MICROSTRUCTURE AND MECHANICAL PROPERTIES OF MULTI-WALLED CARBON NANOTUBE/ALUMINA COMPOSITES PREPARED BY A NOVEL FLOCCULATION METHOD

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Abstract

This paper describes the mechanical properties of multi-walled carbon nanotube (MWCNT)/alumina composites prepared by a novel flocculation technique and spark plasma sintering (SPS) method. The influences of processing parameters including sintering temperature, acid treatment temperature and MWCNT volume fraction on the composites' mechanical properties were investigated. It is found that the well dispersed MWCNTs within the alumina matrix were obtained in the high volume fraction MWCNT composites prepared in this research. Lower sintering temperature and higher acid treatment temperature could lead to the maintenance and increase of bending strength and fracture toughness with the MWCNT fraction of 5 vol.%, even 10 vol.%.

1. Introduction

Engineering ceramics have high stiffness, excellent thermal and chemical stability, along with relatively low density, which make them widely used in a range of applications. Amongst the engineering ceramics, alumina is one of the most commonly used and researched ceramic, whose applications span from high-speed cutting tools, wear resistant parts and dental implants to thermal and electrical insulators [1]. However, besides the apparent merits, such as high hardness, good wear resistance and high thermal and electrical insulation properties, the intrinsic brittleness restricts it from considerable structural occasions. In order to overcome the drawback, incorporation of a second phase including carbon and glass fibers, whiskers and particulates, as the reinforcing agents, have been tried for several decades [1,2].

Since the discovery of carbon nanotubes (CNTs), they become one of the hottest research focuses quickly, among which multi-walled carbon nanotubes (MWCNTs) are attracting more attention because of the relative simple synthesis methods and low cost. The experimental and theoretical results have shown that MWCNTs possess excellent mechanical properties, including good flexibility [3] and high Young's modulus and tensile strength [4], which are regarded as one of the promising reinforcing agents in ceramics. Therefore, there have been very increasing interests in the development of ultra-strong and ultra-tough ceramic based composites containing MWCNTs during the last decade. Among the CNT/ceramic composites, alumina based composite containing MWCNTs is the most studied, and many interesting results have been reported. Ahmad *et al*, reported that the hot-pressed MWCNT/alumina nanocomposites showed 94% and 6.4% simultaneous improvement in fracture toughness and bending strength at 4 vol.% MWCNT addition using sodium dodecyl sulphate (SDS) as effective dispersant [5]. High performance alumina composites were also achieved by a precursor method. Compared to a monolithic alumina, 0.9 vol.% acid-treated MWCNT addition led to 27% and 25% increases in bending strength and fracture toughness, respectively [6]. Besides the enhancement in mechanical properties, the addition of CNTs also has a great influence on the electrical, thermal, and tribological properties and thermal shock resistance. The comprehensive descriptions about the properties of ceramic-based composites containing CNTs have been reviewed by Cho *et al* [7] and Zapata-Solvas *et al* [8].

Up to now, making ceramic composites with single-walled CNTs (SWCNTs) or MWCNTs is still a significant challenge, especially making the composites with high volume fraction CNTs. Tailoring of multifunctional ceramic composites with the desirable mechanical, transport and tribological properties is a long-term topic and becomes more and more attracting. Incorporation of MWCNTs with high volume fraction into the matrix is the premise and guarantee of obtaining composites possessing outstanding transport and tribological properties. However, CNTs tend to agglomerate easily because of large aspect ratio and high surface energy, which has a significant influence on dispersion processing. The aggregates prevent the composites from densification and form cavities in the matrix and have great influence on the effective exploitation of strength and stiffness of CNTs, resulting in decrease of mechanical properties. In the experimental results of Ahmad *et al*, the decrease in mechanical properties except fracture toughness occurred, and the increasing ratio of fracture toughness decreased from 94% to 66%, when the MWCNTs volume fraction was increased from 4 vol.% to 10 vol.% [5]. In the MWCNT-alumina system prepared by the precursor method, even in 3.7 vol.% concentration, the apparent reduction both in bending strength and fracture toughness was observed [6]. Actually, some exciting improvements have been realized in ceramics containing CNTs, but a long and rough pavement still needs to walk. In Ref. [9], an unprecedented enhancement in fracture toughness with large amount of SWCNTs was revealed by Zhan *et al*. They used alcohol to disperse SWCNTs and spark plasma sintering process to synthesize 10 vol.% SWCNT/Al_2O_3 nanocomposite. The fracture toughness of the composite measured by indentation method was reported to be as high as 9.7 $MPa \cdot m^{1/2}$, nearly three times higher than that of pure alumina [9]. However, it is easy to produce overestimated results by indentation method, and the actual value may not be so surprising [10,11]. Currently, Estili *et al*, also conduced some meaningful works in high volume fraction MWCNTs/alumina composites [12]. Nevertheless, how to keep or to increase the mechanical properties with high volume fraction CNTs is still a constant threat to materials researchers.

Therefore, how to disperse CNTs uniformly in ceramic matrix with high CNT content is very challenging, which inspires the development of dispersion techniques. Colloidal method is considered to be one of the most effective routes to disperse CNTs in matrix, in which cationic or anionic surfactants are commonly used [13,14]. However, the amount and influence on the mechanical properties of residual contaminants is unknown, which produces a series of difficulties in material design and estimation. Here, a friendly-material flocculation method was developed in our laboratory. A combination of an acid treatment, a flocculation processing and spark plasma sintering (SPS) was used to prepare high volume fraction

MWCNT/alumina composites without additives in the sintered bodies. In order to find the suitable conditions to keep and to increase the mechanical performances further in high volume fraction MWCNT/alumina composites, effects of processing conditions including the acid treatment temperatures, MWCNTs volume fractions and sintering temperatures on the microstructures and mechanical properties of the composites were investigated in this research.

2. Experimental procedure

2.1. MWCNTs acid treatment

Commercially available MWCNTs, which were acquired from Nano Carbon Technologies (presently Hodogaya Chemical), were used as raw materials. The MWCNTs were synthesized by a catalytic chemical vapor deposition (CCVD) method, and then thermally-annealed at 2600˚C under argon atmosphere. The diameters and lengths of the pristine MWCNTs from transmission electron microscope (TEM, Hitachi HF-2000) and scanning electron microscope (SEM, JEOL JSM-6610) measurements ranged from 18 to 90 nm (average: 41 nm) and from 1.2 to 40.0 μm (average: 8.5 μm), respectively. The acid treatment was conducted in a mixture of sulfuric acid (95 mass%) and nitric acid (65 mass%) with the volume ration of 3:1. The MWCNTs were suspended in the acid mixture at 50, 60, 70, and 80˚C for 2 h each with magnetic stirring. Then the MWCNTs suspension was diluted and washed thoroughly with distilled water to be acid-free. Finally, the acid-treated MWCNTs were dried in an electrical drying oven at 105˚C.

2.2. Fabrication of MWCNT/alumina composites

Alumina powders (TM-DAR, Taimei Chemical) were ball milled and washed by distilled water followed by drying in the oven. After that, the zeta potential of the MWCNTs and alumina suspensions was measured via varying pH using a zeta potential analyzer (ZEECOM ZC2000, Microtec, Japan). Then the MWCNTs and alumina were separately dispersed in distilled water combined with homogenizer for 10 min and sonication for 1 h without any other additions. The pH of the suspensions of the MWCNTs and alumina were adjusted by HCl or $NH_3 \cdot H_2O$ to be the same values on the basis of the zeta potential results. After pH adjustment, the MWCNTs suspension was introduced into the alumina suspension gently. This strategy can prevent re-agglomeration during the process of mixing effectively, and can realize uniform dispersion of the MWCNTs in alumina matrix. The MWCNTs-alumina mixture was then filtered and washed by distilled water when there were no free MWCNTs in the supernatant indicating the complete flocculation between the MWCNTs and alumina powders was achieved. The composites were prepared by SPS (SPS-1050, Sumitomo Coal Mining, Japan) in a graphite die with an inner diameter of 20 mm at 1200, 1300, 1400, 1500, and 1600˚C for 10 min each under a pressure of 50 MPa in vacuum. For the sake of comparison, a monolithic alumina was prepared using similar conditions.

2.3. Microstructural and mechanical characterization

The bulk densities of the samples were measured by the Archimedes method in distilled water. In this study, 2.10 Mg/m^3 and 3.99 Mg/m^3 were adopted as theoretical densities for the MWCNTs and alumina, respectively. Young's moduli of the disk samples were measured by the ultrasonic pulse-echo technique. During the measurements, the times for the transverse and longitudinal waves propagating the samples were recorded. From the time and samples thickness measurement, the velocities for the waves through the samples, and the Young's moduli were calculated finally [5]. The bending strength was measured by the three-point bending method with a span of 12.0 mm and crosshead speed of 0.83 μm/s (0.05 mm/min) under ambient conditions. The test specimens had the dimensions of 2.0 mm (width) × 3.0 mm (thickness) × 20.0 mm (length). The fracture toughness measurement was conducted at room temperature using single edge notch beam (SENB) method, in which the size of test specimens was 2.0 mm (width) × 3.0 mm (thickness) × 15.0 mm (length). A notch with depth and width of 0.3 mm and 0.1 mm was introduced in the center of the specimens. The span and crosshead speed were 8.0 mm and 0.83 μm/s (0.05 mm/min), respectively. All the surfaces of the specimens were finely polished, and the edges were all chamfered. The fracture surface especially the dispersion condition of MWCNTs in the matrix was observed with SEM.

3. Results and discussion

3.1. Influence of sintering temperature

Applying higher sintering temperature could favor the increase in relative density in the densification regime, and could increase the grain size through grain-boundary diffusion in the grain-growth regime [15]. The influences of sintering temperature on relative density, Young's modulus, bending strength and fracture toughness are investigated in the experiments, and the variation curves were displayed in Figure 1.

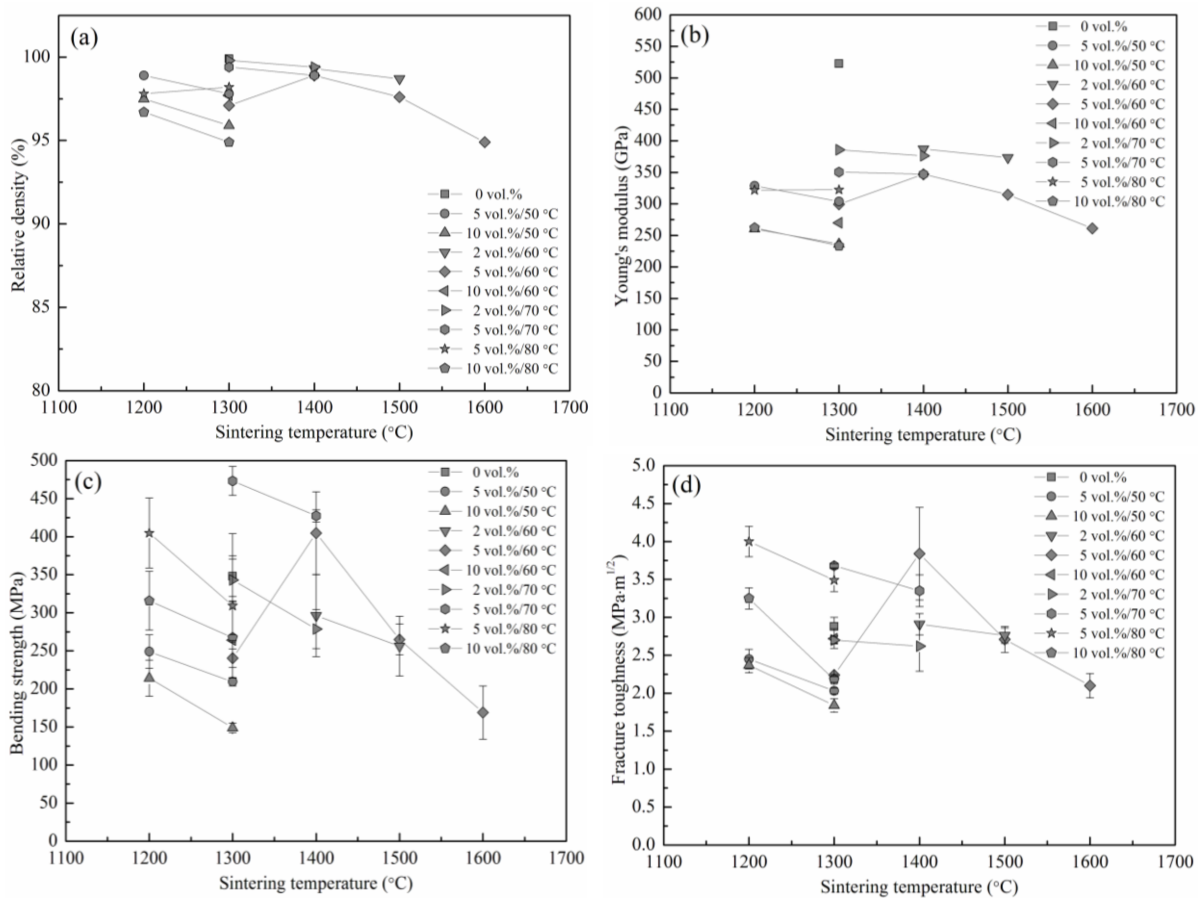

Figure 1. (a) Relative density; (b) Young's modulus; (c) bending strength; and (d) fracture toughness vs. sintering temperature.

From the curves of relative density (Figure 1(a)), all the samples sintered in this experiment show high relative density (> 94%). Among the mechanical properties, Young's modulus is very sensitive to porosity [16]. The sintering temperature and MWCNT addition have impact on densification and porosity, and then have influence on Young' modulus. From Figure 1(b), Young's moduli of the samples show the similar variable tendency with the relative densities. As the curves of bending strength and fracture toughness vs. sintering temperature displayed in Figures 1(c) and (d), even though the exception can be observed, the general trend is visible, that is with the increase of sintering temperature, the mechanical properties decrease no matter what the acid treatment temperature and MWCNT volume fraction are. Lower sintering temperature is beneficial to the good mechanical properties acquirement in the temperature range (1200–1600˚C) in this study.

3.2. Influence of acid treatment temperature

Acid treatment is regarded as one of the most effective methods to functionalize CNTs, which can etch the surface and induce functional groups to improve the dispersion in the matrix and the connectivity between CNTs and the matrix. In this study, several acid treatment temperatures were attempted. The bending strength and fracture toughness as a function of acid treatment temperature, are shown in Figure 2. The acid treatment will affect the dispersion condition of the MWCNTs in distilled water and in the matrix finally, thereby having influence on the mechanical properties of the composites. Indeed, some fluctuations are observed in the figures about bending strength and fracture toughness vs. acid treatment temperature. However, a general and approximate trend that increasing acid treatment temperature can lead to better mechanical properties still can be confirmed. In the range of the acid treatment temperatures (50–80˚C) used in this research, it is possible to realize the improvement in bending strength and fracture toughness at a higher acid treatment temperature.

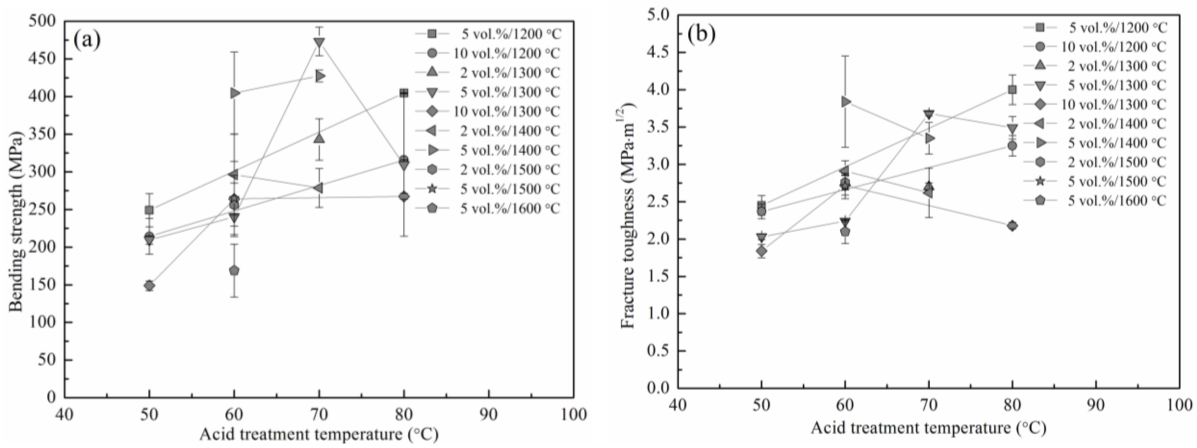

Figure 2. (a) Bending strength and (b) fracture toughness vs. acid treatment temperature.

3.3. Influence of MWCNT volume fraction

It is well known that homogeneous dispersion of CNTs together with suitable interfacial bonding is one of the key factors in preparation of CNT/ceramic composites. Although many interesting results have been obtained in the past decade, the success is almost limited to small amount of CNTs, restricting the potential applications of CNT/alumina composites. In this study, flocculation method and acid treatment technique combined with SPS were used to solve the problems of MWCNT dispersion, interfacial bonding and MWCNT degradation, trying to obtain alumina composites reinforced with higher volume fractions of MWCNTs. The dependences of relative density, Young's modulus, bending strength and fracture toughness on MWCNT volume fraction are shown in Figure 3. As shown in Figures 3(a) and (b), the relative density and Young's modulus decrease with increasing MWCNT content, which is in agreement with many reported experimental results. With regard to bending strength and fracture toughness, the values of the monolith alumina sintered at 1300˚C, which are marked by the dash lines in Figures 3(c) and (d), form the boundary to separate all the data into two parts. Four samples (dash-line circle) show better bending strength when the MWCNT fractions are 5 vol.%, and more samples (dash-line circle) containing 5 vol.% MWCNTs possess better fracture toughness than the monolith. More importantly, the sample prepared in the condition of 1200˚C for sintering temperature and 80˚C for acid treatment temperature surpasses fracture toughness of the pure alumina successfully, when the MWCNT fraction is as high as 10 vol.%. Thus, it is seen that the experimental results circled have been obtained from the processing conditions of the lower sintering temperature and higher acid treatment temperature. This observation is in accord with the previously mentioned trends in Figures 1 and 2. Under the processing conditions used in this research, the intrinsic mechanical properties of alumina are preserved and increased successfully with large amount of MWCNTs. In this case, the electrical conductivity and tribological properties of the alumina composites may be enhanced significantly, which is a fairly good progress in tailoring multifunctional ceramic based composites. Despite of a long way to go to get higher absolute values in mechanical properties, there are still highlights in the results and the developed combination method is promising to achieve large MWCNT content addition in ceramic matrix.

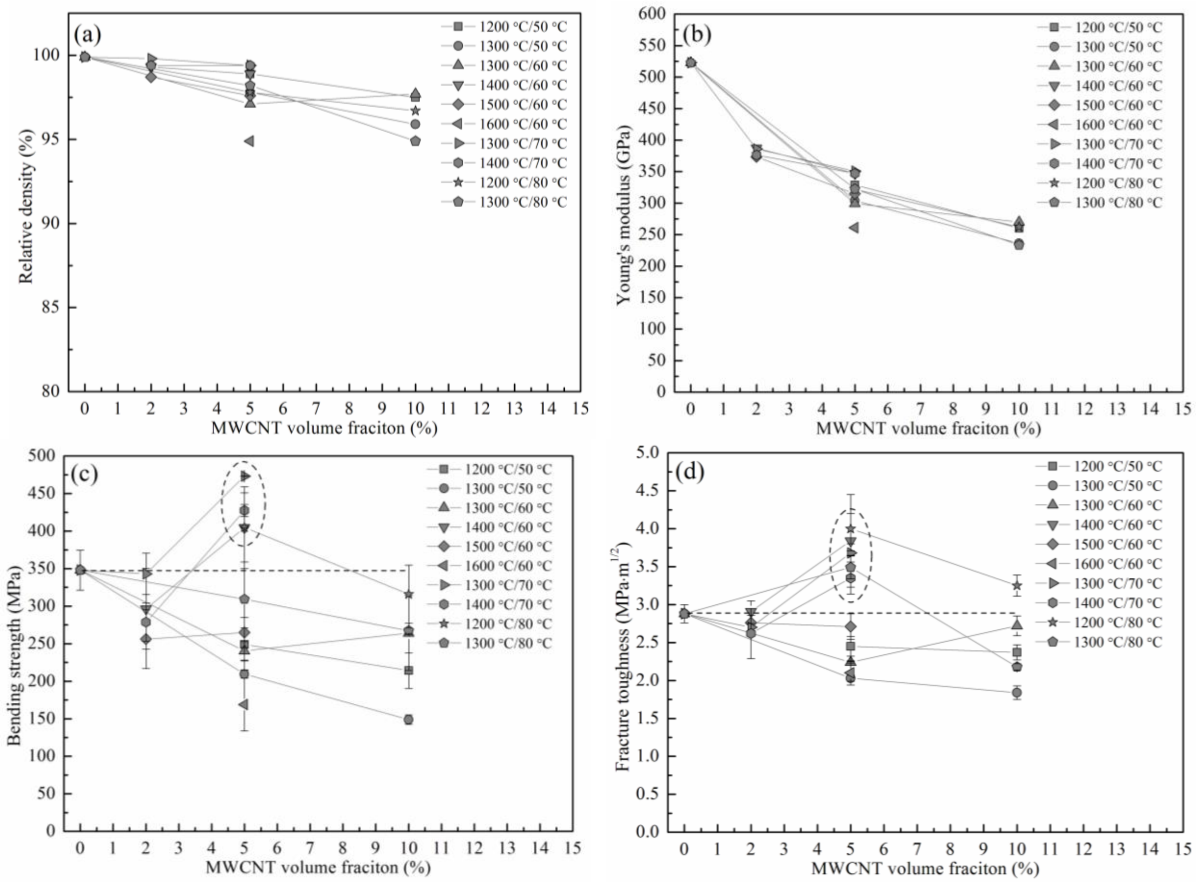

Figure 3. (a) Relative density; (b) Young's modulus; (c) bending strength; and (d) fracture toughness vs. MWCNT volume fraction.

3.4. Fracture surface observation

Well dispersed MWCNTs in the matrix is one of the most influencing factors for the enhancement of mechanical and transport properties. Figure 4 compares the fracture surfaces of the composites containing 5 vol.% and 10 vol.% MWCNTs, in which acid treatment temperature and sintering temperature are 80˚C and 1200˚C, respectively. As seen from the images, successful dispersion of MWCNTs within the alumina matrix is obtained by the flocculation method. At as higher as 10 vol.% MWCNT addition, almost no alumina grains are visible. However, the individually dispersed MWCNTs are still clearly observed, which helps to maintain and surpass the mechanical properties of alumina matrix as shown in Figure 3. Further, the number of observed MWCNTs on the fractures surfaces increases evidently with the increasing MWCNT fraction from 5 vol.% to 10 vol.% in comparison of Figures 4(a) and (b), indicating significant MWCNT loss don't happen during flocculation and SPS process. Theses experimental results indicate that the novel flocculation technique combined with acid treatment and SPS method avoids the problems with MWCNTs segregation and degradation effectively, which is conducive to the improvement of electrical and tribological properties of alumina while maintenance of mechanical properties.

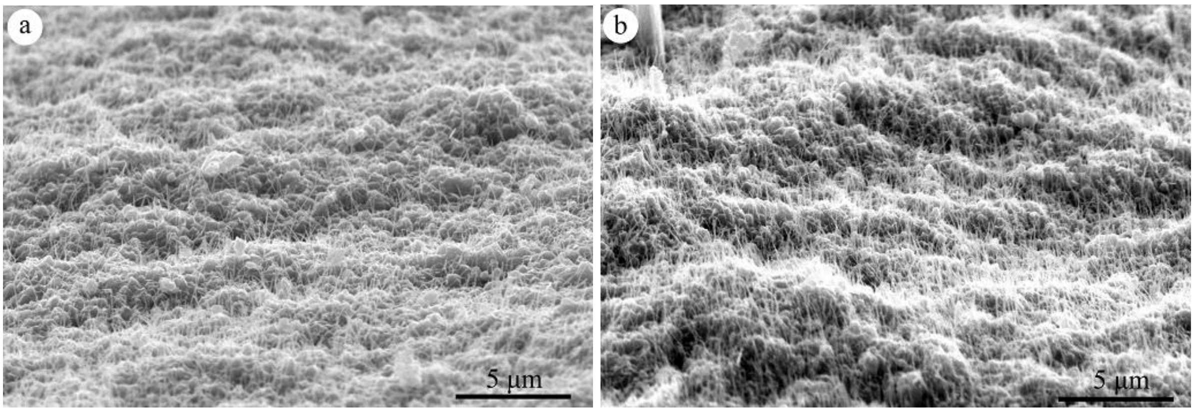

Figure 4. SEM images showing fracture surfaces of the MWCNT/alumina composites with the MWCNT fractions of (a) 5 vol.% and (b) 10 vol.%, respectively.

4. Conclusions

Alumina based composites containing high volume fraction MWCNTs were fabricated by the novel flocculation technique combined with acid treatment and SPS method. Several influencing factors including sintering temperature, acid treatment temperature and MWCNT volume fraction were investigated. In this experimental condition, the MWCNTs was found to be distributed homogenously in the alumina matrix at high volume fraction. Besides, lower sintering temperature and higher acid treatment temperature could lead to the mechanical properties improvement. Some samples containing 5 vol.%, even as high as 10 vol.% MWCNTs could realize the maintenance and increase of bending strength and fracture toughness successfully compared with alumina matrix. The method developed here is a useful technique for fabricating surfactantless and well-dispersed MWCNTs reinforced ceramics especially for high volume content MWCNTs.

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