FABRICATION AND MECHANICAL EVALUATION OF ALIGNED MULTI-WALLED CARBON NANOTUBE SHEET/ALUMINA LAMINATED CERAMIC COMPOSITES

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Abstract

Here we present a simple way of preparing an alumina ceramic material that contains aligned multi-walled carbon nanotube (MWCNT) layers, i.e., aligned MWCNT sheet/alumina laminated ceramics are prepared for the first time by using a filtration technique and spark plasma sintering (SPS) method. It is demonstrated that the introduction of the aligned MWCNT sheets is an effective approach to deflect cracks preventing catastrophic failure whilst raising the fracture toughness from 3.81 ± 0.09 MPa·m$^{1/2}$ to 4.10 ± 0.10 MPa·m$^{1/2}$ and work required to break the samples from 43 ± 7 J/m^2 to 256 ± 70 J/m^2. The electrical conductivities of the composites, containing 0.7 vol.% aligned MWCNT sheets, in directions both parallel and perpendicular to the MWCNT alignment reach values of 858.5 S/m and 117.2 S/m, respectively, compared with that of 10^{-10}–10^{-12} S/m for monolithic alumina samples.

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. Alumina is the most cost-effective and widely used material in the family of engineering ceramics, because of its low sintering temperature and relatively good mechanical properties. However, amongst other engineering ceramics including silicon nitride, silicon carbide and zirconia, alumina is one of the most brittle materials with lower fracture toughness, which restricts its use in a wide array of structural applications. Several approaches have been adopted to improve the brittleness of ceramics [1,2]. Recently, researchers have focused on the carbon nanomaterials, in particular carbon nanotubes (CNTs), which are nanometer-sized tubes of single-walled (SWCNT) or multi-walled (MWCNT) graphene with unique mechanical and chemical properties [3-7], motivating their use in ceramic composite materials as a fibrous reinforcing agent. Moreover, they could confer electrical conductivity to insulating materials due to the excellent electrical properties [8,9]: to avoid the electrostatic charging of insulating ceramics, the electrical conductivity above 0.01 S/m is needed. Therefore, CNTs are anticipated for use as ideal filler for ceramics to enhance their toughness and electrical conductivity. Nevertheless, numerous studies of CNT application to ceramic reinforcement performed for the last two decades have failed to demonstrate their excellent mechanical and electrical reinforcement capabilities for ceramics [10,11]. The toughness and electrical conductivity of CNT/ceramic composites prepared to date are generally inferior to those of theoretically predicted properties, mainly because of poor dispersion, random orientation and inadequate interfacial connectivity between two phases [12,13].

As described above, CNT orientation is one of the important factors in enhancing toughness and electrical conductivity of CNT/ceramic composites. Few efforts have been conducted to fabricate CNT/ceramic composites with unidirectional alignment of CNTs, such as the use of high temperature extrusion technique [14] and electric field-induced alignment technique [15]. Peigney *et al*. [14] exploited that when alumina grains are maintained at sufficiently low sizes (less than approximately 1 μm), they become superplastic, allowing the use of high temperature extrusion technique for the forming of aligned MWCNTs in alumina matrix composites. The authors reported that the composites showed an anisotropy of the electrical conductivity, and conductivity could be adjusted by controlling the MWCNT content. Anisotropic behaviour of the electrical conductivity has been also reported by Zhu *et al*. [15] due to the alignment of MWCNTs using a DC electric field during processing. A difference of 7 orders of magnitude in the electrical conductivity of alumina composites made with 2 wt.% MWCNT that modified by electric field alignment technique was measured from the parallel direction (6.2×10^{-2} S/m) to the perpendicular direction (6.8×10^{-2} S/m).

Here we present a simple way of preparing an alumina ceramic material that contains aligned MWCNT layers, i.e., aligned MWCNT sheet/alumina laminated ceramics are prepared for the first time by using the filtration technique and spark plasma sintering (SPS) method. The aligned MWCNT sheets used in this research are synthesized by a thermal chemical vapor deposition (CVD) method followed by a solid-state drawing and winding technique. It is shown that the aligned MWCNT sheets will deflect cracks preventing catastrophic failure whilst raising the fracture toughness from 3.81 ± 0.09 MPa·m$^{1/2}$ to 4.10 ± 0.10 MPa MPa·m$^{1/2}$ and work required to break the samples from 43 ± 7 J/m^2 to 256 ± 70 J/m^2. Electrical conductivity measurements on the composites reveal that the only 0.7 vol.% aligned MWCNT sheet addition results in about 13–14 orders of magnitude increases in conductivity (858.5 S/m) in the direction parallel to the MWCNT alignment.

2. Experimental

2.1. Preparation of aligned MWCNT sheets

Aligned MWCNT sheets were prepared from a vertically aligned MWCNT array. The MWCNTs with length exceeding 0.8 mm were vertically grown on a Si substrate by the thermal CVD method using an iron chloride powder as precursor of a catalyst. The details of the grown method are described in the reference [16]. The solid-state drawing and winding technique was applied to transform the vertically aligned MWCNT array into aligned MWCNT sheets [17]. The number of plies, i.e., thickness of the aligned MWCNT sheet, could be controlled by varying the take-up number. Here aligned MWCNT sheets with 3 plies were prepared and used for composite preparation. The outer and inner-space diameter of the MWCNTs from transmission electron microscope (TEM, JEM-2100F, JEOL) measurements ranged from 15.6 to 45.2 nm (mean: 31.6 nm) and 3.4 to 19.9 nm (mean: 9.0 nm), respectively. TEM observations revealed that the MWCNTs consist of nested graphitic cylinders that were

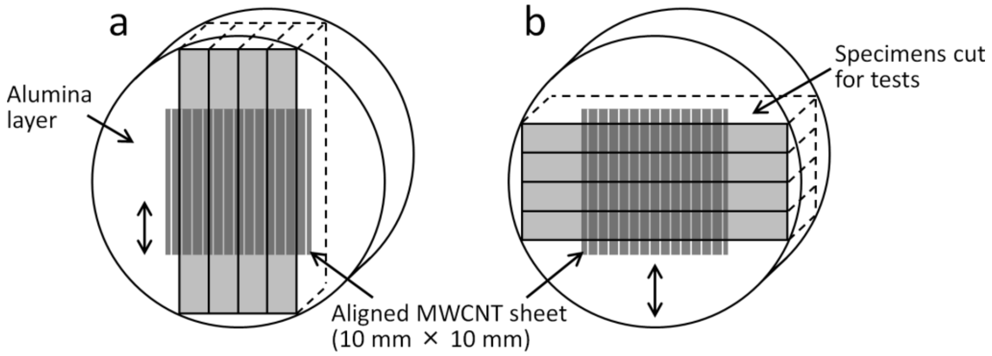

Figure 1. Showing schematics of preparation method of the composites having the aligned MWCNT sheets which oriented (a) parallel and (b) perpendicular direction to the long side of specimens. Double arrows indicate the direction of the MWCNT alignment.

almost perfectly aligned with the nanotube axis, even though structural defects such as gaps between fringes and caps in a central channel were observed for a subset of the MWCNTs. Tensile-loading experiments of individual MWCNTs [18] revealed that nominal (or "engineering") strength and modulus, calculated based on the cross-sectional area of the full specimen, of 5 MWCNTs ranged from ~2.9 to ~7.9 GPa (mean: 5.9 GPa) and ~110 to ~410 GPa (mean: 250 GPa), respectively.

2.2. Fabrication of aligned MWCNT sheet/alumina laminated composites

The procedure for the aligned MWCNT sheet/alumina laminated composite preparation is as follows. First, an α-alumina (TM-DAR, TAIMEI CHEMICALS) was dispersed in isopropyl alcohol (IPA) with the aid of ultrasonic agitation. Next, the alumina-IPA mixture was made into thin sheet, by using the filtration technique, which was then coated with the aligned MWCNT sheet of 10 mm × 10 mm and this process was repeated to give a laminated block approximately 2 mm in thickness. The laminated block was then sintered by spark plasma sintering (SPS, SPS-1050, Sumitomo Coal Mining) at a temperature of 1250˚C under a pressure of 40 MPa in vacuum for 5 min. The prepared specimens were disk-shaped, measuring about 20 mm in diameter and 1 mm in thickness. The specimens were cut using a diamond saw and polished into 2.0 mm (width) × 0.7 mm (thickness) × 15.0 mm (length) pieces, as shown in Figure 1. For the purpose of comparison, samples of monolithic alumina, i.e., composites containing no aligned MWCNT sheets between the alumina layers, are also prepared under the experimental conditions as mentioned above.

2.3. Materials characterization

The fracture toughness was measured by a single edge notched beam (SENB) method under ambient conditions. A notch with a depth of 0.35 mm and width of 100 μm was machined in the center part of the SENB specimens by using a diamond wheel saw with a width of 100 μm. A span length of 8.0 mm and crosshead speed of 0.83 μm/s were applied for the toughness tests. The fracture toughness K_{Ic} is given by the following equation

$$K_{\mathrm{I}c} = \frac{3PL}{2bd^2} a^{1/2} Y \tag{1}$$

where P is the maximum load, L is the span length (= 8.0 mm), b and d are the width (= 2.0 mm) and thickness (= ~0.7 mm) of the samples, respectively, a is the notch depth (= ~0.35 mm)

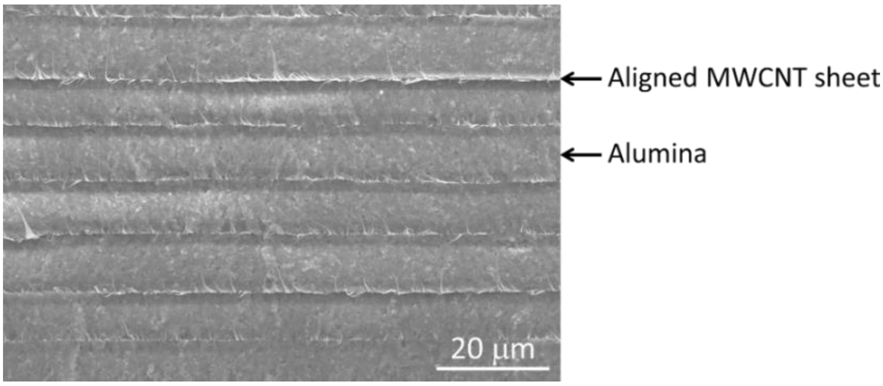

Figure 2. SEM image showing the structure of the laminated composites with approximately 10 μm thick layer of alumina separated by the aligned MWCNT sheets.

and *Y* is a geometrical factor for an edge crack in a three point bend bar. The deflection of the specimens was monitored at the mid-point using a laser scan micrometer (LS-7030M, Keyence) fixed on to the mechanical testing machine (5985, Instron). The electrical conductivity of the samples was measured by using a four-probe technique (2400, Keithley) under ambient conditions with DC currents on parallelepipedic specimens, 2.0 mm (width) × 0.4 mm (thickness) × 10.0 mm (length), in the directions both parallel (Figure 1a) and perpendicular (Figure 1b) to the MWCNT alignment. The microstructures were observed using scanning electron microscopy (SEM, S-4300, Hitachi) and TEM.

3. Results and discussion

The structure of the laminated materials consists of approximately 10 μm thick layer of alumina separated by the aligned MWCNT sheets, as shown in Figure 2. An estimated of the volume fraction of the MWCNTs in the composite was approximately 0.7%, taking 2.10 Mg/m^3 and 3.99 Mg/m^3 as the theoretical values for the MWCNTs and alumina, respectively. In the sample containing no MWCNT layers, there was no visible structure remaining between the alumina layers after sintering. To compare the fracture behavior of the monolithic and laminated samples, containing the aligned MWCNT sheets which oriented perpendicular

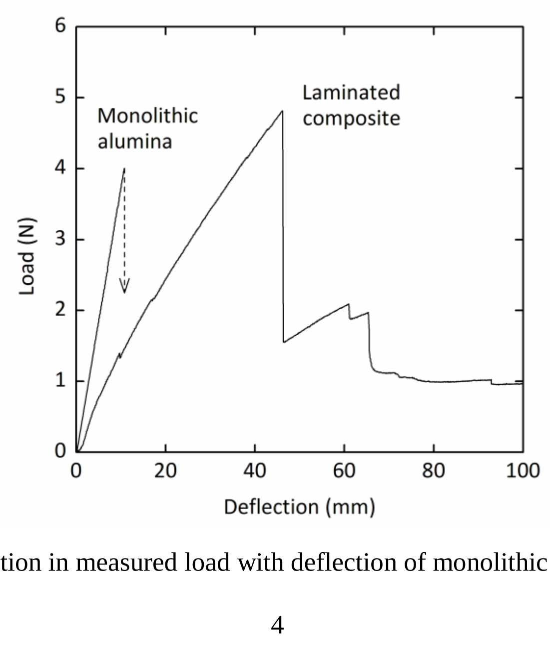

Figure 3. Comparing the variation in measured load with deflection of monolithic and laminated samples.

direction to the crack propagation (Figure 1a), were tested by the SENB method. As expected, the monolithic alumina samples behaved in a linear elastic fashion until catastrophic failure. The laminated composites also deformed in a linear elastic fashion until the crack reached almost the same stress intensity as the monolith, at which point crack growth began. However, rather than travelling right across the specimen, the crack was deflected by one of the aligned MWCNT sheet interface and a delamination crack then grew along the interface. This process was repeated until all the alumina layers had cracked, resulting in a step-like load-deflection response, as shown in Figure 3. The failure of an initial breaking segment corresponds to the maximum load in the load-deflection curve and using equation (1) gives the fracture toughness for three batches of composite of 4.18, 4.16 and 3.95 MPa·m$^{1/2}$ (mean: 4.10 MPa·m$^{1/2}$). In contrast, the fracture toughness for the monolithic alumina was 3.81 ± 0.09 MPa·m$^{1/2}$ and this value was close to the literature value [19].

From Figure 4, it can be seen that the transverse crack does not grow from the tip of the delamination crack, but some distance behind so that the materials is effectively notch insensitive. The work of fracture was calculated by dividing the area under the load-deflection curve by the cross-sectional area of the specimen along the notch plane. This gives the work required to the break the monolithic alumina as 43 ± 7 J/m^2. Even though no significant improvement in the fracture toughness was achieved yet for the composites prepared in this research, the work required to break the laminated composites dramatically increased approximately sixfold (256 ± 70 J/m^2). Note that no apparent difference in both the fracture toughness and work of fracture was observed between the composites having the aligned MWCNT sheets which oriented parallel and perpendicular direction to the crack propagation, suggesting that the composite possesses no in-plane anisotropic properties in mechanical aspects.

Next, we investigated the microstructures of the fracture surface of the composites having the aligned MWCNT sheets which oriented perpendicular direction to the crack propagation. As shown in Figure 5a, numerous individual MWCNTs protrude from the fracture surface, which had not been obtained until now for ceramic composites reinforced by randomly oriented MWCNTs. Lengths of MWCNTs protruding from the fracture surface are in the range approximately 0 to 30 μm. Most MWCNTs appear to be well aligned in the composite, as examplified in Figure 5b. Furthermore, numerous MWCNTs that bridged the about 10–15 μm wide transverse and delamination cracks were observed (Figure 4b). Even though the fracture properties of fiber reinforced composites are well known to be dominated by the fiber bridging

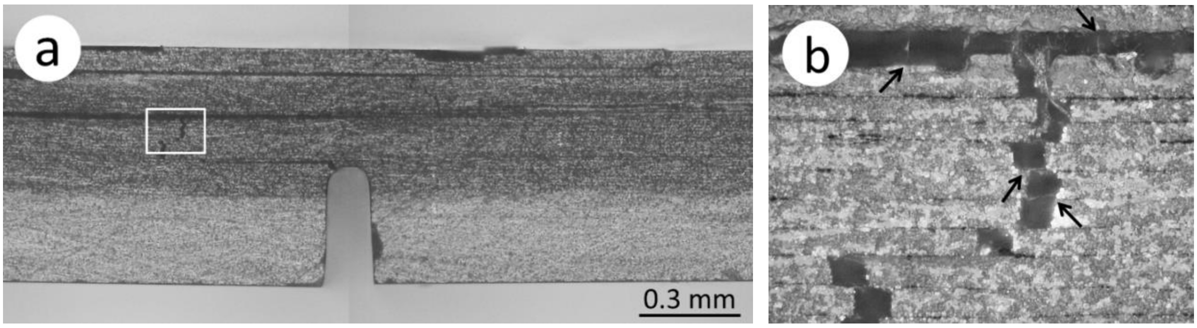

Figure 4. Images of the composite after the toughness test. (a) Transverse crack growth from the notch is deflected, giving rise to a delamination crack. (b) Enlarged image, taken from the square area in image (a). The arrows in image (b) indicate MWCNTs that bridged the 10–15 μm wide transverse and delamination cracks.

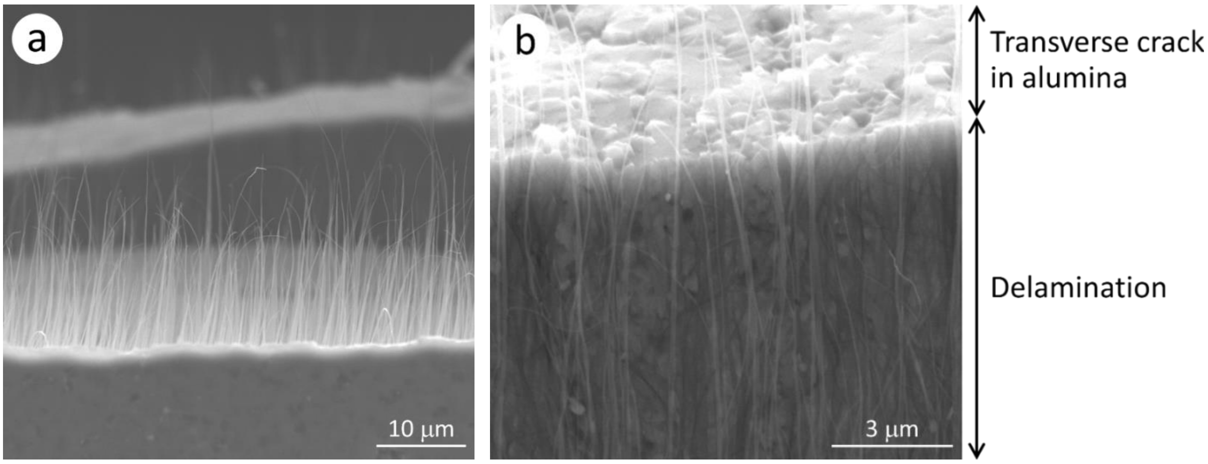

Figure 5. Fracture surface of the laminated composites having the aligned MWCNT sheets which oriented perpendicular direction to the crack propagation. (a) Numerous individual MWCNTs protrude from the fracture surface. (b) Most MWCNTs in the composites are well aligned.

force resulting from debonding and sliding resistance (which dictates the major contribution to the toughness), the crack bridging behavior observed here is unlikely to make a major contribution to the fracture energy due to the low volume fraction of the MWCNTs.

Highly aligned nature of MWCNTs in the composites motivated our research of the electrical properties through the electrical conductivity measurements. The current-voltage characteristics of the aligned MWCNT sheet/alumina laminated composites were investigated on parallel (Figure 1a) and perpendicular (Figure 1b) to the MWCNT alignment. The measured conductivity in the parallel direction of 858.5 S/m is higher than that in the perpendicular direction (117.2 S/m), and the anisotropy ratio is approximately 7.3: this ratio is quite similar as observed for aligned MWCNT sheets [20]. There are a few papers that reports significantly high electrical conductivity of alumina composites made with larger amount of MWCNTs (Table 1). In this research, however, addition of only 0.7 vol.% aligned MWCNT sheets to alumina lead to the increase in the electrical conductivity by about 13–14 orders of magnitude compared with that of the monolithic alumina (10^{-10}–10^{-12} S/m [21]). Such dramatic improvement of the conductivity may be attributable to the good electrical conductivity of the MWCNTs along with the highly aligned nature of MWCNTs in the composites.

MWCNT orientation	MWCNT content [vol.%]	Conductivity [S/m]	References
random	3.7	65.3	[21]
random	9.1	567	[22]
random	10	1140	[23]
alignment	1.2–3.3	1.58	[14]
alignment	3.7	0.062	[15]
alignment	0.7	858.5	Present work

Table 1. Comparison of the electrical conductivities of MWCNT/alumina composites. MWCNT content written in weight fraction in the references [14,15,22] were converted into volume fraction, taking 2.10 Mg/m^3 and 3.99 Mg/m^3 as the theoretical values for MWCNTs and alumina

4. Conclusions

In this research, aligned MWCNT sheet/alumina laminated composites has been prepared for the first time by using the filtration technique and SPS method. It has been demonstrated that the introduction of the aligned MWCNT sheet was an effective approach to deflect cracks preventing catastrophic failure, i.e., the fracture behavior of the laminated composites was quite different from that of the monolithic alumina. Relative to the monolithic alumina samples, the fracture toughness and work required to break the composites for cracks propagating normal to the MWCNT alignment was increased from 3.81 ± 0.09 MPa·m$^{1/2}$ to 4.10 ± 0.10 MPa·m$^{1/2}$ and 43 ± 7 J/m^2 to 256 ± 70 J/m^2, respectively. We have then also shown that the composites demonstrated high anisotropy in the electrical conductivity: the measured conductivity in the parallel direction of 858.5 S/m was higher than that in the perpendicular direction (117.2 S/m). Addition of only 0.7 vol.% aligned MWCNT sheets to alumina led to the increase by about 13–14 orders of magnitude compared with that of monolithic alumina samples.

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