Effect of sintering temperature on densification and mechanical properties of pressureless sintered CNT-alumina nanocomposites

N Bakhsh1, F A Khalid1 and Abbas S Hakeem2
1Faculty of Materials Science and Engineering, Ghulam Ishaq Khan Institute of Engineering Sciences and Technology, Topi, KPK, Pakistan
2Centre of Excellence in Nanotechnology, King Fahd University of Petroleum and Minerals, Dhahran, Kingdom of Saudi Arabia

E-mail: khoja72@gmail.com

Abstract. Carbon nanotubes (CNTs) exhibit excellent mechanical, electrical and thermal properties thus have been considered for applications in the production of nanocomposite materials. This work presents results of sintered CNTs-reinforced alumina nanocomposites that can be used for many structural and engineering applications. Gas purging sonication (GPS) was used to achieve homogeneous dispersion of CNTs in alumina powder. Nanocomposites were synthesized by conventional pressureless sintering technique using varying amounts of CNTs in alumina matrix. Densification, hardness and fracture toughness of the resulted nanocomposites were examined. It is found that considerable improvement in fracture toughness at 1 wt% CNT-alumina nanocomposite has occurred. Role of CNTs in improving the fracture toughness of nanocomposites is explained which is attributed to well known bridging and pullout mechanism of CNTs in the matrix.

1. Introduction
Carbon nanotubes (CNTs) have excellent properties and a distinct structure that have fascinated the researchers’ interest worldwide. The high values of modulus (1 TPa), tensile strength (upto 100 GPa), large aspect ratio (1000-10,000) and low density of CNTs are being utilized to improve the toughness and strength of materials in various composite systems, including polymer, metal, cermets and ceramic matrix composites [1].

The higher degree of entanglement between CNTs; due to their high aspect ratio and strong Van der Waals forces, restrict them to get full benefits out of each individual CNT. Various chemical and physical methods are used for the exfoliation and dispersion of CNTs in the matrices. These methods include surface functionalization, shear mixing, high energy ball milling, ultrasonication and gas purging sonication etc. [2-9]. Ceramic materials possess high brittleness and low fracture toughness and low thermal stability which are undesirable for various engineering applications[10]. Alumina is extensively being used for many engineering utilities but; its toughness is too low to make it feasible for several advanced applications [11, 12]. The introduction of CNTs in alumina matrix enhances its mechanical properties by the suppression of grain growth during sintering and well known mechanism of CNTs pull out, crack bridging between grains during load applications. The improved fracture toughness and moduli of CNT-alumina nanocomposite makes it a strong candidate for efficient structural material suitable for many advanced engineering applications [2, 13]. Several sintering
techniques such as hot isostatic pressing, hot pressing, microwave sintering and spark plasma sintering (SPS) have been used to improve the mechanical properties of alumina and other ceramics [13-17]. However, all these processes impose many geometrical limitations to the sintered products and hence require simple shapes for the sintering purposes. Thus pressureless sintering technique is still widely being used due to its accommodation of intricate sintered parts [18]. The sintering of CNT-alumina nanocomposites was carried out by the same authors at 1600°C and the data had been published in reference [9]. Sintering at a further higher temperature is thought to be investigated to optimize the temperature range using pressureless sintering technique.

In the present work, pressureless sintering of CNT–Al₂O₃ nanocomposites is carried out at 1700°C in an inert atmosphere. The Vickers hardness and fracture toughness of the CNT–Al₂O₃ nanocomposites containing 1, 2 and 3 weight % CNTs are investigated. Synthesis and processing parameters are optimized and presented to explain the role of CNTs in CNT-alumina nanocomposites showing better fracture toughness at 1wt% CNT-alumina nanocomposites.

2. Experimental Procedure

Multiwalled Carbon nanotubes (diameter 10-40 nm) were purchased from Sun Nanotech, China. The reported purity level of CNTs was greater than 90%. α-Alumina powder, with an average particle size around 400 nm and purity >99%, was procured from Nabond Technologies, China. The as-received CNTs and alumina powder were separately dispersed in de-ionized water through sonication and ball milling to get homogeneous and de-agglomerated suspensions. The suspensions were mixed together through a unique mixing and dispersion technique, which consisted of simultaneous sonicating and purging of nitrogen gas through the solution till no sonicating effects could be observed in the thick slurry. This novel technique of sonicating and purging with N₂-gas for the de-agglomeration of CNTs and alumina resulted in a uniform mixture of the composite powder [9]. The slurry was dried at 120°C for 24 hours before sieving it through a 250 mesh to homogenize the particle size of the resultant composite powder. The powder was uniaxially pressed in a steel die to get pallets suitable for handling during the sintering process. The sintering was carried out at 1700°C for 15 minutes in flowing argon.

Particle size of alumina powder was analyzed with the help of Microtrac S3500 particle analyzer. Scanning electron microscope (Philips XL30) was used for microstructural investigation. Vickers hardness tester (DVK-2) was used for fracture toughness measurements with a load of 10 kg. A microhardness tester with Vickers’ sensor was employed for the measurement of hardness at 200g load with 15 seconds of dwell time.

3. Results and Discussion

3.1. Morphology of CNTs and alumina powder

SEM image shown in figure 1(a) displays the surface features and morphology of as-received CNTs used in current research.

![Figure 1. SEM images of (a) as-received CNTs, (b) alumina powder.](image-url)
These highly entangled and agglomerated CNTs have diameter in the range of 10-40 nm with a length of few microns. The alumina powder particle size ranges from less than 100 to 500 nm with irregular shape morphology as shown in figure 1(b). The approximate average particle size of the starting alumina powder is 0.4µm as shown in figure 2.

### 3.2. Sintering and Densification

The sintering process has produced a near full densification of around 99% for monolithic alumina. However, the addition of CNTs results in the reduction in final density of alumina nanocomposites as shown in figure 3. Density of the nanocomposite at 1 wt% CNT-alumina is achieved as 98.6% as compared to corresponding theoretical density, which is higher than the similar nanocomposites sintered at 1600°C [9]. The mass transportation caused due to bulk diffusion and pores elimination are most important reasons for enhanced densification of alumina [19].

Further addition of 2 and 3wt% CNTs in alumina result in reduced density values of 96.1 and 95.1 % respectively as compared to their corresponding theoretical densities. This reducing trend in density with increased CNT contents is due to CNTs stagnation at the grain boundaries which results in
impeding the grain growth at the sintering temperature. The higher degree of CNT-agglomerations at a high CNT-concentration and the nano to submicron size range of alumina powder has the inherited porosity which also results in decreased densification of the nanocomposites [18-22].

3.4. Fracture Behavior and Phases

Figure 4 (a) reveals the SEM image of fractured surface morphology of alumina after sintering at 1700°C for 15 minutes. The finer alumina grains are surrounded by larger ones thus filling the gaps between the grains that help in enhancing the density of the sintered alumina. Average grain size of the sintered monolithic alumina lies between 6 ± 1µm. The fractured surface of pure alumina reveals mostly the intergranular fracture along with transgranular behaviour. The SEM image of fractured surface from 1 wt % CNT-alumina nanocomposite shows uniform and reasonably good dispersion of CNTs in the alumina matrix as shown in figure 4(b). The addition of 1 wt% CNTs to alumina results in the decrease in average grain size to approximately 1.2 µm after sintering compared to monolithic alumina. The decreasing trend in grain size due to addition of CNTs is in accordance with the previous literature [9, 18].

![Figure 4. SEM images of the fractured surface of: (a) monolithic alumina, (b) 1wt%CNT-Al₂O₃, (c) 2wt%CNT-Al₂O₃ and (d) 3wt%CNT-Al₂O₃ nanocomposites.](image)

The decrease in the grain size of CNT-alumina nanocomposite can also be attributed to the well dispersed nanosize carbonaceous impurities present in the as-received CNTs. This has also been confirmed that the addition of CNTs not only results in the pinning of grain boundaries but also retards the grain growth during sintering as described in reference [13]. Pull out pattern of CNTs indicates that these are embedded in the alumina grains and tied them up and hence resulted in the improved mechanical properties. At 2 and 3 wt% CNTs in alumina, the agglomeration can be observed as shown in figure 4 (c and d). The SEM images of CNT-alumina nanocomposites also depict the same
intergranular and transgranular fracture modes [9]. The images show no evidence of CNTs degradation reflecting that the CNTs can withstand at 1700°C in an inert atmosphere using conventional sintering.

3.5. Mechanical Behavior

Figure 5(a) shows the comparison of hardness of sintered monolithic alumina and CNT-alumina nanocomposites. The monolithic alumina has a hardness of 27.5 GPa after sintering at 1700°C which is better than sample sintered at 1600°C as reported in the previous work [9]. At a concentration of 1wt% CNTs in alumina matrix, the hardness is reduced by 9% compared to monolithic alumina. On further increasing the concentration to 2 and 3wt% CNTs, the hardness values follow the same decreasing trends with 27% and 40% respectively compared to monolithic alumina.

![Figure 5(a)](image_url1)

**Figure 5(a).** Hardness comparison of alumina and alumina-CNTs nanocomposites.

Figure 5(b) shows the comparison of fracture toughness of CNT-alumina nanocomposites with monolithic alumina. Fracture toughness of monolithic alumina after sintering is determined as 3.50 MPa m$^{1/2}$. On addition of 1wt% CNTs, fracture toughness of the nanocomposite is improved by 10% which is attributed to better dispersion of CNTs using gas purging sonication, reduced grain size of alumina, and crack deflection and bridging due to CNTs [1, 18, 19]. On further increasing the CNTs concentration, fracture toughness results have shown a decreasing trend but still maintaining a higher value compared with monolithic alumina.

![Figure 5(b)](image_url2)

**Figure 5(b).** Fracture toughness comparison of alumina and alumina-CNTs nanocomposites.

4. Conclusions

(1) The CNT-alumina nanocomposites were fabricated by a novel mixing technique of simultaneous sonication and gas purging prior to conventional sintering at 1700°C.

(2) Microstructure analysis presented a uniform distribution of 1wt% CNTs which were strongly bonded with the matrix and revealed a decrease in grain growth due to pinning effect showing an improvement in fracture toughness by 10% over monolithic alumina.

(3) Pressureless sintering at 1700°C provided better densification and hardness at 1wt% CNT-alumina nanocomposite but deteriorated the fracture toughness as compared to sintering at 1600°C.

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