rapid heating rates and short dwell times to maintain the structural integrity of the CNTs. The results from this work rule out hot pressing as a method for the preparation of ceramic CNT composites because of the long times at high temperatures involved in this processing route.
# Chapter 8. Thermal Transport Properties

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8.1 Introduction

The aim of this work was to investigate the effect of CNTs and nano porosity on the thermal diffusivity of structural ceramic materials. There is currently a limited amount of literature relating to the effect of CNTs on the thermal properties of ceramics although there are reports on both Al₂O₃ and TiN that suggests they do increase the thermal conductivity of the matrix [9, 96].

The effect of porosity on ceramic materials is well studied with increased porosity leading to considerably lower thermal diffusivity values. This is due to the porosity scattering phonons within the structure [132-135]. Research by Deng et al. found that an organised uniform structure reduced the thermal conductivity more than when a non-uniform dispersion of porosity was used [132]. This work aimed to investigate the effect of CNTs on the thermal properties of PSZ and the effect of a low content (0.5-2 vol%) of nanostructured porosity formed by the oxidation of carbon nanotubes could have a significant impact on the thermal transport properties of the ceramic matrix.

The materials investigated were PSZ and B₄C. These materials have widely different thermal conductivity values and were used to give a broad understanding on the effect of the second phase, either CNT or porosity. Both PSZ and B₄C were prepared with 0.5 and 2 vol% CNTs to give samples with CNT contents below and above the percolation threshold respectively. To investigate the effect of porosity the CNTs were thermally oxidised leaving a ceramic matrix with an interconnected network of porosity equal in volume to the CNTs that were in the sample.
8.2 Experimental

The materials used and the setup of the sample and die for sintering are described in section 3.1. Once the sample reached 450° C they were sintered at a heating rate of 200°C/min and a cooling rate of 150°C/min. All the PSZ and PSZ-CNT samples were sintered at 1200°C and the B₄C and B₄C-CNT samples were sintered at 2100°C. These sintering temperatures were chosen to attain materials with a density of >98% for all samples whilst not exposing the samples to excessive sintering conditions that would lead to significant grain growth or degradation of the CNTs if possible. The dwell time at the sintering temperature was 5 minutes in all cases. All the samples had a uniaxial pressure of 50MPa applied during sintering. During heating this pressure was applied at 1000°C over a period of one minute and then removed gradually upon cooling from the sintering temperature to 1000°C. A pressure of 16MPa was used below 1000°C during both the heating and cooling steps to ensure good electrical contact between the rams and the die assembly. The density was measured as described in section 3.3. It was measured both after sintering and after burning out the CNTs to determine the latent porosity of the sample. The CNTs were burnt out by heating the samples at 3°C/min up to 850°C before a 2 hour dwell time and allowing the furnace to cool naturally.

The thermal diffusivity was measured using a Netzsch LFA 457 microflash laser flash system. Measurements were taken at room temperature and then at 100°C and every 100°C thereafter up to a maximum temperature of 1000°C. Three measurements were taken at each temperature in all cases and the average value was used for the analysis. A period of 2 minutes between laser shots was used for all samples to ensure there was thermal stability across the sample. As well as this all measurements were done in an inert argon atmosphere and maintained a temperature stability of ±1°C for all shots.
Chapter 8. Thermal Transport Properties

8.3 Results

The thermal diffusivity of the PSZ and PSZ CNT composites is shown in figure 8.3.1. At room temperature, the thermal diffusivity increases with increasing CNT content. The thermal conductivity of the monolithic PSZ decreases rapidly initially before beginning to plateau at around 350°C, and is essentially constant by ≈600°C and even shows a slight increase by 1000°C. Using a specific heat capacity value of 0.510 J/gmK from the literature for the PSZ it was possible to determine the thermal conductivity at room temperature to be 2.9 W/mK [136]. This value is comparable with that obtained by several other research groups indicating an accurate measurement for the thermal diffusivity of the samples [136-138]

The CNT composites however do not show this same trend; instead, there diffusivity values decrease steadily to 1000°C. Both the 0.5 and 2 vol% composites show similar behaviour with increasing temperature. The 2 vol% diffusivity value drops below the monolithic PSZ at ≈900°C compared to ≈550°C for the 0.5 vol% sample, this difference is due to the higher diffusivity value of the 2 vol% composite rather than a change in mechanism with CNT content.

The CNTs were then burnt out of the PSZ 0.5 vol% and 2 vol% composites the thermal diffusivity values were measured again and compared to the monolithic ceramic. The results are shown in figure 8.3.2 and show a decrease in the thermal diffusivity for both CNT composites across the entire temperature range. The 0.5 vol% composite gave a clear decrease with the curve now reaching a minimum between 500 - 600°C and then increasing slowly up to 1000°C. The 2 vol% sample does not follow the same pattern with a higher thermal conductivity than the 0.5 vol% composite although it did remain lower than the monolithic ceramic across the temperature range.
Chapter 8. Thermal Transport Properties

Figure 8.3.1: Thermal diffusivity of PSZ and PSZ CNT composites between room temperature and 1000°C

Figure 8.3.2: Thermal diffusivity of PSZ and porous PSZ between room temperature and 1000°C
Table 8.3.1 shows the density of the PSZ and PSZ CNT samples after sintering and then after the CNTs were burnt out. The first observation is that after sintering all the samples had a density >98% so were considered acceptable for the analysis. The 0.5 vol% composite behaves as expected with a reduction in both the mass and the final density of the sample. The 2 vol% composite however, shows the mass loss as expected but then exhibits a marginal increase in the density suggesting some sintering has occurred during the annealing.

<table>
<thead>
<tr>
<th>Sample</th>
<th>After Sintering</th>
<th>After Oxidation</th>
<th>Mass of Samples (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Density (g.cm(^3))</td>
<td>Theoretical Density (%)</td>
<td>Density (g.cm(^3))</td>
</tr>
<tr>
<td>PSZ</td>
<td>6.09</td>
<td>99.5</td>
<td></td>
</tr>
<tr>
<td>PSZ 0.5 vol% CNTs</td>
<td>6.01</td>
<td>98.2</td>
<td>5.94</td>
</tr>
<tr>
<td>PSZ 2 vol% CNTs</td>
<td>5.98</td>
<td>99.6</td>
<td>6.03</td>
</tr>
</tbody>
</table>

The thermal diffusivity of the B\(_4\)C and B\(_4\)C CNT composites tested is shown in figure 8.3.3. All three composites show very similar thermal diffusivity values across the temperature range. There are not the clear differences observed for the PSZ and CNT composites. After annealing the composites were retested and the results shown in figure 8.3.4 and shows there is no significant effect of annealing the samples. Using a literature value of 1.1 J/gmK for the specific heat capacity of B\(_4\)C, it was possible to calculate the thermal conductivity as 32.4 W/mK at room temperature of the monolithic ceramic in this research [139]. This corresponds with values obtained previously by other research groups and showed that the thermal diffusivity values obtained in this research for the monolithic ceramics are accurate [140].
Chapter 8. Thermal Transport Properties

Figure 8.3.3: Thermal diffusivity of $\text{B}_4\text{C}$ and $\text{B}_4\text{C}$ CNT composites between room temperature and 1000˚C

Figure 8.3.4: Thermal diffusivity of $\text{B}_4\text{C}$ and porous $\text{B}_4\text{C}$ between room temperature and 1000˚C
The density of the $\text{B}_4\text{C}$ and $\text{B}_4\text{C}$ CNT composites is shown in table 8.3.2. As with the PSZ and PSZ CNT samples the densities in all cases is $>98\%$ and therefore considered acceptable for the analysis. Both samples showed a mass loss after annealing as expected and the densities changed in a similar way to the PSZ composites. The 0.5 vol\% composite shows a slight reduction in the density whereas the 2 vol\% composite does not.

Table 8.3.2: Shows the change in measured and theoretical densities for $\text{B}_4\text{C}$, $\text{B}_4\text{C}$ 0.5 & 2 vol\% CNT composites before and after burning out

<table>
<thead>
<tr>
<th>Sample</th>
<th>After Sintering</th>
<th>After Oxidation</th>
<th>Mass of Samples (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Density (g.cm$^3$)</td>
<td>Theoretical Density (%)</td>
<td>Density (g.cm$^3$)</td>
</tr>
<tr>
<td>$\text{B}_4\text{C}$</td>
<td>2.50</td>
<td>99.2</td>
<td></td>
</tr>
<tr>
<td>$\text{B}_4\text{C}$ 0.5 vol% CNTs</td>
<td>2.48</td>
<td>98.8</td>
<td>2.45</td>
</tr>
<tr>
<td>$\text{B}_4\text{C}$ 2 vol% CNTs</td>
<td>2.47</td>
<td>100</td>
<td>2.47</td>
</tr>
</tbody>
</table>
8.4 Discussion

The addition of CNTs and nano porosity to ceramic matrices has shown interesting results. In the case of PSZ the presence of CNTs enhances the thermal diffusivity, particularly at lower temperatures, whilst a network of porosity appears to decrease the thermal diffusivity. For the B₄C however, there does not appear to be any significant effect on the diffusivity with either the addition of CNTs or porosity.

In the case of PSZ increasing CNT content causes the thermal diffusivity to increase at room temperature. The change in thermal diffusivity with temperature is more pronounced in the case of the CNT composites with both the 0.5 and 2 vol% composites showing similar shape curves up to 1000°C. The monolithic PSZ did not show the same reduction and instead begins to plateau from 350°C upwards. This has been seen in previous work and is followed by an increase in thermal diffusivity over 1000°C [138]. It can be attributed to passing the Debye temperature for PSZ at which point the crystal structure is in its highest normal vibrational mode [141]. In practical terms this results in a plateau of the thermal diffusivity because no additional thermal energy can stored in the system. CNTs have a significantly higher Debye temperature of >1000°C, this is the cause of the lower thermal diffusivity values of the CNT composites at higher temperatures as the CNTs have vibrational modes which are only activated above the Debye temperature of the PSZ [142]. Previous work on the thermal conductivity of ZrO₂ has found that decreasing the grain size decreases the thermal conductivity [137]. The presence of the CNTs reduced the grain size of the PSZ as demonstrated in chapter 6 and the increase in the thermal diffusivity caused by the presence of CNTs is greater than the effect of the reduction in grain size.

The addition of porosity to ZrO₂ has been widely studied to reduce the thermal conductivity of ZrO₂ ceramics [136, 138, 143-144]. One area they are widely used in is that of thermal barrier coatings for components such as gas turbine blades. The thermal conductivity and fracture toughness of partially
stabilised ZrO$_2$ is higher than the fully stabilised cubic form, this means the partially stabilised form is often used to reduce the risk of mechanical failure of the component [136]. There is then a trade off between the volume content of porosity and the mechanical properties. In this work the sample containing 0.5 vol% porosity shows a diffusivity reduction compared to the monolithic ceramic and the plot now follows the same shape reaching a plateau at 500 – 600 °C. The behaviour of the 2 vol% porous sample did not follow the trend of decreasing thermal diffusivity with increasing porosity. There was a reduction compared to the monolithic ceramic but it is higher than the 0.5 vol% composite. This is because of the increase in density during annealing for the 2 vol% composite. The samples were annealed at 850°C for 2 hours, this is below the sintering temperature of PSZ, however, the increase in density appears to show otherwise. The formation of porosity at the grain boundaries when the CNTs are oxidised is able to close up at this low temperature. This must be because it is a percolating network as it is not observed in the case of the 0.5 vol% composite where a reduction in density was observed, as expected.

The thermal diffusivity of B$_4$C appears unchanged with the addition of CNTs as well as porosity. It is worth noting that the thermal diffusivity of the B$_4$C is an order or magnitude higher than that of PSZ making it harder to increase the value further. The counterpoint to this, however, is that porosity should have more of an impact on the thermal diffusivity because it is lowering it from a higher starting point. The samples did exhibit a weight loss during annealing which suggests there was carbon present to burn out, however a Raman scan of the sample showed that the CNTs had reacted with the matrix during processing and left only residual D and G peaks. The loss of the majority of the CNTs within the sample during sintering explains why the samples did not exhibit the differences observed for the PSZ.
8.5 Conclusion

This research found that the inclusion of CNTs in a matrix does increase the thermal diffusivity of ceramic materials at low temperatures. A 2 vol% CNT composite showed ≈25% increase in thermal diffusivity at room temperature. This shows that with low CNT content the thermal properties of a ceramic can be significantly influenced. The CNTs also inhibited the thermal transport mechanisms at high temperature and both composite samples had a lower thermal diffusivity than the monolithic ceramic at 1000°C due to the very high Debye temperature of the CNTs and could allow the development of composites with novel thermal properties. The thermal diffusivity of PSZ can be reduced by the oxidation of CNTs to leave a residual porosity within the sample although when a percolating network of CNTs is used the temperature required to close the porosity is significantly lower than must be used during sintering. The B$_4$C did not exhibit any significant changes to its thermal properties; this could in part be down to the higher thermal diffusivity of B$_4$C but is more likely to be caused by the damage to the majority of the CNTs during sintering causing the microstructure of the samples to be very similar in all cases.
9. Conclusions

9.1 Conclusion

This work was a comprehensive investigation on the sintering behaviour of ceramics CNT composites. The sintering and grain growth mechanisms along with their associated activation energies were calculated for a series of ceramic and ceramic CNT composites. The structural integrity of the CNTs was also investigated to help identify suitable sintering routes for ceramic CNT composites. Finally the effects of low volume contents of CNTs on the thermal properties were investigated.

CNTs play an important role in the sintering of structural ceramics. It was found that for PSZ composites the addition of a 2 vol% CNTs had a dramatic effect on the sintering activation energy, reducing it by 62% this was due to the presence of a percolating network of CNTs enhancing the sintering mechanism of grain boundary diffusion that was displayed by the partially stabilised PSZ. The addition of 0.5 vol% CNTs had little effect on the sintering behaviour of PSZ and showed an activation energy essentially the same as that of the monolithic ceramic. The effect of CNTs on the sintering behaviour of B$_4$C was complicated by the reduction of the oxide layer on the surface of the B$_4$C grains. The 2 vol% CNT composite showed a reduction in the sintering activation energy of 38% and appeared to show a shift in the sintering mechanism. Bulk diffusion was exhibited by the monolithic B$_4$C and the composite with 0.5 vol%, however, the 2 vol% composite showed a combination of bulk diffusion and grain boundary diffusion. This apparent change in sintering mechanism could have been caused by the reduction of the surface oxide allowing diffusion along the grain boundary. The B$_4$C 0.5 vol% composite showed similar behaviour to the PSZ 0.5 vol% composite with an activation energy the same as that observed for the
monolithic ceramic. This further reinforces the idea that for the addition of CNTs to enhance sintering the formation of a percolating network was critical.

The effect of CNTs on the grain growth mechanism and activation energy of PSZ was investigated across a range of temperatures and dwell times. CNTs do not wet well with ceramic materials and their presence at the grain boundaries results in a 22 and 19% increase in the grain growth activation energy for the 0.5 and 2 vol% composites respectively with the values for the 0.5 and 2 vol% composites within the margins of error. The additional energy was needed to drag the CNT through the matrix along with the grain boundary. Unlike the sintering activation energy this process was not dependant on the formation of a percolating network of CNTs although retardation of grain growth is enhanced with increasing CNT content.

The degradation of CNTs during processing is a critical area of research that could go some way to explaining the discrepancies currently in the literature relating to the effect of CNTs on the properties of ceramics. In this work it was found that there was significant degradation of CNTs in a PSZ matrix from 1500°C and potentially lower. The rate of degradation is dependent on both sintering temperature and time and the use of long sintering dwell times (>15 min) results in severely damaged CNTs. This shows that the use of hot pressing to consolidate ceramic CNT composites is not appropriate.

The inclusion of CNTs in a PSZ matrix has been shown to increase the thermal diffusivity compared to the monolithic ceramic at room temperature. With increasing temperature, however, the thermal diffusivity of the PSZ reaches a plateau above 600°C whereas the CNT composites continue to fall up to 1000°C. Burning the CNTs out of the composite and measuring the thermal diffusivity of a nano porous structure decreased the thermal diffusivity in both the 0.5 and 2 vol% materials. Interestingly the reduction was greater in the case of the 0.5 vol% composite because it was a non percolating network
and resulted in trapped porosity when it was burnt out. In the case of the 2 vol% composite, however, the sample showed an increase in density after burning out the CNTs because the percolating network of nanostructured porosity was able to close at 850°C, several hundred degrees below the sintering temperature. In the case of the B₄C the thermal diffusivity was not influenced by the presence of either the CNTs or the porosity. This is believed to be due to the higher thermal diffusivity of the monolithic ceramic negating any increase caused by the CNTs, and also the partial reaction of the CNTs with the oxide layer on the surface of the B₄C grains.
10. Future Work

10.1 Future Work

i. An investigation into the effect of graphene, fullerenes and carbon black on the sintering activation energy of structural ceramics would be a natural progression of this work. It would provide a valuable insight into the role of carbon, in its various allotropes on the sintering of ceramics, by SPS.

ii. A study on the sintering activation energy of CNTs with other matrix materials such as silicon nitride (Si$_3$N$_4$) would allow further comparison of the effect of CNTs on sintering behaviour. With the experience gained from studying the effect on PSZ and B$_4$C, it is apparent future work should be carried out on a material that does not react with carbon at high temperatures in the same way B$_4$C did. It is also important to pick a powder that has a single sintering peak spread over as wide a temperature range as possible to allow the comparison of a range of temperatures.

iii. There is also scope for additional research on the grain growth behaviour of ceramic – carbon composites to be investigated. The use of graphene as a grain growth inhibitor should be examined and compared with the values for the CNTs. It would also be informative to investigate the effect of the aspect ratio of the CNTs to optimise the grain growth retardation for a given volume content of carbon.
iv. An investigation into the effect of coating the CNTs in the matrix material would potentially allow the CNTs to wet during sintering and not just sit at the grain boundary and would allow a comparison of the grain size and grain growth activation energy with the uncoated CNTs.

v. The thermal properties of ceramic-carbon composites should be investigated with a focus on producing materials with a higher carbon content that does not form a percolating network which can close easily during the oxidation process. Graphene and fullerenes are ideal candidates for this because of their plate and spherical structures; this means a higher loading is needed to produce a percolating network than for CNTs.

vi. Further work on the reaction of $\text{B}_4\text{C}$ with the CNTs is needed to fully understand the role of CNTs on the sintering. This could be achieved with a TEM investigation of the interface after a heat treatment across a range of times. Raman spectroscopy should be used to reinforce the results. A comparison of the Raman spectra should provide information on when the reaction between the two phases begin to react.

vii. The mechanical properties of ceramic CNT composites is an area that needs extensive research using well prepared and characterised materials. One area that should be investigated is that of the interface bond between the CNT and the matrix. A study measuring the force required to pull CNTs out of a fracture surface with an AFM tip would allow for a comparison between oxide, carbide and nitride ceramic materials although it would be critical to ensure the microstructure of the matrices, and the structural condition of the CNTs be constant.
11. References


Chapter 11. References


Chapter 11. References


12. Publications

