MEASUREMENTS OF CARBON NANOTUBE TENSILE STRENGTH AND MECHANICAL PROPERTIES OF CARBON NANOTUBE/ALUMINA COMPOSITES PREPARED BY PRESSURELESS SINTERING

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Abstract

In this research, the effects of MWCNT addition on mechanical properties of pressureless sintered MWCNT/alumina composites were investigated by using four types of MWCNTs having different nanostructures and fracture characteristics. Tensile-loading experiments revealed that there was an optimal annealing temperature for improving the fracture properties of MWCNTs. MWCNTs treated at 1800˚C, 2200˚C and 2600˚C displayed enhancements to their nominal tensile strengths by factors of ~5.3, ~5.2 and ~1.8, respectively, compared to MWCNTs treated at 1200˚C. Fracture tests of MWCNT/alumina composites showed that the MWCNTs annealed at 2200˚C was the most effective in improving the bending strength and fracture toughness of the MWCNT/alumina composites. These experimental results implied the effectiveness of the use of MWCNTs having a much higher load carrying capacity for preparation of tougher ceramic composites.

1 Introduction

Novel materials and processing routes provide opportunities for the production of advanced high performance structures for different applications. Ceramic matrix composites are one of these promising materials. Engineering ceramics such as Al_2O_3, Si_3N_4, SiC and ZrO_2 produced by conventional manufacturing technology have high stiffness, excellent thermostability and relatively low density, but brittle nature restricted them from many structural applications [1]. Several approaches have been adopted to improve the fracture toughness of ceramics. As one possible approach, incorporation of particulates, flakes and short/long fibers into ceramics matrix, as a second phase, to produce tougher ceramic materials is an eminent practice for decades [2,3]. Recently, researchers have focused on the carbon nanomaterials, in particular carbon nanotubes (CNTs), which are nanometer-sized tubes of single- (SWCNTs) or multi- layer graphene (MWCNTs) with outstanding mechanical, chemical and electrical properties [4], motivating their use in ceramic composite materials as a fibrous reinforcing agent. However, most results for strengthening and toughening have been disappointing, and modest improvement or even deterioration have been reported in CNT/ceramic composite materials [5], presumably owing to the difficulties in homogeneous dispersion of CNTs in the matrix and in formation of adequate interfacial connectivity between two phases. Although several techniques have been proposed to improve dispersibility of CNTs in ceramic matrix and to control interface connectivity in the studies previously reported [5], these routes involved additional processes, thus, limit easy processing and wider use of such composites In addition, pressure-assisted sintering methods such as spark plasma sintering (SPS) and hot pressing (HP) are the two techniques that have been commonly employed to prepare CNT/ceramic composites [5]. However, these methods are inappropriate for producing components with complicated shapes. Furthermore, work done to date has utilized CNTs with a variety of different nanostructures, with the choice of CNT materials often dictated by availability or processing considerations. Thus, effects of different CNT nanostructures on the microstructure and mechanical properties of CNT composites have heretofore not yet been addressed.

In this research, we compared four types of MWCNTs having different nanostructures and fracture characteristics as a fibrous reinforcing agent in alumina. Structures-properties relationship of these MWCNTs was investigated through transmission electron microscope (TEM) observations and tensile-loading experiments with individual MWCNTs. Alumina composites made with the above-mentioned MWCNTs were prepared by a simple mechanical mixing method followed by pressureless sintering. The effects of tensile strengths of the MWCNTs on mechanical properties of the resultant composites were investigated. Achieving tougher ceramic composites with MWCNTs is discussed based on these results.

2 Materials and testing methods

2.1 Tensile-loading experiment sample preparation

Chemical vapor deposition-grown MWCNTs followed by a series of high temperature annealing at 1200˚C, 1800˚C, 2200˚C and 2600˚C were used as a starting material for preparation of MWCNT/alumina composites. Tensile-loading experiments were carried out using an *in-situ* scanning electron microscope (SEM, JEOL, JSM-6510) method with a nanomanipulator system [6]. Further details of the sample preparation are described elsewhere [6]. The atomic force microscope cantilevers served as force-sensing elements and the applied force was calculated from the angle of deflection at the cantilever tip [6]. A crosshead speed, i.e., movement rate of the cantilever, of about 100 nm/s was applied for the pullout tests. Each MWCNT diameter was measured by TEM (Hitachi HF-2000).

2.2 Preparation and evaluation of MWCNT/alumina composites

A typical synthesis procedure for the composite preparation is as follows. Four types of the pristine MWCNTs were separately dispersed in isopropyl alcohol (IPA, Wako Pure Chemical Industries) with the aid of ultrasonic agitation. An alumina powder (TM-DAR, Taimei chemicals) was added to the MWCNT-IPA slurry and mechanically mixed using a planetary centrifugal mixer at 2000 rpm for 30 min. The resultant mixture was dried in an air oven at 60˚C. 24 mm diameter pellets were formed by uniaxial dry pressing at 200 MPa followed by cold isostatic pressing at 200 MPa. The composites were prepared by pressureless sintering (TG2162, Toei Scientific Industrial) in a graphite crucible in resistance heated graphite element furnace at a temperature of 1400˚C under flowing Argon-Hydrogen mixtures. The bending strength and fracture toughness of the composites was measured by the three-point bending method and by the single-edge notched beam (SENB) method, respectively. A notch with depth and width of 0.3 mm and 0.1 mm for the SENB tests was cut in the center part of the test specimens. The bending strength (σ_b) and fracture toughness (K_{Ic}) are given by the following equations:

$$\sigma_b = 3P_bL / 2bh^2 \tag{1}$$

$$K_{Ic} = \left(3P_b L / 2bh^2\right) \cdot a^{1/2} Y \tag{2}$$

where P_b is the maximum load, L the span length, b the specimen width, h the specimen thickness, a the notch depth and Y the dimensional factor. All surfaces of the specimens were finely ground on a diamond wheel, and the edges were chamfered. Raman scattering spectroscopy (Jobin-Yvon T64000, Horiba) was used to analyze the defect rate of carbon nanotube structure. Measurements were carried out at room temperature using an Ar ion laser in a backscattering.

3 Results and discussion

It was demonstrated from the nanostructural analyses and the tensile-loading experiments that the different annealing temperatures led to different nanostructures and tensile strengths of MWCNTs. We used Raman spectroscopy to analyze the disordered structure of carbon present in the MWCNTs. As shown in Fig. 1, the Raman scattering spectrum of the MWCNTs displayed a pair of bands around 1360 cm^{-1} (D-band) and 1590 cm^{-1} (G-band). The intensity ratio I_G/I_D (R value) is known to depend on the number of defects in the CNTs. The R values of the samples increased with increasing annealing temperature, indicating that the defective carbon networks in the structure decreased after high temperature annealing. This implies that the defective carbon networks transformed into a stable graphite planer structure by annealing process. However, the Raman analysis provides no information about the structure of the MWCNTs. Thus, structural observation of these samples was carried out by TEM. TEM images of the MWCNTs treated at the different annealing temperatures are shown in Fig. 2. For the MWCNTs annealed at 1200˚C, disordered and undulated fringes are typical characteristics, showing a highly disordered nanostructure. When the annealing temperature increases up to 2600˚C, graphene walls tend to be aligned with the tube axis, indicating that highly disordered nanotubes are developed into a highly crystalline structure. In order to understand the structures-properties relationship of these MWCNTs, we investigated the mechanical behavior of the MWCNTs using the nanomanipulator tool described previously.

Fig. 3 shows the relationship between the annealing temperatures and the fracture properties of the MWCNTs. Here, the tensile strength was calculated based on the cross sectional area of

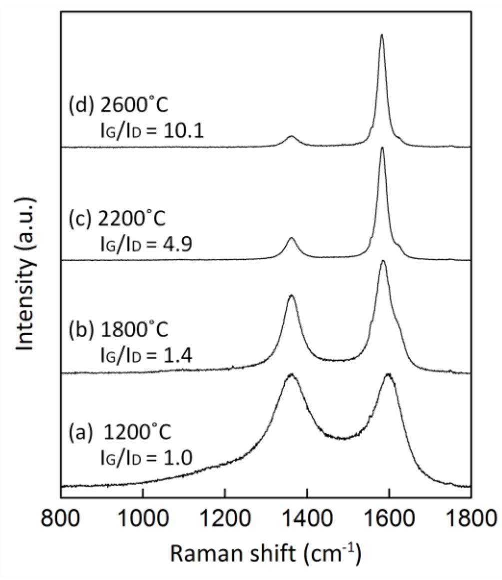

Figure 1. Raman spectra of MWCNTs annealed at temperatures of (a) 1200˚C, (b) 1800˚C, (c) 2200˚C and (d) 2600˚C, respectively. The Raman intensity ratio I_G/I_D estimated from the peak position of the D-band and G-band are also indicated.

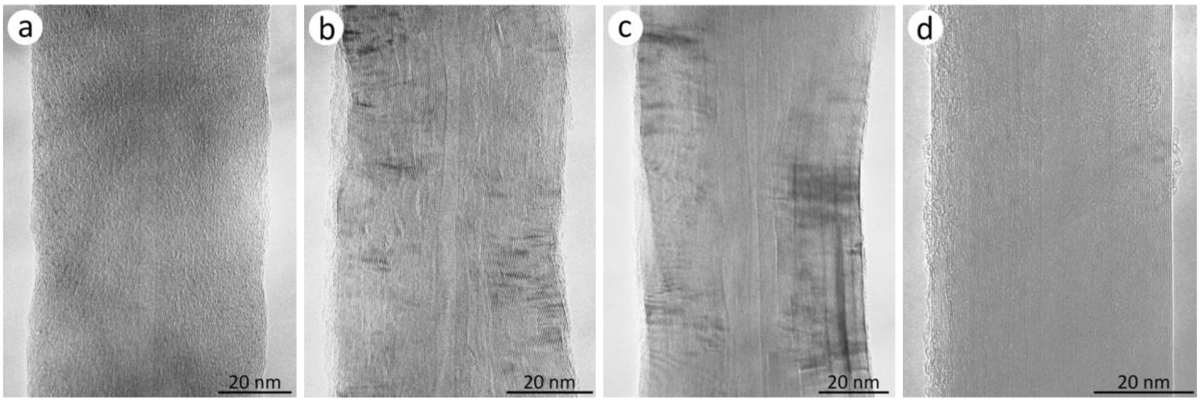

Figure 2. TEM images of MWCNTs treated with different annealing temperatures. Annealing temperatures are (a) 1200˚C, (b) 1800˚C, (c) 2200˚C and (d) 2600˚C, respectively.

the full specimen. It is clear that there is an optimal annealing temperature for improving the fracture properties of the MWCNTs. Breaking force and nominal tensile strength were simultaneously increased around at 1800˚C~2000˚C, and then they were decreased gradually with increasing annealing temperature. The MWCNTs treated at 1800˚C, 2200˚C and 2600˚C displayed enhancements to their tensile strengths by factors of ~5.3, ~5.2 and ~1.8, respectively, compared to the MWCNTs treated at 1200˚C. TEM observation of the broken nanotube fragments revealed a variety of fracture patterns. They are presented as examples of what happens as a result of loading to breaking. The MWCNT treated at 2600˚C broke in the outer shells and the inner core was pulled away from the outer shells (Figs. 4A-4D), i.e., they underwent failure in a "sword-in-sheath" fracture mode, as observed for arc discharge-grown MWCNTs under tensile loading [7]. The other types of the MWCNTs failed leaving either a very short sword-in-sheath failure or a "clean break", as exemplified in Figs. 4a-4f. These results suggested that the improvement of tensile strength may be due to the moderate development of crystal structure by the annealing treatment. The irregular shell structure of the MWCNTs treated at the moderate annealing temperatures may be facilitated by a significant intershell load transfer.

The variability in the MWCNT strengths motivated our research of the mechanical properties of the composites prepared with the MWCNTs having different fracture characteristics. We prepared the MWCNT/alumina composites by using the pressureless sintering method, and

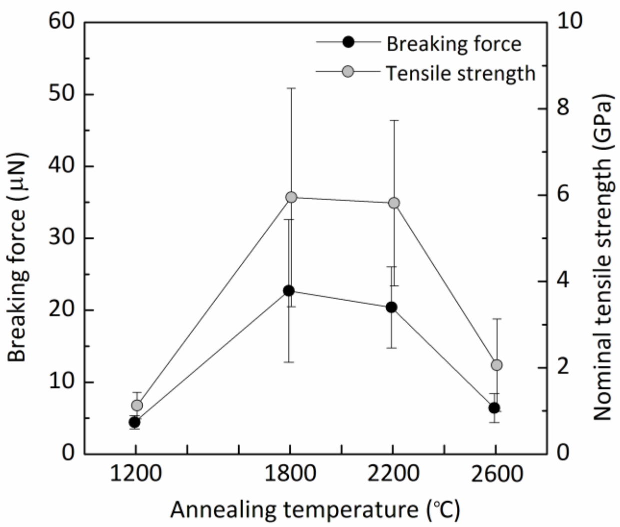

Figure 3. Breaking force and nominal tensile strength of single MWCNTs as a function of MWCNT annealing temperature.

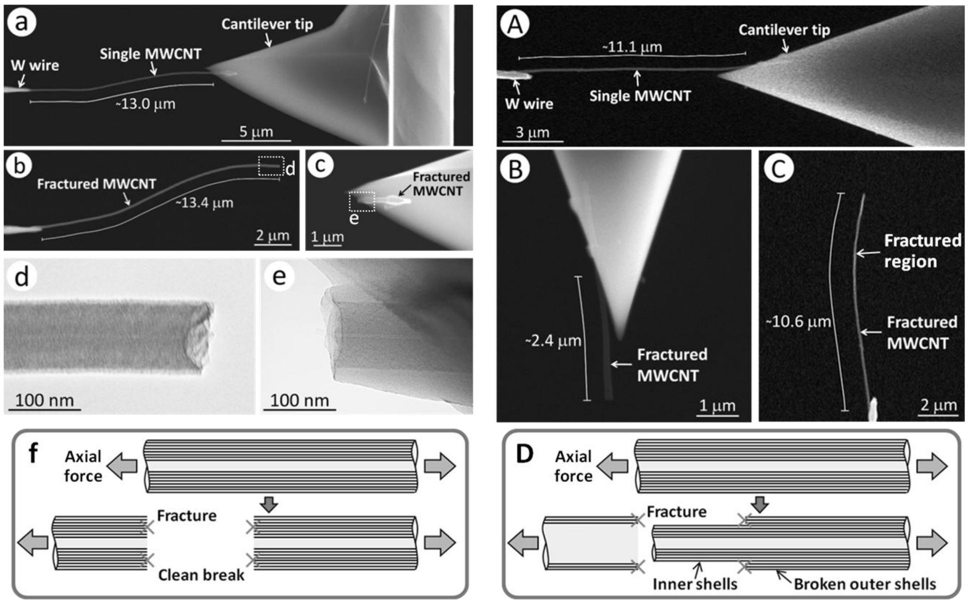

Figure 4. Two series of SEM and TEM images for each of two individual MWCNTs, captured before and after their breaking. Annealing temperatures of samples are (a-f) 1800˚C and (A-D) 2600˚C, respectively.

investigated the fracture properties of the resultant composites. Results obtained from the fracture tests revealed that even though there is no clear correlation between the fracture properties of the composites and the tensile strengths of the individual MWCNTs, the MWCNTs having higher tensile strength seems to lead to higher mechanical properties of the composites. Fig. 5 displays the dependence of the bending strength and the fracture toughness on the MWCNT content in the composites. There are few papers which report significant improvement in the mechanical properties such as toughness [8], and the improvement by MWCNT addition has been limited so far in previous studies [5]. In our composites, however, the bending strength and the fracture toughness simultaneously increased with the addition of a small amount of the MWCNTs. The composites made with the MWCNT treated at 2200˚C showed both higher bending strength and fracture toughness than those of the composites made with the other types of MWCNTs. The bending strength and fracture toughness of the composite containing 0.9 vol.% MWCNT treated at 2200˚C reached 742.6 ± 13.1 MPa and 5.83 ± 0.19 MPa·$m^{1/2}$, respectively, and were approximately 25% and 45% higher than the MWCNT-free alumina. A large increase in the fracture properties may be attributed to the use of the MWCNT having a higher load carrying capacity. However, according to the current

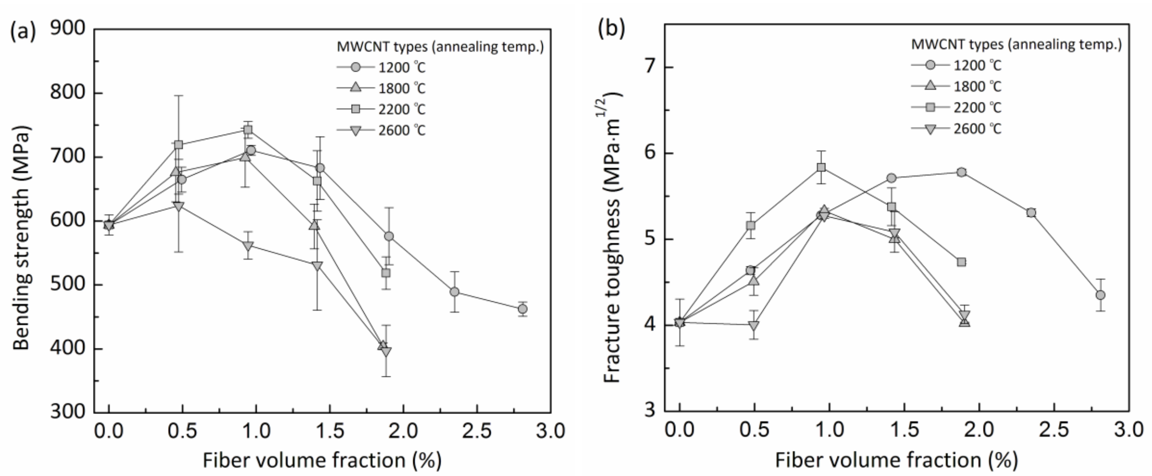

Figure 5. (a) Bending strength and (b) fracture toughness of the MWCNT/alumina composites as a function of MWCNT content.

SEM observations on the composite fracture surfaces, the dispersibility of the MWCNTs in the matrix appears to be different among the four types of the composites. It has been recognized that surface conditions of CNTs have an impact on the dispersibility of CNTs in solvents [9]. In this research which used four types of the MWCNTs having different surface structures, the dispersibility of the MWCNTs in the alumina matrix is expected to depend on the MWCNT types. Further researches are needed to accurately clarify quantitatively the contribution of the MWCNT strength to the enhanced mechanical properties of the composites prepared in this research.

The strengthening and toughening mechanisms of composites by fibers are now well established [2,3]; central to an understanding is the concept of interaction between the matrix and reinforcing phase during the fracture of the composite. The fracture properties of such composites are dominated by the fiber bridging force resulting from debonding and sliding resistance, which dictates the major contribution to the strength and toughness. To obtain in-depth understanding of fracture mechanisms of our composites, microstructural observation was carried out using SEM and TEM. SEM images shown in Fig. 6 display the morphology of the fracture surface of the composites. From the fracture surface, the following features can be noted. First, as shown in Fig. 6a, the fracture surface of the composite exhibits protruding MWCNTs from the crack flank. Most of MWCNTs are located in the intergranular phase, and their lengths are in the range 0~10 μm. Similar observations were made by others types of the composites. The average grain sizes of alumina matrix in the 1.9 vol.% MWCNT composites were typically 1.0~1.2 μm, which were smaller than the grain size of 1.40 ± 0.16 μm observed in the MWCNT-free alumina sintered under the same conditions. Second, in the case of the smaller amount of the MWCNTs, no severe phase segregation was observed for all types of

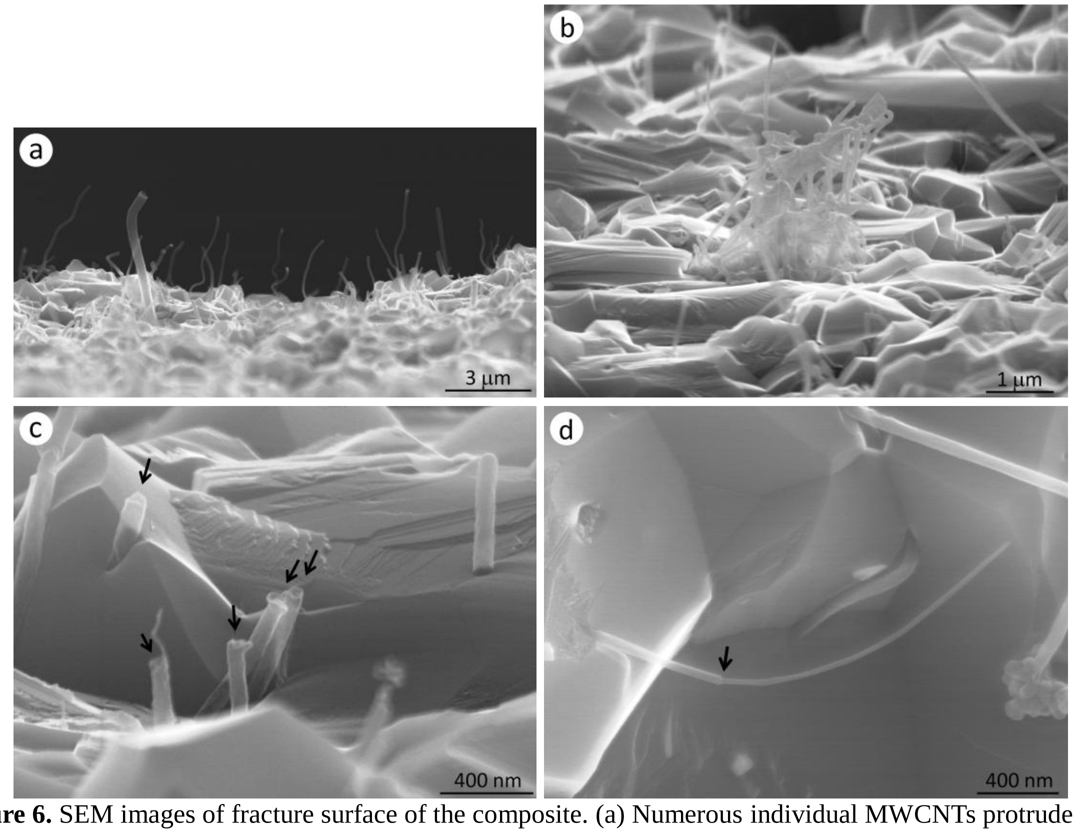

Figure 6. SEM images of fracture surface of the composite. (a) Numerous individual MWCNTs protrude from the clack plane. (b) Presence of clustered MWCNTs in the composite. (c,d) Some MWCNTs have broken in the multi-wall failure. MWCNT annealing temperatures and volume fractions are (a) 1200˚C, 2.8%, (b,c) 1800˚C, 0.5% and (d) 2600˚C, 0.5%, respectively. Black arrows in (c) and (d) indicate the location where the MWCNT undergo failure.

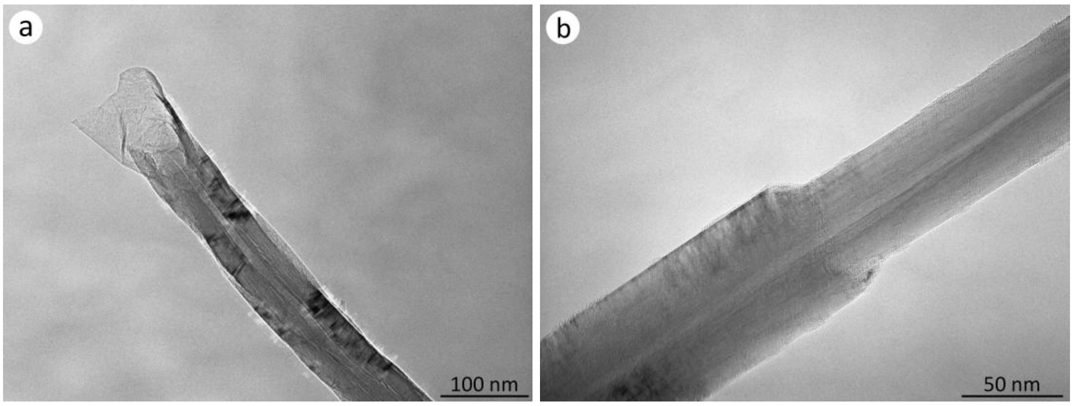

Figure 7. TEM images of the fracture surface of composites. MWCNT annealing temperatures and volume fractions are (a) 2200˚C, 0.5% and (b) 2600˚C, 0.5%, respectively.

the composites. In contrast, some clusters were present at the higher MWCNT contents as exemplified in the microstructures of the composite containing 1.9 vol.% MWCNTs (Fig. 6b). The degradation of both bending strength and fracture toughness observed for the composites with larger amount of the MWCNTs may be primarily attributed to the presence of such clustered MWCNTs. Because the cluster of MWCNTs has poor load-carrying ability, the effect of this kind of clustered MWCNTs in the matrix may be similar to that of pores [10]. Note that even though some clusters were observed for all types of the composites, the number of the clusters in the composite made with MWCNT treated at 1200˚C appeared to be much smaller compared with the other types of the MWCNTs. Third, some MWCNTs on the fracture surface showed a clean break near the crack plane, and that the diameter of the MWCNT drastically slenderized toward their tip, as illustrated in Figs. 6c and 6d, respectively. TEM was used to further examine the detailed morphology of the fractured MWCNTs.

The TEM observations on the fracture surface demonstrated that MWCNT failure was evidently observed for all types of the MWCNTs, as exemplified in Fig. 7. At least, 25% MWCNTs appear to fail leaving either the clean break or sword-in-sheath failure. As shown in Fig. 7a, the MWCNT failure is clearly observed for the composite made with 0.5 vol.% MWCNT treated at 2200˚C. The same fracture morphology is observed in the tensile-loading experiments of the MWCNTs treated at 1200˚C, 1800˚C and 2200˚C (Figs. 4a-f). In contrast, the MWCNT treated at 2600˚C underwent failure in the sword-in-sheath fracture mode (Fig. 7b). This morphology is quite similar as observed in the fracture morphology of the MWCNTs treated at 2600˚C under tensile loading (Figs. 4A-4D). As shown in Fig. 7b, outer-walls having approximately 25 shells were observed to break up at the location where the MWCNT undergo failure, and that the edges of the broken outer shells were observed to be perpendicular to the cylinder axis. These observations demonstrate that the multi-wall failure is an intrinsic and inherent characteristic of the MWCNT/alumina composites. Furthermore, the multi-wall failure has also been confirmed in our recent study for arc-discharge-grown MWCNTs, as well as chemical vapor deposition-grown MWCNTs [11]. Based on these results, we suggest that the multi-wall failure is the major cause for the modest enhancement in the fracture properties of MWCNT-based ceramic composites.

4 Conclusions

It has been demonstrated that by varying the annealing temperature, the nanostructures and the fracture properties of MWCNTs could be tailored. The Raman spectroscopy analyses and the TEM observations showed that the disordered structure of the MWCNTs transformed into a stable graphite planer structure by annealing process. The improvement in the tensile strength observed for the MWCNTs annealed at 1800˚C and 2200˚C may be due to the moderate development of the crystal structure by the annealing treatment, i.e., a significant inner-walls load distribution may be facilitated by the irregular wall structure. We have then also shown that the use of the MWCNTs having higher load carrying capacity could be effective method for the enhancement in the mechanical properties of MWCNT/alumina composites. The composites made with the MWCNTs having a higher tensile strength showed both higher bending strength and fracture toughness than those of the composites made with the other types of the MWCNTs. The investigation of the fracture surfaces via TEM gave evidences for limited improvement in the mechanical properties of the composites prepared in this research. All types of the MWCNTs used in the present research underwent multi-wall failure during crack opening in the composite. Our finding suggests that the design of tougher composites with MWCNTs as a fibrous reinforcing agent will need to account, or in some way circumvent, the MWCNT failure reported here.

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References

[1] Mukerji J. Ceramic matrix composites. *Defence Science Journal*, **43**, pp. 385-395.

[2] Evans A.G. Perspective on the development of high-toughness ceramics. *Journal of the American Ceramic Society*, 73, pp. 187-206 (1990).

[3] Hull D., Clyne T.W. *An Introduction to Composite Materials*. Cambridge University Press, Cambridge (1996).

[4] Thostenson E.T., Ren Z., Chou T.W. Advances in the science and technology of carbon nanotubes and their composites: A review. *Composites Science and Technology*, **61**, pp. 1899-1912 (2001).

[5] Cho J., Boccaccini A.R., Shaffer M.S.P. Ceramic matrix composites containing carbon nanotubes. *Journal of Materials Science*, **44**, pp. 1934-1951 (2009).

[6] Yamamoto G., Suk J.W., An J., Piner R.D., Hashida T., Takagi T., Ruoff R.S. The influence of nanoscale defects on the fracture of multi-walled carbon nanotubes under tensile loading. *Diamond and Related Materials*, **19**, pp. 748-751 (2010).

[7] Yu M.F., Lourie O., Dyer M.J., Moloni K., Kelly T.F., Ruoff R.S. Strength and breaking mechanism of multiwalled carbon nanotubes under tensile load. *Science*, **287**, pp. 637-640 (2000).

[8] Zhan G.D., Kuntz J.D., Wan J., Mukherjee A.K. Single-wall carbon nanotubes as attractive toughening agents in alumina-based nanocomposites. *Nature Materials*, **2**, pp. 38-42 (2003).

[9] Chen J., Hamon M.A., Hu H., Chen Y., Rao A.M., Eklund P.C., Haddon R.C. Solution properties of single-walled carbon nanotubes. *Science*, **282**, pp. 95-98 (1998).

[10] Yamamoto G., Omori M., Yokomizo K., Hashida T., Adachi K. Structural characterization and frictional properties of carbon nanotube/alumina composites prepared by precursor method. *Materials Science and Engineering B*, **148**, pp. 265-269 (2008).

[11] Yamamoto G., Shirasu K., Hashida T., Takagi T., Suk, J.W., An J., Piner R.D., Ruoff R.S. Nanotube fracture during the failure of carbon nanotube/alumina composites. *Carbon*, **49**, pp. 3709-3716 (2011).