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Development of CNT Based Matrix for Mechanical Shielding Application

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the field Abstract— Recent advancements in Nanotechnology has basically led to improvement in the structural properties of Carbon Nanotubes (CNTs). These CNTs have been found to possess superior mechanical properties than their metal and ceramic matrix counterparts. This paper is aimed at suggesting an alternative to the use of traditional metal or ceramic matrix by using finely dispersed CNTs for penetration resistance against high momentum external impact.

Keywords—Nanotechnology, CNTs, penetration resistance, external impact

INTRODUCTION

In the initial design phase of any equipment the possibility of external impact should be considered to be another major parameter which is scalable to the conventional design considerations. The possible scenarios where such design can prove to be instrumental are impact of a meteor with a spacecraft, a loose aircraft blade striking the surrounding containment or crashing of an automobile during day to day travelling. In military the possible conditions requiring heavy protection would range from small bullets striking the jackets of soldiers to major projectiles being targeted at larger vehicles such has tanks and Humvees. All these situations can be dealt with by using armor protection that is light and has high mechanical strength at the same time, such that it does not affect the mobility of the end user. The protection of ground forces and heavy military equipment is nearly impossible without the use of ceramic or metal matrix composites Composite structures are best suited for such kind of military application because of their low density and high mechanical strength. In situation where a medium weight projectile incident on the armor, using only composite structures is simply not sufficient. In such cases composite material are combined with ceramic matrix to reduce the impact on the armor and the gross weight of the machinery by a huge margin. Nanocomposite is a multiple phased rigid material wherein minimum one phase has at least one dimensional configuration of less than 100 nanometers. This definition includes porous, colloidal and copolymer substances but is traditionally considered to be a composite of bulk matrix and nano-dimension phase which differ in characteristics due to dissimilar structural and chemical All major properties of the nanocomposite will vary widely than its parent combined materials. Size limit proposed for mechanical strengthening application is greater than 100 nanometers which inhibits matrix dislocation under high incident mechanical force. The usual ceramics that are reinforced with CNTs are alumina, silica, zirconia, silicon nitride or silicon car-bides, etc. Under consideration of greater hardness Al₂O₃ is the most viable ceramic option but due to low fracture resistance and brittle characteristics, it has limited application. Many attempts have been made to improve the mechanical properties of ceramics through incorporating CNTs in ceramic matrix. Recently, researchers developed CNT based Al₂O₃ composite using plasma spray method which resulted in an increase in the fracture toughness by nearly 43% [1] and an elastic modulus of 200% with reference to pure Al₂O₃ [2]. This paper suggests the use of CNTs in conjunction with Al₂O₃ for greater mechanical rigidity.

SYNTHESIS OF CNT BASED AL₂O₃

A. Required Raw Material for Nanocomposite Synthesis

Very few researchers prefer using SWCNT (Single walled Carbon nanotube), due to much higher cost and clustering problems as compared to MWCNT (Multi walled Carbon nanotubes) which reduces overall cost and increases homogeneity in the matrix. The diameter and length of the MWCNT should be between 5-124 nanometers and 0.5-160 micro-micrometer, respectively with purity and special surface area ranging from 80-98% and 25-300 meter²/gram, respectively. There are few researchers who prefer using gamma or delta Al₂O₃ powder because these options are lowtemperature metastable forms of crystalline Al₂O₃ and they convert to a stable alpha-phase on heating above 1150°c. Al₂O₃ has much lower particle size and higher surface area as compared to reactive alpha-Al₂O₃ that also helps in reducing sintering temperature required for achieving desired margin of densification.

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2

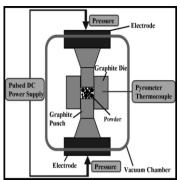


Fig. 1 Spark Plasma Sintering

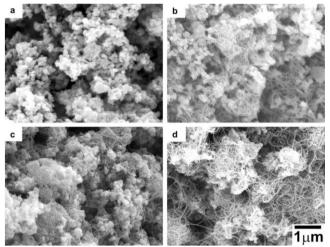


Fig. 2 FESEM images of the CNT- Al_2O_3 nanocomposites (SM)

B. Preparation of CNT Based Nanocomposites

CNTs are grown directly on Al2O3 by using Co(NO₃)₂.6H₂O as a catalyst precursor agent [3]. To use the precursor on the Al₂O₃, CR30 Al₂O₃ powder is mixed with ethanol, which is followed by sonication for a duration of 15 minutes. The mixture is then dried at 130°C for overnight which is followed with grinding into fine powder. For larger scaled production of CNT, Co/Al₂O₃ powder is loaded into a fused quartz tube. For small scale use, Co/Al₂O₃ powder is dispersed in a Molybdenum boat and put in fused quartz tubes which are thereby inserted in a horizontal furnace. Fused quartz stirrers are included in the system to achieve uniform exposure to the gases required for reaction. In this paper, we refer composite growth by Molybdenum boat and stirrer as 'BM' and 'SM' mode, respectively. Acetylene, hydrogen and argon gas in ratio of 1:4:6 and flow rate of 1100 sccm (standard cubic centimeter per minute), is usually introduced in the reaction chamber through distilled water bubbler enabling CNT growth. The production process of CNTs is operated at 750°C for 15 minutes. As shown in Fig. 1, The CNT- Al₂O₃ composite is then placed in a 15 mm diameter graphite die, which is sintered in vacuum inside a Spark Plasma Sintering unit. The conditions for the process are guided by a pressure of 100 MPa with temperature in the range of 1150 or 1450°C, heating rate 100°C/min, hold time of 10 minutes and pulse duration 12 milliseconds. Hence, as shown in Fig. 2 CNT- Al₂O₃ composite is obtained [8]. In this paper, greater emphasis is on the mechanical characteristics of nanocomposites engineered by SM, as they show much better CNT yielding, mechanical and density properties than by BM method.

III. RESULTS AND DISCUSSION

A. Structure of CNT-Al₂O₃ nanocomposite

Fig. 4 shows the image of the type of alumina powder considered in this paper. The average size of the particles is 150-300 nm, Fig. 2(a)-(d) shows the images of CNT- Al₂O₃ nanocomposites created by SM on Co/Al₂O₃ with Co content in the range of 0.5, 1.0, 2.0, and 4.0 wt.%, respectively. The content of CNTs in the nanomaterial increases with the catalyst. Very few CNTs are found in nanocomposite composed of 0.5 wt.% of Co/ Al₂O₃ and the distribution is sparse as shown in Fig. 2(a). When the ratio increases to 1.0 and 2.0, uniformly distributed CNTs and small bundles are found in the matrix (Fig. 2(b) and (c)). As the ratio reaches 4.0 wt.%, greater CNTs and clusters of CNTs are found as shown in Fig. 2(d). Some Al₂O₃ nanoparticles are wrapped around by these CNTs. The diameter of CNTs is nearly 10-40 nm, and the length is approximately 1–7 um. The diameter of the CNTs increases with cobalt concentration. FESEM images of CNT- Al₂O₃ generated by BM with Co/ Al₂O₃ in the ratio of 1.0 and 5.0 wt.% are shown in Fig. 3(a) and (b). The two processes of BM and SM of 1.0 wt.% Co/Al2O3 do not show any notable difference in the uniformity and distribution of CNTs.

B. Variation of relative density with CNT content

After the production of the CNT- Al₂O₃ composite powder, spark plasma sintering is used to consolidate the nanocomposites. The densities of the CNT- Al₂O₃ composites sintered at varied temperatures are lower than pure Al₂O₃. With the increase in CNT content the density of the CNT- Al₂O₃ first increases to maximum and then starts decreasing. The nanocomposites sintered at 1150°C and 1450°C have peak densities at different CNT content. At temperature of nearly 1150°C, the composite having 8.2 wt.% CNT has peak density of 2.5 g/cm3, while for temperature of 1450°C, the peak density of 3.1 g/cm3 is usually found for nanomaterial with 7.3wt.% CNT content [9]. On comparing the CNTs grown on 1.0 wt.% in SM and BM, the density of the SM sample is found to be lower than BM. This is caused due to greater yield of light-weighted CNTs in the composite generated by SM. The density of the CNT- Al₂O₃ composites do not decrease linearly with an increase in the CNT composition but the porosity changes inversely with density of nanocomposites.

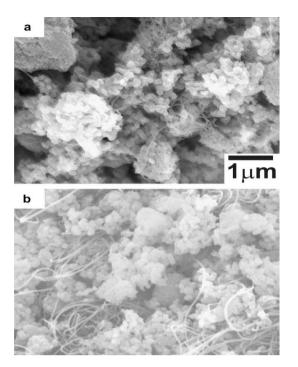


Fig. 3 FESEM images of the CNT- Al₂O₃ nanocomposites (BM)

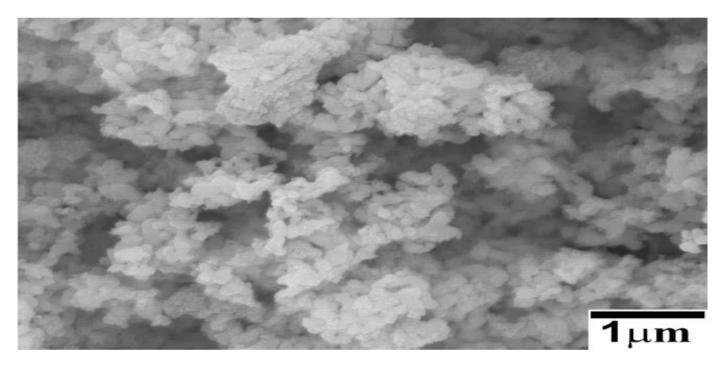


Fig. 4 FESEM image of the original alumina powder

C. Mechanical properties of the CNT– Al_2O_3 nanocomposites The Vickers hardness is a function of the CNT content in CNT- Al_2O_3 nanocomposite. The toughness is dependent on the CNT content and sintering temperature. At temperature of 1150^{0} C, the hardness of variable CNT content samples is lower than pure Al_2O_3 , while is higher at 1450^{0} C. In Fig. 5, the hardness increases rapidly when the CNT content increases from 3.19 to 7.39 wt.% in the nanocomposites, then

it decreases gradually with CNT content from 7.39 to 19.1 wt.% (SM). A sharp decrease in the hardness is observed for the nanocomposites with 20.5 wt.% CNT content (BM). The peak hardness of the composites can be reached with the CNT content of 6–8 wt.%. For instance, the 7.39 wt.% CNT–Al₂O₃ composite shows the hardness of 2.29 GPa (Giga Pascal) at 1150°C and 9.98 GPa at 1450°C. Apart from the CNT content and sintering temperature, the observed increase

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in porosity with the CNT content above the optimal value also plays an important role in the modified hardness of composites. The increase of CNT content above the optimal value reduces the densification of the nanocomposite which decreases its hardness. The increase in the CNT content makes the composite loose due to agglomeration. During sintering, due to transfer of stress to the CNTs, separation from the matrix becomes easier, which leads to the decrease in mechanical strength [4]. The reduced density of CNTmatrix has been spoken about by multiple reports in the past [5,6] but its exact mechanism is yet to be clearly understood. The densification of ceramic composites, removal of pore and mass transportation via bulk and surface diffusion are two factors which ultimately decide the density. Henceforth the variation of sintering property should be in consideration with these few points. It has been found that CNTS in grain boundaries prevent closing up of these gaps. The Fig. 6 confirms the survival of CNTs in composite after SPS treatment [8]. On comparing the FESEM images before (Fig. 2) and after (Fig. 6) of SPS procedure, no major change in the quantity and distribution of CNTs is observed in the nanocomposites. To accomplish effective enhancement in the mechanical properties in CNT reinforced nanocomposites, the matrix interface should be neither be too weak nor strong [7]. Such interface is required in the CNT-Al₂O₃ composite such that the de-cohesion of the interfaces can enable energy absorption under stress through CNT pull-outs [5].

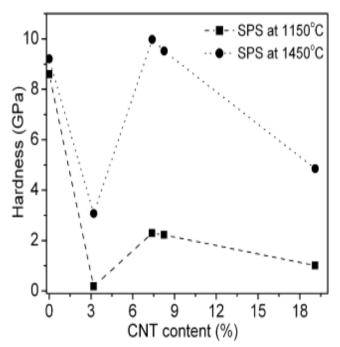


Fig. 5 Vickers hardness of the CNT-Al2O3 (SM)

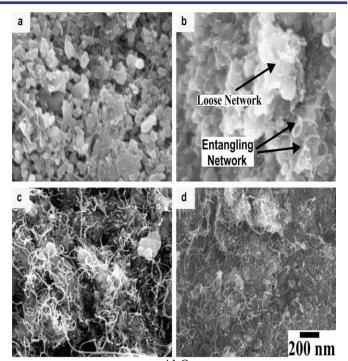


Fig. 6 Fracture surfaces of CNT- Al₂O₃ nanocomposites (SM) sintered at different temperatures

D. Potential Applications in Mechanical Sheilding

Given the improvement in fracture toughness and other advantages of electrical and thermal nature, Al₂O₃ reinforced with CNTs are a promising raw material in the world of automotive and aerospace engineering. In relation to the enhanced mechanical performance of Al₂O₃, the wear resistance characteristics of these nanocomposites can be suitable for a number of applications in artillery and projectile firing chambers. As shown in Fig. 7, CNT based composites can be layered between two sheets of armor of any device to be protected from high impact, providing much greater fracture strength. They are also suitable for structural applications, such as ball bearings, seals, bullet proof armor for vehicles and ground personnel and various cutting tools.

As the research is progressing in the world of nanotechnology, better CNTs-reinforced nanoceramics with phenomenal properties are expected and which may substitute various automobile and aerospace components in the not so distant future. Also, owning to their various functionalities these CNT based composites have great potential for third generation nano-device technologies. Carbon nanotubes are an ideal raw material for bulletproof vests with relation to their unique combination of exceedingly high elastic modulus and enormously high yield strain. SWCNTs can be characterized by a Young's modulus of nearly 1000 GPa, where strength ranges from 13 to 53 GPa and strain for failure due to tensile force is predicted to be ~16%. The specific gravity of SWCNTs is nearly 1.5 g/cm3, therefore one may expect the ballistic performance parameters to range from 2708 m/s to 4326 m/s. These values are similar to the previously found value of 3000 m/s by Alan Windle for ballistic performance parameters of CNTs [9]. When compared with other alternative fibers suitable for ballistic application the CNT embedded ceramics have great potential in the world of bullet-proof armor systems.

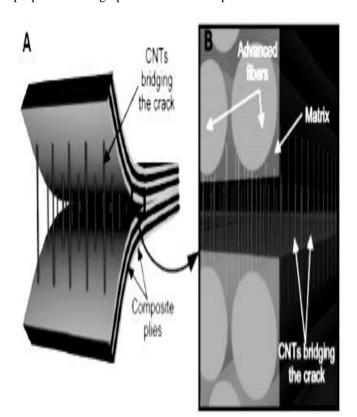
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Fig. 7 CNTs bridging ceramic fracture

IV. CONCLUSION

The study of Al₂O₃ reinforced with carbon nanostructures (CNTs and graphene) have been thoroughly reviewed. Successes in the purification and dispersions of MWCNTs are somehow satisfactory, however SWCNTs need further research and standards for CNT dispersion are vital for addressing the quality and reliability with confidence. CNTsreinforced ceramics follow the combined advanced toughening mechanisms of CNT's stretching/uncoiling and the classical fiber pullout theory, as an energy dissipating process. Rough surface and Nano pits of MWCNTs explain the strong interface connections with ceramic matrix and the confirmation of the formation of intermediate Al₂O₃ phases at the interface further strengthens these explanations. Conclusively, problems of reinforcing MWCNTs into ceramics have been solved to some extend. Despite challenges and controversial issues, CNTs have successfully enhanced the toughness and other properties of brittle ceramics and converted them into useful materials for next generation applications. It is clear that graphene can play an important role as filler in ceramics according to publications. However, work on graphene ceramic composites is in its early stages and there are still considerable works that need to be done in order to optimize their processing, microstructure and interfacial properties to obtain better multifunctional properties from graphene-ceramic composites.



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