SPARK PLASMA SINTERING OF MONOLITHIC

SILICON CARBIDE AND SILICON CARBIDE-

GRAPHENE COMPOSITE

By

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Abstract:

Ball milled α – SiC (2.73 μm) was consolidated rapidly using spark plasma sintering at 1800, 1900, and 2000 ℃ under 90 MPa pressure and 20 min of soaking time. Relatively high densification (>90% relative density) was achieved at 2000 ℃. The densification stages were identified, and a three stage densification process was proposed. The formal densification study was performed using the model proposed by Ashby, and the dominant mechanism for densification was determined to be grain boundary accommodated diffusion controlled creep. The formal grain growth mechanism was also investigated, and similar result was found. The value of stress exponent was calculated as 1.1, and the activation energy needed for final stage densification was found to be $\approx$ 427 - 500 KJ/mol. Also, nano-grain clustering was identified as an auxiliary mechanism from microstructural analysis.

The reinforcement of SiC was done with 1, 2, and 3 vol.% graphene. Mechanical characterizations were performed on the reinforced ceramics, and inter-granular fracture was seen. Graphene didn't cause any improvement in hardness of SiC, but showed substantial improvement in flexural strength. Graphene proved to be very useful in restraining grain growth, but decreased the density of monolithic SiC.

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CHAPTER I

INTRODUCTION

1.1 Introduction

Ceramic materials are well known for their excellent mechanical, chemical and thermal properties such as hardness, strength, wear resistance, stiffness, heat resistivity (refractoriness), anti-oxidation and thermal conductivity. They are also known for their great electrical properties. Mechanical and electrical applications at an elevated temperature have been seen as a key factor in state-of-the-art modern ceramic technology, as the refractoriness has been identified as the main attraction for ceramics with a very high melting point.

Among all the modern ceramic materials, structural ceramics are of great promise in the field of advanced engineering and industries [1,2,3,4,5]. Several efforts have been made in the past to analyze and enhance the properties in some potential structural ceramic systems (Y-TZP, Al_2O_3, SiC, Si_3N_4). These ceramics are very attractive because of their potential for thermal and mechanical properties; especially hardness, flexural strength, and creep behavior at high temperatures. Silicon Carbide (SiC) is a great structural material used in various industrial purposes and carries a great potential for automotive vehicles, abrasives, and tool materials with the atmosphere thermally and aerodynamically rough. In addition to that, SiC has a very high melting point. That is why, SiC is a great choice for high temperature mechanical and electrical applications.

Producing dense bulk structure from SiC powder, using powder metallurgy techniques is still a big challenge in the industries. That is why the densification characteristics are very important for the mass production of SiC from powder contents. Although, a lot of investigations have been done to improve the properties of SiC in various processes, the densification behavior of SiC has been neglected especially in the consolidation techniques such as hot pressing and spark plasma sintering [6,7,8,9,10,11,12].

Spark plasma sintering [13] (SPS) is a very recent technique being widely used successfully to manufacture alloys, ceramics, bulk metallic glasses, and metals [14,15,16,17]. Several authors have confirmed this novel technique to be very effective in restricting the grain growth. Spark plasma sintering uses both pressure and Joule heating through pulsed electric current to consolidate the powder compact. As a result, much shorter and faster densification is achieved compared to that in hot pressing. Again, only a few studies have been done on the densification mechanisms that take place in the powder matrix [18,19,20]. Although these mechanisms are still a matter of debate, an acceptable and logical densification mechanism will be tried to be found in this research work.

The application of SPS is still limited for SiC because of its poor sinterability. Because of low self-diffusion and a high melting point, a very high temperature is needed to completely consolidate SiC through sintering. The challenge is to identify the controlling mechanism responsible for densification in SiC, especially at high temperature. The relation between grain growth and densification is of great importance as necking is a crucial characteristic in ceramic sintering.

Reinforcements are often used for improving the mechanical and chemical properties of SiC. Although, it can withstand very high temperatures because of its high melting point, there is still opportunity to improve the strength properties of SiC. Recent investigations have indicated

that Graphene is a very promising candidate for reinforcing ceramics [21]. Graphene has excellent mechanical and electrical properties which have made it a prime choice as reinforcement in SiC [22,23,24,25].

In this chapter, the basic properties of SiC and Graphene are briefly discussed along with the Spark plasma sintering mechanism. Also, the application and previous works on SiC will also be reviewed.

1.2 SiC

SiC is a naturally stable group IV compound. It shows excellent semi-conductivity and other wide range of useful properties. Jons Jacob Berzelius was the first person to report a chemical bond between Silicon and Carbon [26]. In 1824, he speculated this phenomenon in one of his produced samples. In 1885, the Cowles brothers invented the Electric Smelting Furnace [27]. Acheson adopted this new technology, and wanted to substitute diamond by a new abrasive and cutting material, because of the high expense associated with diamonds. He mixed coke and silica in the furnace, and was able to produce a new crystalline product, which he named 'Carborundum' [28]. He introduced its proper formula, SiC. This 'Carborundum' had great properties such as high hardness, refractibility, and infusibility. In 1893, Professor Frazier discovered 'polytypism' in SiC, which will be discussed in detail later in this chapter [29]. The first actual application study began with the production of LED (Light Emitting Diode) from SiC in 1907 [30]. It took a long time for SiC to be used in gross industrial production. The first blue LED was introduced in the market in late 1980s, which was the only commercial blue electroluminescent light source at that time [31].

Research and affiliated works related to SiC received more interest in the late 1970s and late 1980s, as two important discoveries were made. First, the seeded sublimation growth was

invented by Tairov and Tsvetkov [32] and second, the high quality step-controlled epitaxy [33] could be made. Since then, SiC has been a prime candidate in material research for various purposes throughout the world.

1.2.1 Crystallographic structure and properties of SiC

The crystallographic structure of SiC needs to be discussed in detail, because it shows a unique crystalline structure named as 'Polytypism'. The compounds and elements appearing in more than one crystalline form, is called 'Polymorphism'. Generally polytypism is described as one-dimensional variation of polymorphism [34]. This phenomenon occurs with different stacking sequences of a basic core structure. In SiC, although a two dimensional variation of polymorphism is seen; it is still described as polytypism for simplification. Till now, almost 200 polytypes of SiC have been invented [35,36].

The vigorous investigations related to the polytypism started back in the early 20th century through X-ray and goniometric studies. The Arnt and Hausmann study discarded the possibility of the existence of a second formula for silicon carbide other than SiC [37]. Early crystallographic studies were done through the goniometric measurements by Acheson [38], Baumhauer [39,40,41], Becke [42,43], Negri [44,45], Peacock et al. [46,47] and Cortellezzi and Schroeder [48]. The true structural studies began after 1919, when Hull [49,50] and Ott [51,52,53,54,55,56] reported crystal modifications of SiC. It continued with more investigations by Thibault [57,58,59], Ramsdell [60,61,62,63,64,65,66] Mitchell [67,68], and many others for the next 50 years.

The basic building block of a SiC crystal is a tetrahedron of four carbon atoms with a silicon atom in the center. There is a particular distance between the two adjacent atoms, and also between each carbon and the silicon atom. **Figure 1.1** shows the arrangement in a tetrahedron

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where the distance between the carbon and silicon atoms is 1.89Å, and the distance between the carbon atoms is 3.08Å [69]. The tetrahedron generally comes in two types. They are 180° apart from each other.

Figure 1.1: Characteristic unit Tetrahedron building block in SiC crystal [69]

All polytypes of SiC crystals are comprised of hexagonal frames of SiC bilayers. These layers are the same for all lattice planes. Successive layers can arrange among themselves either in parallel or anti-parallel directions. If the possible positions are A, B and C, then there exists one polytype with a pure cubic stacking sequence of ABCABC…. in [111] direction, which is named as cubic SiC crystal. Thibault named the structure β-SiC, and Ramsdell named it 3C-SiC. The number '3' stands for the number needed for periodicity. This cubic form is similar to the structure of zinc blend (ZnS) or diamond with individual tetrahedron.

The pure hexagonal stacking with ABAB…. sequence in the [0001] direction is called wurtzite (2H-SiC), where the two nearby SiC bilayers are in opposite directions to each other. **Figure 1.2** shows the stacking sequence in the parallel and anti-parallel directions [70].

Figure 1.2: Tetrahedron orientation in successive hexagonal bilayers in a) parallel, and b) anti-parallel directions [70]

All other polytypes are the blend of pure cubic and hexagonal bonds. Most other common polytypes are, hexagonal 4H-SiC and 6H-SiC, and polytypes with rhombohedral symmetry, 15R-SiC [34]. In 4H-SiC, there are equal numbers of cubic and hexagonal bonds present. In 6H-SiC one-third of the bonds are hexagonal and the rest are cubic. The stacking sequence for these polytypes would be ABCB….., ABCACB..…., and ABCBACABACBCACB………. Again, the numbers in the polytypes denote the number of layers needed for periodicity.

Figure 1.3 shows the five most common crystal structures of SiC described by Ott in five modifications. He described the cubic 3C-SiC structure as 'amorphous' because of the very fine powder structure found in his research, but should not to be confused with the glassy amorphous structure. The hexagonal structures or the mixed structures are also called α-SiC.

The color variation in the different crystal structures is one of the interesting features of SiC. Gasilova et al. [71,72] and Taylor et al. conducted a study for their sample produced through thermal reaction in furnaces for different starting materials (mostly graphite, silicon and graphite,

and SiO$_2$). They found that, β-phase yields a lighter appearance in color which is mostly greenish and darker green. The α-phase produces darker phases such as light grey, dark grey, and black. This evidence is not always conclusive because some of the 6H phases also appear to be in green and darker green. Also, the color depends on the impurity. The dark black color is mostly due to the mixture of 4H and 6H. The relative proportion of the phases depends on experimental conditions mostly on annealing temperatures and operating cycles.

SiC has a wide bandgap depending on the binding energy. It varies from 2.4 eV for 3C-SiC to 3.33 eV for 2H-SiC, hence, it can be used in a broad range of high temperatures. The bandgap for 6H-SiC is 3.023 eV and 3.27 eV for 4H-SiC [73,74].

The lattice parameters are of a great indication of the geometry of the different crystal structures in SiC. They were computed by numerous authors over the years. **Table 1.1** shows the crystal parameters of common modifications of SiC crystals.

Figure 1.3: Common polytypes of SiC (after H. Ott)

Table 1.1: Lattice parameters of different polytypes of SiC

Geometry of Unit Cell	Lattice Parameters (Å)	Reference
2H	a = 3.073 c = 5.048	Sokhor et al. [75]
2H	a = 3.073 c = 5.048	Adamsky and Merz [76,77]
3C	c_0 = 4.34	Thibault [57], Mitchell [68]
4H	a = 3.073 c = 10.053	Mitchell [68], Thibault [57], Ott [56], Wychoff [78]
4H	a = 3.09 c = 10.08	Kimoto et al. [79]
6H	a = 3.073 c = 15.079	Ott [51,52], Michell [68], Thibault [57]
6H	a = 3.09 c = 15.12	Kimoto et al. [79]
15R	a = 3.073 c = 37.7 α = 13 ˚54-1/2'	Mitchell [68], Ott [54], Wyckoff [78]

We can see that, the largest bandgap is associated with the 2H-SiC structure; therefore, it has the highest binding energy. Judging by the lattice parameters, Mesquita [80] suggested, 2H structure is the densest one, whereas 3C is the most open structure.

Raman spectroscopy studies are a very good reference of the characteristics of different crystal structures. Numerous investigations have been done on the polytypes of SiC [81,82,83,84,85,86,87,88,89,]. Raman spectra are highly dependent on the stacking sequence and isotropy. SiC polytypes show peaks for a range of frequencies. For folded acoustic mode, the frequencies are 100-700 cm^{-1} (except for 3C-SiC because of its isotropic structure). For folded optical mode, they vary from 700 to 1000 cm^{-1}. Nakashima et al. [89] and Feldman et al. [83,84] conducted a study on different polytypes and found similar results. They quantified the results on the basis of reduced wave vectors (x) on the phonon mode in the basic Brilloin zone. 'x' depends on the number of atomic layers on the stacking unit and number of atoms in the unit cell. Both of the results are presented in **Table 1.2** for comparison.

The properties, which were discussed before, are the indications of general characteristics of polytypes of Silicon Carbide. Other than those mentioned above, SiC also shows some unusual and interesting characteristics which are discussed below.

1. **Zig-Zag Stucture:** It is illustrated that, the hexagonal frames act as sheets of spheres in SiC crystals, and these sheets are same for all lattice planes. But the relative position of the plane above or below somewhat shifts to fit in the open spaces with the adjacent layer creating two inequivalent positions on the adjacent layers, hence the zig-zag structure is created. It is an active mechanism for achieving closed-pack orientation. Mitchell**Error! Bookmark not defined.** described this phenomenon as a horizontal translation of the layers with the vertical displacement along the c-axis. He mentioned that, this horizontal displacement is necessary to maintain the 'zig-zag chains'.

Table 1.2: First order Raman Spectra of different polytypes of SiC

Polytype	$x=$ q/q_{max}	Planar Acoustic — FTA (folded transverse acoustic)	Axial Acoustic — FLA (folded longitudinal acoustic)	Planar Optic — FTO (folded transverse optic)	Axial Optic — FLO (folded longitudinal optic)	Reference
3C	0	-	-	796	972	Nakashima [89]
3C	0	-	-	796$\pm$2	972$\pm$2	Feldman [84]
2H	0	-	-	799	968	Nakashima [89]
	1	264	-	764	-	
4H	0	-	-	796	964	Nakashima [89]
	0.5	196, 204	-	776	-	
	1	266	610	-	838	
4H	0	-	-	797	964-971	Feldman [84]
	0.5	204, 196	-	776	-	
	1	266	610	-	838	
6H	0	-	-	797	965	Nakashima [89]
	0.33	145, 150	-	789	-	
	0.67	236, 241	504, 514	-	889	
	1	266	-	767	-	
6H	0	-	-	797	964-971	Feldman [84]
	0.33	149, 145	-	788	-	
	0.67	241, 236	508, 504	777, 769	889	
	1	262	-	766	-	
15R	0	-	-	797	965	Nakashima [89]
	0.4	167, 173	331, 337	785	932, 938	
	0.8	255, 256	569, 577	769	860	
15R	0	-	-	797	964-971	Feldman [84]
	0.4	167, 172	331, 337	785	932, 938	
	0.8	254, 256	577, 569	769	860	

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2. **Growth Theory:** The eminent reason for polytypes formation or the growth theory in SiC is still a matter of debate. Multiple theories have been formulated, but no single simple theory could be established satisfactorily. Earlier it was suggested that, the impurities in SiC are mainly responsible for creation of different polytypes in SiC. Lundqvist [90] and Zhdanov, Minervina [91,92] were the main advocates of this impurity theory. However, due to lack of evidences and its failure to analyze the long period chain structure like 1560H [93], this theory failed to gain the confidence of the scientists. The most popular and well accepted theory for growth is the 'screw dislocation theory'. It says that, polytypes are formed by a spiral growth around a screw dislocation, and different polytypes are defined by the step height of the growth spiral. Frank [94] and Amelinckx [95] established this theory. Screw dislocation can almost describe any polytype formation which is why it is the more polular one. Vand and Hanoka [96] proposed a modification to this theory by describing the screw dislocation to be formed by an epitaxial growth from a foreign body. Jagodzinski [97] proposed a different modification to this theory. He assumed the cubic polytype to be most stable, and the other polytypes could be formed from this cubic structure resulting from the ordering of the stacking faults.

3. **Polytypic Transition:** Because of the low bandgap, 3C structure is generally a low temperature stable polytype. Baumann [98] and Taylor et al. [72] showed that the SiC formation had a clear transition point around 2000-2100 ℃. After this temperature β-SiC is reformed to α-SiC. But this theory is debatable. Shaffer [70] reported that, β phase can be formed by rapid reaction from Silicon, while slow quasi-equilibrium cooling produces α phase. The reverse transformation from β to α is also possible depending on impurities or reaction atmosphere. The transformations are presented below in **table 1. 3.**

Table 1.3: Polytypic conversion criteria for SiC

Transformation	Condition	Reference
6H → 3C	Nitrogen impurity	Page [99]
α ↔ β	Nitrogen pressure control	Slack and Scace [100]
6H → 4H → 2H	Boron/Aluminum impurity	Page [99]
4H → 6H	Boron and Aluminum impurity	Page [99]

From the presented data it is evident that, the p-type impurities work as α-SiC stabilizer and n-type impurities tend to stabilize β-SiC environments.

1.2.2 Some Physical properties of SiC

SiC shows a band of density values varying from 3.16 to 3.3 g/cm^3. The density variation depends on the temperature and the primary polytype formation in a particular crystal. Different authors measured the density of SiC as a function of temperature for different polytypes. The values are presented in **table 1.4.**

Table 1.4: Density of different crystal structures of SiC

Polytype	Density (g/cm^3)	Temperature (K)	Reference
2H	3.21	293	Merz et al. [101]
3C	3.17	300	Sheets et al. [102]
3C	3.21	300	Taylor et al. [103]
3C	3.21	300	Mesquita [80]
6H	3.21	300	Mesquita [80]
6H	3.29	300	Taylor et al. [103]

Young's modulus of SiC is highly dependent on the size of the sample (mainly thickness). **Table 1.5** shows the Young's modulus values for different doping conditions, and also for a wide range of thickness values.

Table 1.5: Young's Modulus of SiC

Conditions	Thickness (mm)	Yung's modulus (GPa)	Reference
297K undoped	3.13	392	Neudeck et al. [104]
297K undoped	2.35	447	Neudeck et al.**Error! Bookmark not defined.**[104]
297K undoped	1.29	442	Neudeck et al. [104]
297K undoped	10	448	Wuttig et al. [105]
297K Al-doped, 3C	10	694	Wuttig et al. [105]

Thermal conductivity of SiC has been studied with the addition of doping materials. Thermal conductivity upto 5 W/cm/K has been reported in literature. **Table 1.6** shows some thermal conductivity values for SiC for different doping conditions.

Table 1.6: Thermal conductivity of SiC

Polytype	Thermal conductivity (W/cm/K)	Doping Condition	Reference
4H	3.7	-	Taylor et al. [106]
3C	3.2	-	Taylor et al. [106]
6H	3.6	Nitrogen doped	Pettenpaul et al. [107]
6H	3.6	Nitrogen doped	Pettenpaul et al. [107]

6H	3.6	Nitrogen doped	Pettenpaul et al. [107]
6H	2.31	Aluminum doped	Pettenpaul et al. [107]
6H	4.9	-	Slack [108]

Table 1.7 shows some miscellaneous properties of SiC. Note that, the specific heat is dependent on temperature.

Table 1.7: Miscellaneous properties

Property	Value	Condition	Reference
Poisson's ratio	0.183-0.192	Room temperature	Shackelford and Alexander [1]
Bulk modulus (6H)	14.01	10^6 psi, 20 ℃	Shaffer [109]
Specific heat α	 0.22 cal/g/ ℃ 0.28 cal/g/ ℃ 0.3 cal/g/ ℃	 200 ℃ 1000 ℃ 1400 – 2000 ℃	Sheets et al. [110]
β	0.27 cal/g/ ℃ 0.35 cal/g/ ℃	700 ℃ 1550 ℃	Shaffer [109]

1.2.3 Applications of SiC

Silicon carbide shows a multi-variegated application in the modern day semiconductor, tool, abrasive, nuclear and biomedical industries [111,112,113,114]. The applications are discussed below in four categories.

1. Silicon carbide has had a great impact on the mechanical application for over 70 years now. Abrasives, tools, armors, pipe linings, valve faces, bearings, pump components have seen the effectiveness of SiC for a combination of properties, such as, high melting point

(2800 ℃), wear resistance, corrosion resistance and hardness compared to low density. Significant amount of SiC is being used to manufacture refractory brick material. Prolonged use of high purity SiC is being considered in different machine components for its anti-oxidation properties. The development of SiC, as a potential component in vehicular gas turbines is one of the newest technology evolving in the modern time [115,116]. The other interesting characteristics of SiC are, high temperature shock resistance and high temperature modulus of ruptur [117].

2. SiC has its biggest market share in semi-conductor and electrical components since 1893. As mentioned earlier, it all started with a simple LED production, but gradually the market has grown as big as 400 million USD for MESFET production (according to Yole Development market study, 2007) [118]. This market is projected to be worth of 10 billion USD for power-device production, as studied by the same authority. Although it was estimated for fully grown and developed SiC production. This just gives a rough idea of what can be accomplished from the processing of SiC. The SiC Schottky diode [119,120,121] market was estimated to see a market share of 250 million USD in 2007**Error! Bookmark not defined.**[118]. So, the question is what makes SiC different over the traditional Si and GaN based components. The answer lies in the theoretical indicator for performance called the 'Figure of Merit'. These parameters are considered to be the indicator for a high-power, high-frequency application namely Johnson Figure of Merit (JFOM) [122], Keyes Figure of Merit (KFOM) [123] and Baliga Figure of merit (BFOM) [124]. JFOM emphasizes on the breakdown field and saturated drift velocity. Keyes proposed his parameter on the basis of thermal conductivity, speed of light in vacuum and dielectric constant. But the most acceptable is BFOM, which is based on breakdown field and low-carrier field mobility. The comparative values for different systems are shown below in **table 1.8.**

Table 1.8: Figure of merit for most common materials in high-power, high-frequency use. Values are normalized to Si (Ref: Kordina and Saddow) [125]

Material	JFOM	KFOM	BFOM
Si	1	1	1
GaAs	9	0.41	22
6H-SiC	900	5	920
4H-SiC	1640	5.9	1840

It is obvious from the high values of Figure of Merit compared to other materials (especially Silicon) that, SiC has the upper hand in the field of electrical performances. These factors are the critical indicators used to describe the efficacy of any potential semiconductor material.

Commercial availability of SiC substrates and the bulk wafer production of 6H and 4H type of polytypes, helped SiC emerge as the leader and pioneer in the semiconductor industry [126]. The three most common forms of SiC crystals (3C, 4H and 6H) have been widely used for all sort of high power and high frequency applications namely Bipolar Junction Transistor (BJT) [127,128], Metal Semiconductor Field Effect Transistor (MESFET) [129,130], Junction gate Field Effect transistor (JFET) [128,131], Metal Oxide Semiconductor Field Effect Transistor (MOSFET) [132,133] and Thyristo [134].

Figure 1.4 shows the predicted market for high power application of SiC over the period of 10 years. The next upcoming impact is expected on HEV's (Hybrid Electric Vehicles). On the other hand, power factor corrector (PFC) share is expected to decrease.

Figure 1.4: SiC market share prediction for high power application (by Yole Developpement) [135]

3. SiC/SiC nano-fiber composites has its fair share in the nuclear fusion reactor because of the low radio-activity of the neutron irradiation, corrosion resistance and high temperature strength [136,137,138]. Blanket design utilizing SiC/SiC [139,140,141] for fusion reactors are the one of the most promising discovery in the field of nuclear science since 1990s, especially for the Gas cooled Fast Reactors (GFR) [142]. The chemical vapor infiltration (CVI) technique has been broadly used to manufacture high quality SiC/SiC composites which gives excellent properties and high quality crystalline structure, but is proved to be expensive and slow [143,144,145]. So newer techniques like Reaction Sintering (RS) [146] and Nano-infiltration and Transient Eutectic Phase (NITE) [147,148] process are developed which facilitates complex shape manufacturing and great material properties with low cost. Very high conductivity of 50 W/mK has been reported for RS processing [146]. Kohyama et al. conducted research on irradiation studies of SiC/SiC composites prepared with NITE process. His study showed no

significant swelling and degradation of fracture toughness even at high temperatures of 1600℃.

4. The biocompatibility and chemical inertness have made SiC a supreme leader when it comes to the application in biomedical devices. SiC has literally been used in almost every parts of human body, from coatings for bone prosthesis for hip joint [149] to making durable dentures [150]. SiC has also been used as coating for Body Mass Index (BMI) devices [151], Myocardial Heart Probes [152] and Coronary Heart Stents [153]. SiC is particularly attractive because of its MEMS (microeletromechanical systems) and NEMS (nanoeletromechanical systems) applications. BioMEMS are of great potential because the MEMS give great performance in harsh conditions. They show high resistance to chemical susceptibility and oxidation [154,155] in such conditions. The 6H and 4H substrates are being used in preparing bioMEMS. These substrates show a wide variety of applications such as, pressure sensors [156], accelerometer [157] and biosensors [158].

1.3 Graphene

Graphene (one of the carbon allotropes) is the newest wonder in the field of material science and engineering because of its multi-variegated excellence in properties. It is a two dimensional form of carbon monolayer with a honey comb structure [159]. For a long time it was believed that, the 2D variation of carbon allotrope would not exist without a 3D base and the thermodynamic instability was defined with respect to Fullerene (another allotrope of carbon) [160] for a monolayer having the thickness value less than 20 nm according to the AB Initio calculation [161]. But the groundbreaking discovery by Geim and Novoselov [162] through conducting experiments on graphene and its properties, established the first real evidence of

stable carbon monolayered structure, and its limitless possibility in electronics, mechanics and optics. Geim and Novoselov [163,164,165] continued their experiments on graphene which eventually rewarded them Nobel Prize in experimental physics in 2010. Graphene has surprisingly unique properties such as anomalous (half-integer) quantum Hall effect (QHE) [164], very high electron mobility (250000 cm^2/Vs) at room temperature [162,163], exceptional thermal conductivity (as high as 5000 W/m/K) [166] and super high Young's modulus (1 TPa) [167].

1.3.1 Crystal structure and properties of Graphene

As mentioned earlier, graphene layers are made of a honey-comb structure which consists of two basic sub-lattices, where these sub-lattices are two triangular shaped structures shown in **figure 1.5.** Each triangular sub-lattice combines with another similar structure, and creates hexagonal net which is called the honey-comb structure. The distance between two Carbon atoms is 1.42 Å and they are connected to each other by σ or sp^3 bond. But two neighboring layers are connected by π or sp^2 bonds along the z direction. Each carbon atom possesses this π bond which are then hybridized together to form π and π* bands [168]. The inter-planar distance of ideal graphite has been calculated as 3.45 Å, but successive planes can rotate with each other resulting the inter-planar distance to increase [169].

Traditional semiconductors have a finite bandgap whereas graphene shows a nominal bandgap of zero which is quite different. Generally it is regarded that graphene mono-layers have a thickness of 3 Å, which is twice the bond length [170] of C-C.

Figure 1.5: Atomic structure of graphene; (a) Honey-comb structure of graphene monolayer, triangular sub-lattices create hexagonal continuous structure. (b) π-π^* band structure of graphene, red and blue layers are valence and conduction π bands respectively (courtesy: Geim and Mcdonald [171])

Raman spectroscopy can be used to determine the number of graphene layers present in a sample. Graphene shows three most dominant peaks which are G band (results from in plane vibration of sp^2 bond) ~ 1580 cm^{-1}, 2D (G$^{'}$) band (results from two phonon resonance process) $\sim$ 2680 cm^{-1} and D band (results from disorder/defects in the atoms) ~ 1350 cm^{-1} [172,173].

The shape of the 2D peak and its intensity relative to the G peak can be used to determine the number of layers in graphene. Single layer graphene can be characterized by a long sharp peak, whereas milti-layers result in a broader and asymmetric Lorentzian 2D peak (shown in **figure 1.6**) [174]. In this aspect, it is generally assumed that more than 10 layers of graphene contribute towards formation of graphite. It will be evident from the property table of graphene in the next section.

Fig. 1.6: Raman spectra for graphene layer dependence, N = number of layers of graphene on Si/SiO$_2$, also raman spectrum of bulk graphite is shown; figure adopted from Cooper et al.**Error! Bookmark not defined.**[170]

1.3.2 Important physical properties of Graphene

Graphene shows extraordinary properties both in electrical and mechanical regime. As we are more interested in the mechanical aspect of graphene, some important properties related to the strength and thermal conductivity are presented below.

Table 1.9 shows the young's modulus and intrinsic strength, σ_{int} for graphene, which are direct indicators of exceptionality of graphene in mechanical strength. Note that, single layer graphene shows more strength value than the multi-layered one, which suggests that, graphene is superior to graphite in properties.

Table 1.9: Some mechanical properties of graphene

Different Graphene materials	Characterization technic	Properties	Reference
Mono layer	AFM	E = 1$\pm$0.1 TPa σ_{int} = 130$\pm$10 Gpa at ϵ_{int} = 0.25	Lee et al. [167]
Mono layer Bi layer Tri layer	AFM	E = 1.02 TPa, σ_{int} = 130 GPa E = 1.04 TPa, σ_{int} = 126 GPa E = 0.98 TPa, σ_{int} = 101 GPa	Hone et. al. [175]
Multi-layer	Raman	Strain $\sim$ 1.3% (tension) Strain $\sim$ 0.7% (compression)	Tsoukleri et al. [176]

Thermal conductivity is also very important in mechanical design assemblies. **Table 1.10** shows the experimental values of thermal conductivities from different graphene samples. It shows a range of values as high as 3000 – 5500 W/m/K for single layer graphene but shows a very low value for reduced graphene oxide.

Table 1.10: Thermal conductivity of graphene

Different Graphene materials	Characterization technic	Thermal conductivity (W/m/K)	Reference
Mono layer	Confocal micro-Raman	4840 – 5300 at RT	Balandin et al. [166]
Suspended graphene flake	Confocal micro-Raman	4100 – 4800 at RT	Ghosh et al. [177]
Single layer (suspended) Single layer (SiO$_2$ support)	Thermal measurement method Do	3000 – 5000 at RT 600 at RT	Seol et al. [178]
Reduced graphene oxide flake	Electrical four-point measurement	0.14 – 0.87	Timo et al. [179]

1.4 Spark Plasma Sintering

Sintering is a long established and sufficiently old process, which had been used for more than 6000 years now. It is a process of consolidating powder materials which was popular in making bricks, pottery and compacting precious metals [180]. The term spark plasma sintering (SPS) deserves more explanation, as it is unique in its concept of using Joule heating for consolidation rather than some external heating source as used in conventional hot pressing (HP) or hot isostatic pressing (HIP). The spark plasma sintering constitutes of a simultaneous action of electric current and uniaxial mechanical pressure to consolidate powder to form a bulk shape or sample. It all started with a US patent in 1922 [181], although a dense particle or shape building technique by axial pressure and current to sinter metallic particle was also studied by Hoyt [182] in 1927. The rise and commercialization of SPS technique as a mainstream processing technique took some time, as most of the SPS related patents saw daylight after 1990 and in the beginning of 2008 [183]. Although this very process was developed in United States but it was taken over by Japanese investigators. The earlier machineries related to SPS were developed and manufactured along with most of the publications related to SPS being done by them. Nowadays, the Chinese researchers are working more on these processing techniques, and both Japanese and Chinese researchers have developed SPS technique as an emerging solid state science.

1.4.1 Mechanism and advantages of SPS

As mentioned before, SPS technique utilizes a pulsed high DC current with a simultaneous uniaxial pressure. The pulse frequency can vary, but studies found that change in frequency has no significant effects on densification of compact. The applied current and load may be constant or may vary during the sintering cycle in different thermal cycles. The densification is much quicker and takes very little time compared to the HP or HIP processes. The

heating process uses electric current, which makes it much more rapid and efficient heating technique than conventional heating processes in HP. It gave rise to the belief that, pulsing of current gives rise to a plasma state (hence the name SPS) of material which is responsible for such quick heating and densification of the powder compact. It is still a matter of debate, as conflicting views and results showed no presence of plasma. Also no clear evidence was found supporting the claim [184]. Thus some researchers are negligent to call this process SPS, rather they gave rise to new names such as, pulsed electric current sintering (PECS), electric pulsed assisted consolidation (EPAC), electric current activation of sintering (ECAS), pulse discharge sintering (PDS), field activated sintering technic (FAST) etc.

The heating process takes place in a confined structure, created by a 'die' and a 'punch' in SPS. As the whole assembly must be conducting to pass the current, often graphite dies and punches are used, but not limited to, as other materials (tungsten carbide, copper, steel etc.) are also used. Die is a closed boundary cylinder, where a hole is drawn throughout the middle and punches act as plunger to create the pressure. The limiting pressure of graphite dies and punches are generally around 100-140 MPa, as it depends highly on the material's rupture criteria. Very high heating rate is achievable and 1000 ℃/min is reported. **Figure 1.7** shows the schematic of the SPS process and charging between the particles.

Figure 1.7: Schematic of spark plasma sintering mechanism [185]

The powder compact can be insulating or conductive, but as the powder is loaded in the graphite or metallic die, the whole setup becomes electrically conductive and the pulse or high DC current activates the powder bed. It also supplies the necessary driving force, which is enhanced by the applied pressure. Often pressure is applied after the current is applied, but both can be and have been applied together. Higher heating rates provide additional driving force and the densifying mechanisms, such as grain or lattice diffusion are activated. Xie et al. [186] investigated the effect of pulse frequency on densification but concluded that, it had no effect on microstructure and density. They found similar results for pulse DC and constant DC current. On the other hand, the application of current greatly affects the densification and grain growth, as reported by Ghosh et al. [187]. They found grain growth retardation in spark plasma sintered tetragonal yttria-stabilized zirconia (YSZ), with the application of an electric field of about 4 V/cm.

The basic sintering process can be categorized into two, resistance sintering (RS) and electric discharge sintering (EDS). The main difference lies in the application procedure of the current.

RS uses low voltage high current, in the form of direct or pulsed DC or alternating current (AC), whereas EDS uses the electrical energy stored in a capacitor bunk with a sudden release of the energy. Between these two RS is more common and widely used. The thermal cycles for SPS are follows:

- Ramping or heating

- Dwelling or soaking (holding at a particular temperature)

- cooling

Figure 1.8: Difference between the temperature profiles and heating arrangements in a) HP, and b) SPS [188]

As stated before, the main difference between SPS and conventional hot pressing, is the heating criterion. **Figure 1.8** shows the basic difference between these two. T_I and T_A are the temperatures of the center and powder edge respectively. It is clearly evident that, the heating curves are much consistent and smoother in case of SPS, than HP resulting in uniform dissipation of heat and energy circulation. As a result, SPS facilitates the densification process in shorter time, thus reducing material loss due to vaporization [189]. Especially for synthesis of ternary phases like Ti_3SiC_2, SPS eliminates the formation of intermediate phases by the dissipation of heating power to the contact points of the particles. Homogeneous distribution enhances mass transfer in both micro and macro level, which ultimately results in high density values for ternary alloys in a very short time. Because the process is very fast, SPS imparts high densification rate with less power needed. It is also economically viable with noticeable property enhancement for various materials. SPS ensures great increase in superplasticity of ceramics [190], property enhancement in ferroelectrics [191], improved magnetic properties [192], improved thermoelectric properties [193], enhancement in oxidation and corrosion resistance [194], remarkable improvement in mechanical properties [195], improvement in microstructure [196] and electric properties [197] without any significant grain growth. **Table 1.11** gives an idea of the superiority of SPS process over HP. Munir et al. [198] calculated the diffusion coefficients of Ni for both SPS and HP processes. SPS shows higher coefficient of diffusion, hence facilitates the densification.

Table 1.11: Diffusion coefficients of Ni in SPS and HP of Ni/Cu spheres

Sintering process	Temperature applied (℃)	Hold time (s)	D_{Ni} ($\times 10^8$) (m^2/s)
SPS	1000	300	3.564
	1100	300	9.239
HP	1000	2700	1.111

	1100	2700	2.142

1.4.2 Application of SPS

The application of SPS process is well distributed throughout the material science regime. Shorter time and application of low temperature create the possibility of minimal grain growth. Following discussion will give some idea about the vast application contour of SPS.

1. SPS has been successfully implemented to sinter ceramic materials and their composites, with an increase in their mechanical properties, such as fracture toughness and flexural strength. Harimkar et al. investigated the sintering behavior of ZrB_2/SiC and ZrB_2/CNT, and found the effectiveness of SPS in ceramic processing. He showed that, shorter time in operation cycle doesn't allow any thermal reaction between the particles.

2. SPS process has been used to make near-net-shapes, as Galy's [199] research attempt with manufacturing Al_2O_3 spheres from Al_2O_3 powder in only a single step, proved to be very successful as a manufacturing technique for net shape production.

3. SPS is also very effective in producing complex material with complex crystal structures. Wang et al. [200] was able to produce glass phase of zeolite by SPS from crystalline powders based on an approach best known as order-disorder transformation.

4. A great advantage of SPS process is its ability to sinter and densify nanostructured and intermetallic substances. Reduction in ductile-brittle temperature was achieved using this technique [201,202].

5. SPS has been very useful in sintering porous materials, as Kun et al. [203] was able to sinter porous stainless steel, which had higher compressive strength than that of the samples prepared by HP.

6. In electronics, the grain size effect on the material of interest has been investigated for a long time. Okamoto et al. investigated the grain size effect on sintered Scandia stabilized Zirconia, and the fine size of the grain produced, could suppress the formation of less conductive rhombohedral phase.

7. SPS technique is also implemented to sinter transparent materials [204]. Research on transparent alumina has shown that the decrease in pore size decreases light scattering, hence enhances transparency.

8. Functionally graded materials (FGM) [205] and joining of materials [206] have also been achieved by spark plasma sintering and more research works are being done in this field.

1.5 Previous works on densification study of ceramics or similar materials

Very few studies have been performed on the densification behavior of ceramic materials, as the mathematical models developed are still being debated by various researchers. Most of the ideas developed on the dominant densification mechanism are identified as grain boundary or lattice diffusion enabled creep. Surface diffusion is considered as a very early stage mechanism of a sintering process. It is hardly considered as a densification mechanism by any of the authors. **Figure 1.8** delineates some idea about the densification mechanisms and the matter transport during consolidation. Different prominent and widely received mechanisms are discussed in the following section.

Figure 1.9: Six distinct mechanisms responsible for densification in sintering of polycrystalline ceramics; only 4-6 are the densifying mechanisms (Ref: M.N. Rahaman) [207]

1.5.1 Nabarro-Herring vacancy creep:

Nabarro [208] and Herring [209] proposed that, the self-diffusion within a solid would cause a solid to creep for releasing the stress applied. That is why, this model is also known as stress directed vacancy diffusion model. It involves material transport from the faces under compressive stress (higher chemical potential) to faces under tensile stress (lower chemical potential). In other words, it lets vacancies to move from tensile to compressive faces, thus creating a vacancy concentration gradient from faces under tension to that of compression. For

polycrystalline compound like SiC, it can be seen as atoms transferred from grain boundaries under compression to grain boundaries under tension. According to the model,

$$J = D_0 exp\left(-\frac{Q}{RT}\right)\frac{1}{c_0}\frac{c_0}{d\Omega}\left[exp\left(\frac{\sigma\Omega}{kT}\right) - exp\left(-\frac{\sigma\Omega}{kT}\right)\right] \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (1.1)$$

Where,

J is the vacancy flux ($D/c_0.\dot{c}$), D is atom diffusion coefficient, c_0 is equilibrium vacancy concentration, $\dot{c}$ is vacancy concentration gradient, R is gas constant, d is grain diameter, k is Boltzmann constant, Q is activation energy for diffusion, T is temperature, σ is stress, D_0 is temperature independent diffusion constant, and Ω is volume of vacancy.

1.5.2 Modified Coble creep for hot pressing:

Mater transportation or diffusion along grain boundaries in a polycrystalline solid is commonly known as Coble creep, named after R.L. Coble [210]. This creep model could only provide an approximation of densification rate in a sintering process, like hot pressing. In this model, atomic flux terminates at pore surfaces, while grain size remains constant during creep. It is not true for hot pressing, as path length for diffusion and grain size both increase during hot pressing. Coble's creep model, as shown in equation (1.2), was still used in some of the earlier work though.

$$\frac{1}{\rho}\frac{d\rho}{dt} = \frac{HD\phi^n}{G^m kT}p_a^n \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (1.2)$$

Where, H is a numerical constant, D is diffusion coefficient of the rate controlling process, Φ is stress intensification factor, G is grain size, k is Boltzmann constant, T is absolute temperature; m, n are grain size and stress exponents respectively.

1.5.3 Ashby creep model:

Ashby creep model [211] is widely used for investigating the densification behavior in ceramics and other polycrystalline materials. It provides a good relation for grain size, stress exponents, and of course activation energy. This model can be used for SPS processing by the following equation,

$$\ln\left(\frac{T}{\mu_{eff}}\frac{1}{D}\frac{dD}{dt}\frac{dT}{dt}\right) = -\frac{E}{RT} - p\,lnG + n\,ln\left(\frac{\sigma_{eff}}{\mu_{eff}}\right) + K \dots\dots\dots (1.3)$$

Where, D is instantaneous relative density, K is some constant, μ_{eff} = instantaneous shear modulus, T is absolute temperature, n is stress exponent, σ_{eff} is effective macroscopic stress, E is activation energy, G is grain size, P is grain size exponent, R is gas constant.

Values of m and n dictate the mode of densification. Ashby proposed some combinations of two exponents.

If the grain boundary is the perfect source of vacancies:

1. $n = 1$, $p = 2$; densification proceeds by grain boundary sliding accommodated by volume diffusion

2. $n = 1$, $p = 3$; densification proceeds by grain boundary sliding accommodated by grain boundary diffusion

If the grain boundaries are not the perfect sources of vacancies:

1. $n = 2$, $p = 1$; densification proceeds by grain boundary sliding accommodated by an in series (interface reaction/lattice diffusion) mechanism

2. $n = 2$, $p = 2$; densification proceeds by grain boundary sliding accommodated by an in series (interface reaction/grain boundary diffusion) mechanism

Higher values of n generally govern mechanisms facilitated by dislocation climb controlled mechanism.

1.5.4 Previous data on densification of some important ceramics

Table 1.12 features some of the past works related to the mechanisms described and also some other mechanism proposed by other researchers.

Table 1.12: Previous densification studies on ceramics in different sintering mechanisms

Material investigated	Consolidation process	Process parameters	Model for densification	Mechanism identified	Calculated activation energy (KJ/mol)	Maxi-mum density (%)
Yttria stabilized zirconia (Y-TZP) [212]	Two-step Isopressing	40-350 MPa 200-1400 ℃ 5 ℃/min	Young & Cutler[Ɨ]	Grain boundary diffusion	130±20 300±40	99.9
Hydroxyapat-ite [213]	Cold pressing, Furnace sintering	100 MPa 750-1250 ℃ 5 ℃/min 30 ℃/min	Dilatometry	Grain boundary diffusion	-	98.2
HfB$_2$ [214]	HP	800 MPa 1400-1900 ℃ 10 min	Nabarro-Herring vacancy creep	Stress directed vacancy difussion	-	100
Zirconia (TZ3Y) [215]	HP	100 MPa 950-1200 ℃ 25 ℃/min 15 min	Ashby creep	Grain boundary sliding accommodated by grain boundary difussion	450±25 280±25	99.5
Al$_2$O$_3$ doped with CaCO$_3$ and TiO$_2$ [216]	SPS	50 MPa 800-1200 ℃ 100 ℃/min 5-15 min	Ashby creep	Grain boundary sliding accommodated by oxygen grain boundary difussion	300±50	≈100
α-Al$_2$O$_3$ [217]	Cold isostatic pressing, Constant heating rate sintering	200 MPa 5 ℃/min 2h	Johnson[*]	Grain boundary diffusion	356 492	99
Zirconia (TZ3Y) [218]	SPS	950-1200 ℃ 5-180 min 50 ℃/min 100 MPa	Ashby creep	Grain boundary sliding accommodated by interface reaction/lattice reaction of Zr^{4+} ion	450	100
Zirconium oxy carbide [219]	SPS	2155-2460 ℃ 2-20 min 25, 50, 100 MPa 100 ℃/min	Ashby creep	Inter granular glide at low temp, dislocation climb at higher temp	687-774	100

Ɨ = Young and Cutler [220], * = Johnson [221]

1.6 Recent works and data on mechanical properties of SiC

SPS added a new dimension in material science research because of its ability to provide various properties and quick densification in polycrystalline and ceramics materials. That is why many investigators have computed impressive works on SiC using this technique. Some of them are presented below.

1.6.1 Consolidation data of SiC by SPS

Table 1.13: Recent works on SiC by consolidated by SPS

Material and initial particle size	Processing parameters	Max. final grain size	Maximum Relative density (%)	Mechanical properties			Ref.
				Max. Hardness (GPa)	Max. Flexural Strength (MPa)	Max. Fracture toughness (MPa m$^{1/2}$)	
β-SiC (16.6 nm by pyrolysis)	1700-1900 ℃ 73 MPa 185 ℃/min 10 min	1.1 μm	96	25	-	6	Lamello et al. [222]
β-SiC (30 nm by plasma enhanced CVD)	1650-2200 ℃ 50-150 MPa 1-30 min 100-200 ℃/min	2.39 μm	98±0.6	-	-	-	Lara et al. [223]
SiC (0.5 μm)	1750-1850 ℃ 1-10 min 50-100 ℃/min 75 MPa (pressure applied at sintering temperature) 75 MPa (pressure applied at 1000 ℃)	2.4 μm	92 80	-	-	-	Guillard et al. [224]
SiC (0.5-1 μm form granules of 80-100 μm by fluidized bed binderless granulation)	800-1860 ℃ 50 MPa 5 min 150 ℃/min	2.05 μm	98.5	28.5	395	4.5	Zhang et al. [225]
β-SiC (prepared by author by ball milling from Si and C, 5-20 nm in agglomerates of 50-150 nm)	1700-1950 ℃ 70 MPa 10-20 min 180 ℃/min	-	98	20.59	520±50	3.6±0.6	Yamamoto et al. [226]

Ohyanagi and Yamamoto et al. [227,228] conducted research on cubic SiC powder and was able to densify to an impressive level of 98%, without the aid of any additives or sintering aids even at 1700 ℃. They proposed an idea of a disorder-order transformation of the crystalline structure. Starting powder was ball milled from raw Si and C powder for 0-48 hrs, and successfully produced β-SiC with an average particle size of 5-20 nm in 50-150 nm agglomerates. Their observation was validated by Halder-Wagner method from the XRD data and TEM analysis.

Figure 1.10: Disorder-order transformation in SiC and densification characteristics study by XRD; a) comparison in density of SiC sintered at different temperature with commercial powder b) XRD data for samples sintered at different temperature [227,228]

Figure 1.10 shows the disorder-order transformation. A sudden rise of density at 1700 ℃ indicates a transformation of ordering in crystalline structure. They compared their result with a sintered sample from commercially available SiC with 30 nm of particle size, but ended up densifying that sample only up to 80%. The XRD analysis supports their claim of ordering at 1700 ℃. Until 1650 ℃ the disordered structure showed broader hump (also at point (a)) in the

peaks of SiC, but right after 1700 ℃ the peaks tend to get narrow and showed an increment in symmetry. Also a new characterizing peak at point (b) exists after 1700 ℃, showing the ordering of the structure. They were able to retain nano-structure as, the maximum grain size was 60 nm at 1900 ℃.

1.6.2 SPS data of SiC composites

SiC has been reinforced with various and multiples of reinforcements such as Carbon nano tube (CNT), alumina, aluminum, SiC fibers, Si_3N_4 etc. As, our proposed research will be dealing with graphene as a reinforcement, so only CNT reinforcement of SiC will be discussed in this section. Since CNT and graphene share similar aspect in properties and they are both polytropes of C.

Table 1.14: Processing of SiC-CNT composites by various techniques

Material	Processing technic	Hardness (GPa)	Flexural strength (MPa)	Fracture toughness (MPa m$^{1/2}$)	Reference
Si (30-50 nm) + MWCNT (dia. 60-100 nm)	Sonication of Si in MWCNT, Cold press at 2 GPa and 8 GPa, annealing at 1770 and 1970 K produced SiC-MWCNT composite	20-21	-	6.8-7.1	Wang et al. [229]
B-SiC (80 nm) + CNT (dia. 30-40 nm) + 0-1% B_4C	Cold pressed at 40 MPa, HPed at 2273 K and at 25 MPa	-	375.8 (for 10% CNT + 1% B_4C), 100.3 (for 10% CNT)	1.85 (for 10% CNT + 1% B_4C), 3.86 (for 10% CNT)	Wu et al. [230]
SiC (30 nm) + MWCNT coated with SiC (dia. 20-50 nm) + 2% B_4C as additive	SPS 1800 ℃ 40 MPa 5 min	30.6	-	5.4	Morisada et al. [231]
Carbonized α-SiC + CNT	Reactive infiltration enabling of SiC with molten Si at 1400 ℃, Reaction bonding with CNT	-	144.6 for 0.6% CNT	-	Chou et al. [232]

1.6.3 Previous work on ceramic-graphene composites

Not much of research has been done on the mechanical characterization of graphene reinforced ceramics. Only alumina and silicon nitride matrix have been tried for reinforcement consolidated by SPS. Both of them are presented below with some of their properties.

Table 1.15: Manufacturing and properties of different ceramic-graphene composite by SPS

Material	Processing parameters	Hardness (GPa)	Fracture toughness (MPa m$^{1/2}$)	Reference
Al_2O_3 + GO†	1300 ℃ 50 MPa 3 min 100 ℃/min	-	5.21	Wang et al. [233]
α-Si_3N_4 + 0.02-1.5% graphene mixture by Colloidal dispersion	1500-1700 ℃ 35 MPa 2-5 min	15.7-22.3	2.7-6.6	Corral et al. [21]

†GO = Graphene oxide

Corral et al. [21] found surprisingly good property in terms of fracture toughness of the graphene reinforced Si_3N_4. They showed an impressive 235% increase of toughness from the monolithic Si_3N_4 (2.7 MPa m$^{1/2}$) to 1.5% graphene- Si_3N_4 (6.6 MPa m$^{1/2}$).

Figure 1.11: SEM pictures showing a) and b) crack propagation and graphene bridging c) fracture surface showing graphene network of graphene reinforced Si_3N_4

The SEM pictures above show the graphene wrapping of the cracks propagated, which blocks the growth of crack and eventually increases strength and hardness. Also the graphene network can be seen (shown in **figure 1.11**).

1.7 Motivation and hypothesis

1. As discussed in the literature review, it is evident that only a handful studies have been performed on the detailed densification mechanisms, especially on ceramics manufactured by SPS. No formal densification studies have been performed on SiC especially consolidated by SPS.

2. A detailed grain growth study which relates with density and microstructure has not been investigated for spark plasma sintering process yet. Minimal grain growth is expected while achieving higher density.

3. Identification of densification stages involved in SiC system is necessary for better understanding of the basic phenomenon that takes place while denfication, which is important in doping studies and property enhancement. The densification stages have not yet been identified for SiC manufactured by SPS.

4. Recent experiments and results involving the reinforcement of Si_3N_4 with graphene showed a new direction in property analysis and reinforcing SiC with graphene. An improvement of mechanical properties is expected.

1.8 Proposed research and scope of work

A detailed densification and grain growth study will be performed from the ram displacement and grain growth data. The criterion governing the densification mechanism will be identified. Microstructural study for SiC will be carried out to analyze the topological structure and densification mechanism. Reinforcement by graphene of SiC will be discussed for 1, 2, 3 volume% of the total volume manufactured by SPS. Finally mechanical characterization will be performed for SiC-graphene reinforced samples.

CHAPTER II

EXPERIMENTAL DETAILS

2.1 Starting powder

The staring powders that were used in densification studies and mechanical testing are as follows:

- α-SiC (Silicon carbide powder, superfine, 600 grit, product no # A13561, Alfa Aesar USA)

- Graphene (average diameter: 30 μm, thickness: 20 nm, source: American Elements)

Following nomenclature was used for the various samples:

Table 2.1: Nomenclature used for various samples manufacture by SPS

For densification of monolithic SiC		For SiC - graphene ceramics	
Names	Sintering temperature	Names (all sintered at 2000℃)	Volume fraction of graphene
S1800	1800℃	SiC-1G	1% of total volume
S1900	1900℃	SiC-2G	2% of total volume
S2000	2000℃	SiC-2G	3% of total volume

2.2 Experimental Procedure

2.2.1 Mechanical Milling:

Commercially available SiC powder (99.99% pure, source: Alfa Aesar, USA, initial particle size of 600 grit ~ 20 μm) was used as the raw powder for the densification studies under SPS treatment, as well as for the mechanical characterizations. The raw SiC powder used for the densification studies, was ball milled in a Tungsten Carbide jar with the aid of Tungsten Carbide balls for 45 mins with a ball to powder weight ratio of 1:5 at 700 rpm with 5 mm diameter balls. The purpose of this operation was to effectively reduce the particle size of the powder before the green compact was subjected to any sort of thermal load or hot isostatic pressure. This study shows the effectiveness of ball milling procedure, as sufficient milling successfully reduced the particle size, which was used as the starting particle size for all the calculations. During ball milling it was ensured that, no structural damage occurred to the participating particles. That's why careful measures were taken as the ball milling operation was performed inside a Glovebox in inert nitrogen with the aid of wet medium. Acetone was used as a process control agent.

Graphene (average diameter: 30 μm, thickness: 20 nm, source: American Elements) was used as a reinforcement for all of the composite compositions of SiC-G (generic name used for all graphene reinforced SiC with 1, 2, 3 vol% of graphene). The milling of the SiC-G composites was done in two stages. In the first stage, only SiC powder was ball milled for 30 mins at 700 rpm. In the second stage, graphene was added and milled again for 15 mins at 300 rpm. This was done to prevent any sort of structural damage to graphene and also to SiC powder. It should be mentioned that, for better dispersion, graphene platelets were ultrasonicated in acetone for 10 mins before they were added to SiC for milling. 0.2% of Polyacrylic acid (PAA) was also added to the SiC - graphene mixture inside the jar and milled together to ensure better dispersion.

Mechanical milling was carried out in a high energy planetary ball mill (Fritsch planetary micro mill, 'pulverisette 7' premium line) as shown on **fig. 2.1.** In this planetary ball milling machine, the jars are clamped to the sun disk, and high amount of centrifugal force is generated during milling. In 'pulverisette 7' model of ball milling machine the rotation speed could be as high as 1100 rpm and generates 150% more energy resulting reduction in grinding times. This ensures breaking into ultra-fine powders. This special planetary milling machine has been used successfully to create nano-particles. Self-lock technology is a great feature in this ball milling machine, which automatically check the lock of the jars before milling, and shuts off the operation in case of any imbalance.

Fig 2.1: High speed ball milling machine

2.2.2 Spark Plasma Sintering

      The manufacturing of SiC and SiC-G composites were done by a SPS model 10-3 manufactured by Thermal Technologies LLC (Santa Rosa, CA, USA). The basic features of this model are presented below:

Table 2.2: Specification of SPS system used for experiments

Parameters	Range of values
Maximum load	10 ton
Maximum current	3000 Amp (three 1000 amp unit)
Maximum voltage	5 V
Pulsing frequency	Straight DC or 4 to 900 ms
Pulsing sequence	Off time 0 to 9 ms
Maximum heating rate	600 ℃/min
Maximum sintering temperature	2500 ℃
Vacuum used	10^{-2} torr by vacuum pump
Pressure control	Digital servo valve hydraulic press, minimum pressure 3 MPa
Cooling mechanism for heating chamber	Inert gas flow
Temperature measurement	K type thermocouple for < 1000 ℃ Single-color optical pyrometer (Raytek, RAYMM1MHVF1V for higher temperature, adjustable to all three axes

Figure 2.2 shows the components of the SPS machine that was used to consolidate the samples.

Figure 2.2: SPS machine components (Thermal Technology LLC)

The powder bed was inserted into the graphite die-punch assembly. A thin graphite sheet was inserted on top of the powder on both sides for easy removal of the samples. Also graphite cloth was used (can be seen in **figure 2.3**) for reducing radiation loss. The graphite dies were capable of handling a maximum of 100 MPa pressure. They were 20 mm in diameter and had a thickness of 10 mm. Two 30 mm punches were used to provide the pressure. **Figure 2.4** shows the pyrometer which was used.

Figure 2.3: Graphite-die assembly

Figure 2.4: Raytek single color pyrometer

All the SPS tests were conducted under inert argon atmosphere with a fixed heating rate of 100℃/min. Different temperatures (1800℃, 1900℃ and 2000℃) were used to sinter the SiC green compact in order to obtain the densification rate and behavior. All the sinterings were performed under a fixed pressure of 90 MPa. The optimum soaking time was determined to be 20 mins for all the experiments. Punch displacements were recorded all the way through the experiments to study densification. Pyrometer was used to accurately measure the temperature which shows the real temperature within an error range of +25℃ to -25℃.

The green density for the compact was measured at the initial condition of the experiments. The pre-compaction pressure for the SPS system was 5 MPa. The initial height of the powder bed was measured very carefully after applying the 5 MPa pressure at room temperature. Throughout the experiment, the instantaneous heights were precisely measured using the punch displacement data. For a fixed diameter of the samples (which is 20 mm in this case), the instantaneous density can be found from the following relation:

$$D = (\frac{H_f}{H})D_f$$ …………………………………………………………………………………….. (2.1)

Where, D is the instantaneous density, H_f is the final height of the sample, D_f is the final density of the sample, and H is the instantaneous corrected height of the compact.

Because of the high temperature, the graphite die and punches expand, so correction was needed for the swelling and expansion of graphite die and punches. A 'blind test' was performed in order to achieve the real shrinkage of compact to eliminate the expansion effect. Thus the corrected ram displacement curve was found. Blind test was done by subjecting the die and punches to the similar SPS conditions for 1800, 1900 and 2000℃ using the same 90 MPa pressure without any powder. The blind ram displacement curves were subtracted from the punch displacement data which was obtained having the powder inside, and thus real ram displacement curves were plotted.

2.2.3 Sample preparation

The sintered SiC and SiC-G samples were taken out by a hand hydraulic press shown in **figure 2.5a.** The samples were then polished by diamond plates of grades of 30 μm, 9 μm, 6 μm. After that, polishing was done by the diamond solutions of 3 μm, 1 μm and finally followed by 0.5 μm alumina solution for mirror polish. **Figure 2.5b** shows the polishing machine used (MoPao 160E grinder polisher). They were cleaned afterward by ultrasonic cleaner and dried in hot air flow.

Figure 2.5: a) Hand hydraulic press b) Polishing machine

2.3 Material characterization

2.3.1 Relative density measurement

The relative density calculation was done according to the ASTM C380-00 standard. The bulk density was calculated by Archemedes' principle through following relation,

$$\rho = \frac{m_1}{m_3 - m_2} \rho_w \quad \text{.. (2.2)}$$

Where, ρ is the calculated density, ρ_w is the density of water (0.998 at 25 ℃), m_1 is the mass of the sample measured in air, m_3 and m_2 are masses of the saturated sample measured in air and water.

The relative density was calculated by following relation,

$$Relative\ Density = \frac{Density\ of\ sintered\ samples}{True\ Density} \times 100\ \% \quad \text{... (2.3)}$$

True density was calculated by a Helium Pycnometer, and used to calculate the relative density. The open porosity was found by the following relation,

$$\pi_o = \frac{m_3 - m_1}{m_3 - m_2} \times 100\ \% \quad \text{.. (2.4)}$$

Finally closed porosity was found by the following equation,

$$\pi_c = (100 - \pi_o - relative\ density)\ \% \quad \text{... (2.5)}$$

2.3.2 Phase & Surface morphological Analysis

2.3.2.1 X-Ray Diffraction

The phase analysis of the sintered samples was done using X-ray diffraction (XRD), which was carried out by a Philips Norleco X-ray diffractometer operating with Cu K_α radiation

(λ = 1.54178 Å) at 45 kV and 40 mA. The XRD was performed with a diffraction angle (2θ) range varying from 10 to 90° with a step increment of 0.02°/s. High Score Plus software, which is based on ICDD PDF2 database, was used to determine the formed phases.

2.3.2.2 Surface morphology, Microstructure and Grain size measurement

The surface morphology was analyzed by Scanning Electron microscopy (SEM) [FEI Quanta 600 field-emission gun Environmental SEM (JSM-6360, JEOL)] on the fracture surfaces to investigate the microstructure development and fracture behavior. Necking and pore geometry were observed in details. Grain growth was also measured from the SEM pictures taken from the etched surfaces using the line-intercept method. At least 100 grains were taken into account to measure the average grain size. Modified Murakami's reagent (30g $K_3Fe(CN)_6$, 3g NaOH, 60 ml distilled water at 110℃ for 10 min) was used to etch the surface.

2.4 Mechanical Characterization

2.4.1: Micro-hardness

The hardness of the sintered samples was measured by a Clark Instruments, USA; Model no: CM-700AT using Vicker's micro-indendation on the polished and flat surfaces. A load of 9.8N was used with a holding time of 15s for all the hardness values obtained. The indents were taken on the polished surface to get clear and valid indents. Minimum of 20 measurements were taken for an average value of hardness.

2.4.2 Flexural strength

The flexural strength of the sintered composites and the monolithic SiC was measured by a Ring-on-Ring (RoR) test method using a table-top test frame (Instron 5567, Instron Corporation, Norwood, Massachusetts, USA, ASTM C1499-05). All the samples were prepared with a physical dimension of 20 mm diameter and the thickness was kept less than 2 mm. The support and loading ring diameter were 15 mm and 5 mm. A displacement controlled loading rate of 0.5 mm/min was implemented to measure the flexural strength,

$$\sigma_{RoR} = \frac{3P}{2\pi t^2}\left(\frac{(1-v)(a^2-r^2)}{2R^2} + (1+v)ln\frac{a}{r}\right) \dots\dots\dots\dots (2.6)$$

Where,

P is the applied load (N), v is the Poisson's ratio (SiC: 0.19, G: 0.17), a is the radius of the support ring (m), r is the radius of the load ring (m), R is the radius of the sample (m) and t is the thickness of the sample (m) [234].

CHAPTER III

RESULTS AND DISCUSSION

3.1 Densification of Monolithic SiC

3.1.1 Relative density and densification cycle

The densification data has been analyzed for both the pure SiC which is shown in **table 3.1.** Both the temperature and reinforcement effect have been thoroughly studied on SiC system. For a particular processing parameter (in this case 2000℃, 90 Mpa and 20 min) the monolithic SiC showed the maximum relative density close to 90%. The lower sintering temperatures resulted in poor density values for SiC. Again the pressure and soaking time were kept constant for all the samples to simplify the analysis. The pressure and soaking time were determined by trial and error after performing a series of experiments.

Table 3.1: Relative density of the spark plasma sintered SiC (90 MPa pressure and 20 min soak)

Sintering temperature (℃)	Relative Density (%)	Open porosity (%)	Closed porosity (%)
1800	78.55±2.22	19.6 ± 2.01	1.94 ± 0.86
1900	85.96 ± 0.93	11.25 ± 1.13	2.78±0.6
2000	90.32±1.4	5.36 ± 1.39	4.32±0.64

The variation in density in pure SiC with the change in temperature and pressure can be explained from **figure 3.1.** It **s**hows the shrinkage/displacement of ram with different sintering cycles for pure SiC green compact. Pure SiC shows a three-stage dependence on both temperature and pressure, as the particles undergo continuous compression and joule heating. These stages are denoted as I, II and III. A downward motion in the displacement corresponds to effective compression of the compact and an upward motion denotes the opposite. The data shown in **figure 3.1** is normalized and shown for the deformation starting at 6th min (around∼600℃) of the actual cycle. Because the temperature was measured by a pyrometer, there was a response lag between the measured and process temperature at the very beginning of the operation. But both the temperatures became gradually similar as the operation was continued for longer time and the 6th minute was identified as the starting point for analyzing the raw data. **Figure 3.1** also shows the temperature cycles, under which the green compact was subjected to during the consolidation process. Only the heating and the soaking periods are shown and available for analysis, as it is well-established that the densification process takes place in the first two stages, and cooling doesn't really have any substantial effect on densification in a spark plasma sintering process. The thermal cycles are evenly matched with the corresponding ram displacement curves, as the beginning of the dwell periods can be identified easily in the figure for better understanding. It can be mentioned that, the cycles are 1 min apart from each other as the cycle for 2000℃ being the longest which ran up to 40 mins.

Fig. 3.1: Ram displacement and soaking stages of Spark Plasma Sintered SiC at different temperature

The stage I shows the effect of applied pressure immediately after the compaction starts on the particles. Stage I is all about compression that the particles go through, meaning that the temperature is yet to play a role on the densification or consolidation process. In this stage, generally the particles start to rearrange among themselves and slide or go through the time-independent plastic deformation. But, for a very hard particle like SiC, it is most unlikely to occur a large or substantial amount of plastic deformation. Several studies [235,236,237] have shown that, the yield strength of SiC in our sintering temperature zone is at least 200 MPa, which is a lot higher than that of our applied pressure. According to Arzt et al. [238], the minimum threshold pressure needed for the particles to undergo a plastic deformation for the application of hot isostatic pressure up to 90% relative density, is:

$$P_{min} = \frac{3\sigma_y}{4\pi}(D - D_0)[160(D - D_0) + 16] \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \text{(3.1)}$$

Where σ_y is the yield strength of the particle, D and D_0 are the relative and green density of the compact.

The first stage I (maximum deformation 0.5 mm) in **figure 3.1** stays active until the thermal expansion of the particles occur near about 11th min of the sintering cycle (corresponds ~ 1100℃ in the heating cycle). It doesn't really have an effect on the density achieved in the initial stage. The compact and pores, both tend to expand during cycle II. It results relative ratio of the volume between grains and pores to be essentially the same as achieved at the end of stage I. This idea can be misleading as the thermal expansion seems to decrease the density of the sample as seen from the ram displacement data. But close inspection and understanding showed that, the density stays constant during this expansion cycle denoted by II. The punch displacement again increases during the third and final stage of the densification denoted by III for 1900℃ and 2000℃. This stage starts nearly at 19th minute of the sintering cycle for both 1900 and 2000℃, which corresponds to a temperature range of~1830-1850℃ in the operating cycle. The II to III transition points indicates the starting of the soaking time for 1800 and 1900℃. It is noticeable that, the sample sintered at 1800℃ doesn't show any compression at all in stage III which indicates that the temperature isn't enough to activate the temperature dependent diffusion mechanisms which is responsible for the further densification of the samples. Thus the minimum temperature required for the effective and higher level of densification is identified as 1830-1850℃. Even the sample sintered at 1800℃ could not go up to that particular temperature. It still goes through some sort of densification, possibly through the dominant mechanisms activated in high temperature in a less degree or through the other auxiliary mechanisms such as, grain rotation, particle/grain clustering and sliding [239]. This finally results in a relative density value close to 80%. But for the sample sintered at 1900 and 2000℃ there is a very active mechanism, possibly creep that takes the density to the final stage. Several previous studies [240,241,242,243,244] have established the fact that, the dominant densification mechanism in

pressure sintering is thermally activated diffusion controlled creep. This mechanism will be discussed in detail later in this chapter.

The sample sintered at 1900℃ shows a maximum deformation value of 0.8 mm in stage III, but the sample sintered at 2000℃ shows almost five times more punch displacement (close to 4 mm) at its soaking period. Increment of 100℃ temperature facilitates densification where grain growth is at its highest. The punch displacement is almost 4 mm for the sample sintered at 2000℃. At the lower levels of densification (～85-90%), the grain growth is relatively low because of the high volume fraction of long/continuous pores [245]. But for the second phase of the densification, when density values are over 90%, these elongated pores gradually turn into isolated pores, which are mobile throughout the compact. This facilitates the rapid grain growth at higher sintering temperature. At this stage, the closed isolated pores cannot pin the grain boundaries anymore to stop the grain growth. The grain growth data has been presented in **figure 3.3** in the upcoming section, where an increase in grain growth is seen with the increase of sintering temperature and corresponding final relative densities.

Figure 3.2 shows the variation in pressure needed (**equation 3.1**) to achieve different relative density values through plastic deformation for SiC particle having yield strength of 200 MPa at 1900℃. The applied 90 MPa pressure line shows the amount of densification achieved over the green density which in the case is close to 67%. The green density is calculated at a value of 0.60 which is close to the value of packing factor (0.64) in randomly oriented packing (a common assumption in modeling the densification characteristic for ceramics).

Fig. 3.2: Minimum pressure needed for plastic deformation in spark plasma sintered SiC up to 90%

From the figure above, it is clearly seen that only 7% densification is possible through plastic deformation when the yield strength is 200 MPa, i.e. another 30% volume fraction is available in open and close pores which still exist after the initial compression. So a higher density values found in the experiment are related to some other time dependent densification mechanism. But the importance of stage I is far more than just a mere measure of 7%, it starts the powder particles to create grains through necking. A constant applied pressure throughout the sintering process helps the compact to achieve grain accumulation and sliding. This will be discussed later

3.1.2 Relative density and grain growth

The average grain sizes for samples sintered at 1800 ℃ and 1900 ℃ are relatively low (3.4 μm and 4.75 μm respectively), but a rapid grain growth is seen for 2000 ℃. For this temperature grain size was calculated as 7.93 μm. Corresponding density value of 90% supports the validity of high grain growth, as resulted in simultaneous pore diameter reduction. For lower temperatures, the grains did not get enough time to grow to reduce the pore diameter and resulted in smaller grain size. On the other hand, higher level of density could be achieved with the sacrifice of grain size. **Figure 3.3** shows the relation between grain growth and corresponding relative density. It should be mentioned that, the true density was found to be 3.2 g/cm^3.

Figure 3.3: Average grain size variation and relative densities with increasing sintering temperatures

3.1.3 Microstructural analysis

When pressure is applied at the sintering process, the neighboring spherical contacts begin to deform and start to impinge on each other. This creates necking on the grain boundaries. This neck shape depends on the relative contribution of the densification mechanisms involved. According to Swinkels et al. [241], in case of diffusion, the pores tend to round up or spheroidize. On the other hand, plastic flow and creep produce cusped pores. General observation is, the irregular pore shape occurs as a combination of the above mentioned two shapes, as the densification process is a combination of the mentioned mechanisms. **Figure 3.4** shows the SEM pictures taken from the polished and etched surfaces from the three temperatures. Grain size distribution can be seen from the pictures.

Fig. 3.4: SEM pictures taken from the etched surfaces of samples sintered at a) 1800, b)1900 and c) 2000 ℃

Figure 3.5 contains the SEM pictures taken from the fractured surfaces of the different samples sintered at different temperatures (1800℃, 1900℃ and 2000℃ samples are denoted by **a), b)** and **c)** respectively), which clearly shows the pore shape and distribution as well as the necking on the grain boundaries. In **figure 3.5(a) - (c)** the semi-cusped semi-round pore is clearly marked by the red solid arrows. The long and elongated pores are visible in **Figure 3.5(a) - (b),** which are widely spread throughout the matrix. The average pore diameter is 10 μm in the sample sintered at 1800℃ whereas it is reduced to 7 μm in 1900℃ sample. For temperature at 2000℃ it is furthermore contracted through the widening of grains, as the pores are no longer connected in a network, rather they are isolated to separate random locations which consolidates the powder matrix into the final stage. The average pore diameter is less than 5 μm at 2000℃. The neckings, among the particles are shown by the dashed green arrows, creates grains from the powder particles. More number of neckings means less volume of porosity, as 2000℃ shows the highest number of neckings which transform the pores to separate island like structures. For 1800℃, the number of neckings is too low to efficiently consolidate the particles, as the SEM picture shows loosely connected particles, and also a lot of free particles can still be seen.

One important phenomenon was found during sintering process, which is the presence of growing grains even at 2000℃ as marked by blue dotted arrows in **fig. 3.5(c).** This is understandable, as the complete densification could not be achieved in our experiments. But, the presence of these on-growing necks indicates that, higher temperature or pressure may expedite the necking process to some degree which may lead towards the complete consolidation.

Fig 3.5: SEM pictures taken on the fracture surfaces from sample sintered at a) 1800℃ b) 1900℃ c) 2000℃; d) Micrograph showing Clustering of nano-grains at 2000℃; Red solid line arrows show the semi-round semi cusped pores, green dashed arrows show the developed necks in between the grains and blue dotted arrows show the growth of grains

Figure 3.5(d) shows the clustering of nano-grains which is an auxiliary densification after creep. This has an effect on densification. The nano-crystalline grains convert from high angle grain boundaries to low angle grain boundaries through grain boundary migration. This is generally done by grain rotation, and at higher temperature grain coalescence and high grain growth may take place through this curvature driven grain boundary migration. These nano sized grains tend

to eliminate porosity volume as they accumulate with their neighbors, and later they- transform to a bigger grain and achieve higher density values.

3.1.4 Formal densification mechanism analysis

The relative density of the sintered SiC samples was calculated at different sintering times using equation 2.1 for both samples sintered at 1900 and 2000℃. **Figure 3.6 and 3.7** shows the variation in relative density and corresponding densification rate, $\frac{1}{D}\frac{dD}{dt}$ with time for both of the samples respectively. Evidently the amount of diffusion controlled creep is very low for 1800℃ hence only the above told temperatures have been analyzed. It must be noted that, the density and densification rate curves are normalized and presented for temperatures beginning at 1850℃ and above, which refers to the third stage in ram displacement curve. As the initial compression had a little impact on the density values and the expansion cycle had no impact on the densification. It was assumed that, at 1850℃ both the samples start from a density value of 67% (achieved at the end of compression stage), and reach to the maximum value at the end of their respective thermal cycles.

Fig. 3.6: Relative density variation and densification rate for spark plasma sintered SiC at 1900℃ at stage III

Fig. 3.7: Relative density variation and densification rate for spark plasma sintered SiC at 2000℃ at stage III

Both the relative density figures clearly show a rise in their values in the third stage of densification as described earlier, and the critical temperature is close to 1850℃. For the sample sintered at a higher temperature, it shows a higher density value in the end because of the thermally activated diffusion mechanisms. Higher temperature certainly helps the sample to achieve higher density with the expense of higher grain growth. Note that, for both of the samples the densification process is not complete. This is probably because of the low initial densification through the plastic deformation for the samples sintered. For 2000℃, the increment in the density values is continuous, but more rapid after a certain time. In this case, that occurs just before the 9th minute of stage III (corresponds to the 27th minute of the total cycle). For 1900℃, the densification tends to slow down after the initial rise in stage III.

These phenomena showed that, a very high densification rate occurs at the final stage of the densification process for 2000℃, but not so much for 1900℃. This concept is clearly understandable from the densification rate calculated for both of the temperatures in stage III. For the sample sintered at 2000℃, **figure 3.7** shows that, the maximum densification rate occurs at the middle of the soaking period (just after the 10th minute of the final stage). It clearly indicates that, the densification process of SiC is a late densification process which results in the sacrifice of the full densification. Because of the plastic flow the densification process is very slow at the very beginning. Gradually, the density starts to increase in the final stage as soon as the compact enters stage III, because of the creep mechanism. So, we see a rise in the densification rate, except a little drop just after the 8th minute of stage III, which is more of a randomness in the analyzed behavior. Towards the very end the densification becomes slow again because the diffusion processes become slow, and gradually approaches to zero. The curvature driven grain boundary diffusion [239] probably needs more temperature in case of SiC.

On the other hand, the densification rate for 1900℃ shows a complete opposite response presented in **Figure 3.6**. As the compact enters in stage III, the rise in the density values is

sufficiently high to elevate the rate to reach to its maximum at around the 1st minute (corresponds to 20th minute of the original cycle and 1900°C), but soon slows down as the soaking period is already started. The reason is that, the powder compact didn't experience higher temperature to enhance the density. There are some high and low points on the densification curve, but those are again attributed to the randomness of the densification behavior. At around 5th, 8th-13th and 15th minute, some high regions of densification rate values occurred, but they failed to govern the density to the highest level because of the exposure to the lower temperature.

Obviously, some crucial assumptions were taken into consideration when the relative densities and densification rates were calculated. Most importantly, it was assumed that the final density and height of the sample are achieved at the end of the dwell period, i.e. cooling has no substantial effect on the densification process of the compact as stated before. The densification rate, $\frac{1}{D}\frac{dD}{dt}$ observation is very important in this densification study, as it governs the dominant mechanism in active densification.

As mention earlier diffusion controlled creep was attributed as the dominant densification mechanism in spark plasma sintering at high temperature, so matter transport in high temperature pressure sintering can be correlated to the high temperature creep through some previous works [240,246,247].The steady-state creep strain can be expressed in terms of densification rate through the following equation:

$$\dot{\varepsilon} = \frac{d\varepsilon}{dt} = \frac{1}{D}\frac{dD}{dt} = A\frac{\Phi\mu_{eff}b}{kT}\left(\frac{b}{G}\right)^m\left(\frac{\sigma_{eff}}{\mu_{eff}}\right)^n \quad \text{..(3.2)}$$

Where $\dot{\varepsilon}$ is the creep rate, D the instantaneous relative density, A is a constant, Φ the diffusion coefficient, μ_{eff} the instantaneous shear modulus, b the Burgers factor, G the grain size, k the Boltzmann's constant, T the absolute temperature, m the grain size exponent , n is the stress exponent and σ_{eff} the effective macroscopic stress.

According to Helle et al. [242], the conversion of effective applied stress from the original macroscopic load can be expressed through the equation:

$$\sigma_{eff} = \frac{1-D_0}{D^2(D-D_0)}\sigma_{macro} \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \quad (3.3)$$

Here, D_0 is the green density of the compact and D is the instantaneous density.

The effective shear modulus is linked to the effective Young's modulus of SiC through the well-known mechanics relation,

$$\mu_{eff} = \frac{E_{eff}}{2(1+\vartheta_{eff})} \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \quad (3.4)$$

Where ϑ_{eff} is the effective Poisson's ratio.

Now effective Young's modulus for a porous material like ceramics can be found from its theoretical modulus suggested by Lam et al. [248]

$$\frac{E_{eff}}{E_{th}} = 1 - \frac{P}{P_0} \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \quad (3.5)$$

Here E_{th} is the theoretical Young's modulus found from a well-known literature value. P and P_0 are the fractional porosities of the powder bed and green compact, which can be described by following,

$$P = 1 - D \quad \& \quad P_0 = 1 - D_0 \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \quad (3.6)$$

Combining equation (3.4), (3.5) and (3.6) we can write,

$$\mu_{eff} = \frac{E_{th}}{2(1+\vartheta_{eff})}\frac{D-D_0}{1-D_0} \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \quad (3.7)$$

So relation (3.2) can be modified as,

$$\frac{1}{\mu_{eff}}\frac{1}{D}\frac{dD}{dt} = C\frac{e^{-\frac{E}{RT}}}{T}\left(\frac{b}{G}\right)^m\left(\frac{\sigma_{eff}}{\mu_{eff}}\right)^n \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \text{ (3.8)}$$

Where, E is the apparent activation energy for the diffusion mechanism controlling densification; C is a new constant and R the gas constant.

Interpretation of two exponents 'm' and 'n' is very important, because their values are the key factors in determining the corresponding mechanisms responsible for densification. So determining these two factors is crucial also for the activation energy calculation responsible for densification through creep. The Young's modulus E_{th} has been considered as 400 GPa (a common value found from the literature). We can assume the average grain size to be constant under an isothermal condition. With that being said, $\left(\frac{b}{G}\right)^m$ can be taken as constant, and for a fixed temperature where the activation energy is also unchanged we can find the value of n from a $\ln(\frac{1}{\mu_{eff}}\frac{1}{D}\frac{dD}{dt})$ vs $\ln(\frac{\sigma_{eff}}{\mu_{eff}})$ curve using **equation (3.8),** where the slope of the curve gives the value of n. The densification mechanism was characterized successfully upon the value of n. Using the previous equations the values of σ_{eff} and μ_{eff} are tabulated and the graph is plotted for 1900 ℃ and 2000 ℃ as these two temperature clearly showed **better** response to creep than 1800 ℃. **Figure 3.8** gives the value of n in two different temperatures. The slopes for both the temperatures at 1900 and 2000 ℃ are found to be 0.86 and 1.34. Assuming the average the value of n was decided to be ≈ 1.1.

For activation energy calculation using the same **equation (3.8)** a $\ln(\frac{T}{\mu_{eff}}\frac{1}{D}\frac{dD}{dt}\left(\frac{\mu_{eff}}{\sigma_{eff}}\right)^n)$ vs $\frac{1}{T}$ curve was plotted as the equation (8) can be reformed as following,

$$\ln\left(\frac{T}{\mu_{eff}}\frac{1}{D}\frac{dD}{dt}\left(\frac{\mu_{eff}}{\sigma_{eff}}\right)^n\right) = -\frac{E}{RT} + K \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \text{ (3.9)}$$

Where, *K* is some constant.

Figure 3.9 shows the plot described for activation energy. The activation energy was calculated as the energy needed to reach the final density region for both of the sample i.e. 85-90 % for 1900 ℃ and 90-95% for 2000 ℃. Again, the value is found from the slope of the curve and it is calculated as 427 KJ/mol which converts to approximately 4.43 eV.

Both the stress exponent curve show high degree of fit as did the Arrhenius plot so energy value obtained is rounded up for convenience.

Fig. 3.8: Linear regression to calculate stress exponent, n at a) 1900 ℃, b) 2000 ℃

Fig. 3.9: Activation energy (Arrhenius) plot for spark plasma sintered SiC for 1900 and 2000 ℃

Although the exact densification mechanism is very difficult to point out, but based on the activation energy and stress exponent values an acceptable model has been tried out. As the quantitative investigations have been performed, the three most dominant and understood mechanisms related to diffusion are diffusion through pore surface, grain boundary and lattice. It is evident that, activation energy values are relatively lower for the grain boundary diffusion than that of lattice diffusion (Atkinson et al.) [249]. Surface diffusion is a low temperature activated process supported by other authors [250]. Also, it is more common in case of nano-grained powders. On the same note, surface diffusion generally more common for the materials sintered near 1500 ℃. On the other hand grain boundary diffusion and lattice diffusion which are the other two dominant diffusion processes occur at very high temperature, especially lattice diffusion. Activation energy for grain boundary diffusion for Carbon in SiC has been calculated to be 3.1 – 6.2 eV which shows that the value obtained is within the range of the reported activation energy values for Carbon in SiC [251]. But the reported values for lattice diffusion of Si and C in SiC are

much higher than that of the grain boundary diffusion mechanism. Also, because of the entrapped pores present in the sintered SiC samples over 1900℃, the possible densification mechanism is attributed to grain boundary diffusion or grain boundary sliding accommodated by grain boundary diffusion of matter. The melting point of SiC is close to 2800℃ and some authors reported lattice diffusion to be the dominant mechanism when the sintering was done well over $0.7*T_m$ (Andrienvskii et al. [252] and Sarian et al. [253,254]). Also a low value of n ($n \leq 2$) [255] suggests that, the densification process is more relevant to Coble Diffusion creep [210].

3.1.5 Formal grain growth analysis

The grain growth has been thoroughly analyzed, and used for further analysis for a grain growth mechanism. From the grain growth (**Figure 3.3)** data, it is seen that for a particular temperature the average grain diameter is very high. This rapid grain growth is responsible for densification process as it diminishes the volume fraction of porosity within the compact. At 2000℃, this rapid grain growth is clearly visible and calculated as 7.93 μm. The initial particle diameter was calculated as 2.73 μm, and the growth of this extent requires some sort of diffusion mechanism which transpires in higher temperature. So the mechanism responsible for grain growth will be discussed based on the grain size data from **figure 3.3.**

Grain growth by different atomistic mechanism can be predicted by a very well established equation of the following expression: [256]

$$G_t{}^n - G_0{}^n = Kt \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (3.10)$$

Where G_t and G_0 are the grain sizes at time t and t = 0, n is the grain growth exponent and t is the time of operation. K is defined by,

$$K = K_0 exp\left(-\frac{E}{RT}\right)\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (3.11)$$

Where, E is the activation for operating mechanism or grain growth, R is the gas constant; T is the absolute temperature and K_0 is the diffusion coefficient.

Now, this new exponent denoted by n is quite different than the stress exponent described earlier. The value of n characterizes the operative mechanism responsible for growth rate. In a porous material grain growth is controlled by pore mobility not by the mobility of the grain boundary. For this sort of cases, $n = 2$ defines the grain growth controlled by grain boundary diffusion, $n = 3$ governs the growth either by diffusion through lattice or volume or a liquid phase at the grain boundary, $n = 4$ means growth controlled by surface diffusion.

Equation 3.11 can be transformed as following:

$$lnK = lnK_0 - \frac{E}{RT} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (3.12)$$

The grain size data was analyzed according to **equation 3.10** and **3.12** for $n = 2$, 3, and 4 as mechanisms governed by these three values are most common diffusion mechanisms active in porous ceramics. As the densification rate was not very high at the beginning, so the grain growth for all temperature were assumed to be of normal growth, although very high densification rate at the beginning of the sintering process may lead to prolonged or abnormal grain growth in ceramics.

Figure 3.10, 3.11 and **3.12** portrays $ln[(G_t{}^n - G_0{}^n)/t]$ vs 1/T curves for n = 2, 3, 4 respectively. A least square regression was performed to fit the data for achieving straight lines. Each time the statistical stability was measured through the correlation coefficient. Also the activation energies were calculated.

Figure 3.10: Least square fit for Arrhenius plot for *n* = 2

Figure 3.11: Least square fit for Arrhenius plot for *n* = 3

Figure 3.12: Least square fit for Arrhenius plot for *n* = 4

The Arrhenius plots for activation energy for different grain growth exponent show sufficiently high degree of fit (0.99966, 0.99819, 0.99637 for *n* = 2, 3, 4 respectively) with the maximum r = 0. 99966 for n = 2. This indicates that, for the assumption of grain boundary diffusion it is most likely be the dominant mechanism responsible for grain growth and densification. The activation energy calculated is 500 KJ.mol, which again converts to 5.18 eV which close to the value obtained by the approach involving creep before. Again, this value of activation energy falls within the reported value of C diffusion in SiC through grain boundary.

At higher temperature, grain deformation through creep aided by grain boundary diffusion is more predictable, as the surface diffusion mechanisms are activated at a relatively lower temperature. Based on the data presented on **figure 3.10** diffusion of C in SiC through grain boundary seems to be more logical, as the controlling mechanism during the sintering process of SiC. There is a good chance of surface diffuse taking place at the earlier stage during heating up, and that may contribute to the grain coarsening process. For high temperature

sintering, there is a good chance that the grain boundaries are more mobile than usual, and if it gets higher than the pore mobility, the pores may take place within the grains which can be seen in the SEM pictures. These residual pores may shift towards the grain boundary through a slower mechanism, but the chances for that is too low as the densification process seems to be much faster.

From the Arrhenius plot, the calculated diffusion coefficient for grain boundary diffusion is $K_0 = 6.77*10^{-3}$ m^2/s. The proposed grain growth equation is:

$$K = 6.77 \times 10^{-3} m^2/s \times exp\left(-\frac{500KJ/mol}{RT}\right) \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (3.13)$$

3.2 Densification and mechanical characterization of SiC-G composites

3.2.1 Densification of SiC-G composites and grain growth

The addition of graphene content on the SiC matrix has a very diverse effect on the densification behavior of the SiC-G composites. Addition of graphene greatly to decreases the density, and also the amount of open porosity increases for the SiC - graphene composites. The density values for the composites are pretty close, but it lowest for 3vol% addition of graphene.

Table 3.2: Relative density of SiC and SiC-G composites sintered at 2000℃

Sample	Relative Density (%)	Open porosity (%)	Closed porosity (%)
SiC	90.32±1.40	5.36±1.59	4.33±0.64
SiC + 1G	83.77±0.93	14.08±1.95	2.15±2.27
SiC + 2G	84.00±1.28	15.04±1.93	0.95±0.72
SiC + 3G	82.01±0.71	15.51±1.34	2.48±0.92

This incident can be explained from the grain growth data for sintered SiC and SiC-G samples. The grain growth data has been analyzed in **figure 3.13,** as can be seen that with little addition of graphene decreases the grain growth or at least blocks it. More dispersed graphene throughout the matrix has a tendency to block the grain growth in ceramics as, C has been successfully used in the past to block or hinder grain growth. That is why C is still a good additive or sintering aid when it comes to the matter of consolidating harder materials like SiC or Si_3N_4.

Fig. 3.13: Grain size variation of SiC and SiC-G composites with increment of graphene content

From the figure above it is clearly evident that graphene sheets are acting as effective grain growth blocking agent. For SiC-1G and for SiC-2G the grain growth decreased from an average value of 7.93 μm to $\sim 3 - 3.4$ μm. As discussed earlier, smaller grains cannot facilitate densification because they tend to give rise to interconnected porosity, which governs the consolidation process. The mobility is transferred to matter but not to pores, as elongated pores rarely move throughout the matrix area. This causes lower values in the density of SiC-1G and

SiC-2G samples. For 3% addition of graphene to the SiC matrix the scenario remains the same, as more graphene addition doesn't help to achieve higher density values for the ceramic matrix, rather it tends to decrease the grain size to a higher degree. As a result, the density value again decreases more for 3% graphene added samples. Note that, the true densities for 1, 2 and 3 vol% of graphene were found to be 3.3, 3.32 and 3.3 g/cm^3 respectively.

3.2.2. Phase analysis of SiC and SiC-G samples

The phase analysis was done by XRD for the sintered SiC and SiC-G composites. **Figure 3.14** shows the XRD analysis of the samples sintered at 2000 ℃.

Fig. 3.14: XRD analysis of sintered SiC and SiC-G samples sintered at 2000 ℃

From the data above, it can be seen that, along with the SiC crystals some peaks of WSi$_2$ are also seen. It probably developed during the ball milling of SiC for size reduction. As high speed (700

rpm) was chosen for effective size reduction, some W could diffuse into the matrix from the jar and the balls and created a secondary phase. But the intensity of these peaks is very low, and the relative content of this phase is also low. The peak near 27˚ corresponds to C (graphene), but the source of this peak can be attributed to two reasons. Either the amount of graphene directly shows a peak in the XRD, or it can be generated from the residual C left on the polished surface. As graphite sheet was used to sinter the samples, some extra C can be present on the surface of the samples sintered.

3.2.3 Microstructural analysis

The microstructural analysis of the SiC-G samples was done from the SEM images. The pictures taken from the fractured surfaces of the samples show the distribution of graphene network inside the ceramic matrix. **Figure 3.15** shows the SEM pictures taken from the polished and etched surfaces of the graphene composite samples. The grain size distribution can be seen from these images.

Fig. 3.15: SEM pictures taken from the etched surfaces of sintered a) SiC+1G, b) SiC+2G and c) SiC+3G

Figure 3.16 shows the morphology in SiC-2G and SiC-3G samples. The agglomeration for the SiC-3G sample can be seen in **fig. 3.16a**. For the 2% graphene reinforcement the graphene network can be seen in **fig 3.16b** and **3.16d.** The pulled out graphene sheets is also seen. **Fig. 3.16c** shows the cracking in the SiC-2G grains due to flexural test and it appears to be a trans-granular failure.

Fig 3.16: SEM pictures taken from the fractured surfaces of SiC-G samples; a) agglomeration of graphene sheets in SiC-3G sample, b) pulled out graphene sheets in SiC-2G sample, c) cracks in SiC-3G samples (yellow arrows show cracks), trans-granular failure d) graphene network in SiC-2G sample (red arrows show graphene sheets)

3.2.4 Mechanical properties of SiC and SiC-G ceramic samples

The hardness and flexural strength data have been analyzed and normalized for all the samples. **Figure 3.17** and **3.18** show the hardness and flexural test data with the reinforcing content respectively. The hardness of the SiC and SiC-G composites varied from ~19-21 GPa, which is not considered as a considerable improvement in the hardness values. Although the SiC-

2%G showed the maximum value~21 GPa, it again decreased for SiC-3%G sample. Even the monolithic SiC and SiC-1%G showed nearly the same hardness. This is logical from the fact that SiC is a hard material, and so a softer material like carbon doesn't really strengthen the composite. No other hardening mechanism is prominent. Although graphene tends to block the grain growth, but finer grain doesn't really help in hardening the matrix.

On the other hand, there was definite improvement seen in flexural strength at 2% reinforcement in SiC. It shows a flexural strength close to 223 MPa, which is 23% higher than that of the monolithic SiC having the strength of 184 MPa. SiC-1%G showed almost the same strength as pure SiC, even slightly less because of the less value in density. For SiC-3%G sample, flexural strength decreases rapidly because of the agglomeration of the graphene platelet inside the matrix of SiC, which creates weak spots in the matrix material facilitating failure. But for the SiC-2%G, there is definitely some sort of strengthening effect is going on, which is attributed to the grain and graphene pull-out mechanism [21]. The fractured surfaces of the samples have been analyzed under SEM. **Figure 3.16a** shows the agglomeration of the graphene platelets and **figure 3.16c** shows cracks developed in the matrix. **Figure 3.16d** shows the pulled out grains which is a common phenomenon in SiC particles.

Fig. 3.17: Hardness of graphene reinforced SiC samples manufactured by spark plasma sintering

Fig. 3.18: Flexural strength of graphene reinforced SiC samples manufactured by spark plasma sintering

Bellosi and Sciti reported very high flexural strength of 750 MPa at room temperature and 550 MPa up to 1000 ℃ for β-SiC hot-pressed with sintering aids (Al_2O_3-Y_2O_3 and La_2O_3-Y_2O_3). These values great decrease after 1300 ℃ and became as low as 183 MPa. At high temperature the sintering aids tend to soften the grain boundary, hence lower flexural strengths were found. Although, Bellosi and Sciti [257] found very high flexural strength at room temperature because of the ultrafine and highly pure SiC was used. Also, nearly full densification was achieved in their experiments.

The values reported in this research work were found for pure SiC, and it was sintered with the help of no aids. As a result, there should not be a temperature degradation effect on the flexural strength values. Also, the percentage change in the values found in the samples cannot be directly compared with the percentage change found in Bellosi's samples at high temperatures. Probably, different combination of milling balls (elliptical, round, cylindrical etc.) may have decreased the particle size more effectively and produced better densification, had we used them. Also, graphene hindered the grain growth by a degree, which decreased the density. That is why, higher value than 221 MPa could not be found for the graphene reinforced samples. But, it is

clear that; graphene has a strengthening effect in SiC even if the densities for the graphene reinforced samples were lower. 2vol% of graphene in SiC showed the maximum flexural strength and indicates the strengthening mechanism taking place in SiC matrix.

CHAPTER IV

CONCLUSION

Conclusion

SiC and SiC-Graphene composites have been successfully consolidated by spark plasma sintering; even though the full density could not be achieved. Densification stages have been identified successfully. The dominant and responsible mechanism for densification was found to be the grain boundary diffusion controlled creep or grain boundary sliding accommodated by grain boundary diffusion. Also a low contribution from the plastic deformation and nano grain clustering were seen. The activation temperature of this thermally activated diffusion mechanism was identified as 1830℃. The densification process was found to be very rapid towards the very end of the sintering process, and takes place at a relatively higher temperature. 2000℃ and 90 MPa were decided to be an optimal combination of parameters for processing SiC. The pure SiC and SiC-G composites were exposed to the mechanical characterization. Flexural strength was greatly improved (23% for SiC-2G sample than monolithic SiC sample) through two mechanisms such as, grain pull-out and graphene sheet pull-out, although the values found are relatively lower than that of the reported ones. Addition of graphene didn't show any effect on hardness. Values found were very close to each other. Graphene was found to be very effective in restraining grain growth.

CHAPTER V

FUTURE WORK

Future Work

1. Fracture toughness measurement of graphene reinforced SiC ceramic.

2. Raman spectroscopy of graphene reinforced SiC to identify if any deformation or structural damage is done to the graphene sheets at higher temperature.

3. Oxidation characterization of graphene reinforced SiC.

4. Investigation on additives as sintering aids for Silicon carbide and related mechanical characterization.

5. Effect of WSi_2 formation on the properties of SiC.

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