EXPERIMENTAL INVESTIGATION ON THE FABRICATION OF CONDUCTIVE CERAMIC COMPOSITE

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CERTIFICATE

I hereby certify that the work being presented in the dissertation entitled "**EXPERIMENTAL INVESTIGATION ON THE FABRICATION OF CONDUCTIVE CERAMIC COMPOSITE**" in partial fulfillment of the requirement of the award of the Degree of master of technology and submitted to the Department of Mechanical Engineering of Lovely Professional University, Phagwara, is an authentic record of my own work carried out under the supervision of Mr. Mandeep Singh (Asst. Professor) Department of Mechanical Engineering, Lovely Professional University. The matter embodied in this dissertation has not been submitted in part or full to any other University or Institute for the award of any degree.

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This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

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Signature of Examiner

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TABLE OF CONTENTS

1. INTRODUCTION

A ceramic is an inorganic non-metallic solid made up of either metal or non-metal compounds shaped and hardened on exposing to high temperatures. Most of the ceramics are hard, corrosion-resistant and brittle. The word ‘ceramics’ in present times holds a broader meaning. Traditional ceramics are clay-based, but advanced ceramics are being developed utilising a wide range of inorganic non-metals. Advanced ceramic materials possess enhanced properties such as superior mechanical strength as a result of its hardness and modulus of elasticity, chemically stable, high values of stiffness alongwith strength at elevated temperatures on comparison with conventional ceramics and also have a great potential to solve a wide number of material challenges in advanced technological applications. These properties are comparatively better than polymers or metals, therefore allowing monolithic ceramics capable of being used in applications as aerospace, military, power generation, transportation, biomedical sciences and electronics.

Numerous applications making use of ceramic parts require the fabrication of complex shapes and high accuracy, which is challenging for ceramic materials considering the high hardness of ceramics. But the drawbacks of ceramics are that, brittleness of ceramic materials as a result of occurrence of ionic and weaker covalent bonds. Low fracture toughness is a key drawback in ceramics, which reduces the capability of ceramics to be implemented in structural applications. To solve the above stated problems, most of the research’s purpose done till date was to improve ceramic toughness, electrical conductance and mechanical strength either by modifying the grain structure of nanocomposites, or by incorporating reinforcement, or by simultaneously using both. Improvement in mechanical properties of ceramics lead to improvement of strength and toughness of ceramic composites. This leads to difficulty in machining of composites using conventional methods and moreover it is expensive and difficult to fabricate complicated shapes. Electron discharge machining is a possible alternative but requires materials to be electrically conducting, so as to be used as workpiece to have a certain value of conductivity i.e > 1 ohm^{-1} cm^{-1}. Addition of conductive 2nd phase such as carbide nitride or boride particles or SiC fibres can cause enhancement in electrical conductance of silicon carbide based composites. [1]

It is also stated that enhancing electrical conductivity of ceramics can lead them to be machined on EDM, as an alternative to expensive manufacturing processes. As far as EDM is put in consideration, it can only be performed on materials with electrical conductivity > 0.3-1 Sm^{-1}. Some studies also yielded that EDM can performed successfully on ceramic materials if electrical resistivity was < 100 Ohm cm [7].

The reinforcement of electro-conductive second phases in ceramic matrix has proved to be an affordable alternative to reduce the limiting properties of ceramics, and it is one of the approaches to harness the excellent properties of the reinforcement for various applications by incorporating the material in composite materials. Electrically conducting secondary phases used in most researches are found to CNTs (carbon nanotubes), r-GO (reduced graphene oxide) or GNPs (graphene nanoplatlets). As already stated, carbon nanotube (CNT) and graphene provides new opportunities to fabricate composite materials having improved electrical conductance alongwith mechanical properties enhancment.

CNT possess superior electrical properties when equated to different materials to be used as reinforcement. But it was stated that the issue with fabrication of CNT is acquiring uniform scattering of the CNTs in matrix. Also the CNTs can get damaged at elevated temperatures and highly reactive environments [2]. CNTs possess exceptional thermal, mechanical and electrical properties. But difficulties in material fabrication and the costs has limited work on nanotube-reinforced composites. Connections among Carbon Nanotubes is a point-to-point interaction contact, which leads to high resistance, whereas graphene being a 2-Dimensional material is linked by an area-to-area interaction contact, which results in improved chances of touching one-another and lesser electrical resistivity is observed [7]. However one more of the challenging tasks is homogenous scattering of carbon reinforcement in the matrix, and it is expected that by a proper dispersion of nanotubes into appropriate matrices the fabricated composites will have enhanced properties. Nanotubes reinforced in ceramic matrices show the problem of agglomeration and damage of nanotubes.

In recent times, an increasing interest in use of graphene as an electrically conducting reinforcement is observed because of its 2D structure. Many research findings on composites with graphene as reinforcement, focused on polymer-based

composites, show that graphene has led to enhancement of electrical conductivity and mechanical properties. Earlier research findings have concluded that graphene sheets have improved Global Mechanical and electrical properties of polymer based composites [3].

One of the ceramics, Alumina is a poor conductor of electricity and to be machined on EDM its electrical conductivity needs to be enhanced. Increase in conductivity of an insulating material is a function of concentration and aspect ratio of the reinforcement. In general, the conductivity increases with growing filler content and above a critical concentration, named "percolation threshold", the fillers particles start to form linkages with one another to form conducting paths across the non-conducting matrix and hence enhancing the electrical conductivity of the composite [7]. However, a better scattering of the reinforcement in the ceramic matrix remains as a major challenges for achieving the desired conductivity in an effective way for graphene as well.

The blend of better mechanical properties and functional properties such as resistance to oxidation, bio-compatibility and electrical conductivity to make GNP-MMCs/CMCs (graphene nanoplatlet-metal matrix composite/ ceramic matrix composite) an exciting field. Powder processing/ Powder metallurgy is frequently opted technique for graphene reinforced MMC/CMC. Initial mixing powder is critical for homogenous mixing or dispersion of GNPs, as it influences mechanical, electrical properties etc. [15]

Graphene mainly exist in monolayer form, other than that multilayer, excessively thin materials made by exfoliation of graphite, that forms a vital commercial concern as fillers for composites. Graphene oxide and various chemically altered graphene, and carbon materials fabricated off of graphene or graphene oxide as precursors as thin as to the atomic level, which can be arranged in stacks, bent into folds, wrinkled, or pillared into numerous 3D structures, available commercially. At present, graphene sheets are made through exfoliation of expanded graphite, but mechanical ball milling offers a feasible option for graphene sheet preparation [3]. Most of the materials just came into existence, and are fascinating in their own terms, from viewpoint of science and technology. Together with graphene they create a group of ultra-thin, 2D carbon materials, dimensions in transverse direction and widths of these materials fall in ranges from 10 nm to micrometers to even larger dimensions, and dimensions in transverse directions can possibly affect

percolation thresholds, band gaps, cell interactions, and various related behaviours of the material.

Graphene and its derivatives are classified as below, *Graphene*, *Multi-layer graphene (MLG)*, *Few-layer graphene (FLG)*, *Graphene nanosheet*, *Graphene microsheet*, *Graphene oxide (GO)*, *Reduced graphene oxide (rGO)*. Graphene materials (also graphene-based materials, graphene nanomaterials, graphene-family nanomaterials) – predominant terms for the collection of 2D materials defined above that contain the word ‘‘graphene’’, including all above mentioned classifications. *Graphene nanoplatlets* [22].

Various researchers have stated enhancement in mechanical properties like fracture toughness, hardness on reinforcement of secondary phases, especially CNTs, Graphene, GO etc. into ceramic matrices. Also the fabricated composite materials were observed to have a better electrical property of conductance, to many orders up than the matrix material without the reinforcement. Various methods of sintering have been opted for making the composites, namely Conventional sintering, Hot Isostatic pressing, High frequency induction heating, 2-step sintering process, and the newest of all is Spark plasma sintering (SPS) or sometimes called as flash sintering. The only disadvantage with using conventional sintering is that, to achieve full densification of prepared composites they require higher values of sintering temperatures (1700-2100 degree Celsius), because this method does not include pressure on the sample during sintering, but attaining higher temperature is not economic. As observed in SPS the temperature of sintering required are comparatively lesser (1400-1600 degree Celsius) than those required in conventional sintering and also the properties are also better in SPS fabricated samples as depicted by most recent researches.

In a research work it is stated that > 99% densification of CNT-Alumina composite at 1500 degree Celsius sintering temperature by pressureless/conventional sintering, Similarly, the consequence of lesser temperature conventional sintering of alumina matrix composite reinforced with graphene is not thoroughly explored, that too in an environment having sintering additives which will help in the composite densification at comparatively lower sintering temperatures. [21]

2. REVIEW OF LITERATURE

Martin et al. (1989) [1] Enhancement in electrical conductivity of alumina based composite due to sintering in vacuum was observed by incoporation of Titanium carbide particles with the average size of particle equal to 1.5 micrometres without disintegration of conductive particles. Mixing for production of whisker reinforced Alumina is difficult. An appropriate blend of ball milling ultrasonication and Turbo mixing was utilised for uniformly mixing TiC particles with Al_2O_3 and ZrO powders along with silicon carbide whiskers. A new original and patented mixing method was utilised which led to uniform microstructure. To achieve complete densification of the green sample, they were subjected to hot pressing in graphite dies at 1600 degree Celsius under vacuum. Increasing the whisker content for getting high electrical conductivity will cause a problem in sintering. To get hold of this problem, addition of TiC particles of 30 wt. % with respect to Zirconia toughened Alumina matrix was carried out. It was concluded in the work that mechanical properties of SiC whisker reinforced Alumina, had bending strength decreased on incorporating Titanium carbide particles. Even though the values for bending strength for Titanium carbide content of 30 vol. % is still large, approximately around 850 MPa. It was seen that mismatch of thermal expansion between TiC particles and Al_2O_3 matrix was very less so as to induce significant stresses.

Curtin et al. (2004) [2] Fabrication method used was CVD (Chemical vapour deposition). It was also observed that small diameter and large aspect ratio of nanotubes can make it difficult to get a homogenous mixture of the two phases before sintering or hot pressing. Conventional hot pressing/Isostatic pressing methods were used for the production of the nanotube reinforcement composites. Presence of CNTs prevents the grain growth during high temperature processing of various composite materials. Also on XRD analysis of composites made by high temperature fabrication of ceramic matrix can create difficulty in identification of CNTs in the final composite, especially the ones having low volume fraction of CNTs as reinforcement. It was also observed that in order to retain the nanotube

structure a different processing technique should be implemented known as SPS (Spark Plasma Sintering).

Ting He et al. (2009) [3] In this work Alumina / graphene composite powder was fabricated by SPS technique. Ball milling yielded 3-4 nm graphene sheets after a milling time of 30 hours. A difference in graphene and CNT as reinforcement was that, graphene was found easy to be homogeneously distributed in matrix. The starting material in this work was natural graphite approximately 320 mesh size and 99.9% pure, Alumina 99.9% average particle size 150 nm, volume ratio of graphene to Alumina was 5:95. Powder was mixed and wet milled with ethanol at room temperature for 10 to 50 hours on conventional planetary ball mill. Weight ratio of balls to powder was 30:1, rotation rate of while was 250 RPM. After drying and sieving, powder was placed in graphite die and samples were hot pressed in vacuum by SPS. Heating rate of 80-100°C/min., pressure of 60 MPa was applied before temperature reached 1100° C, then the samples were held at 1400° C for 3 minutes at a pressure of 60 MPa and was then allowed to cool naturally. After 10 hours of ball milling large stacks of graphene sheets were not significantly broken and deformed. Average cross section size of graphene sheets in microstructure was observed to be 50 nm, where as some reached 150 nm and 6-8 nm of thickness of edges was observed. It was also observed that increasing the milling time, i.e. 30 hours, graphite flakes size decreased and graphene sheets thinned. Rolling up of graphene sheets happened, leading to nanotube like morphology. Further increasing the milling time to 50 hours, graphite layers were broken as a result of which graphite flakes became smaller. Significant grain size reduction was observed in Alumina on graphene addition. It was concluded that increasing the milling time resulted in reduction of grain size of bulk Alumina / graphene, which indicates tiny graphene sheets restricted grain growth of Alumina and that the fine grains would induce high strength in composites.

Fan et al. (2010) [4] In this work, exfoliation of commercially expandable graphite by heating to 1000 degree Celsius in 60s in nitrogen atmosphere was done. Then the expanded graphite was ground with a-Al_2O_3 (100 nm using a planetary mill for 30 h. Si_3N_4 balls and nylon vials were used and the N-methyl-pyrrolidone (NMP) was chosen as the dispersal media. After ball milling the composite powders were

dried by the rotary evaporator. Finally the residual solvent was removed in forming gas at 600 degree C. Powders were sintered in vacuum, soaking time of 3 min, heating rate 140 K/min, uni-axial pressure of 60MPa, was applied from 1000 degree Celsius upwards and maintained during dwell at 1300 degree Celsius. DC conductivity of composite exhibited rise of 8-10 orders in magnitude. Al_2O_3 is an insulator with extremely low electrical conductivity but showed a sharp increase as the content of GNSs was close to percolation threshold (3 vol. %). Temperature dependence of DC electrical conductivity was also analysed for 3.5-4.5 vol. % GNS in temperature range of 2-300 K. Conductivity was found to be increasing linearly with temperature, reason being increasing in carrier concentration. The conductivity achieved 5709 S/m when composite had 15 vol. % GNSs, which was 170% higher compared to the best result previously reported in CNT/Al2O3 composites.

Wang et al. (2011) [5] In this work it was stated that in order to attain homogeneous Dispersion of GNS in alumina matrix, an electrostatic attraction between jio and aluminium particles is required followed by subsequent reduction. Ultrasonication was opted for exfoliation of graphene oxide, then 20 grams of Alumina having 70 mm average size was added to 100 ml water and was subjected to ultrasonication for a period of half hour, then 1 litre of graphene oxide suspension 0.5mg/ml was dripped gradually into Alumina suspension with mechanical stirring. Hydrazine monohydrate was used to reduce the powder for 24 hours at 60 degree Celsius. Resulting powder was then hot pressed by Spark plasma sintering in vacuum atmosphere at a pressure of 50 MPa, at 1300 degree Celsius with the heating rate of 100 degree Celsius/ min. In Argon atmosphere for 3 mins. Samples of sizes diameter 30 mm x 10mm, which were then cut to 4 mm X 22 mm pieces for testing fracture toughness. Results show that relative densities of 96% were observed in resulting composites. An improvement of 53% in fracture toughness of GNS alumina composites was observed (5.21 MPa-m^1/2). Addition of zns lead to grain refinement of Alumina from 1 micrometre to 500 nm. And enhancement in electrical conductivity was seen at room temperature the resulting compose it had the conductivity of 172 SM which is 13 orders of magnitude better as compared to pure alumina. The improvement in the electrical conductivity was related to the formation of nanosheet electrical pathways in the matrix.

Sarkar et al. (2012) [6] 5 different samples of MWCNT/ Alumina nanocomposites from 0.15 vol. % - 2.4 vol. % were fabricated using simple wet mixing of as received commercial precursors followed by pressureless sintering in Argon at three different temperature conditions i.e. 1500 degree Celsius, 1600 degree Celsius, 1700 degree Celsius. MWCNT of > 95 wt. % purity, 60-100 nm diameter, and length of the order 5-15 µm, Alumina powder with surface area 8.9 m^2/g and average particle size of 0.5 µm were used as starting material. Green billets were prepared by cold isostatic pressing at pressure of 150 MPa. Further the samples were sintered at three different temperatures for 2 hours each in graphite resistance heating furnace in static Argon at a pressure of 35 to 70 KPa with a heating rate of 10 degree Celsius per minute. Densification of composites sintered at relatively lower temperatures of about 1500 degree Celsius was less than 90% but was approximately 99% on sintering at 1700 degree Celsius. Samples with 0.3 vol. % MWCNT, sintered at 1700 degree Celsius for 2 hours in Argon environment lead to an increase of approximately 23% in hardness and 34% in fracture toughness as compared to monolithic Alumina, whereas composites containing 0.15 vol. % MWCNT/Alumina showed highest improvement in bending strength of 20% as compared to monolithic Alumina. After sintering at 1500 degree Celsius and 1700 degree celsius in an inert atmosphere MWCNT was preserved with formation of internal bamboo structure. Work results differ from those reported in **[21],** where pressureless sintering at 1500 degree Celsius for less than 2 hours was sufficient to achieve 100% relative density of pure Alumina and greater than 92% for MWCNT (0.5 vol. %) / Alumina composite, most probably due to enhanced dispersion of filler, better matrix-reinforcement interaction, much higher green density of specimen compacted at 310 MPa isostatic pressure. It was also stated that MWCNT / Alumina nanocomposite can successfully be consolidated at high temperature up to 1700 degree Celsius by pressureless sintering in inert atmosphere without damaging MWCNTs strength stability.

Centeno et al. (2013) [7] Graphene-alumina composite produced by SPS with enhancement in electrical and mechanical properties as compared to monolithic alumina. SPS allowed one step in-situ reduction of GO during sintering. Graphene platelets provided the composite with a crack-bridging reinforcing mechanism by acting as elastic bridges to avoid crack propagation. Graphene content as low as

0.22 wt. % led to an increase of 50% in Mechanical properties of Alumina and an enhancement in electrical conductivity up to 8 orders of magnitude. 2nd phase incorporation leads to mechanical property improvement, especially fracture toughness. Composite preparation was done using colloidal method for mixing 40 g. alumina powder with 150 nm particle size and 100 ml water with PH 10 using NH4OH. Samples after sintering were in the form of discs with diameter of 20 mm and 5 mm thickness. Complete densification of Alumina by SPS is reached at 1300 degree Celsius. 99% densification was seen after 1500 degree Celsius of sample for 1 minute. Average particle size of 150 nm of Alumina after sintering turned into 4 micrometre. The percolation threshold was observed to be 0.2 wt. %, but electrical conductivity increases even above percolation threshold.

Liu et al. (2013) [8] Starting powders used for this work was Alpha Alumina powder having purity of 99.85 % and an average particle size of 150 nm, having surface area of 10 m^2/gm, and GPL used were stacks of graphene sheets 6 to 8 nm in thickness and Lateral dimension of 15 to 25 micrometres. Milling was carried out in riconia container using Zirconia balls at a ball to powder ratio of 2. Build mixture was heated at 90 degree Celsius for period of 3 days to completely dry it and further the dried powder was grounded and sieved by 140 mesh. Sintering in a vacuum of 5 Pa, under Universal pressure of 50 MPa was applied throughout the cycle. The starting temperature was preset to 400 degree Celsius and was taken upto 1500 to 1550 degree Celsius at a heating rate of 100 degree Celsius per minute with a soaking time of 3 minutes during sintering. Results depict and improvement in flexural strength and fracture toughness of composites reinforced with 0.38 vol. % GPL by 30.75 % and 27.20 % as compared to monolithic Alumina. Pull out and Crack deflection toughening mechanisms are observed on fracture surfaces of the resulting composite.

Kim et al. (2014) [9] In this work the starting powders used were, Alumina powder with a grain size <2..2 micrometre, 99.9% purity, length < 2 micrometre and thickness less than 2 nm and the devil reinforcement were added in 1 wt. % and 3 wt. %. High energy ball mill was used for mixing at 250 RPM for a time period of 10 hours using tungsten carbide balls of 9 mm diameter as the grinding media inside a stainless steel vessel. The selected weight ratio of balls to powder was 30:1.

HFIHS apparatus involving use of 15 kilowatt power supply was used, which induces current through the sample and 50 KN of uniaxial pressure was applied. Vacuum of 5.33 Pa was created in the system and a uniaxial pressur of 80 MPa was applied, after that the induced current was activated and was continued to maintain till densification rate reduced to negligible. Heating rate adopted for the process was 1400 degree Kelvin per minute, in the current was turned off at the end of process to allow the sample to cool down at room temperature. Average grain sizes for samples of Alumina, Alumina-1 wt. % graphene and Alumina-3 wt. % graphene were observed to be 62, 43 and 31 nm respectively. The used process proved to be an efficient method for the densification of nanostructure alumina and graphene composites as the resulting composites had a relative density of 99.7% and 99.6% for 1 and 3 weight percent graphene reinforcement. Maximum value for vicker's hardness and fracture toughness observed and 3 weight percent graphene reinforcement and the values were 20.1 GPa and 5. MPa-m^1/2.

Ashwath et al. (2014) [10] This work focuses on the effects caused by reinforcement percentage and ball milling on Mechanical properties of aluminium alloy metal matrix composites. Average particle size of matrix metal is 10 micrometre, reinforcement used are silicon carbide 10micrometer, Alumina 10 micrometer, graphene 10nm. High energy ball milling was carried out on the Powder and as the average particle size was in microns and sufficient enough to be compacted, therefore ball milling was acted as a medium for mixture of powders rather than for the breaking down of particles and retain finer grains. Ball milling was carried out at 150 RPM for 20 minutes. Green compacts were made on Universal testing machine by application of uniaxial pressure of 650 MPa. Samples were subjected to microwave sintering at 550 degree Celsius for 15 minutes with the heating rate of 10 degree Celsius per minute. Three different composites of reinforcement with 10, 15 and 20 wt. % were prepared. Samples were then subjected to hardness measurement after 2 months dealing with samples broke down with the stated reasoning the reinforcement percentage, heating rate and aging. It was stated that considering graphene as reinforcement, the reinforcement composition should be less than equal to 1 wt. % to attain good compact for centring and get improved Mechanical properties.

Magnani et al. (2014) [11] In this paper a two-step sintering of SiC (commercially available) was performed at 1980 degree Celsius with boron carbide and carbon as additives. Starting material was α-SiC ready to press powder, and the samples created were a disc of dia. 40mm and thickness of 3mm, uniaxial pressing- at load 200MPa. Atmosphere created had graphene resistant high temperature furnace in flowing Argon at 1atm. The process depicted in this paper involved comparison, like conventional heated sample at 2130 degree Celsius for 1 hour and the two-step sintering process carried out the sintering at two temperatures 2030 degree Celsius and 1980 degree Celsius for 7 hours. Conventional method's temperature of sintering is around 2130 degree Celsius, with an after sintering density of 98.6%, whereas the two-step sintering process had a sintering temperature of 1980 degree Celsius with an after sintering density of 98.4%. Al_2O_3 and Y_2O_3 were opted as aids for sintering, but the only drawback or shortcoming of using sintering aids is that sintering aids/additives can cause reduction in hardness and flexural strength at high temperature.

Ahmad et al. (2015) [12] High frequency induction heat sintering was utilised for production of high density (> 99.5%) Alumina nanocomposites reinforced with graphene. Mixed powders were exposed to temperatures upto 1500° C with exfoliated graphene nanosheets as reinforcements with 0.25-3 wt. %. 4 gram loose composite for each composition was prepared, then prepared samples of nanocomposites were consolidated in graphite dies at different temperatures ranging between 1400 to 1500 degree Celsius and uni-axial pressures of 30, 50 and 60 MPa. Samples for made in form of discs with diameter 10 mm and 3 mm thickness, under vacuum level of 45 Torr, load was then applied and temperature was raised at 150 degree Celsius per minute to attain a certain temperature. Pure Monolithic Alumina reference samples were also made through same processing conditions for comparison. On adding 0.25 and 0.5 wt. % GNS, around 20 to 46% decrement in mean particle size was observed. GNS addition seemed to encourage wrapping of a number of Al_2O_3 particles with subsequently prohibited grain growth. Nanocomposites sintered at 1400 degree Celsius under 30 MPa displayed inadequate densification and became slightly better at 50 MPa of applied pressure, depicting that external pressure is an important sintering parameter which fastens the densification process during HFIHS by offering extra force to reduce gaps and

attain preferred position and achieve densities close to theoretical values. An improvement of 4 and 7% respectively in microhardness was observed for 0.25 wt. % and 0.5 wt. % GNS, in comparison to monolithic Alumina samples. Reduction of 6% and 15% respectively in values of hardness was observed for 1.5 wt. % and 3.0 wt. % GNS, this reduction was attributed to apparent variations in shape of grains and lubrication properties of graphene. A two stage toughening mechanism is explained in the work. A theoretical model charting stick-slip phenomenon rising from Graphene Nanosheet elasticity and the complicated interlayer friction is proposed to account for longer GNS pull out segments and superior toughness.

Li et al. (2016) [13] Graphene was used as an additive to enhance fracture toughness of SiC ceramic. The mixtures of SiC, graphene, B_4C, and PF were ball-milled in a Nylon pot with SiC balls and ethanol for 24 h. After ball-milling, the blend was dried, crushed, sieved, and uni-axially dry pressed to shapes of circular sheet samples with a diameter of 65 mm and a thickness of 6 mm under 30 MPa. Subsequently, the samples were isostatically pressed under 200 MPa for 300 s. Fracture toughness, bending strength, micro-hardness increased initially, then decreased with contents of graphene increasing from 0-5 wt. %. Highest fracture toughness of the order 5.65 MPa $m^{1/2}$ at 1 wt. % graphene sintered conventionally at 2130 degree Celsius for 1 hour in Argon, and the observed results showed an improvement of 22.6% greater than SiC without graphene. Highest bending strength value of 434.14 MPa was observed at a graphene content of 0.5 wt. % and value of micro-hardness observed was 29.21 GPa at graphene content of 2 wt. %. Solid state pressureless sintering of SiC using B & C as sintering aids exhibit excellent corrosion resistance, strength, hardness from room to elevated temperature. As graphene contents increased form 0-5 wt. %, relative density of SiC samples reduced monotonically from 99.18% to 96.66%, while an increase in electrical conductivity from 0.2 to 1.82 S/m , nearly one order of magnitude.

Belmonte et al. (2016) [14] The study proposed two approaches to overcome the toughness limitation of SiC i.e. to enhance the fracture toughness by, inducing in-situ growth of elongated SiC grains through thermal treatments or by developing carbon-fibre or SiC-fibre reinforced SiC composite. In both the approaches, fibres/elongated grains deflect or bridge the cracks, ultimately limiting growth of

cracks. Graphene nanoplatlets and reduced graphene oxide (r-GO) were used as fillers to develop reinforced SiC/graphene composite. The mechanical properties of the material were investigated as a function of type of graphene source and graphene content. 5% vol. of r-GO resulted in the enhancement of properties in the resulting composite when compared to SiC, with 162% increment in fracture toughness and 61% (600 MPa) increase in strength. Key factors observed to promote the crack-shielding mechanism were stated as the preferential alignment of graphene fillers, their dimensions and the Graphene-SiC mechanical interlocking. In case of SiC-graphene composites by in-situ growth of graphene sheets (3-4 vol. %) into bulk SiC ceramics during spark plasma sintering process, which improved fracture toughness and resistance to cone/ring cracking under contact stress. r-GO arise as the best graphene fillers considering outstanding toughness and strength with an addition of 5 vol. % . For GNPs 10 vol. %, maximum improvement was observed of about 86% enhanced toughness and constant strength.

Nieto et al. (2016) [15] The two-dimensional structure of graphene provide a greater specific surface area in comparison to CNT or graphite, hence providing a higher area to interact with the matrix material. This graphene possessing 2D structure is suitable in metal/ ceramic matrix composites in which fabrication methods make use of elevated pressures. Flat morphology of graphene is more apt in surviving the high pressure processing than the tubular structures of CNT (carbon nano-tubes) which makes them susceptible to buckling or fracture. Researchers have used varying type of CVD (Chemical vapour deposition) called as thermal and plasma to synthesize single to multilayer graphene. Graphene layer thickness is dependent on substrate rate, gas flow rate, cooling rate, and other operating conditions too. CVD method produces high purity graphene, few layered (<10), structures close to perfect and crystallographic orientation. It was also stated that around 50% of the researches on structural graphene made use of graphene which was commercially available as reinforcement phase. Graphene should be properly distributed in the matrix without formation of clusters so as to take benefit of high surface area and nano-structure. Similar to CNTs, a similar issue with blending graphene is inhibition of cluster formation, so the blending process of ceramic matrix and graphene powder needs sufficient energy which is greater than the high surface energy of graphene which is responsible for GNP cluster formation. Ball

milling and ultrasonication are 2 key tools for making powder blends. Future aspects as stated in the paper are advanced processing for composite designs to optimize the GNP content, grain size etc. or from application point of view, composites can be investigated for tribological properties ad high temperature behaviour.

Liu et al. (2016) [16] Conventional powder compaction and sintering will prove to be an economic alternative to expensive processes like vacuum hot pressing, hot rolling, and hot extrusion process. At elevated pressures of compaction, aluminium alloy powders provided full densification. Variety of pressures have been implemented for production of SWNT/MWCNT-AMCs and graphene and its derivatives reinforced AMCs, and the range of pressure lies from 50 to 600 MPa. Archimedes method was utilised to calculate density of green sample and sintered sample, which was seen to be higher for higher applied pressures. Maximum density obtained at 560 MPa and it was 88.5% of the theoretical pore free density. Vicker's hardness test was done to test sample hardness, 0.3 wt. % of r-GO showed an improvement of 32% in hardness (34.5 +/- 3 HV) and 0.15 wt. % GNS should an increment of 43% (37.6 +/- 2.3 HV) in hardness over pure aluminium (26 +/- 1.3 HV). Even at higher pressures of 560 MPa pores were still evident between larger particle powder for r-GO and GNS reinforced AMCs. GNS is better reinforcement as compared to r-GO. GNP reinforced aluminium composite can possibly increase use of aluminium material by providing higher strength to weight ratio.

Liu et al. (2016) [17] Graphene nanoplatlet reinforced (0.75-1.48 vol. %) alumina matrix composite, in this work was produced and sintering was performed on the sample in an inert atmosphere of gas in a pressureless furnace. The starting materials were subjected to ball milling in a planetary ball mill for 2-hours at 100 revolutions per minute in a cylindrical shell made up of Zirconia, with Zirconia balls as the grinding/milling media. Ball-Powder ratio was chose to be 2. The slurry mixture produced by milling was then heated at 90 degree Celsius for 3 days in an oven to dry completely. Dried powder was ground and then sieved through a 140 mesh, further the dried and sieved powders were used to form green compacts by making use of cold Isostatic pressing. The green compacts prepared were sintered in tube furnace at a sintering temperature of 1650 degree Celsius, soaked for 2.5-3

hours with a continuous flow of inert gas at the rate of 8 l/min. The resulting composites were found to possess a relative density of 95.6-99.2% as compared to alumina alone. Also enhancement in mechanical properties was observed, like a maximum improvement of 60% in flexural strength and an enhancement of 70% in fracture toughness on addition of 0.75 vol. % GPL was observed in the prepared composites. Pull-out mechanism of toughening, along with the strengthened interaction of GPL and Alumina matrix were stated to be the reasons of the observed increment in properties.

Grigorev et al. (2017) [18] Study on graphene reinforced Al_2O_3-SiCw ceramic composites was carried out. Well dispersed ceramic-graphene oxide powder was fabricated using a colloidal processing route. Dense composites were obtained via Spark plasma sintering, a technique capable of reducing oxide to graphene in-situ during sintering process. Various samples with different concentrations of graphene were prepared, among all the samples 0.5 vol. % of graphene in composite showed highest flexural strength, fracture toughness, hardness with extremely good dispersion of graphene within the ceramic matrix, also enhancing the electrical conductivity making it EDM machinable. SPS is a fast solidification technique which allows high quality and uniform compacts to be sintered rapidly at comparatively lower temperature than conventional sintering. The main problem targeted in this study was that conventional machining processes involves hard tools or abrasives for material removal of softer material to take place and obtain a desired shape. High hardness, brittle nature and lack of electrical conductivity makes it difficult to machine ceramic materials, if the electrical conductivity of ceramics can be enhanced, they can be made eligible for machining on EDM. EDM requires material to have resistivity less than 100-300 ohm-cm for efficient machining, Al_2O_3, SiC have high resistivity, so to enhance the electrical conductivity Graphene oxide was added to ceramic matrix.

Alam et al. (2017) [19] Powder processing of GNP-Alumina was carried out for composite preparation. Ultrasonication was done in presence of Acetone for a time period of 2 hours to make a slurry of desired ratio. Slurry prepared after ultrasonication was ball milled at 150 rpm for ½ hour by making use of Zirconia balls (diameter 20 mm) as milling media in a planetary ball milling apparatus. Ball

to powder ratio selected was 10:1. Toulene was used as wetting media during milling. Milled slurry was heated and dried at 80 degree Celsius for 12 hours. The powders prepared after the above processing was further processed for fabrication of composites by both SPS (Spark plasma sintering) and Conventional sintering techniques to compare the results. For conventional sintering, green compacts were made on a compaction machine having applied pressure uni-axially, at a value of 388 MPa. Green compacts are further sintered at a temperature of 1650 degree Celsius for three varying sinter times of 2h, 3h, and 4h under inert conditions. For SPS samples, carried out at a temperature of 1450 degree Celsius for 5 minutes opting a heating rate of 100 degree Celsius/ minute, with samples subjected to 50 MPa pressure during sintering. The atmosphere consisted of 6 Pa vacuum and highly pure Argon was allowed to flow into the chamber at the rate of 2 l/min. Results for conventionally fabricated samples displayed 87% relative density at a reinforcement concentration of 3 vol. % GNP, whereas for SPS processed samples the value for relative density was as high as 99.6%. Hardness improvements was noticeable of all at 3 vol. % GNP reinforcement, maximum hardness value of samples fabricated through conventional method was 2.3 GPa after sintering at 1650 degree Celsius for 3 and 4 hours both, but on comparing with the samples fabricated by SPS the highest hardness value was observed to be 10.9 GPa, which was about 4.5 times than that of the former processing technique. It was also observed that the hardness values dropped as the reinforcement values exceeded 3 vol. %, similarly the wear resistance increased till 3 vol. % only. Maximum value of fracture toughness via both processing techniques was observed at 0.8 vol. % GNP, a value of 4.1 MPa $m^{1/2}$.

Cygan et al. (2017) [20] Alumina-xGO composites were fabricated using powder metallurgy, where x = 0.2, 0.5, 0.7, 1.15, 2 wt. %. For uniform Dispersion of graphene oxide ultrasonication was carried out in isopropyl alcohol for 30 minutes. Attrition type mill was used to get blend graphene oxide in Alumina in presence of isopropyl alcohol for a time period of 8 hours .To reduce the chances of contamination the grinding media used was made up of Alumina. Slurry mixture was dried followed by sieving through 0.5 mm sieve, to make sure that the reinforcement was a uniformly dispersed. The resulting dried and seed powder mixture was then subjected to Spark plasma sintering. Sintering process parameters

were optimised in this work with the variables being dwell time, temperature of sintering, heating rate. The optimised sintering parameters used in the work or 1450 degree Celsius sintering temperature, heating rate of 250 degree Celsius per minute, 4 minutes of Dwell time at an applied pressure of 35 MPa in vacuum atmosphere. For comparison come to an end forced Alumina samples centred at 1400 degree Celsius and 1450 degree Celsius were used for reference. Result certified that Spark plasma sintering carried out at 1450 degree Celsius and showed full densification of the samples. At sintering temperatures of 1400 degree Celsius and 1450 degree Celsius, an enhancement in fracture toughness was seen in samples with 0.5 wt. % graphene oxide as compared to pure Alumina samples, with 35% and 75% enhancement in fracture toughness at sintering temperatures of 1400 degree Celsius and 1450 degree Celsius respectively. Further increment in reinforcement lead to reduction in values of fracture toughness of the composite and the reasons stated was the formation of agglomerates which become sites of stress concentration.

3. OBJECTIVES

- Enhancement of mechanical as well as functional properties of resulting composite.
- Achieve uniform reinforcement dispersion into the matrix and its role towards densification and grain refinement.
- Increasing electrical conductivity of ceramic matrix composite.

4. SCOPE OF STUDY

- This study is focussed on fabrication of conducting ceramic by addition of graphene in order to enhance the mechanical and functional properties of the resulting ceramic matrix composite, and make the suitable to be used in various advanced technological applications. Also the resulting ceramic matrix composite is expected to have enhanced electrical properties on addition of graphene as the reinforcement.

5. MATERIALS TO BE USED

- **Alumina:** Procured from Almatis (Germany), grade CL 5000 (> 99.8% purity) having specific surface area of 0.2-0.35 m^2/g. Average particle size of 50-95 µm and density of the order 2.35-2.42 g/cc.
- **Graphene:** Procured from Platonic Nanotech (India), Lab grade graphene produced by chemical exfoliation method, having purity > 98%, thickness of 2-5 nm, length of 2-5 micron. Average number of layers 1-4, with an average surface area of 240 m^2/g.

6. EQUIPMENT

- **Ball milling apparatus:** A machine which is used for grinding and/or blending/mixing materials to be used in various applications, one of which is ceramics. It works on the principle of impact and attrition, reduction of particle size is done by the impact of balls (grinding media) falling under action of gravity as the container/drum rotates. The apparatus consists of a hollow cylinder rotating about its central axis. The cylindrical shell consists of grinding media (balls), most preferably made up of Tungsten Carbide, Zirconia, chrome steel, ceramic etc. Length and diameter of the cylindrical shell are nearly equal.
- **Compaction machine:** Compaction is a process carried out to form green compacts of required composition of powders to be sintered. Compaction is carried out by application of high pressures. Generally the pressure application is done vertically, with punch applying pressure on the powder in the die to take the shape and size of die and the compact is then ejected out.
- **Vacuum furnace:** Vacuum furnace would be required to carry out the sintering process by predetermining the maximum temperature, heating rate, cool-down conditions of the composite.
- **SEM, XRD apparatus:** SEM (Scanning electron microscopy) and XRD (X-Ray Diffraction) are imaging techniques used to analyse the surface topography and microstructure of the prepared composite and the starting materials as well.
- **Hardness tester:** Hardness refers to the property of a material to resist indentation. Generally Vicker's Hardness test is carried out in related researches. The underlying principle of the hardness test is to analyse the ability of a material to resist plastic deformation.
- **Fracture toughness testing apparatus:** Fracture toughness of any material is defined as the ability of material to resist brittle fracture when a crack is already present. Fracture toughness is one of the key properties of concern in CNT/graphene reinforced ceramics.

7. RESEARCH METHODOLOGY

The following process chart shows the steps to be followed in fabricating and testing of the composite.

Procurement of raw material

Evaluation of raw material powder properties

Mixing of raw materials in definite proportions

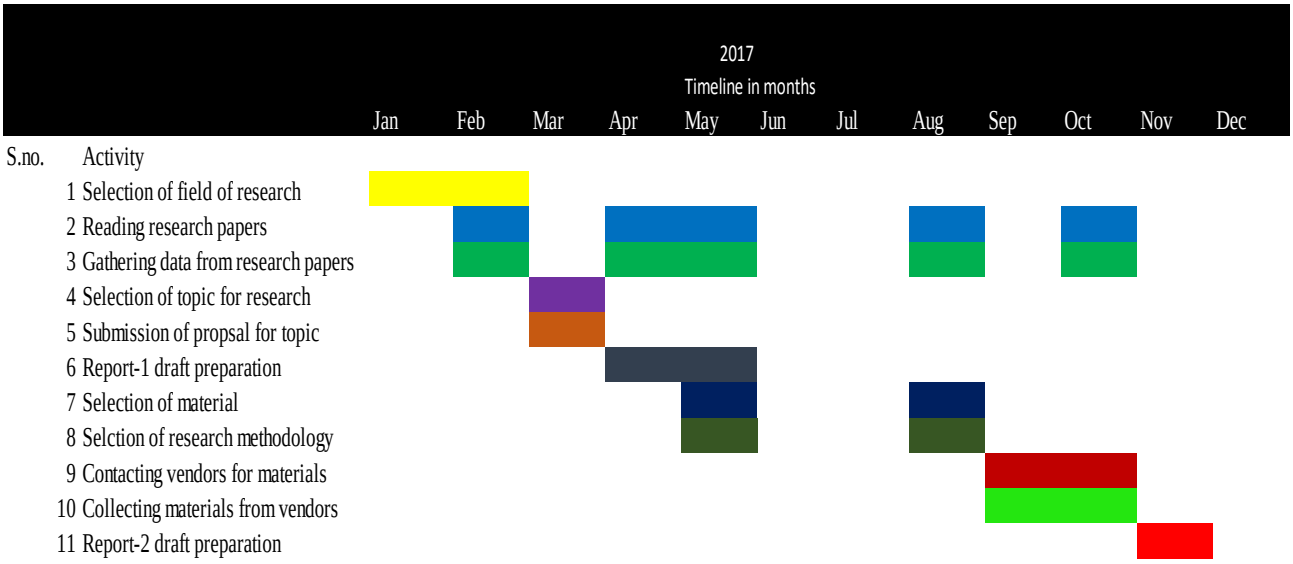
Compaction

Sintering

Evaluation of the composites properties

Results and disscusion

8. WORK PLAN: GANTT CHART



9. EXPECTED OUTCOMES

- Attain uniform dispersion of reinforcement in the ceramic matrix.
- Enhancement in fracture toughness, hardness and strength of the resulting ceramic matrix composite as compared to starting ceramic.
- Improvement in electrical conductivity of ceramic matrix composite.

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