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Spark plasma sintering of ceramic matrix composite based on alumina, reinforced by carbon nanotubes

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Abstract. Alumina composites reinforced with 3 vol.% multi-walled carbon nanotubes (MWCNTs) were prepared by spark plasma sintering (SPS). The influence of sintering temperature (1400-1600 °C) on the composites microstructure and mechanical properties was investigated. Microstructure observations of the composite shows that some CNTs site along alumina grains boundary, while others embed into the alumina grains and shows that CNTs bonded strongly with the alumina matrix contributing to fracture toughness and microhardness increase. MWCNTs reinforcing mechanisms including CNT pull-out and crack deflection were directly observed by scanning electron microscope (SEM). For Al_2O_3/CNT composite sintered at 1600 °C, fracture toughness and microhardness are 4.93 MPa·$m^{1/2}$ and 23.26 GPa respectively.

1. Introduction

Carbon nanotubes are widely used as reinforcements in polymers, metals, and ceramics to improve their mechanical and functional properties [1]. CNT has been considered as an ideal candidate for reinforcing/functioning elements because of small size, low density, high aspect ratio, and outstanding mechanical, electrical, and thermal properties. The demand for advanced composite materials comprising of high performance characteristics and improved functional properties is always rising [2]. Alumina, along with other ceramics like zirconia, silicon nitride, tungsten carbide, titania, etc., is not only being used as a biomedical material but also for high temperature applications in aerospace and automobile industries. This is due to its high hardness, good wear resistance, thermal/electrical insulation properties and excellent chemical inertness. But the main problem associated with alumina is its low fracture toughness which sometimes hinders its application as a structural material [3, 4]. Various types of particulate, whisker and fiber reinforcements have been used to improve the fracture toughness of alumina in the last few decades. In this regard, CNTs are achieving a lot of attention as a reinforcement candidate due to their good thermal stability up to 1800 °C [5] and excellent mechanical properties after sintering with alumina. CNTs connect the alumina grain boundaries and retard grain growth resulting in the grain refinement during the sintering at elevated temperatures which help in the improvement of fracture toughness, Young's and shear modulii [6]. The toughening mechanism of CNT-alumina composites is mainly attributed to the crack deflection at CNT-alumina interface, crack bridging and CNT pull-out from alumina grains [7]. Most studies have been based on laboratory-scale self-made composite powders, which cannot meet the

requirements of wider applications. In the present study, commercial Al_2O_3/CNT composite powders were used as raw materials and sintered by spark plasma sintering.

2. Materials and methods

Commercial α-Al_2O_3/CNT composite powder (Applied Carbon Nanotechnology Co., Ltd., Korea) with MWCNT contents of 3 vol.% were used as the starting powder. The particle morphology of initial composite powder and microstructures of the fracture surfaces were observed by means of a scanning electron microscope (JSM-7500FA, JEOL). A small amount of composite powder was dispersed onto a TEM grid to be characterized by transmission electron microscopy (TEM, JEM-2100F, JEOL). The measurements of particle size distribution of composite powder by means of laser diffraction method were performed with SALD-7101 (Shimadzu). Composites were prepared by spark plasma sintering (SPS-515S, Syntex) in a graphite die with an inner diameter of 15 mm at different sintering temperatures (1400, 1500, and 1600 °C), constant load of 40 MPa, heating rate 100 °C/min, and holding time 10 min. After sintering, the composites were allowed to cool naturally to room temperature. The density of the sintered disk-shaped composites was determined using the geometrical method. The theoretical densities were calculated according to the rule of mixtures, in which densities of 3.99 g/cm^3 and 2.10 g/cm^3 were assumed for the alumina and MWCNTs, respectively [8]. The relative density ρ is the ratio of the measured density to the theoretical density. Measurements of the microhardness H_V were performed with a PMT-3M (LOMO) microhardness tester under ambient conditions. The Al_2O_3/CNT composites were indented using a Vickers diamond pyramid with a load of 4.9 N applied on the surface for 15 s. At least 10 measurements were carried out for each sample. The diagonal lengths of the indents were measured using the attached microscope, converted to Vickers hardness number (HV) and further converted to GPa. A Vickers hardness tester TP-3R-1 was used for fracture toughness measurements using a load of 49 N. The fracture toughness values K_{IC} were calculated using the Anstis method [9]:

$$K_{IC} = 0.016 \left(\frac{E}{H_V}\right)^{1/2} \left(\frac{P}{c^{3/2}}\right),$$

where E is the Young's modulus, H_V is the microhardness, c the radial crack length generated by Vickers's indentation and P the load at failure.

3. Results and discussion

Figure 1a shows morphology of the Al_2O_3/CNT raw powder. The alumina particles are irregular in shape with size ranging from 100 nm to 9 μm. Aggregation of alumina particles is not observable.

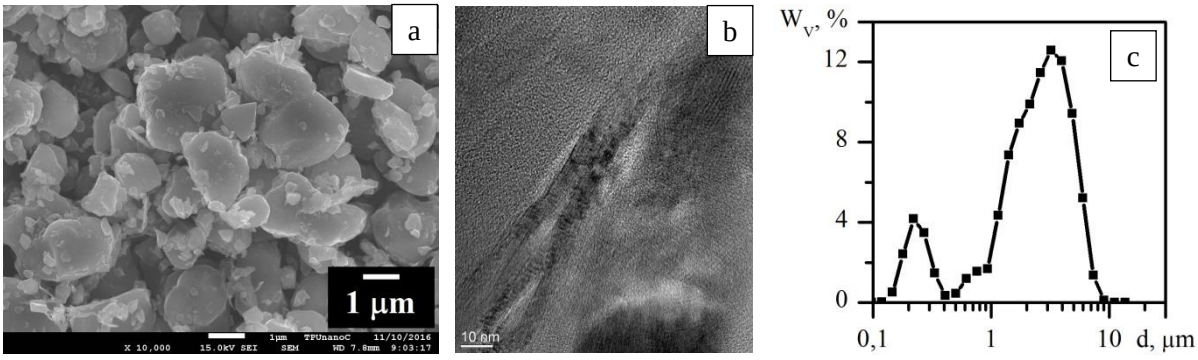

Figure 1. (a) SEM image showing morphology of composite powder, (b) TEM image showing morphology of MWCNT and (c) particle size distribution of composite powder.

Figure 1c shows the particle size distribution of composite powder. The average particle size of powder is approximately 1.7 μm. TEM images shown in Figure 1b display the morphology and surface features of the CNTs used in this research. The surface of the CNTs is not smooth, and hollow

core and numerous graphitic layers of the CNTs are clearly visible, although the layers are not concentrical and some compartments exist.

Let us now examine the three SEM micrographs of the sintered products obtained by SPS. First of all, it is seen that all of the samples, consist of 1-2 μm sized grains (Figure 2a, b, c) and there is no evidence of CNTs damage during sintering. Employing the SPS sintering, the densification of samples can be realized in short time without a considerable grain growth process. The CNTs are located mainly in the inter-granular places and in some cases incorporated into grains. As can be seen (Figure 2c), CNTs were distributed inside the alumina grains and strongly bonded with the alumina matrix.

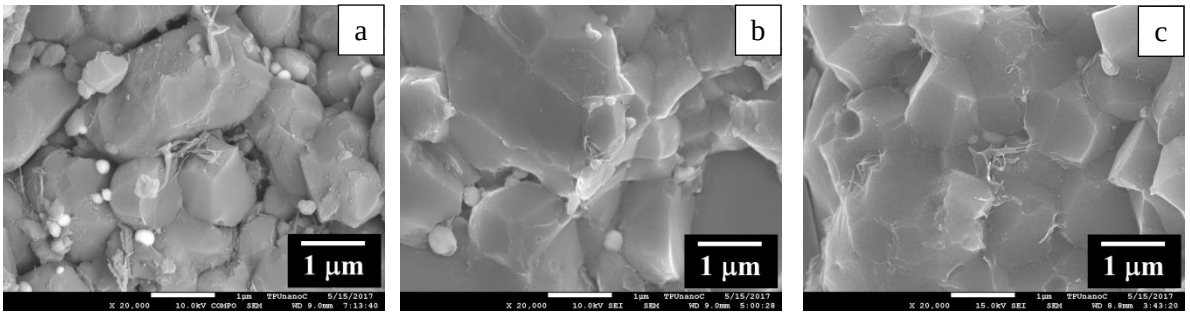

Figure 2. SEM images of the fractured surface of composites sintered at temperatures: (a) – 1400; (b) – 1500; (c) – 1600 °C.

As the sintering temperature rises from 1400 to 1600 °C, the density of the Al_2O_3/CNT composite increases (Table 1). It is evident that the temperature increase intensifies the processes of diffusion in solid and plastic deformation with attainment of creep threshold stress, and, therefore, of the material yield [10]. In this case, the whole free volume in solid is filled with the material, pore disappear, and a compressed (monolith) compound is formed (Figure 2c).

Table 1. Properties of Al_2O_3/CNT composites.

T (°C)	ρ (%)	H_V (GPa)
1400	89.80	14.69
1500	97.84	17.52
1600	98.60	23.26

Microhardness of composite Al_2O_3/CNT is 14.69 GPa after sintering at 1400 °C. With increasing the sintering temperature to 1500 and 1600 °C, microhardness values increase by 19 % and 58 % respectively (Table 1). For comparison, in [11-13] composites Al_2O_3 containing 3, 2.4 and 0.9 vol.% of MWCNTs fabricated by SPS had microhardness values of 18.40, 18.50 and 17.00 GPa, respectively. The composite Al_2O_3 with 2.5 vol.% of MWCNT obtained by hot pressing [14] and Al_2O_3 composite with 0.1 wt.% of MWCNT were densified by pressureless sintering [15] had microhardness values of 18.00 and 16.66 GPa, respectively. It is also worth noting that at a load of 4.9 N, no cracks appeared on the sample surfaces, which indicates an exceptionally high fracture toughness of the samples.

More detailed views about the characteristics of microstructure of composites are shown in Figure 3a, b. MWCNT tend to assemble in bundle of nanotubes as can be seen in Figure 3a which consist of several tubes and aligned along their length in van der Waals bonding with one another. CNT bundle (d ~ 180 nm) is embedded into the matrix and this bundle is divided into three little bundles (Figure 3a, d ~ 20-35 nm). MWCNTs, which seem to have been entrapped in the matrix grains during SPS, are cut near the grain surface (Figure 3b). As shown in Figure 3b, observed the formation of strong interface between CNTs and matrix. Also shown clear evidence of pulled-out

CNTs, which indicates that the CNTs bear significant stress by sharing a portion of the load and, at the same time, toughen the matrix by a bridging effect.

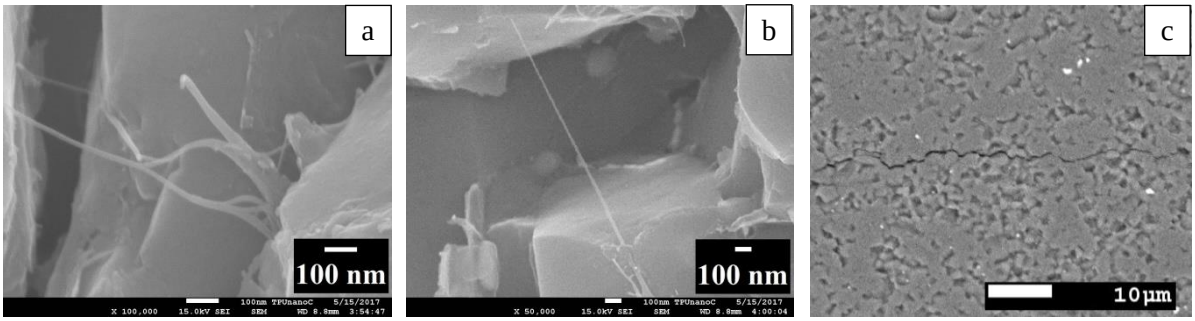

Figure 3. (a, b) SEM images of the fractured surface and (c) SEM images of crack on the surface of composite by indentation.

The fracture toughness of the Al_2O_3/CNT composite after sintering at 1600 °C is measured to be 4.93 MPa·$m^{1/2}$, which is high enough due to crack deflection, crack bridging and pull-out mechanism [16, 17]. The improvement in fracture toughness is also attributed to minimization of CNTs damage during sintering [18]. The crack is characterized by a small number of deviations at large angles and therefore, a very tortuous path occurs explaining the high efficiency of the deflection mechanism and therefore, an increase in fracture toughness (Figure 3c). MWCNT pull-outs were also detected on the fracture surface suggesting a strong bonding between CNT and Al_2O_3 matrix and significant load transfer from the matrix to carbon nanotubes during loading. In intergranular fracture the crack propagates along the grain boundary thus consumes more fracture energy, which is favorable for the increment of fracture toughness. However, our results shows that the toughness of the Al_2O_3/CNT composite sintered at 1600 °C is 4.93 MPa·$m^{1/2}$, which is 105 and 83 % increase in toughness over pure alumina with the same-as grain size (1.66 and 2 μm) 2.41 and 2.70 MPa·$m^{1/2}$ respectively [19, 20].

The SPS method has been useful to give high mechanical properties of the Al2O3/CNT composites. The SPS technique is a pressure-assisted fast sintering method based on high-temperature plasma momentarily generated in the gaps between powder materials by electrical discharge during on-off direct current pulsing. It has been suggested that the direct current pulse could generate several effects such as spark plasma, spark impact, Joule heating, and an electrical field diffusion [21]. Through these effects, the formation of a comparatively stronger bond between MWCNTs is expected for the SPS samples.

4. Conclusions

The investigated composites produced by SPS of the Al_2O_3/CNT composite powder presented strongly bonded CNTs with the alumina matrix. Microstructure investigation of the samples showed that structure of the composite sintered at 1600 °C is comprised of densely sintered grains of alumina surrounded by carbon nanotubes and some CNTs embedded into the alumina grains. The Al_2O_3/CNT composites thus fabricated showed effectively enhanced hardness and toughness compared to monolithic materials, which is based on the mechanisms CNT pull-out, CNT bridging and crack deflection. Multi-wall carbon nanotubes are attractive materials for reinforcement (strength and toughness) of ceramics and strong bonding of CNTs with matrix play an important role for reinforcement.

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