# Microstructure development and fracture toughness of acid-treated carbon nanofibers/alumina composites

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In this study, carbon nanofibers (CNFs) having different amounts of defect were prepared by acid-treating for 0.5, 1 and 5 h and were combined with alumina. Then, the influence of the amount of defect on the CNFs on microstructure development of the CNFs/alumina composites and relationship between the fracture toughness and the average alumina grain size was investigated. The intensity ratio of D-band to G-band (D/G) in Raman spectra of the CNFs increased from 0.34 for pristine CNFs to 0.95 for the CNFs acid-treated for 5 h with the acid-treatment time, which indicates that the amount of defect on the CNFs increased with the acid-treatment time. The alumina grain growth in the dense composites sintered at 1200–1300°C was not influenced by the amount of defect on the CNFs, however, the composite containing CNFs having the moderate amount of defect (D/G = 0.56) showed the slowest alumina grain growth rate at 1350–1450°C. The fracture toughness of the composites containing the CNFs acid-treated for 0.5 h increased with a decrease in average alumina grain size and reached 5.6 MPa·m<sup>0.5</sup> at the average alumina grain size of 0.84  $\mu$ m, which was 60% higher value compared to monolithic alumina (3.5 MPa·m<sup>0.5</sup>). However, fracture toughness of the composites containing CNFs acid-trease in average alumina grain size, showed the maximum values of 5.0 and 4.5 MPa·m<sup>0.5</sup> at average alumina grain size of 1.3 and 1.6  $\mu$ m, respectively, and decreased as the average alumina grain size decreased further. The maximum fracture toughness of the composite containing the CNFs acid-treated for 5 h was lower than that of the composite containing the CNFs acid-treated for 5 h was lower than that of the composite containing the CNFs acid-treated for 1 h.

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# 1. Introduction

Alumina ceramics have been widely used as engineering materials, medical materials, electrical insulators and optical materials due to their high wear resistance, thermal resistance, chemical durability, biocompatibility, hardness, strength and electrical resistance.<sup>1)–3)</sup> However, the brittleness of alumina ceramics limits their application fields, so the improvement of the toughness is required.

It seems that carbon nanotubes (CNTs) are the best reinforcement fibers to improve the mechanical properties of alumina ceramics because CNTs have incredible mechanical properties and high aspect ratio.<sup>4)–11</sup> However, CNTs have two embarrassing properties to be combined with alumina ceramics. First, CNTs are tangled with each other and often form large agglomerates.<sup>12)–21</sup> Second, CNTs are hydrophobic and so interfacial compatibility between CNT and alumina grain is poor.<sup>22</sup> In order to fabricate the reliable CNTs/alumina composites with higher toughness and higher strength, the uniform dispersion of CNTs in the composites and the enhancement of interfacial compatibility between CNT and alumina grain have been required.<sup>19)–31</sup>

In our previous study,<sup>32)</sup> carbon nanofibers (CNFs), which are a kind of multi-walled CNTs (MWCNTs), were high-dispersion-treated in order to disentangle agglomerates of the CNFs. The high-dispersion-treatment is one of the mechanical dispersion

technique using an ultra fine grinding machine which is similar to wet jet milling. In this treatment, the CNFs were passed through slit like channels using high pressure ethanol fluid (200 MPa) with a small amount of dispersants. Consequently, uniform and dense composites were successfully fabricated. Also, the fracture toughness of the composites increased with a decrease in average alumina grain size. This indicates that the fracture toughness of the composites could be improved by controlling the microstructure.

There are many studies on acid-treated CNTs/alumina composites. 13),14),16),26),27),29)-31),33)-35) The acid-treatment of CNTs has been recognized as an useful method for inducing defects with hydrophilic functional groups on the CNTs.27),31),36)-41) The hydrophilic functional groups on the CNTs improve the dispersibility of the CNTs in polar solvents27),36) and enhance the interfacial compatibility between CNT and alumina grain.<sup>29),30)</sup> Estili et al. acid-treated MWCNTs using the acid mixture (conc.  $H_2SO_4$ :conc.  $HNO_3 = 3:1 v/v$ ) under the optimized reflux condition and obtained MWCNTs individually decorated alumina with intimate bonding.<sup>29),30)</sup> Consequently, the composite showed 70% increase in fracture toughness due to crack deflections and frictional pull-outs of the MWCNTs, originated from the high interfacial compatibility and wetting between the MWCNTs and alumina. Wei et al. acid-treated MWCNTs using the acidmixture (conc.  $H_2SO_4$ :conc.  $HNO_3 = 3:1 \text{ v/v}$ ) under application of ultrasonic and prepared the composite using the acid-treated MWCNTs. The obtained composite showed 79% increase in fracture toughness.<sup>34)</sup> Yamamoto et al. induced nanodefects on

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MWCNTs during the acid-treatment in the acid mixture (conc.  $H_2SO_4$ :conc.  $HNO_3 = 3:1 v/v$ ), and fabricated the composite using the MWCNTs with nanodefects. The obtained composite showed 25% increase in fracture toughness through mechanical interlocks originated from a nanoscale anchor effect on the nanodefect of the MWCNTs.<sup>31)</sup> In this way, the acid-treatment of MWCNTs improved the fracture toughness of the composites. However, there are no reports on the influence of amount of defect on the CNTs on sintering behavior and mechanical properties of the composites.

In this study, in order to prepare CNFs having different amounts of defect, CNFs were acid-treated for different periods of time. The acid-treated CNFs were mixed with high purity alumina powder and the acid-treated CNFs/alumina composites were fabricated. And the influence of amount of defect on the CNFs on microstructure development of the composites and relationship between the fracture toughness and the alumina grain size was investigated.

#### 2. Experimental procedure

## 2.1 Acid-treatment of CNFs

CNFs (VGCF-S; diameter: 100 nm, length:  $10-20 \,\mu$ m, Showa Denko, Japan), which are a type of MWCNTs, were acid-treated for 0.5–5 h using the acid mixture (conc. H<sub>2</sub>SO<sub>4</sub>:conc. HNO<sub>3</sub> = 3:1 v/v) under application of ultrasonic in order to prepare the hydrophilic CNFs having different amounts of defect. The acid-treated CNFs were filtered, rinsed with distilled water and freeze-dried. In this study, the CNFs acid-treated for 0.5, 1 and 5 h were described as AT05-CNFs, AT1-CNFs and AT5-CNFs, respectively.

In order to compare with the acid-treated CNFs, the highdispersion-treated CNFs,<sup>32)</sup> which had smaller amount of defect and hydrophobic surface compared to the acid-treated CNFs, were also used and were described as HDT-CNFs.

# 2.2 Preparation of composites

The AT05- or AT1-CNFs were dispersed in ethanol solution dissolving a small amount of polyvinylbutyral (PVB) as a dispersant by ultrasonic. The AT05- or AT1-CNFs ethanol suspensions were kept quietly for 3 days to sediment remaining bundles or agglomerates of the CNFs into the bottom layer of the suspensions. Then, the upper layer of the suspensions were elutriated to obtain well dispersed CNFs suspensions. The AT5-CNFs were dispersed in ethanol without any dispersant by ultrasonic.

The acid-treated CNFs suspensions were mixed with high purity alumina powder (TM-DAR, purity 99.99%, average particle size  $0.1 \,\mu$ m, Taimei Chemicals, Japan) by ball-milling for 24 h. The obtained slurries were dried and then passed through a 100-mesh sieve. In this way, the powder mixtures containing 0.4–1.6 wt % CNFs were prepared.

The powder mixtures were compacted by cold isostatic pressing (CIP) at 200 MPa and sintered in a vacuum at 1150–1450°C for 0.5–6 h. Then, the sintered composites were treated by hot isostatic pressing (HIP) at 180 MPa in a nitrogen atmosphere to be densified further. The temperatures and times of HIP were the same as those of sintering in vacuum but the composites sintered in vacuum at 1450°C for 4 h or 6 h were treated by HIP at 1450°C for 2 h.

#### 2.3 Estimation of composites

The bulk densities of the composites were measured using the Archimedes method. The relative densities were calculated using the bulk densities of the composites and the theoretical densities of alumina  $(3.987 \text{ g/cm}^3)$  and VGCF-S  $(2.0 \text{ g/cm}^3)$ . The microstructures of the composites were observed using a scanning electron microscope (SEM) and a transmission electron microscope (TEM).

The fracture toughness was measured using the Vickers indentation fracture method. The composites were finally polished to a mirror finish using diamond slurry with a particle size of 1  $\mu$ m, and then a 196.1 N load was applied on the polished surface for 10 s. The crack-to-indent ratios (c/a) were larger than 2.5<sup>42)-44</sup>) in every indentation, where c is the half-length of the surface radial crack and a is the half-diagonal length of Vickers indent. So the fracture toughness was calculated by the Miyoshi's formula<sup>45</sup>) Eq. (1):

$$K_{IC} = 0.018 \left(\frac{E}{H}\right)^{0.5} \cdot \frac{P}{c^{3/2}}$$
 (1)

where E is the Young's modulus of the specimen, H is the Vickers hardness of the specimen and P is the applied indentation load.

The alumina grain sizes of the composites, which were polished and thermally etched in air at 50–75°C lower temperatures than the sintering temperatures for 1 h, were measured using the line-intercept method<sup>46)</sup> on the SEM photographs. The measured individual grain size was the maximum length of the grain, which is described as tangent diameter,<sup>47),48)</sup> in the specified direction. The average alumina grain size was determined from the sizes of about 200 grains.

# 3. Results and discussions

## 3.1 Acid-treatment of CNFs

SEM images of the pristine and acid-treated CNFs are shown in Fig. 1. Cracks and flaws were observed on the surface of a few AT5-CNFs but not observed on the surface of AT05- and AT1-CNFs. The CNFs were not shortened by the acid-treatment. Also, the nanodefects reported by Yamamoto et al.<sup>31</sup>) were not observed in this study. Raman spectra of the acid-treated CNFs measured using infrared ray of the wave length of 785 nm are shown in Fig. 2. D-band (defect-mode) and G-band (E<sub>2s2</sub> mode) were observed at 1315 and 1582 cm<sup>-1</sup>, respectively. The intensity ratio of D-band to G-band (D/G) increased with the acidtreatment time as shown in Fig. 2(b) while it did not alter after ball-milling or high-dispersion-treatment as shown in Fig. 2(c). These results indicate that the defects were induced on the CNFs by the acid-treatment and increased with the acid-treatment time. As the results, the acid-treated CNFs, especially AT5-CNFs, dispersed uniformly in ethanol by ultrasonic though the pristine CNFs did not dispersed in ethanol by ultrasonic and formed large agglomerates.

#### 3.2 Densification behavior of composites

Relative densities of the 0.4–1.6 wt % CNFs/alumina composites sintered in vacuum at 1150–1450°C for 2 h are shown in **Fig. 3.** At 1150°C, the acid-treated CNFs/alumina composites had higher relative densities than the HDT-CNFs/alumina composite, as shown in Fig. 3(a). The 0.4 wt % HDT-CNFs/ alumina composite was densified rapidly at range of 1150– 1200°C and reached relative density of 99% at 1250°C. However, the 0.4 wt % acid-treated CNFs/alumina composites were densified slower at range of 1150–1350°C than the 0.4 wt % HDT-CNFs/alumina composite and reached relative density of 99% at 1400°C. On the other hand, the relative densities of the composite sintered in vacuum became lower with an increase in the CNFs content, as shown in Fig. 3(b). These results were



Fig. 1. (Color online) SEM images of (a) pristine, (b) AT1- and (c) AT5-CNFs. The arrows indicate cracks on AT5-CNFs.



Fig. 2. (Color online) (a) Raman spectra of the pristine and acid-treated CNFs, (b) change in the intensity ratio of D-band to G-band (D/G) of CNFs with acid-treatment time and (c) the D/G value of the pristine, ball-milled, HDT- and AT1-CNFs.

observed not only for AT1-CNFs/alumina composite but also for HDT-, AT05- and AT5-CNFs/alumina composites.

By the subsequent HIP treatment, the 0.4 wt % AT05-CNFs/ alumina composite sintered in vacuum at  $1250-1350^{\circ}$ C was densified to relative density of more than 98%, and the 0.4 wt %AT1- and AT5-CNFs/alumina composites sintered in vacuum at  $1250-1350^{\circ}$ C were densified to relative density of more than 99%. However, the 0.8 wt % AT1-CNFs/alumina composite sintered in vacuum were not densified further by the subsequent HIP treatment. Therefore, the microstructure development and fracture toughness of the 0.4 wt % CNFs/alumina composites, which densified to the relative density of more than 98%, were discussed in following paragraphs.

#### 3.3 Microstructure development of composites

SEM images of fractured surfaces of the  $0.4\,wt\,\%$  CNFs/ alumina composites sintered in vacuum at 1250 and 1450°C for

agglomerates of the CNFs were not observed in all composites. At 1250°C, most CNFs were distributed uniformly at intergranulars of alumina, regardless of acid-treatment time of CNFs, and the obvious difference in the microstructure of these composites was not found. At 1450°C, many HDT-, AT05- and AT1-CNFs were still distributed uniformly at intergranulars of alumina. However, some HDT-CNFs were gathered at the same sites of the intergranulars of alumina and formed bundles as enclosed by the circle in Fig. 5(a). In the AT05- and AT1-CNFs/alumina composites, a few bundle consisting of 2-3 CNFs were observed. In the AT5-CNFs/alumina composite sintered at more than 1350°C, a large number of CNFs entered intragranulars of alumina as shown in Fig. 5(f) and bundles of the CNFs were hardly observed. The CNFs sinking in the alumina grains as shown by the arrow in Fig. 5(c) were observed frequently in the composites containing acid-treated CNFs. When the sinking

2 h, and then treated by HIP are shown in Figs. 4 and 5. Large

CNFs fell out the alumina grains as shown by arrows in Fig. 5(e), the traces of the CNFs, which are like channels, remained there. While the HDT-CNFs having a smaller amount of defect (D/G = 0.34) rarely sank in the alumina grains, the AT05- and AT1-CNFs having a larger amount of defect (D/G = 0.56 and 0.59) sank in the alumina grains and the AT5-CNFs having a much larger amount of defect (D/G = 0.95) not only sank in the alumina grains but also entered the grains. These results suggest that the interfacial compatibility between CNF and alumina grain was enhanced by inducing defects on the CNFs.



Fig. 3. (Color online) (a) Relative densities of the  $0.4 \text{ wt} \% (\square) \text{ HDT-}$ , ( $\bigcirc$ ) AT05-, ( $\diamondsuit$ ) AT1- and ( $\bigtriangleup$ ) AT5-CNFs/alumina composites sintered in vacuum at various temperatures for 2 h. (b) Relative densities of the ( $\diamondsuit$ ) 0.4, ( $\bigcirc$ ) 0.8 and ( $\blacksquare$ ) 1.6 wt % AT1-CNFs/alumina composites sintered in vacuum at various temperatures for 2 h.

TEM images of the 0.4 wt % AT05- and AT5-CNFs/alumina composites are shown in **Fig. 6**. Almost interfaces between AT05-CNF and alumina grain were clear, and lattice images of alumina and ordered inner-walls of AT05-CNFs were also observed clearly. However, interfaces between AT5-CNF and alumina grain were not always clear. In addition, disordered inner-walls of AT5-CNFs were frequently observed near the non-clear interface between AT5-CNF and alumina grain. The non-clear interface might have more intimate bonding than the clear interface because the defect induced on the CNFs enhanced interfacial compatibility between CNF and alumina grain.<sup>29),30)</sup> Therefore, AT5-CNFs having a much larger amount of defect might bond more intimately to alumina grains.

Relationships between sintering temperature and average alumina grain size of the 0.4 wt % CNFs/alumina composites are shown in Fig. 7. Alumina grains in all composites grew larger with an increase in sintering temperature. The composites sintered at the same temperatures in the range of 1200-1300°C showed almost the same average alumina grain sizes (around 0.4, 0.8 and 1.2 µm for the composites sintered at 1200, 1250 and 1300°C, respectively), regardless of acid-treatment time of the CNFs. However, at 1350°C, the average alumina grain sizes of the AT05-, AT1- and AT5-CNFs/alumina composites (1.3, 1.6 and  $1.8\,\mu m$ , respectively) were smaller than that of the HDT-CNFs/ alumina composite (2.0 µm), in addition, it was smaller as the acid-treatment time of the CNFs was shorter. At 1450°C, while the average alumina grain sizes of the AT05- and AT1-CNFs/ alumina composites (1.8 and 2.1  $\mu$ m) were smaller than that of the HDT-CNFs/alumina composite (2.5 µm), that of the AT5-CNFs/ alumina composite (2.6 µm) was as large as that of the HDT-CNFs/alumina composite. These results indicate that the grain boundary migration of alumina was influenced by the amount of defect on the CNFs and the composite containing CNFs having a moderate amount of defect (D/G = 0.56) showed the slowest alumina grain growth rate at higher temperatures (1350-1450°C).

Schematic illustrations of microstructure development of the dense composites containing a smaller amount of CNFs such as 0.4 wt % are shown in **Fig. 8**. Generally, when the dense alumina ceramics are sintered further, the alumina grow extremely. When second phase particles are doped in alumina, the inclusion



Fig. 4. SEM images of fractured surfaces of the 0.4 wt% (a) HDT-, (b) AT05-, (c) AT1- and (d) AT5-CNFs/alumina composites sintered in vacuum at 1250°C for 2 h and then treated by HIP.



Fig. 5. (Color online) SEM images of fractured surfaces of the 0.4 wt % (a) HDT-, (b) and (c) AT05-, (d) and (e) AT1-, and (f) AT5-CNFs/alumina composites sintered in vacuum and then treated by HIP at 1450°C for 2 h. The circle in (a) shows a bundle of CNFs in the composite. The arrow in (c) shows a sinking CNF in an alumina grain and the arrows in (e) show a CNF fell out the surface of alumina grains.



Fig. 6. (Color online) TEM images of the 0.4 wt % (a) AT05- and (b) AT5-CNFs alumina composites sintered in vacuum and then treated by HIP at 1350°C for 2 h. The bold arrows indicate the direction parallel to inner-walls of the CNFs.

particles can either (1) move along with boundaries offering little impedance; (2) move along with boundaries with the inclusion mobility controlling the boundary velocity; or (3) be so immobile that the boundary pulls away from the inclusion, depending on the relative values of the boundary driving force, the boundary mobility and the inclusion particle mobility.<sup>49)</sup> At lower sintering temperatures (1200–1300°C), the average alumina grain sizes of the composites did not depend on the amount of defect on the CNFs, as shown in Fig. 7. Such microstructure could be shown as an illustration in Fig. 8(a). When the composites were sintered at higher temperatures (1350–1450°C), the alumina grain boundaries migrated to the directions of solid arrows in Fig. 8(a)

and the CNFs in the composites migrated to the directions of dotted arrows in Fig. 8(a) with the alumina grain boundaries. It was easy for the HDT-CNFs having a smaller amount of defect to migrate rapidly on alumina grain boundaries, which is just like a water drop on the leaf of lotus. That is, the HDT-CNFs could move along with boundaries offering little impedance, which is corresponding to above (1). So the HDT-CNFs were gathered at the same sites of grain boundaries and formed bundles of the CNFs. Consequently, the grain growth retardation effect of the HDT-CNFs on the alumina grain was smaller at higher temperatures, especially at 1450°C, and the alumina grain growth progressed much more, as shown in Fig. 8(b). On the other hand,

because the AT05-CNFs had a larger amount of defect than the HDT-CNFs, it was not easy for the AT05-CNFs to migrate rapidly on the alumina grain boundaries. That is, the AT05-CNFs moved along with boundaries with the CNFs mobility controlling the boundary velocity, which is corresponding to above (2). So the AT05-CNFs were distributed at intergranular even at higher temperatures and did give a larger grain growth retardation effect to the alumina grain growth, as shown in Fig. 8(c). It was very difficult for the AT5-CNFs having a much larger amount of defect to migrate on the alumina grain boundaries at higher temperatures. That is, the AT5-CNFs were so immobile that the boundary pulls away from the CNFs, which is corresponding to



Fig. 7. (Color online) Relationships between sintering temperature and average alumina grain size of the 0.4 wt % ( $\Box$ ) HDT-, ( $\bigcirc$ ) AT05-, ( $\diamondsuit$ ) AT1- and ( $\triangle$ ) AT5-CNFs/alumina composites sintered in vacuum at various temperatures for 2 h and then treated by HIP.

above (3). Therefore, the AT5-CNFs entered alumina grains at higher temperatures and the alumina grains in the AT5-CNFs/ alumina composite grew much larger than those in the AT05-and AT1-CNFs/alumina composites, as shown in Fig. 8(d). Consequently, the alumina grain became as large as those in the HDT-CNFs/alumina composite at 1450°C, as shown in Fig. 7. Because the AT1-CNFs had a larger amount of defect than the AT05-CNFs but had a smaller amount of defect than the AT05-CNFs, they played an intermediate role between the AT05-CNFs and the AT5-CNFs. Therefore, the average alumina grain size of the AT1-CNFs/alumina composite became smaller than that of the AT5-CNFs/alumina composite but became larger than that of the AT05-CNFs/alumina composite at higher temperatures.

# 3.4 Fracture toughness of composites

In this study, the fracture toughness of the 0.4 wt % AT05-CNFs/alumina composite sintered in vacuum at 1250°C for 2 h and then treated by HIP was the highest (5.6 MPa·m<sup>0.5</sup>), which was 60% higher value compared to fracture toughness of mono-lithic alumina (3.5 MPa·m<sup>0.5</sup>).

Relationships between facture toughness and average alumina grain size of the obtained composites are shown in **Fig. 9**(a). Fracture toughness of the 0.4–2.5 wt % HDT-CNFs/alumina composite increased rapidly with a decrease in average alumina grain size. <sup>32)</sup> Similarly, fracture toughness of the 0.4 wt % AT05-CNFs/alumina composite increased with a decrease in average alumina grain size. However, fracture toughness of the 0.4 wt % AT1- and AT5-CNFs/alumina composites increased with a decrease in average alumina grain size, showed the maximum value at average alumina grain sizes of 1.3 and 1.6 µm, respectively, and decreased as the average alumina grain sizes decreased further. The maximum value of the fracture toughness of the AT5-CNFs/alumina composite was lower than that of AT1-CNFs/alumina composite.

The Vickers cracks on many CNFs/alumina composites were not almost deflected, but bridgings and/or pull-outs of the CNFs



Fig. 8. (Color online) Schematic illustrations of microstructure development of dense CNFs/alumina composites. (a): the microstructure of the composites sintered at lower temperatures, which did not depend on the amount of defect on the CNFs. When these composites sintered at higher temperatures, alumina grain boundaries migrated the direction of the solid arrows in (a) and CNFs migrated the direction of the dotted arrows in (a). (b), (c) and (d): the microstructure of the composites sintered at higher temperatures, which were containing CNFs having a smaller amount of defect (HDT-CNFs), a larger amount of defect (AT05-CNFs) and a much larger amount of defect (AT5-CNFs), respectively.



Fig. 9. (Color online) (a) Relationships between fracture toughness and alumina grain size of the ( $\Box$ ) 0.4–2.5 wt% HDT-, 0.4 wt% ( $\bigcirc$ ) AT05-, ( $\diamondsuit$  and  $\blacklozenge$ ) AT1- and ( $\bigtriangleup$ ) AT5-CNFs/alumina composites. The AT1-CNFs/alumina composite in which crack deflections were observed was shown by closed-mark ( $\blacklozenge$ ). SEM images of (b) crack bridgings and pull-outs of CNFs in a Vickers crack on the AT05-CNFs/alumina composite sintered in vacuum at 1250°C for 2 h and then treated by HIP, (c) Vickers crack on the AT1-CNFs/alumina composite sintered in vacuum at 1450°C for 4 h and then treated by HIP, and (d) fractured CNFs in a Vickers crack on the AT1-CNFs/alumina composite sintered in vacuum at 1250°C for 2 h and then treated by HIP. The insertion in (b) is a lower magnification image of (b).

were observed in the cracks, as shown in Fig. 9(b). This means that the enhancement of the fracture toughness of almost all the composites resulted from the bridgings and/or pull-outs of CNFs. However, only in the 0.4 wt % AT1-CNFs/alumina composites sintered at 1450°C for 2-6 h and then treated by HIP, not only bridgings and/or pull-outs of CNFs but also crack deflections were observed, as shown in Fig. 9(c) and the composites were shown by closed mark  $(\spadesuit)$  in Fig. 9(a). The average alumina grain sizes of these composites were relatively large  $(2-3 \mu m)$  and these composites showed larger fracture toughness than other composites with the same average alumina grain size of 2-3 µm. Such crack deflections have been observed for CNTs/alumina composites prepared using acid-treated CNTs.14),29),35) It is considered that they might be caused in the composites which contained CNTs having a moderate amount of defect (D/G = 0.59 in this study) and had larger average alumina grain sizes (more than 2.1 µm in this study). On the other hand, some fractured CNFs exposed their inner-walls in the crack, as shown by arrows in Fig. 9(d). Such fractures of CNFs are called the "sword-in-sheath fracture", 50) and they were rarely observed in Vickers crack and fractured surface of the HDT-CNFs/alumina composite. These results indicate that strength of the CNFs, especially that of outer-walls, was degraded by the acid-treatment.

The CNFs are bended at intergranulars of alumina in the composites due to the superior flexibility, as shown in **Fig. 10**.



Fig. 10. (Color online) SEM image of the bending CNF in the 0.4 wt% HDT-CNFs/alumina composite sintered in vacuum at 1450°C for 2 h. The arrows indicate the interior compressive or tensile stress.

Such bending is one of the unique property of CNFs, which is different largely from the property of ceramic whiskers and fibers. It was reported in our previous paper<sup>32)</sup> that because the number of bendings per CNF could increase with a decrease in average alumina grain size and the resistance for bridging and/or pull-out of the CNFs could be increased with an increase in the number of bendings per CNF, the fracture toughness of the HDT-CNFs/alumina composites increased with a decrease in average alumina grain size. Because of the similar reason, the fracture toughness of the AT05-CNFs/alumina composites increased with a decrease in average alumina grain sizes and that of the AT5-CNFs/alumina composites increased with a decrease in average alumina grain sizes in the range of 1.6-2.8 µm. Also, because the CNFs acid-treated for longer times might bond more intimately with alumina grains, they showed a larger resistance for bridging and/or pull-out. Consequently, the acid-treated CNFs/alumina composites showed a higher fracture toughness than the HDT-CNFs/alumina composite in the average alumina grain size range of 0.8-2.5 µm, especially, AT1-CNFs/alumina composite showed a much higher value in the average alumina grain size range of 2.1-2.5 µm due to not only bridgings and/or pull-outs of the CNFs but also the crack deflections.

The compressive stress was loaded to the inside of the bending CNF and the tensile stress was loaded to the outside of the bending CNF, as shown by arrows in Fig. 10. Such internal stress should be larger as the bending state of the CNFs was sharper. When the external tensile stress was applied for the CNFs by the cracks propagation, the external and the internal tensile stress was loaded to the outside of the bending CNFs. The total tensile stress should be larger as the bending state of the CNFs was sharper. As the alumina grain became finer, the CNFs were bended more sharply in the composites. The other side, the strength of the CNFs was lowered by the acid-treatment. Therefore, the acid-treated CNFs in the composite having finer alumina grains were fractured more easily when cracks propagated in the composites. This is the reason why the fracture toughness of the AT1- and AT5-CNFs/alumina composites showed the maximum value at average alumina grain sizes of 1.3 and 1.6 µm, respectively, and decreased as the average alumina grain sizes decreased further. In particular, the CNFs acid-treated for longer times such as the AT5-CNFs were fractured much more easily in the composites having finer microstructures by a smaller external tensile stress because such CNFs were bonded much more intimately with alumina grains and had a lower strength. Consequently, the maximum fracture toughness of the AT5-CNFs/

alumina composite was lower and appeared at larger alumina grain sizes than that of the AT1-CNFs/alumina composite. So if the AT05-CNFs/alumina composite have much finer average alumina grain size, fracture toughness of the composite will be decreased.

The acid-treated CNFs/alumina composites showed higher fracture toughness than the HDT-CNFs/alumina composite, particularly in the range of relatively larger average alumina grain sizes. In addition, if the CNFs show a much higher compatibility to alumina such as the AT5-CNFs and have a higher resistance for tensile load, the fracture toughness of the composites will be dramatically improved, particularly in the range of finer average alumina grain sizes.

# 4. Conclusions

In this study, the influence of the amount of defect on the CNFs on microstructure development and fracture toughness of the CNFs/alumina composites which densified to relative density of more than 98% was investigated.

The defects induced on the CNFs by the acid-treatment influenced the microstructure development of the composites sintered at higher temperatures (more than  $1350^{\circ}$ C). The AT05-CNFs having a moderate amount of defect (D/G = 0.56) migrated more slowly with grain boundaries and controlled the boundary migrations of alumina. Consequently, the composite showed the finest microstructure at such higher temperatures.

The fracture toughness of the composites containing the CNFs acid-treated for 0.5 h increased with a decrease in average alumina grain sizes and achieved and reached  $5.6 \,\mathrm{MPa} \cdot \mathrm{m}^{0.5}$  at the average alumina grain size of 0.84 µm, which was 60% higher value compared to monolithic alumina (3.5 MPa·m<sup>0.5</sup>). However, fracture toughness of the composites containing the CNFs acidtreated for 1 and 5 h increased with a decrease in average alumina grain sizes, showed the maximum values of 5.0 and 4.5 MPa·m<sup>0.5</sup> at average alumina grain sizes of 1.3 and 1.6 µm, respectively, and decreased as the average alumina grain size decreased further. The defects induced on the CNFs by the acid-treatment led to more intimate bonding between the CNF and the alumina grain while they lowered the strength of the CNFs. On the other hand, in the composites having finer alumina grains, the CNFs were bended more sharply along alumina grain boundaries, which caused a larger internal tensile stress along the outside surface of the bending CNF. So the acid-treated CNFs were fractured more easily when cracks propagated in the composites having finer alumina grains. Consequently, the fracture toughness of the composites containing the CNFs acid-treated for 1 and 5 h showed the maximum values and decreased with a decrease in average alumina grain sizes.

On the other hand, because the acid-treated CNFs were bonded more intimately with alumina grains, the composites containing the acid-treated CNFs (D/G = 0.56–0.95) showed higher fracture toughness than the composite containing the HDT-CNFs (D/G = 0.34) in the range of average alumina grain size of 0.8– 2.5  $\mu$ m. Therefore, if the CNFs show a much higher compatibility to alumina such as the AT5-CNFs and have a higher resistance for tensile load, the fracture toughness of the composites will be dramatically improved in the range of finer average alumina grain sizes.

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