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Effect of carbon nanotube additions on the microstructure of hot-pressed alumina

Jeong-Wook An[a,b] and Dae-Soon Lim[a,b,*]

[a]*Division of Materials Science and Engineering, Korea University, Seoul 136-701, Korea*
[b]*Ceramic Processing Research Center, Hanyang University, Seoul 133-791, Korea*

Alumina/carbon nanotube (CNT) composites with different CNT contents were fabricated by hot-pressing to investigate the effect of CNT additions on the microstructure and mechanical properties of the composites. Alumina/CNT powders were obtained by forming the CNTs with the aid of catalyst particles supported on the alumina particles. The CNT contents were varied from 0 to 12.5 wt.% by changing the content of the iron nitrate catalyst precursor. The relative densities and the matrix grain size decreased with increasing CNT content. Hardness reached a maximum with about 4 wt.% added CNT. The effect of CNT additions on microhardness was explained by the matrix microstructure and reinforcement effect of CNT.

Key words: Carbon nanotube (CNT), Alumina/CNT composite, Microstructure.

Introduction

It is well known that the fracture toughness of ceramic materials is strongly dependent on their microstructure. To improve the fracture resistance of ceramic materials, there have been extensive studies on the incorporation of strong ceramic whiskers into ceramic matrices [1-3]. Recent studies of SiC whisker and carbon fiber reinforced ceramics reveal substantial improvements in toughness and wear resistance [4, 5]. Carbon nanotubes (CNTs) have recently been considered as reinforcing elements in ceramic matrix composites due to their unique mechanical properties [6, 7]. The tensile strength and Young's modulus of CNT have been measured to be as high as 200 GPa and 1 TPa, respectively, much higher than that of whiskers [8]. Siegel *et al.* reported that fracture toughness of alumina composites with 10 vol.% CNT added was increased up to 24% compared to monolithic alumina [9]. Controversial results with CNT/alumina composites also have been reported. Laurent *et al.* showed that the reinforcing effect that was expected from the addition of CNT bundles was not observed for CNT/Fe-Al_2O_3 composites [10]. The fracture toughness of CNT/alumina composites was lower than or similar to that of CNT/Fe-Al_2O_3 composites. However, observations by SEM indicated that nanotube bundles could dissipate some fracture energy. In this study, the effect of CNT content on the microhardness of CNT/alumina composites was investigated for better understanding of CNT-matrix interactions and the reinforcement effect of CNT.

*Corresponding author:
Tel : +82-2-3290-3272
Fax: +82-2-929-5344
E-mail: dslim@korea.ac.kr

Experimental procedure

Alumina/CNT composite powders were synthesized by the catalytic decomposition of acetylene over iron catalyst supported on alumina powders. Details of the composite powder synthesis method were reported elsewhere [11]. In brief, alumina/CNT composite powder was synthesized by the catalytic decomposition of acetylene with iron catalyst supported on alumina (iron content: 0.1, 0.5, 1.0 and 5.0 mol%). The production of CNTs was carried out at 750ºC with 2 hour reaction time under C_2H_2:H_2:N_2 gas flow in the ratio 20:100:400 sccm respectively. The weight percent carbon in the composite powder was obtained by an elemental analyzer (Flash EA 1112 series, CE Instruments, Italy).

The synthesized alumina/CNT composite powders were hot-pressed in a graphite die in argon atmosphere at 1800ºC under a pressure of 40 MPa for 1 hour. A pure alumina specimen (0 wt.% CNT content) was hot-pressed at 1300ºC for comparison. Relative densities were measured by the water displacement method assuming that no other forms of carbon were present except CNTs, and the density of the CNTs is the same as that of graphite (2.25 g/cm^3). Hardness was measured using a Vickers microhardness tester (SMV-2000, Shimadzu, Japan) under a load of 2N for 10 seconds. The fracture surfaces of the hot-pressed specimens were examined by a SEM (S-4300, Hitachi, Japan).

Results and Discussion

The carbon content of synthesized alumina/CNT composite powders with 0.1, 0.5, 1.0 and 5.0 iron catalyst content was 2.7, 4.1, 10.5 and 12.5 wt.% respectively. SEM and TEM images of the typical composite powder are shown in Fig. 1. The CNTs were

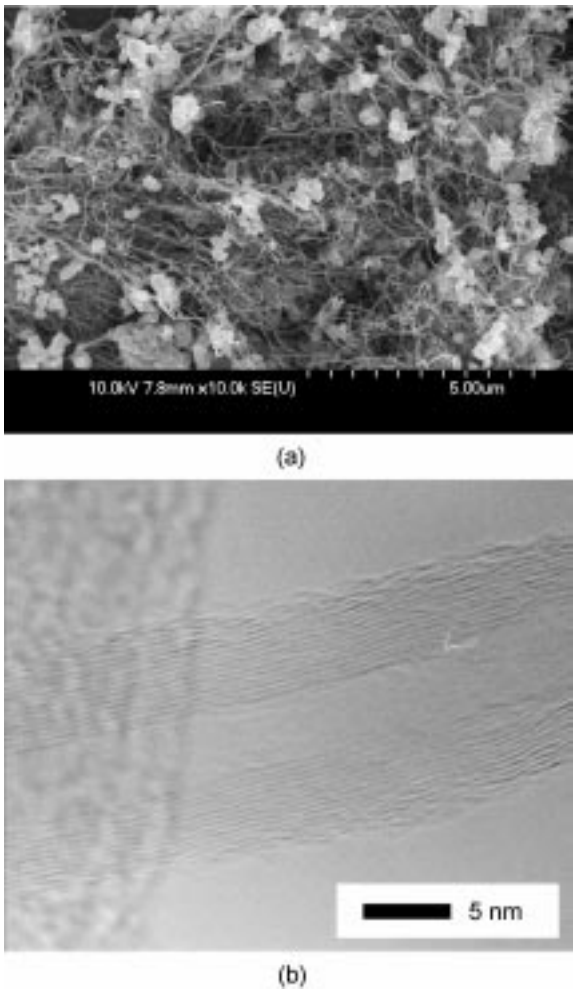

Fig. 1. Typical SEM (a) and TEM (b) micrographs of the composite powder synthesized by catalytic decomposition.

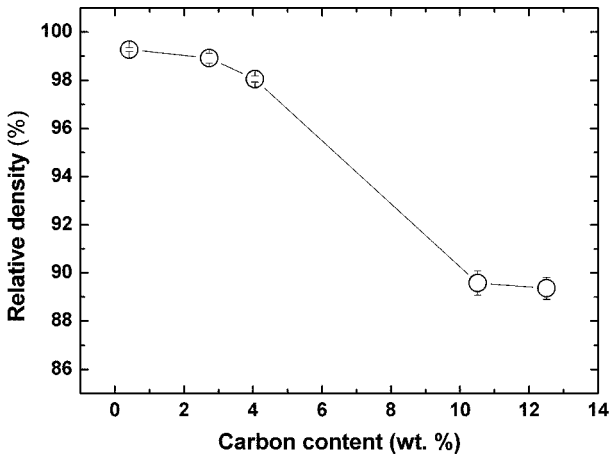

Fig. 2. Variations of the relative densities of samples as a function of the carbon content (CNTs).

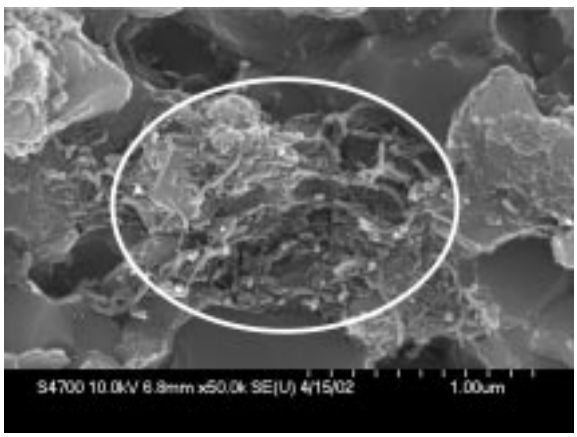

Fig. 3. SEM micrograph of the hot-pressed alumina/CNT composite with 10.5 wt.% CNT. The white circle shows CNT agglomerates in the alumina grain boundaries.

relatively homogeneously dispersed in the powders. The CNTs have a diameter of about 10-50 nm, while their length is about 5-10 μm. Figure 1(b) shows a typical TEM micrograph of a CNT. It clearly shows that the nanotube is a multi-walled hollow tube, not a solid fiber. The fringes on each side of the tube represent individual cylindrical graphitic layers. The CNT has approximately 15 to 20 walls of graphitized carbon. Details of the characterization of the composite powder can be found elsewhere [11].

The synthesized alumina/CNT composite powders were hot-pressed in a graphite die at 1800ºC under a pressure of 40 MPa for 1 hour. The relative densities of specimens as a function of the carbon content (CNTs) are shown in Fig. 2. The addition of CNT up to 4.1 wt.% has no significant influence on the densification behavior, even though the relative density decreases slightly with an increase in CNT content. However, at a higher CNT content (over 10 wt.%), the density decreased significantly. This sintering behavior might be related to the presence of CNTs, which hinders the densification of the composite by the formation of agglomerates at high CNT content. Similar sintering behavior was also reported in whisker reinforced ceramics. Fu *et al.* reported that at a higher SiC whisker content of 30%, the attainable density decreases significantly in SiC whisker toughened alumina composites [12]. Figure 3 shows CNT agglomerates (in the white circle) in grain boundaries of alumina with 10.5 wt.% CNT. This may hinder the grain growth and also adversely affect the mechanical properties.

The microhardness of alumina/CNT composites as a function of the CNT addition is shown in Fig. 4. The hardness shows an increase with increasing CNT content up to a maximum at 4% CNT. Hah *et al*. reported that the hardness of alumina is proportional to $(\text{grain size})^{-1/2}$ [13]. The grain size of composites hot-pressed at 1800ºC are shown in Fig. 5 as a function of the CNT addition. The grain size decreased with increasing CNT content. Because the addition of CNTs in alumina greatly decreases the grain size, a specimen with 0 wt.% CNT was hot-pressed at 1300ºC for comparison. The microhardness with 2.7 and 4.1 wt.%

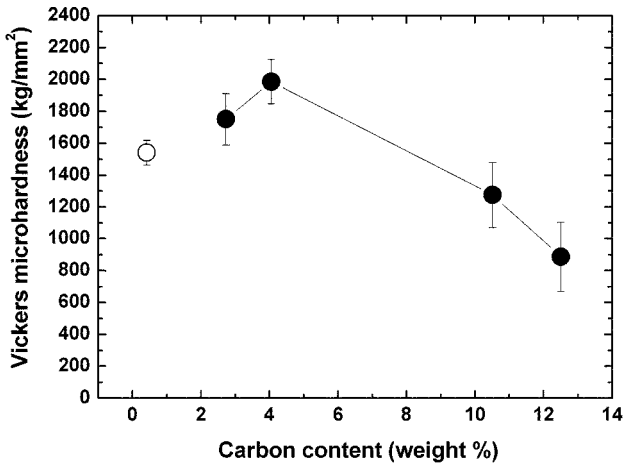

Fig. 4. Variations in the microhardness of alumina/CNT composites as a function of the CNT addition.

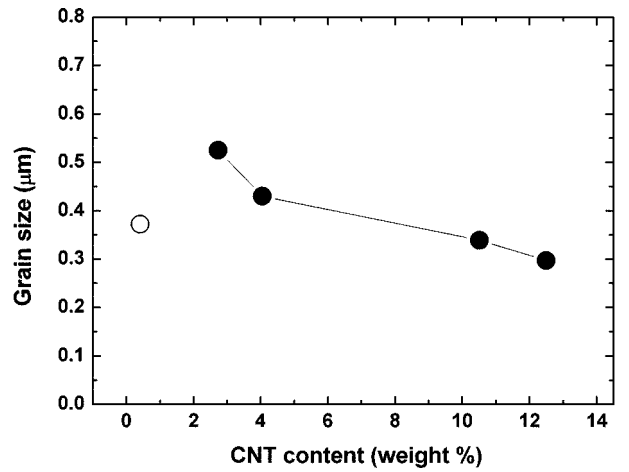

Fig. 5. The grain size of composites hot-pressed at 1800ºC as a function of the CNT addition. *The 0 wt.% CNT addition specimen was hot-pressed at 1300ºC for comparison.

CNT addition is expected to decrease compared to that of 0 wt.% CNT, if only the grain size effect was considered. However, the microhardness of 2.7 and 4.1 wt.% CNT specimens was higher than that of pure alumina. The reinforcement role of CNTs in alumina composite might affect the increase in hardness. Further addition of CNTs over 10 wt.% lowers the microhardness significantly. This phenomenon is probably due to the difficulty in dispersing CNTs homogeneously in the composite and the problem of the poor cohesion between CNTs and the matrix as suggested by Laurent *et al.* [10]. SEM micrographs of the fracture surface morphologies of hot-pressed samples confirm the above description. Figure 6 shows the fracture surfaces of hot-pressed samples containing 2.7, 4.1, and 12.5 wt.% CNT. The CNTs were located in the alumina grain boundaries. Although the hot-pressing temperatures were quite high (1800ºC), the CNTs remain and retain their shape. The grain size of alumina tends to decrease as the CNT content is increased. The cohesion

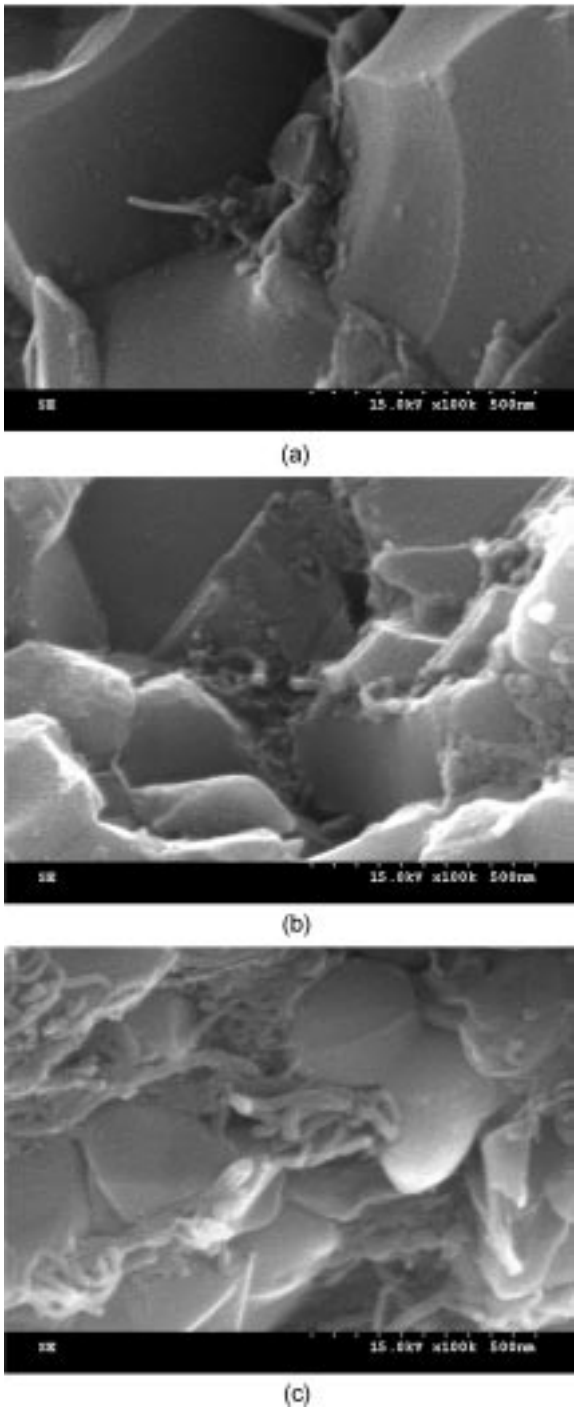

Fig. 6. Fracture surface morphologies of hot-pressed samples with (a) 2.7, (b) 4.1, and (c) 12.5 wt.% CNT content.

between the CNTs and alumina grains appears to decrease as the CNT content is increased.

Conclusions

Alumina/CNT composites with the CNT contents ranging from 0 to 12.5 wt.% were fabricated to investigate the effect of CNT additions on the microstructure. The alumina/CNT composites were obtained by hot-

pressing the alumina/CNT composite powders which had been synthesized by the catalytic decomposition of acetylene over alumina powders impregnated with iron catalysts. The relative densities were lower and the matrix grain size was smaller with increasing CNT content. The enhanced microhardness at 2.7 and 4.1% CNT is a result of the CNTs acting as reinforcing filler in the alumina composite and the grain size effect. However, when the CNT content is over 10%, the mechanical properties are degraded because of the relatively lower density due to the poor cohesion between the CNT and the alumina matrix.

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