Nanotechnology

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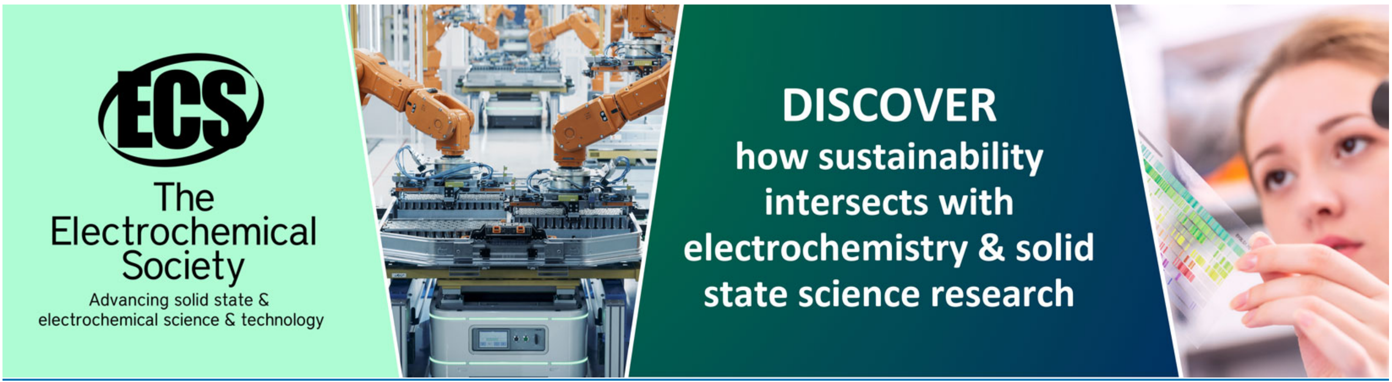
To cite this article: G Yamamoto *et al* 2008 *Nanotechnology* **19** 315708



IOP PUBLISHING NANOTECHNOLOGY

Nanotechnology **19** (2008) 315708 (7pp) doi:10.1088/0957-4484/19/31/315708

A novel structure for carbon nanotube reinforced alumina composites with improved mechanical properties

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Received 26 March 2008, in final form 21 May 2008
Published 24 June 2008
Online at stacks.iop.org/Nano/19/315708

Abstract

Engineering ceramics have high stiffness, excellent thermostability, and relatively low density, but their brittleness impedes their use as structural materials. Incorporating carbon nanotubes (CNTs) into a brittle ceramic might be expected to provide CNT/ceramic composites with both high toughness and high temperature stability. Until now, however, materials fabrication difficulties have limited research on CNT/ceramic composites. The mechanical failure of CNT/ceramic composites reported previously is primarily attributed to poor CNT–matrix connectivity and severe phase segregation. Here we show that a novel processing approach based on the precursor method can diminish the phase segregation of multi-walled carbon nanotubes (MWCNTs), and render MWCNT/alumina composites highly homogeneous. The MWCNTs used in this study are modified with an acid treatment. Combined with a mechanical interlock induced by the chemically modified MWCNTs, this approach leads to improved mechanical properties. Mechanical measurements reveal that only 0.9 vol% acid-treated MWCNT addition results in 27% and 25% simultaneous increases in bending strength (689.6 ± 29.1 MPa) and fracture toughness (5.90 ± 0.27 MPa m$^{1/2}$), respectively.

1. Introduction

Carbon nanotubes (CNTs) have extremely high tensile strength and stiffness [1–7], good flexibility [8, 9], and low density. These superior properties make CNTs attractive for many applications and technologies [10, 11]. In order to take advantage of the intrinsic properties of individual CNTs, various CNT forms [12–19] and composites [20–26] have been demonstrated to overcome the performance limits of conventional materials. Engineering ceramics have high stiffness, excellent thermostability, and relatively low density, but their brittleness impedes their use as structural materials. Incorporating CNTs into a ceramic matrix might be expected to produce tough as well as highly stiff and thermostable ceramic composites. Until now, however, most results for strengthening and toughening have been disappointing, and only little or no improvement of strengthening and toughening has been reported in CNT/ceramic materials. In one study, Padture *et al* [26] used a spark plasma sintering technique to prepare alumina composite containing 10 vol% single-walled carbon nanotubes (SWCNTs). The authors performed single-edge notched beam (SENB) tests on an SWCNT/alumina and alumina-based composite containing graphite particles. The fracture toughness of the SWCNT/alumina composite measured by the SENB method was reported to be similar to that of a graphite/alumina composite. This could be due to the poor connectivity between SWCNTs and alumina matrix [27, 28].

It is well known that the two problems exist in CNT/ceramic composite materials research. The first is the inhomogeneous dispersion of CNTs in the matrix. Pristine CNTs are well known for poor solubilization, which leads to phase segregation in the composite owing to the van der Waals attractive force [29]. Severe structural inhomogeneities

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0957-4484/08/315708+07$30.00

result in the degradation of the mechanical properties of the CNT composite materials [30]. The second problem is the poor connectivity between CNTs and the ceramic matrix, which leads to a limited stress transfer capability from the matrix to the CNTs [27, 28]. The connectivity with the matrix, and uniform distribution within the matrix are essential structural requirements for the stronger and tougher CNT/ceramic composites.

In the majority of the previous studies, alumina powders are mechanically mixed with CNTs in order to prepare CNT/alumina composites. To the best of our knowledge, there is only one report which used a precursor method to prepare CNTs partially coated with alumina particles [31]. Thus, there has been no previous investigation which produced CNT composites using the precursor method. In this study, we show that a novel processing approach based on the precursor method can diminish the phase segregation of MWCNTs, and render MWCNT composites that are highly homogeneous. The MWCNTs used in this study are modified with an acid treatment. Combined with a mechanical interlock induced by the chemically modified MWCNTs, this approach leads to improved mechanical properties. Mechanical measurements on composites reveal that only 0.9 vol% acid-treated MWCNT addition results in 27% and 25% simultaneous increases in bending strength (689.6 ± 29.1 MPa) and fracture toughness (5.90 ± 0.27 MPa $m^{1/2}$), respectively, indicating enhanced stress transfer capability from the alumina to the MWCNTs. The universality of the precursor approach combined with chemically modified MWCNTs will be applicable to a wide range of functional materials.

2. Experimental procedure

The multi-walled carbon nanotubes (MWCNTs) used in this study were kindly provided by Nano Carbon Technologies (Tokyo, Japan), and the purity was claimed to be 99.5% by the producer. The estimated diameter and length of the pristine MWCNTs from scanning electron microscopy (SEM) and transmission electron microscopy (TEM) measurements ranged from 33 to 124 nm (average: 70 nm) and 1.1 to 22.5 μm (average: 8.7 μm), respectively. The pristine MWCNTs were refluxed in 3:1 (volume ratio) concentrated H_2SO_4:HNO_3 mixture at 70 °C for 2 h, washed thoroughly with distilled water to be acid-free, and then finally dried in an oven at 60 °C. A typical synthesis procedure for the composite preparation is as follows. The 50 mg pristine MWCNTs or acid-treated MWCNTs were dispersed in 300 ml ethanol with aid of ultrasonic agitation. 15.2 g aluminum hydroxide (Wako Pure Chemical Industries, Osaka, Japan) was added to this solution and ultrasonically agitated. 73 mg magnesium hydroxide (Wako Pure Chemical Industries, Osaka, Japan) was added to prevent excessive crystal growth. Here, the weight loss of the hydroxides caused by the dehydration process was accounted for in the calculation of the composite composition. The weight loss of aluminum hydroxide and magnesium hydroxide was 34.7% and 31.9%, respectively. The resultant suspension was filtered and dried in an oven at 60 °C. Finally, the product obtained in the previous step was put into a half-quartz tube and was dehydrated at 600 °C for 15 min in argon atmosphere.

The composites were prepared by spark plasma sintering (SPS, SPS-1050 Sumitomo Coal Mining, Tokyo, Japan) in a graphite die with an inner diameter of 30 mm at a temperature of 1500 °C under a pressure of 20 MPa in vacuum for 10 min. For comparison, similar preparation processes were applied while using pristine MWCNTs as the starting material.

The bending strength was measured by the three-point bending method under ambient conditions, in which the size of the test specimens was 2 mm (width) × 3 mm (thickness) × 24 mm (length). The span length and crosshead speed for the strength tests were 20 mm and 0.05 mm min^{-1}, respectively. The fracture toughness was measured by the single-edge notched beam (SENB) method under ambient conditions, in which the size of test specimens was 2 mm (width) × 3 mm (thickness) × 15 mm (length). A notch with depth and width of 0.3 mm and 0.1 mm was cut in the center part of the test specimen. A span length of 12 mm and crosshead speed of 0.05 mm min^{-1} were applied for the toughness test. All surfaces of the specimens were finely ground on a diamond wheel, and the edges were chamfered.

The indentation tests were done on a hardness tester (AVK-A, Akashi, Osaka, Japan) with a diamond Vickers indenter under ambient conditions. The 0.9 vol% acid-treated MWCNT/alumina composite with surface roughness of 0.1 μm (Ra) was indented using a Vickers diamond pyramid with a load of 98.1 N (P) applied on the surface for 15 s. The diagonal (d) and radial crack length (C) were measured by the SEM. The hardness values (H_v) were calculated using the equation $H_v = 0.1891P/d^2$ and indentation toughness values (K_{IC}) were calculated using the Anstis *et al* method, $K_{IC} = 0.016(E/H_v)^{1/2}(P/C^{3/2})$, where E is the Young's modulus ($E = 362.8$ GPa) measured by the pulse-echo method.

Bulk densities of the sintered bodies were measured by the Archimedes method using deionized water as an immersion medium. The nanostructures and microstructures were observed using scanning electron microscopy (SEM, Hitachi S-4300, Tokyo, Japan) and transmission electron microscopy (TEM, Hitachi HF-2000, Tokyo, Japan). The surface roughness was measured by a stylus profilometer (Mitaka Kohki NH-3T, Tokyo Japan). The changes in zeta potentials were measured in 1.0 mM KCl aqueous solution of varying pH using a zeta potential analyzer (ZEECOM ZC2000, Microtec, Chiba, Japan). The pH value of the aqueous solution was adjusted with HCl and NaOH. Zeta potential values were calculated using the Smoluchowski equation. The electrical conductivity of the composites was determined by using a four-probe technique (K-705RS and K-89PS150μR, KYOWARIKEN, Tokyo, Japan) under ambient conditions.

3. Results and discussion

To disperse the MWCNTs homogeneously in the matrix and improve the connectivity between MWCNTs and matrix, we have used acid treatment of the pristine MWCNTs. The rationale behind the acid treatment is to introduce nanoscale defects and adsorb negatively charged functional groups at the

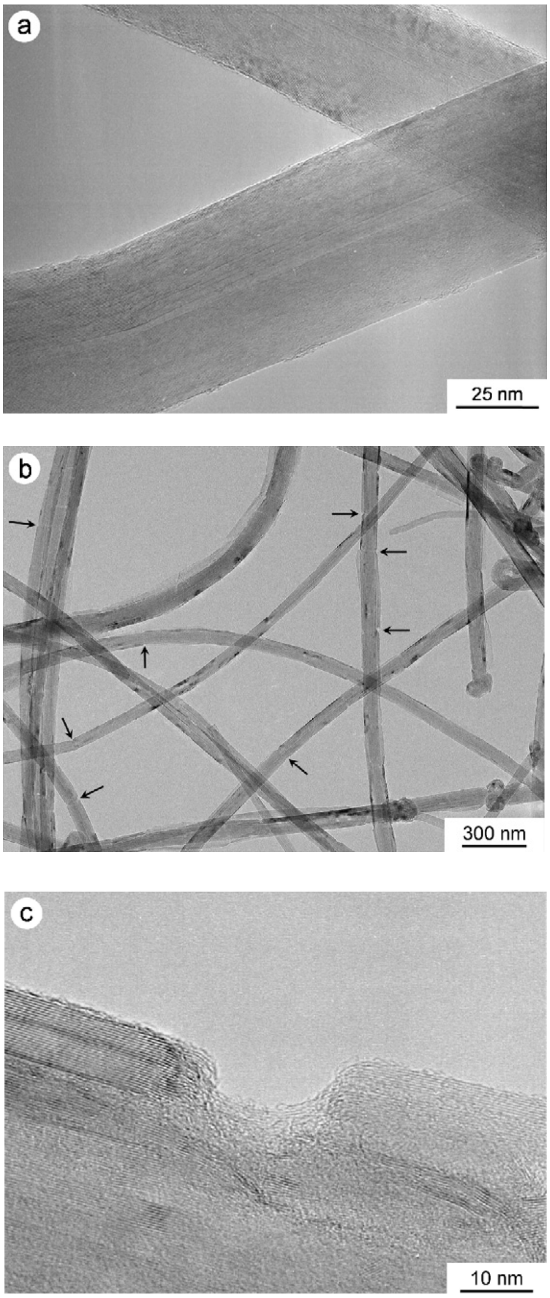

Figure 1. (a) TEM image of the pristine MWCNTs. (b) TEM image of the acid-treated MWCNTs. The arrows indicate the position of the nanodefects. (c) High-magnification TEM image of the acid-treated MWCNT surface.

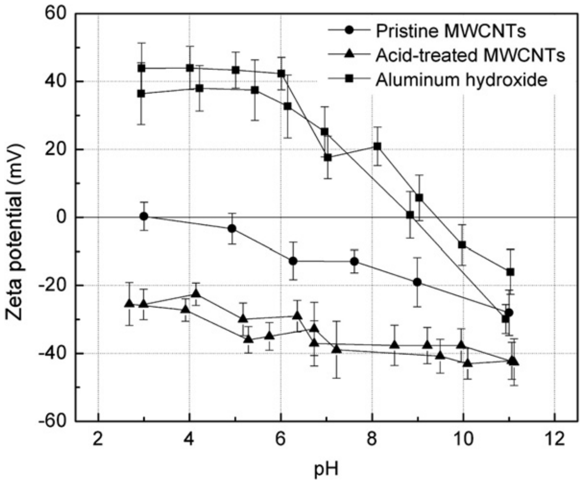

Figure 2. Zeta potential values of the pristine MWCNTs and acid-treated MWCNTs at different pH.

MWCNT ends and along their lengths. The pristine MWCNTs were refluxed in 3:1 (volume ratio) concentrated H_2SO_4:HNO_3 mixture at 70 °C for 2 h, washed thoroughly with distilled water to be acid-free, and then finally dried in an oven at 60 °C. The weight loss of the MWCNTs was less than 7%. Figure 1(a) shows a transmission electron microscopy (TEM) image of the pristine MWCNTs used in this study. It can be seen from figure 1(a) that the pristine MWCNTs have a high crystalline multi-walled structure with no defects on the wall surface. Examination of the acid-treated MWCNTs by TEM revealed that no significant overall damage took place in the MWCNTs during the acid treatment (figure 1(b)). At the same time, a trace amount of multi-walled polyhedra with diameters of typically 100 nm is observed in addition to the MWCNTs; these are a well known by-product of MWCNT synthesis [32, 33]. The detailed structural information of the acid-treated MWCNTs was retrieved from the enlarged TEM image, as shown in figure 1(c). It is demonstrated that with the acid treatment of the MWCNTs, we have successfully introduced nanoscale defects on the surface of the MWCNTs. The depths of the nanodefects are typically 10–20 nm. It has been reported [34] that CNTs can be cut into shorter segments with carboxylic groups by acid treatment of 3:1 (volume ratio) concentrated H_2SO_4:HNO_3 mixture. No such slight change in the length has been found in the acid-treated MWCNTs. The average length of the MWCNTs estimated from scanning electron microscopy (SEM) changed from 8.7 to 8.3 μm after the acid treatment. It has been observed that the surface of the acid-treated MWCNTs is much rougher than that of the pristine MWCNTs. Namely, the acid-treated MWCNTs have irregular surface morphology with mild asperities compared with the smooth surface of the pristine MWCNTs.

The zeta potential values of the pristine MWCNTs and acid-treated MWCNTs at different pH values are shown in figure 2. The isoelectric point (pH_{iep}) for the pristine MWCNTs is located at about 3.0, whereas the acid treatment process makes the surface more negatively charged at tested pH values, and their zeta potential values decreased gradually with increasing pH. The change in the zeta potential may be mainly due to the introduction of more functional groups after the acid treatment [34, 35]. Similar observations have been made by others on acid-treated CNTs [36, 37]. These functional groups make them easily dispersed in polar solvents, such as water and ethanol. Furthermore, it can be expected that the larger electrical repulsive force between the acid-treated MWCNTs will facilitate their dispersion and prevent them from tangling and agglomeration. The zeta potential of aluminum hydroxide, which is used as the starting material for synthesis of alumina, exhibited positive values over a wide pH range (pH = 3–9), while that of the acid-treated MWCNTs was negative in

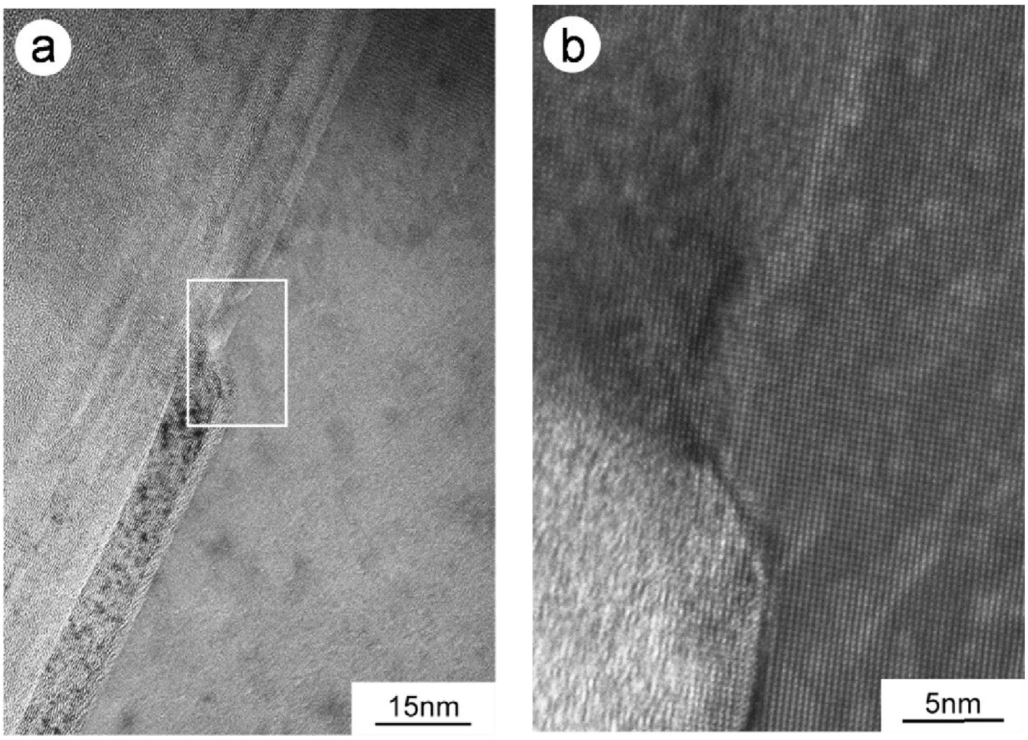

Figure 3. MWCNT morphology in the composites. (a) It is demonstrated that a nanodefect on the acid-treated MWCNT is filled up with alumina crystal. (b) Enlarged TEM image, taken from the square area.

this pH range. On these two colloidal suspensions are mixed, particles of aluminum hydroxide will bind onto the acid-treated MWCNTs because of the strong electrostatic attractive force between them, and this results in a homogeneous MWCNT and aluminum hydroxide solution.

In this study, we used a spark plasma sintering (SPS) method in order to obtain fully dense composites [38]. The physical and mechanical properties, and electrical conductivities of the composites are shown in table 1. The theoretical density values were calculated from the rule of mixtures, assuming the following density values [33]: MWCNTs 2.10 $\mathrm{Mg\,m^{-3}}$, Al_2O_3 3.97 $\mathrm{Mg\,m^{-3}}$, and MgO 3.65 $\mathrm{Mg\,m^{-3}}$. X-ray diffraction analysis of the sintered bodies revealed that the aluminum hydroxide has been transformed to α-alumina during SPS at 1500 °C under 20 MPa. The pure aluminum hydroxide powder can be solidified by SPS to near-theoretical density. The relative densities of both the composites containing 0.9 vol% pristine MWCNTs and acid-treated MWCNTs are also the near-theoretical densities, whereas that of both the composites decreased with increasing MWCNT content. It is well known that CNT aggregates will reduce the relative density of the composite because of their porous rope-like structure. The decreases of the relative density suggest that some MWCNT aggregates remain in the composites. The higher relative density and hardness for the acid-treated MWCNT/alumina composites may be attributed to more homogeneous distribution of MWCNTs compared with the pristine MWCNT/alumina composites, as revealed by SEM observation of the fracture surfaces of the MWCNT/alumina composites. Most of the alumina grains had sizes in the micron range, around 1.5 μm. No clear difference in the grain size is observed between the acid-treated MWCNT/alumina composites and pristine MWCNT/alumina composites, even though the incorporation of MWCNTs seems to suppress the grain growth of alumina [25]. Addition of only 0.9 vol% acid-treated MWCNTs to the alumina matrix increased the electrical conductivity of the composite by about 7–9 orders of magnitude compared with that of monolithic alumina. It is has been reported that the electrical property transition from insulator to conductor, namely the percolation threshold of MWCNT/alumina composite materials, occurs at 0.79 vol% MWCNT content [39]. It is expected that the electrical conductivity is more susceptible to the effect of MWCNT dispersion and length at around 0.79 vol% MWCNT content. The reduction of electrical conductivity of the 0.9 vol% acid-treated MWCNT/alumina compared to the composite made with 0.9 vol% pristine MWCNTs may be attributed to the slight length decrease in the acid-treated MWCNTs.

We now discuss the nanostructures of the acid-treated MWCNT/alumina composites using TEM analysis. An interesting geometric structure was observed between individual MWCNTs and alumina matrix, as shown in figures 3(a) and (b). It is revealed that a nanodefect on the acid-treated MWCNT is filled up with alumina crystal, which may be intruding into the nanodefect during grain growth. This nanostructure is novel in that its structure resembles a nanoscale anchor with an alumina crystal spiking the surface of the MWCNTs.

It has been found that surface modification of the MWCNTs is effective in improvement of bending strength

Table 1. The resultant properties of the MWCNT/alumina composites.

Material	Relative density (%)	Grain size (μm)	Hardness (GPa)	Electrical conductivity (S m^{-1})
Al_2O_3	98.6	1.69	17.3	10^{-10}–10^{-12}
0.9 vol% acid-treated MWCNT/Al_2O_3	99.2	1.65	16.8	1.3×10^{-3}
1.9 vol% acid-treated MWCNT/Al_2O_3	98.9	1.51	15.9	1.3
3.7 vol% acid-treated MWCNT/Al_2O_3	97.7	1.36	13.1	65.3
0.9 vol% pristine MWCNT/Al_2O_3	98.9	1.43	17.0	1.4
1.9 vol% pristine MWCNT/Al_2O_3	98.2	1.57	14.4	15.1
3.7 vol% pristine MWCNT/Al_2O_3	94.1	1.54	11.0	63.4

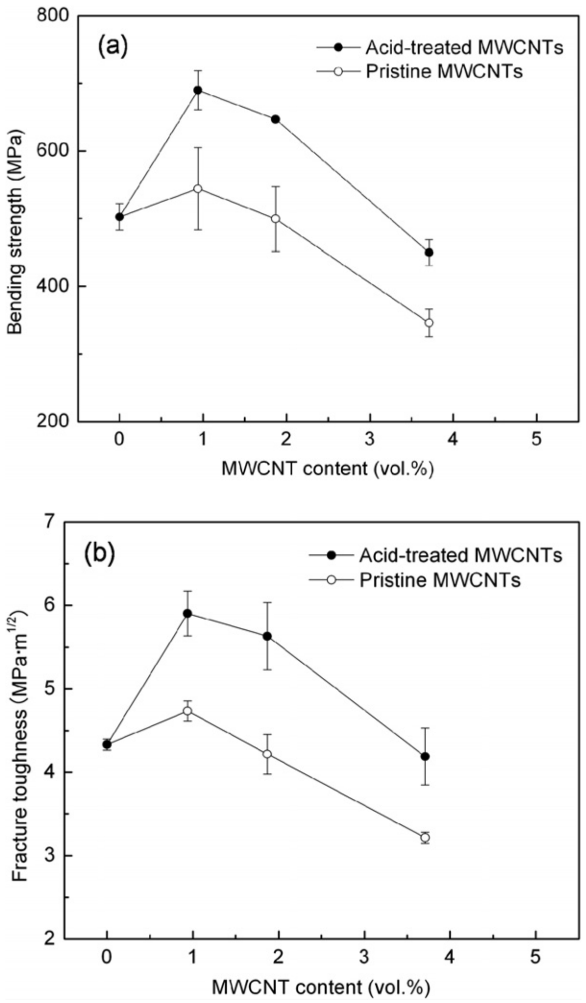

Figure 4. (a) Bending strength and (b) fracture toughness as a function of MWCNT content.

and fracture toughness of the MWCNT/alumina composites. Figures 4(a) and (b) show the dependence of bending strength and fracture toughness on MWCNT content in the composites. There are few papers which report significant improvement in the mechanical properties such as toughness [25], and the improvement by CNT addition has been limited so far in previous studies [20, 26, 40, 41]. In our composites, however, the bending strength and fracture toughness simultaneously increase with the addition of a small amount of the acid-treated MWCNTs. The bending strength and fracture toughness of the 0.9 vol% acid-treated MWCNT/alumina composite reached 689.6 ± 29.1 MPa and 5.90 ± 0.27 MPa $m^{1/2}$,respectively. At the same time, the bending strength and fracture toughness of the acid-treated MWCNT/alumina composites were always higher than those of the pristine MWCNT/alumina composites with identical MWCNT content, indicating enhanced stress transfer capability from the alumina to the acid-treated MWCNTs.

Figures 5(a) and (b) show the microstructure of the fracture surface of the 1.9 vol% acid-treated MWCNT/alumina composite. From the fracture surface, the following features can be noted. First, numerous individual MWCNTs protrude from the fracture surface, and the pullout of the MWCNTs can be clearly observed, which had not been obtained until now for conventional CNT/ceramic composites. The MWCNTs are located in the intergranular phase and their lengths are in the range 0–10 μm. Second, some MWCNTs showed that the diameter of pullout MWCNT drastically slenderized toward their tip (figure 5(b)), quite similar to that observed in a broken MWCNT under tensile load ('sword-in-sheath' failure) [6]. This failure mode of the acid-treated MWCNTs may be due to the enhancement of effective frictional resistance between individual MWCNTs and the alumina matrix. Third, in the case of the smaller amount of the acid-treated MWCNTs, no phase segregation was observed, whereas the composites made with the pristine MWCNTs revealed an inhomogeneous structure even for MWCNT addition as low as 0.9 vol%. These observations revealed that the high structural homogeneity and enhanced frictional resistance of the structural components leads to a simultaneous increase in the strength and toughness of the acid-treated MWCNT/alumina composites. In contrast, for the larger amount of the MWCNTs, the degradation of mechanical properties of both the composites may be primarily attributed to the severe phase segregation. Because a bundle of segregated CNTs has poor load-carrying ability, the effect of this kind of CNT aggregate in the matrix may be similar to that of pores [30].

To understand the fracture mechanism, we conducted complementary indentation fracture tests on the 0.9 vol% acid-treated MWCNT/alumina composite which gave the highest mechanical properties in this study. The tips of the induced radial cracks could be clearly observed on the specimen surface. The Vickers indentation toughness calculated by using the Anstis *et al* [42] equation was 6.64 MPa $m^{1/2}$, which is a slightly larger value than that measured by using single-edge notched beam (SENB) method (5.90 MPa $m^{1/2}$). We were able to observe individual MWCNTs bridging the crack faces (figure 5(c)), quite similar to that observed in MWCNT/polymer composite with improved mechanical

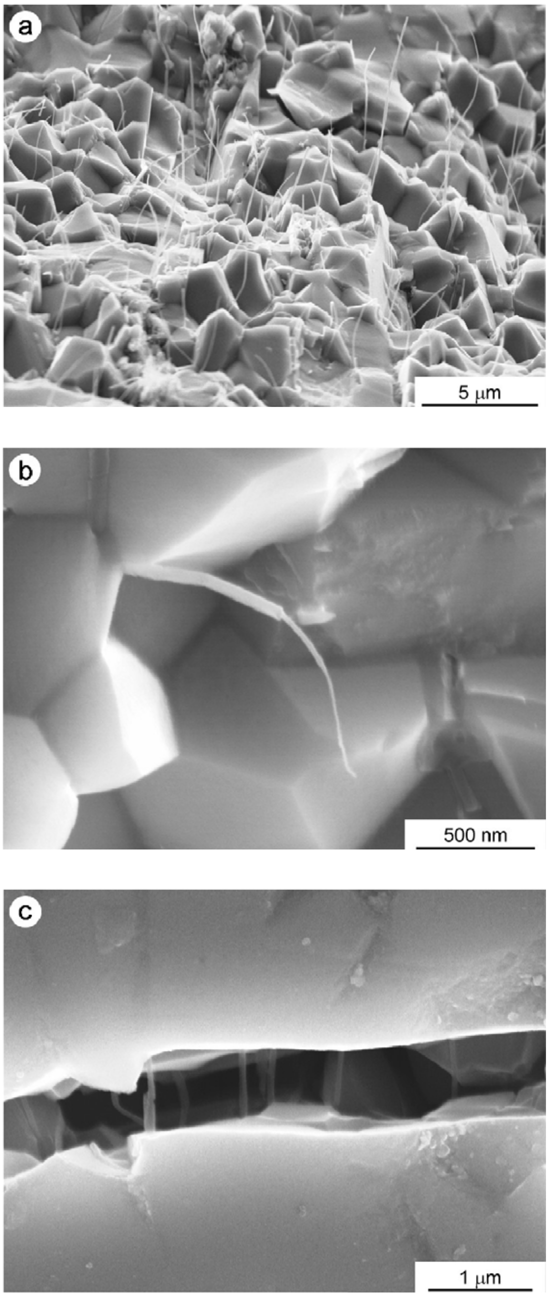

Figure 5. Fracture surface of the acid-treated MWCNT/alumina composite. (a) Numerous individual MWCNTs protrude from the fracture surface. (b) Some MWCNTs that have broken in the outer layers. (c) Numerous stretched MWCNTs that bridged the about 1 μm wide cracks were observed.

properties [43]. The individual MWCNTs are aligned perpendicular to the crack propagation orientation and bridge the crack, thus providing a closure stress across the crack flanks.

The nanodefects on the MWCNTs introduced via the acid treatment process might reduce significantly their intrinsic mechanical properties. However, according to the SEM and TEM observations, no apparent breakage of MWCNTs was noted in general, except for special cases as illustrated in figure 5(b). We infer that the improvement of the strength and toughness may be due to the crack-bridging effect with the enhanced frictional resistance between acid-treated MWCNTs and the alumina matrix through mechanical interlocks.

4. Conclusion

In summary, a homogeneous distribution of MWCNTs in an alumina matrix has been achieved by a novel processing approach based on the precursor method for the synthesis of alumina and acid-treated MWCNTs. Combined with enhanced frictional resistance through the mechanical interlocks induced by the chemically modified MWCNTs, this approach leads to an increase in the strength and toughness of MWCNT/alumina composites. The addition of only 0.9 vol% acid-treated MWCNTs to alumina results in 27% and 25% simultaneous increases in bending strength (689.6 ± 29.1 MPa) and fracture toughness (5.90 ± 0.27 MPa $m^{1/2}$), respectively, indicating enhanced stress transfer capability from the alumina to the MWCNTs. Our present work may give a promising future for the application of MWCNTs in reinforcing structural ceramic components and other materials systems as well. The acid-treated MWCNT/alumina composites may have potential applications to tribomaterials such as joint prosthesis and micro electro mechanical systems (MEMS), because of the CNTs' good lubrication properties [44, 45].

Acknowledgments

This work was supported by the 21st Century Center of Excellence (COE) Program Grant of the International COE of Flow Dynamics, Ministry of Education, Culture, Sports, Science and Technology. The authors thank Mr Y Aizawa of the Fracture and Reliability Research Institute, Tohoku University, and Mr A Okubo of the Institute for Materials Research, Tohoku University, for their technical support. The authors thank Professor Tohji and Mr K Motomiya of the Graduate School of Environmental Studies, Tohoku University, and Mr T Miyazaki of Technical Division, School of Engineering, Tohoku University, for their technical assistance in the TEM analysis. The authors also thank Professor T Ono and Mr N Oda of the Graduate School of Engineering, Tohoku University, for their technical assistance in electrical conductivity measurements.

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