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Fabrication Process and Mechanical Properties of Carbon Nanotube Reinforced Alumina Nanocomposites

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Key Words : Carbon nanotube, Alumina, Nanocomposite, Mechanical properties

ABSTRACT

A novel process to fabricate carbon nanotube (CNT)/alumina nanocomposites, consisting of a molecular level mixing process and an in situ spark plasma sintering process, is proposed. The CNT/alumina nanocomposites fabricated by this proposed process show enhanced hardness due to a load transfer mechanism of the CNTs and increased fracture toughness arising from the bridging mechanism of CNTs during crack propagation

1. Introduction

Since the discovery of carbon nanotubes (CNTs), they have been considered as the most promising reinforcements for composite materials to overcome the performance limits of conventional materials [1–3]. Therefore, there have been several attempts to fabricate CNT/alumina nanocomposites with enhanced hardness and toughness [4–8]. However, previously reported CNT/ceramic nanocomposites show much inferior mechanical properties than expected or, in some cases, even worse mechanical properties than those of monolithic ceramic materials [4–7]. Several processes have been proposed to fabricate CNT/ceramic nanocomposites. Zhan et al. Fabricated CNT/alumina nanocomposite by blending dispersed single-walled nanotubes with nanocrystalline alumina powders, followed by the spark plasma sintering (SPS) process [4]. The CNT/alumina nanocomposite produced shows much enhanced fracture toughness. However, the hardness of the CNT/alumina nanocomposite decreased with increasing CNT content. CNT/oxide nanocomposites have also been fabricated by growing CNTs on powders

mixed with catalyst, followed by the sintering process [5,6]; however, these show little improvement in the fracture toughness. Such results are far from the properties expected, considering the extraordinary mechanical properties of CNTs. There are two main reasons: one is the weak bonding between CNTs and ceramic matrix and the other is the inhomogeneous distribution of CNTs within the ceramic matrix. Recently, CNTs have been homogeneously dispersed within the alumina matrix by the sol–gel process [8]; however, the interfaces between CNTs and alumina matrix are not strong. The most promising process to obtain homogeneous dispersion of CNTs and strong interfacial strength is the molecular level mixing process, consisting of reaction between functionalized CNTs and metal ions in solution, which was originally designed for CNT/metal nanocomposites [9]. In this study, the CNT/amorphous-Al_2O_3 composite powders were fabricated by the molecular level mixing process to obtain strong interfacial bonding and homogeneous mixing between CNTs and Al_2O_3 powders. At the same time, the CNT/amorphous-Al_2O_3 composite powders were consolidated into CNT/alumina nanocomposites by an in situ SPS process.

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2. Experimental Procedures

2.1 Fabrication of CNT/amorphous-Al_2O_3 composite powders

Multi-walled carbon nanotubes fabricated by chemical vapor deposition were obtained from Iljin Nanotech. Co. The CNTs were acid treated with HF, HNO_3 and H_2SO_4 and oxidized at 190℃ for 4 h to remove catalysis particles and to generate functional groups on the surfaces of the nanotubes; the functionalization of CNT can be obtained by acid treatment as reported elsewhere [10–13]. The acid treated carbon nanotubes were sonicated for 24 h in distilled water for homogeneous dispersion. $Al(NO_3)_3$·$9H_2O$ was added into a suspension with the carbon nanotubes and these were sonicated for 24 h. This solution was vaporized by heating to 100℃ and the powders that remained were oxidized at 350℃ for 6 h in air atmosphere. The volume fractions of CNTs varied from 0 to 1.8 vol.%. During the calcination process, the chemical bonding between CNT and amorphous Al_2O_3 matrix was formed and confirmed as shown in Fig. 1a.

2.2 Spark plasma sintering

Spark plasma sintering was carried out with Dr. Sinter 1500 SPS machine from Sumitomo Coal Mining Co. The composite powders were compacted in a graphite mould with a diameter of 8 mm and were heated by pulsed electric current at a vacuum pressure of 1 Pa. The heating rate was fixed as 100℃/min. The hardness of the carbon nanotube reinforced alumina matrix nanocomposite was measured using the Vicker┐s indentation test under a load of 9.8 N and the fracture toughness was evaluated by measuring the crack length generated after indentation.

3. Results and Discussion

The above process can produce homogeneously dispersed CNTs implanted in amorphous Al2O3 powderwith chemical bonding between CNTs and amorphous Al_2O_3. The key feature of this process is that the CNTs and metal ions are mixed homogeneously in an aqueous solution at a molecular level. Therefore, the critical problem of the strong agglomeration of CNTs reported in solid state mixing within a matrix and strong bonding between CNTs and a matrix can be solved by using the molecular level mixing process. The morphology of CNT/Al_2O_3 composite powders showed that the CNTs are homogeneously distributed within the powders as shown in Fig. 1b. In particular, the bridging effect of CNTs across two crack surfaces was observed

when the calcinated composite powder was fractured as shown in Fig. 1c. The composite powders were crystallized and consolidated by the in situ SPS process. SPS enables powder compacts to be sintered by Joule heat and spark plasma generated by pulsed high electric current through the compact [14].
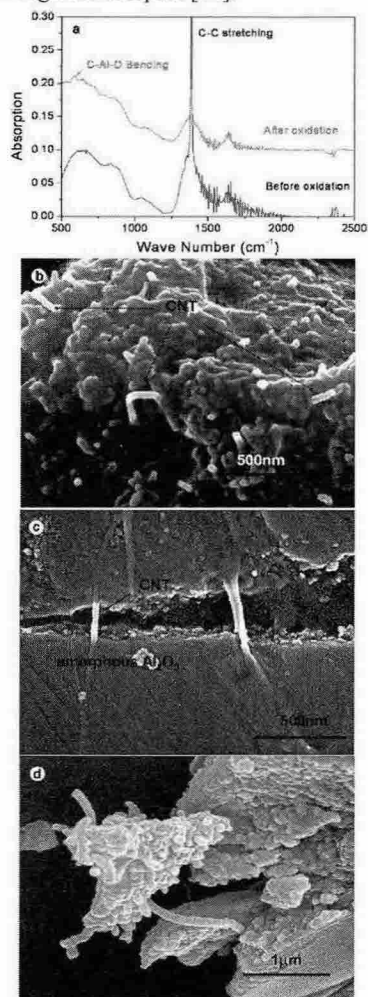

Fig. 1. (a) FT-IR analysis of CNT/amorphous-Al_2O_3 composite powders before and after calcination process. (b) SEM micrographs of surface of a CNT/amorphous-Al_2O_3 composite powder, in which carbon tubes were implanted in amorphous-Al_2O_3 powder. (c) Carbon nanotubes showing the bridging mechanism across a crack in amorphous-Al_2O_3 matrix observed from cross-sectional SEMmicrograp hs of CNT/amorphous-Al_2O_3 composite powders. (d) Small amorphous-Al_2O_3 fragment connected to powder by carbon nanotubes.

Various information on the crystallization, phase transformation and densification of the CNT/amorphous-Al_2O_3 compact was analyzed from the observation of the shrinkage behavior during the in situ spark plasma sintering. In the first stage, the amorphous- Al_2O_3 powders reinforced with CNTs were crystallized at

600℃~800℃ and phase transformation occurred at 1000℃ during in situ SPS. In the second stage, the crystallized Al_2O_3 and CNTs were densified into CNT/a-alumina nanocomposite after SPS at 1500℃ for 5 min as shown in Fig. 2a. The XRD analysis indicates that the amorphous Al_2O_3 powders implanted by the CNTs were sintered into CNT/a-alumina nanocomposite by the in situ SPS process as shown in Fig. 2b. The fracture surface of the sintered CNT/alumina nanocomposite is shown in Fig. 2c.
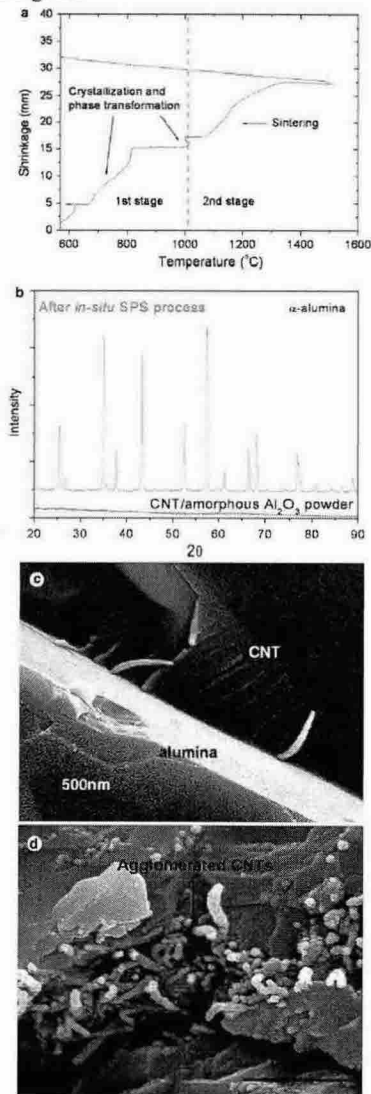

Fig. 2. (a) A plot of shrinkage with increase in temperature during spark plasma sintering of CNT/amorphous-Al_2O_3 powders. (b) XRD analysis results obtained before and after in situ spark plasma sintering of CNT/amorphous-Al_2O_3 powders. (c) The pulled-out carbon nanotubes on the fracture surface of CNT/alumina nanocomposite when the CNT volume fraction was 1.0%. (d) The agglomerated carbon nanotubes and pores on the fracture surface of CNT/alumina nanocomposite with CNT volume fraction of 1.8%.

The CNTs were homogeneously dispersed within grains or at grain boundaries of the alumina matrix. It is also shown that the amorphous alumina matrix is completely crystallized into a crystalline a-alumina phase. The most important feature in the fracture surface of the CNT/alumina composites is that the CNTs are pulled-out during the fracture process. In previous reports on CNT/alumina fabricated by conventional mixing of CNT and alumina powders, most of the CNTs were located at grain boundaries of alumina matrix [4]. However, fractography of the CNT/alumina nanocomposite, fabricated by the molecular level mixing process followed by in situ SPS, shows 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. Therefore, it is expected that the CNTs within the alumina matrix simultaneously strengthen and toughen the alumina matrix. Furthermore, the chemical bonding between the CNTs and the matrix fabricated by molecular level mixing of CNTs and Al ions can enhance the efficiency of load transfer from matrix to CNTs. However, when the volume fraction of carbon nanotube increases over 1.8 vol.%, the CNTs tend to be agglomerated as shown on the fractured surface in Fig. 2d. The mechanical properties shown in Fig. 3 strongly support the suggestion of strengthening and toughening by CNTs in the alumina matrix. The hardness of the CNT/alumina composite increases with increasing CNT volume fraction up to about 1%. However, it decreases when the CNT volume fraction increases above about 2% due to the agglomeration of CNTs as shown in Fig. 2d.
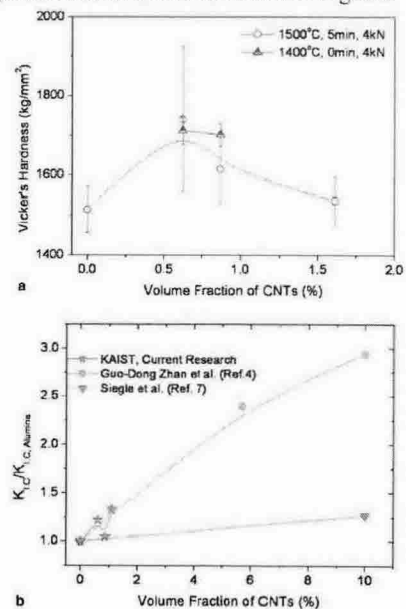

Fig. 3. (a) Variation of the hardness of CNT/alumina nanocomposite with varying CNT volume fraction, and (b) variation of the fracture toughness of CNT/alumina nanocomposite, normalized by that of alumina matrix, with increasing volume fraction of CNTs.

The fracture toughness of the CNT/alumina composite increases with increasing volume fraction of CNTs, which is comparable to the results of other researchers [4–7]. It is concluded that the homogeneous distribution of CNTs within the alumina matrix and the formation of strong interfaces between CNTs and alumina enhances both the strength and the toughness of CNT/alumina nanocomposites. It should be noted that multi-walled CNTs were used in the current research. In previous research, it was suggested that only singlewalled CNTs could improve the fracture toughness of CNT/alumina nanocomposites [4]. However, the multiwalled CNTs in CNT/alumina nanocomposites, fabricated by the process described above, have improved not only fracture toughness but also hardness in this study. Therefore, the homogeneous distribution of CNTs in the alumina matrix and strong interfacial bonding between CNTs and alumina matrix are the most important factors in obtaining strengthening and toughening of CNT/alumina nanocomposites.

4. Conclusions

The CNT/alumina nanocomposites are fabricated by a molecular level mixing process, followed by an in situ SPS process. The CNT/alumina nanocomposites show homogeneously distributed CNTs strongly bonded with the alumina matrix. The CNT/alumina nanocomposites thus fabricated showed an enhanced hardness and toughness compared to monolithic materials, which is based on the load sharing and bridging mechanisms of CNTs in the alumina matrix.

Acknowledgement

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