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# Processing and Characterization of Graphene Reinforced $Al_2O_3$ Composite

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***Abstract*: *Because of stiff competition, industries are in continuous pressure of producing high quality products. To do so, inevitably high quality cutting tools are required. Alumina ($Al_2O_3$) is a quality cutting tool that is used for high speed machining. It is a widely used tool for machining cast iron, hard steels and super alloys. Therefore, the present work has taken up to prepare an alumina cutting tool material. One of the greatest drawbacks of alumina cutting tool material is its low fracture toughness. In the present work, Graphene nanoplatelets (GNPs) are considered the reinforcement in the $Al_2O_3$ceramic matrix to not only improve the fracture toughness but also the other properties. The composites are fabricated by the powder metallurgy route where the powders of raw materials are essentially subjected to compaction and sintering. Once the $Al_2O_3$ composites are fabricated and their properties are tested for their density, hardness and fracture toughness. It is observed that the GNP reinforced composites have much better properties than those of the composites without GNPs.***

***Keywords* : *Graphene nanoplatelets, $Al_2O_3$ cutting tool, powder metallurgy, properties testing***

## I. INTRODUCTION

The present work involves the use of Graphene due to its extraordinary electrical, thermal, and mechanical properties. Graphene nanoplatelets at the nanosize belong to the 2D carbon materials possess the unique properties. There has been a trend to use oxides, carbides and nitrides to be used as the reinforcement in ceramic composites at the micro scale to customize their properties to cater to the specific requirements. The addition of ceramic reinforcement usually improves the hardness but reduces the ductility and fracture toughness. In order to overcome this drawback, reinforcement is to be added at the nano scale. The addition of reinforcement hardly affects the ductility of the composite. The present work deals with the preparation of an advanced composite using the nano reinforcement. Graphene as reinforcement has the advantages of i) better dispersive capability and ii) improved strength and fracture toughness than any other reinforcement. Its high surface-to-volume ration also leads to better properties. Therefore, in the present work, an attempt is made to fabricate the composites using Graphene nanoplatelets as the reinforcement. Though $Al_2O_3$ are way superior to sintered carbides in respect of hot hardness, chemical inertness and stability and resistance to heat and wear, they do not have adequate fracture toughness and strength. Therefore the major objective of the work lies in improving the fracture toughness of the proposed composite though other mechanical properties also get improved during the process.

The objectives are:

- To prepare $Al_2O_3$-GNP ceramic matrix composite by powder metallurgy route
- To evaluate the physical and mechanical properties of the composite and
- To observe the effect of variation of GNP on the improvement of mechanical properties

## II. LITARATURE SURVEY

Alumina is a commonly used material for cutting tool applications. Alumina composites are prepared with a variety of reinforcements such as Zirconia ($ZrO_2$), Titanium Carbide (TiC), Titanium Nitride (TiN) and Titanium Carbo-Nitride (TiCN)[1- 4]. Nearly 40% of TiC or TiCN is used to fabricate super abrasion resistant black ceramics which is extensively used for hardened steels and machining chilled cast iron [2,4]. TiCN is a solid solution of TiN and TiC, which takes the characteristics of both TiC and TiN. Thus, TiCN has better anti-wear capabilities and higher hardness than TiN and TiC [5]. $Al_2O_3$-TiCN ceramic composite consists of Titanium Carbo Nitride grains dispersed in Alumina matrix. Yang et al. [6] investigated the mechanical properties of gas sintered $Al_2O_3$-30%TiCN matrix by varying the sintering temperature and reported the increase in relative density and mechanical properties. Yin et al. [7] reported the raise in relative density, fracture toughness and hardness in $Al_2O_3$/Ti(C,N) ceramic composite prepared by microwave sintering

In the present investigation, it is proposed to achieve the higher mechanical properties than those of the previously reported ceramic composites by reinforcing with Graphene Nano Platelets (GNPs). GNPs offer excellent mechanical properties when they are used as the reinforcing medium.

## III. MATERIALS AND METHODS

$Al_2O_3$ is taken as the matrix phase. Among the Ceramic cutting tools, viz., $Al_2O_3$ and SiC, $Al_2O_3$ is widely used as it has far superior properties in terms of hot hardness, chemical inertness and stability, and resistance to heat and wear. $Al_2O_3$ could withstand roughly even at $2000^0$C in the oxidation atmosphere. In view of the widespread applications, $Al_2O_3$ is considered for improving its properties in the present work.

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$Al_2O_3$/TiCN/GNP-MgO-$Y_2O_3$-Ni - Mo is prepared through the powder metallurgy route. MgO, $Y_2O_3$ are included in the composite as these additives help in grain refinement and densification.

The pure $Al_2O_3$ powders are difficult to sinter, so MgO, $Y_2O_3$ or other additives are normally added to reduce the sintering temperature and accelerate the sintering densification [8]. Besides MgO and $Y_2O_3$, the metallic binders, viz., Ni, Mo are added to the composite as $Al_2O_3$ is highly brittle and hard. The inclusion of the metallic binders gets the composite some ductility and fracture toughness. Without the metallic binders, the component gets a lot of cracks after sintering. Especially in tribological applications, where abrasion is the dominant wear mechanism, TiCN is superior to TiN coating when machining stainless steel, high nickel alloys, cast iron and non-ferrous materials. Excellent surface finishes and close tolerances are obtained, even on super alloys and other difficult to machine materials for which TiC or TiN based coatings cannot be used [9]. $Al_2O_3$ and TiCN were taken at 60 wt% and 30 wt% while the metallic binders, Ni and Mo were each considered at 4.5%. MgO and $Y_2O_3$ were taken as the sintering additives at 0.5 wt% each.

Initially all the components required to prepare the composite were taken in the powder form. The powders along with a particular percentage of GNPs were first ultrasonicated for 10 hours using ethanol as the solvent to attain the uniform dispersion of powders. The obtained slurry was then stirred at 500 rpm for 2 hours using a magnetic stirrer. Then it was transferred to a high energy planetary ball mill with 50 ml vial and tungsten carbide balls for milling. The ball milling was performed for 6hr with an interval pause of 5 min after every 30 min and with a rotational speed of 350 rpm. The obtained mixtures were taken in a crucible and calcinated in air for 30 min. Then the powders were sieved to get ultra-fine powders. There after 2 wt% glycerine was added to improve the binding property of the particles. Once the powder was fed in the die cavity, powder compaction was done using uniaxial pressing in which the powder was placed between the two rigid punches. The powder was compacted with the load of 20Tons with the upward speed of compaction of 2.9mm/sec and downward speed of compaction of 4.7 mm/sec. The powder obtained for different compositions was compacted in unidirectional pressing under the conditions of load 20Tons and holding time of 10-15sec in a metallic die made up of D3 tool steel. To get the required shape, 2ml of glycerin solution was added as binder while compacting it. Cold iso-static pressing was applied to achieve to get uniform compaction in all the directions. In this process, the component to be compacted is subjected to uniform pressure in all the directions through the operating medium of water. A pressure of 450MPa was used in cold iso-static pressing for 60sec. The press took 100sec to reach the specified pressure. In the present case, to avoid the pores developed by escaping gases from organic binders the specimens were kept in the de-binding furnace at 400$^o$C for 1 hour. Heating rate of 3$^o$C/min was used to reach the set temperature. The process was carried out under the pressure of 1 bar in Argon gas. Once debinding is over, the next step is to perform sintering which offers enough strength to the green compact. In the present work, sintering was done through vacuum for which tubular vacuum sintering furnace of 2000$^0$C was used. the pellets were placed in the furnace and sintered at 1500 $^o$C in vacuum at $10^{-3}$ Torr by escalating the temperature in 3 states to evade the formation of residual stress in the pellets. In first state, the temperature of the furnace was considered from room temperature to 500$^o$C in 1 hr 40 min and was given soaking for 10 min, then in second state the temperature was increased from 500$^o$C to 1000$^o$C for 50 min and was given soaking for 10 min and then in final third state the temperature was increased to 1500$^o$C in 2 hr 40 min and was clamped at 1500$^o$C for 90 min for sintering of pellets. Then the furnace was left over for 40 hours for cooling to room temperature. Vacuum of $10^{-3}$ Torr was maintained in the furnace to prevent any kind of oxidation of the compact.

The composites fabricated are shown in where GNP reinforcement was varied from 0 1o 1wt% with the step size of 0.25. The photographs of the samples fabricated are shown in Fig.1.

**Table –I: List of Composites fabricated**

| Sl.No | $Al_2O_3$ | TiCN | GNP | MgO | $Y_2O_3$ | Ni | Mo |
|---|---|---|---|---|---|---|---|
| 1 | 60 | 30 | 0 | 0.5 | 0.5 | 4.5 | 4.5 |
| 2 | 59.75 | 30 | 0.25 | 0.5 | 0.5 | 4.5 | 4.5 |
| 3 | 59.50 | 30 | 0.50 | 0.5 | 0.5 | 4.5 | 4.5 |
| 4 | 59.25 | 30 | 0.75 | 0.5 | 0.5 | 4.5 | 4.5 |
| 5 | 59.0 | 30 | 1.0 | 0.5 | 0.5 | 4.5 | 4.5 |

**Fig.1. Composites fabricated**

## IV. RESULTS AND DISCUSSION

X-ray diffraction (XRD) patterns of synthesised five samples were performed on a PANalytical XPert Pro-diffractometer with CuKa radiation (k = 1.5406 $A^0$). The measurements were made at the room temperature in the range of $0^0$–$80^0$ on 2θ with a step size of $0.05^0$. Field Emission Scanning Electron Microscope (FESEM) images were obtained from a FEI Quanta 200F SEM with gold coating.

Fig.2 shows X-Ray diffraction patterns of five specimens of $Al_2O_3$-TiCN-GNP (ATG) fabricated by varying the GNP weight percentage (wt%), namely $ATG_{(0.0\ wt\%)}$, $ATG_{(0.25\ wt\%)}$, $ATG_{(0.5\ wt\%)}$, $ATG_{(0.75\ wt\%)}$ and $ATG_{(1.0\ wt\%)}$.

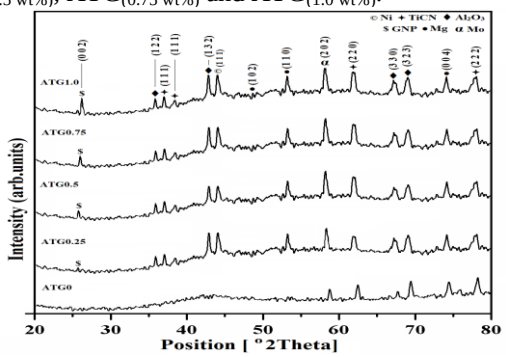


**Fig.2 X-Ray Diffraction patterns of the composites**

All the diffraction peaks of the sintered multi-phase ceramic composite are well matched with the standard diffraction data of JCPDS file Nos. 52-0803, 42-1489 and 75-1621 for $Al_2O_3$, TiCN and Graphene. As no other peaks are detected in the X-Ray diffraction, it is said that the obtained ceramic composites are free of any impurities and no significant reaction between the $Al_2O_3$-TiCN and GNP is said to be taken place.

### A. Density

Theoretical density ($\rho_{th}$): To calculate the theoretical density, rule of mixtures was used. The theoretical density of GNP is very low when compared with any element of the composition. Therefore the addition of GNP reduces the overall theoretical density of the samples.

Sintered density ($\rho_s$): To calculate the sintered density, Archimedes' principle was used. Sintered density of a sample ($\rho_s$) was calculated as the ratio of the weight of the sample in air to the apparent loss of weight when weighed in water.

Relative Density ($\rho_r$)**:**

The degree of sinterability is specified by the relative density. The relative density of sintered Cu–GNP composite was calculated as the ratio of the measured density obtained by the Archimedes' principle ($\rho_r$) to calculated theoretical density ($\rho_{th}$) of the composite.

Table 2 lists the sintering densities and relative densities of the composites.

### B. Porosity

Porosity holds the key for achieving the better mechanical properties. All the material properties get affected by porosity. Density, conductivity, hardness, and strength are influenced by porosity. Fatigue strength is largely impacted by porosity as stress amplification takes place around the pores.

Porosity of the green compact gets reduced by sintering where atomic diffusion takes place at elevated temperature. During atomic diffusion, atoms transfer from one place to another place to occupy the voids so that the voids are filled up. This atomic diffusion is more predominant at higher sintering temperatures. That's why higher sintering temperatures are usually recommended to get reduced porosity levels as more atomic diffusion is enabled at higher temperatures. Porosity values were calculated as per the ASTM standard C1309-85. Porosity was calculated using an image analysis software called "Dewinter". Table 2 lists the porosity values.

**Table 2. Densities and Porosities**

| Sample No | GNP | VHN (GPa) | Fracture Toughness (Mpam$^{1/2}$) |
|---|---|---|---|
| 1 | 0 | 19.38 | 5.14 |
| 2 | 0.25 | 19.42 | 6.63 |
| 3 | 0.5 | 19.46 | 7.01 |
| 4 | 0.75 | 19.48 | 7.18 |
| 5 | 1 | 19.39 | 6.52 |

### C. Hardness

Vickers micro hardness was measured on the sintered samples using a Vickers diamond pyramid indenter. Micro hardness testing was done as per ASTM E-384. To determine the Vickers hardness values of the specimens MHVD-30AP hardness tester is used with a load of 196 N for 60 sec.

The Vickers Hardness (HV) was calculated by optically measuring the diagonal lengths of the impression left by the indenter. The resulting size or depth of the indentation in the surface of the material was measured using the FESEM. Table 3 lists out the hardness values obtained by the composites.

### D. Fracture toughness

In the present work, the facture toughness of the sintered composites was calculated by using the Vickers indentation technique from the following equation [10]:

$K_{IC} = 0.16(c/a)^{-1.5} \times H \times a^{1/2}$

Where

'$K_{IC}$' is indentation facture toughness (Mpa$\sqrt{m}$),

'c' is half of the mean radial crack length (microns)

'H' is the Vickers hardness in (GPa)

The indentation fracture toughness at different percentages of GNPs is shown in Table 3 which shows that the best facture toughness is achieved at 0.75wt%. The facture toughness is continuously increased up to 0.75 wt% and slightly decreased at 1 wt% GNP content due to the agglomerations reported at that percentage.

### E Toughening Mechanisms

In order to deeply analyze the reasons that are responsible for the improved fracture toughness, the fractured surfaces of the proposed GNP reinforced composites are considered.

**Table 3 Hardness and Fracture toughness values**

| GNP | $\rho_{th}$ | $\rho_{s\ (gm/cc)}$ | $\rho_r$ (%) | Porosity |
|---|---|---|---|---|
| 0 | 4.8363 | 4.71 | 97.4 | 6.69 |
| 0.25 | 4.8322 | 4.74 | 98.3 | 6.02 |
| 0.5 | 4.8281 | 4.78 | 99.1 | 5.63 |
| 0.75 | 4.8239 | 4.79 | 99.5 | 3.96 |
| 1 | 4.8198 | 4.7 | 97.6 | 6.66 |

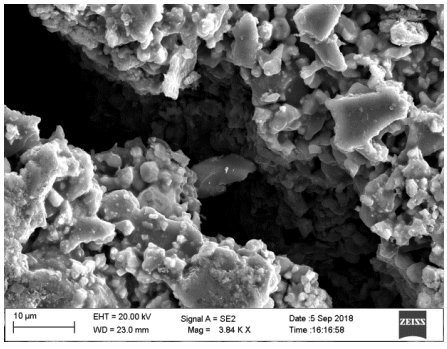


**Fig.3 (a) Crack pullout**

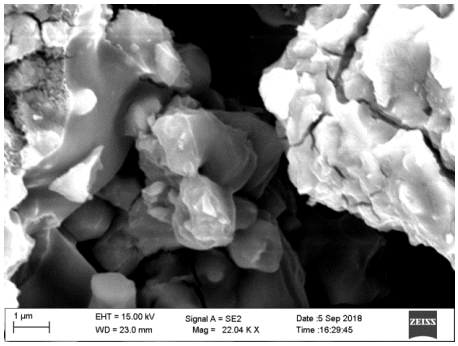


**Fig.3.(b) Deep leftover pit**

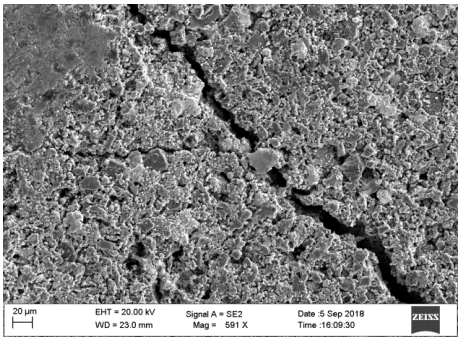


**Fig.3.(c ) Crack bridging**

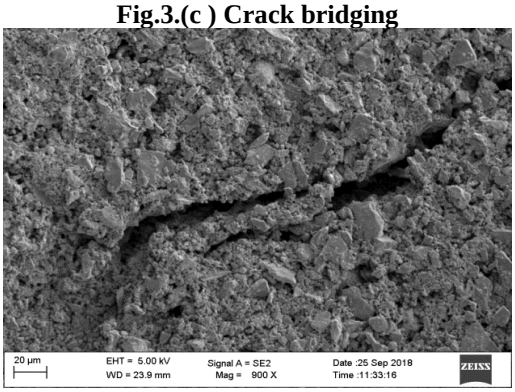


**Fig.3 (d) Crack arrest**

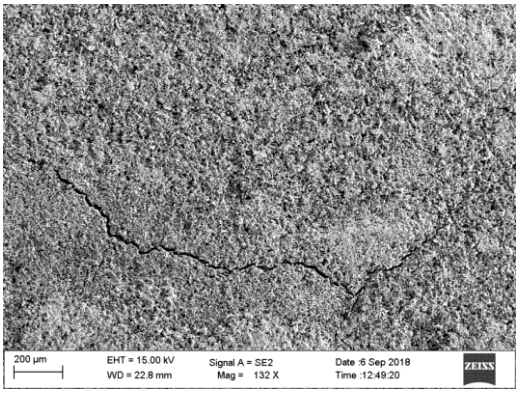


**Fig.3 (e) Crack deflection**

Fig.3 shows the fractured surfaces of the GNP reinforced $Al_2O_3$-TiCN ceramic composites in which, crack pullout, crack bridging and crack deflection are observed. These toughening mechanisms are common in ceramic composites and are reduced by reinforcing fibers; these effects are improved in our present research by using GNPs. GNPs played an important role in changing the microstructure and crack propagation of GNP reinforced $Al_2O_3$-TiCN composites. Fig. 3(a) and 3(b) demonstrate the pull out pattern of 0.75 wt% GNP reinforced $Al_2O_3$-TiCN composite. A deep leftover pit is seen after the pull out of GNPs. Higher interfacial friction against GNPs pull out from the ceramic matrix is provided through the large interfacial area as massive GNPs wrapped around at the grain boundaries.

The large surface area of GNPs require much energy to pull out in comparison with the nano fibre During the sintering, the neighbouring matrix grains of the GNPs offer force which is sufficient to bend the GNPs and embed them between the matrix grains which is accelerated by the interfacial strength. This embedment enables the GNPs to anchor and bind with the matrix grains resulting in enhanced interfacial adhesion [12].

Crack bridging is observed when the GNPs have large angle to the indent crack path. When a crack propagates and meets with Graphene platelet, it is arrested and deflected in-plane as shown in Fig. 3(c and d). It is believed that such a crack deflection mechanism would create a more tortuous path to release stress, which helps increase the fracture toughness. From Fig 3(c) it is very clearly seen that the crack bridge is arisen out of the frictional sliding of the GNPs which brought the two crack surfaces together [11]. Large deflection angles of crack propagation have been marked in Fig 3(e) by the circles.

## V. CONCLUSIONS

$Al_2O_3$-TiCN-GNP composites were successfully prepared by reinforcing GNPs of 0, 0.25, 0.5, 0.75 and 1 wt% through powder metallurgy technique in which sintering was carried out in vacuum.

- The X-Ray Diffraction peaks of all the five specimens prepared revealed the purity of the specimens and were in well confinement with the standard JCPDS data.
- Relative density and hardness values of the composite increase with increase the Graphene content up to 0.75 wt%.
- The maximum relative density and hardness values were observed at 0.75wt% GNP. Maximum relative density and hardness values achieved are 99.46% and VHN 19.48 GPa respectively.
- The effect of GNPs on mechanical properties and toughness mechanisms were studied.
- GNPs with 0.75 wt% morphological images show the existence of different toughening mechanisms. GNPs arrest the crack propagations and offer good crack bridging, crack pull-out and crack deflection.
- Maximum fracture toughness was found to be 7.18MPam1/2 at 0.75wt% while it was 5.147.18MPam1/2 without GNP. Therefore, there's been an improvement of 40% from its initial value. This could be an important finding of the present work as the basic theme of the project is to improve the fracture toughness of the proposed ceramic material.

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