Effects of CNT addition on mechanical properties, electric conductivity and oxidation resistance of Al₂O₃-TiC composite

Hideaki SANO¹, a, Junichi Morisaki¹, Guo Bin ZHENG¹, b
and Yasuo UCHIYAMA¹, c

¹ Graduate School of Engineering, Nagasaki University, Japan
1-14 Bunkyo-match, Nagasaki, 852-8521 JAPAN

a sano@nagasaki-u.ac.jp, b gbzheng@nagasaki-u.ac.jp, c uchiyama@nagasaki-u.ac.jp

Keywords: Al₂O₃-TiC composite, CNT addition, mechanical properties, electric conductivity, oxidation resistance.

Abstract. Effects of carbon nanotubes (CNT) addition on mechanical properties, electric conductivity and oxidation resistance of CNT/Al₂O₃-TiC composite were investigated. It was found that flexural strength, Young’s modulus and fracture toughness of the composites were improved by addition of more than 2 vol% CNT. In the composites with more than 3 vol% CNT, the oxidation resistance of the composite was degraded. In comparison with Al₂O₃-26vol%TiC sample as TiC particle-percolated sample, the Al₂O₃-12vol%TiC-3vol%CNT sample, which is not TiC particle-percolated sample, shows almost the same mechanical properties and electric conductivity, and also shows thinner oxidized region after oxidation at 1200°C due to less TiC in the composite.

Introduction

Al₂O₃-TiC composites are widely used as cutting tools and substrate of magnetic head materials due to their attractive mechanical properties and good electric conductivity. Electric conductivity of the Al₂O₃-TiC composites increased rapidly as a TiC volume fraction increased from 0.20 to 0.23 [1]. The Al₂O₃-TiC composites exhibit electric conductivity of 10⁻¹ S·m⁻¹ and can be cut using wire discharge machining. However, due to the continuous TiC phase, oxidation of TiC proceeds continuously toward the inside of the composite.

Carbon nanotubes (CNTs) possess high mechanical properties, good electric conductivity and high aspect ratio. It is known that CNT/Al₂O₃ composites with a small amount of CNTs exhibit high mechanical properties [2] and good electric conductivity [3]. In this study, to fabricate CNT/Al₂O₃-TiC composites with high mechanical properties, electric conductivity and excellent oxidation resistance, influence of CNT content on these properties of the composites was investigated.

Experimental

Al₂O₃, TiC and CNT were used as a starting powder. Commercially-available Al₂O₃ powder (0.15 µm, > 99.99%, Taimicron TM-DAR, Taimei Chemicals), TiC powder (1-2 µm, > 99 %, TiC-M, Japan New Metals) and various amounts of CNT powder were ball-milled for 20 h in ethanol. CNT was produced by using CCVD (catalytic chemical vapor deposition) method in the condition of 700°C for 1h in atmospheric H₂ carrier gas and C₂H₂ carbon source gas in the tubular electric furnace. Composition of the starting powder is listed in Table 1. The milled powders were then dried under vacuum and hot-pressed in a graphite die with a 25 x 25 x 3 mm³ at 1700°C at 25 MPa under Ar for 1 h. Microhardness, flexural strength and Young’s modulus were measured. For a part of specimens, fracture toughness was evaluated by indentation-fracture (IF) method. Electric resistance was measured by using a 4-probe electric resistance tester. Oxidation test was carried out in a thermogravimetric analyser, in N₂-20 vol.%O₂ with 50 ml·min⁻¹

Table 1 Composition of CNT/Al₂O₃-TiC composites

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Al₂O₃ [vol%]</th>
<th>TiC [vol%]</th>
<th>CNT [vol%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>AT12C0</td>
<td>87.6</td>
<td>12.4</td>
<td>0</td>
</tr>
<tr>
<td>AT12C1</td>
<td>86.7</td>
<td>12.3</td>
<td>1.0</td>
</tr>
<tr>
<td>AT12C2</td>
<td>85.8</td>
<td>12.2</td>
<td>2.0</td>
</tr>
<tr>
<td>AT12C3</td>
<td>84.9</td>
<td>12.0</td>
<td>3.0</td>
</tr>
<tr>
<td>AT12C5</td>
<td>83.2</td>
<td>11.8</td>
<td>5.0</td>
</tr>
<tr>
<td>AT26C0</td>
<td>84.0</td>
<td>26.0</td>
<td>0</td>
</tr>
</tbody>
</table>
from room temperature to 1200°C at a heating rate of 10°C·min⁻¹. Morphology observation and elemental analysis of the samples were performed using scanning electron microscope (SEM) and energy dispersive spectrometer (EDS).

**Results and discussion**

**Porosity and mechanical properties.** The porosity and the mechanical properties of all samples are presented in Fig. 1. The AT26C0 sample is described using solid circle with dotted horizontal line in the figures. The porosity of the samples increased with the increase of CNT content. The AT12C0 sample, which contains no CNT, shows small value in porosity compared with the AT26C0 sample (Fig. 1 (a)). The CNT contents lessened the sintered densities of the nanocomposite [2], corresponding to the pores formed concerned with restricting sintering. The larger pores and agglomeration of CNTs can be observed in the sample containing relatively larger amount of CNT (Fig. 2 (a)). Vickers hardness of the samples decreased with the increasing CNT content (Fig. 1 (b)). Higher TiC content in the Al₂O₃ matrix composites also deteriorated sinterability caused by covalent bond of TiC. The porous structure and CNT aggregates reduced not only the relative density but also hardness. The AT26C0 sample shows slightly higher value in hardness than that of the AT12C0, because TiC is relatively harder than Al₂O₃. However, significant 86% increases in flexural strength were obtained for the AT12C3 sample, in comparison with the AT12C0 sample (Fig. 1 (c)). In contrast, relatively high drop (30%) in flexural strength were observed in the AT12C5 sample than that of the AT12C3 sample. The Young’s modulus of the AT12C3 also shows the highest value of 127 GPa in Fig. 1 (d). Whai, et al. revealed that addition of TiC in the Al₂O₃ matrix resulted in the increase in flexural strength and Young’s modulus due to the improved fracture toughness [4]. The fracture toughness of the AT26C0 (7.3 MPa·m¹/²) is larger than that of AT12C0 (5.7 MPa·m¹/²). It is clearly observed that addition of CNTs in the Al₂O₃-TiC composite also improved the fracture toughness. The AT12C2 samples exhibited the highest value of 6.8 MPa·m¹/². In general, conventional toughening mechanism for fiber-reinforced composites includes fiber pullout and crack bridging. From SEM observation, a few CNTs pullout in the samples observed in a crack formed after Vickers indentation test (Fig. 2 (b)).

**Electric percolation by conductive materials.** Fig. 3 shows the electric conductivity of sintered samples with volume fraction of CNT. The electric conductivity of the composites increases with the increase of CNT content, and exhibits a typical insulator-conductor transition between volume
fraction of 1 and 3 vol.% of CNT. Because TiC and CNTs are metallic conductors, and Al$_2$O$_3$ is insulator, the electric percolation is achieved by forming CNT and TiC network in the Al$_2$O$_3$ matrix. The AT26C0 sample shows higher electric conductivity (4.6 S·m$^{-1}$) than that of the AT12C0 sample (2.6·10$^{-6}$ S·m$^{-1}$). It was found that the percolation threshold concerning to the electric conductivity of the Al$_2$O$_3$-TiC composite was in the range of 0.20 to 0.23 in volume fraction of TiC [1]. Ahmad, et al. demonstrated that addition of MWNTs in Al$_2$O$_3$ matrix results in the dramatic increase of around eight orders of magnitude in the conductivity due to the percolation threshold in the well-dispersed MWNTs / alumina composites containing 0.45 mass% of MWNTs [3]. In this study, the AT12C2 sample containing 2 vol.%-CNT, which is about 1 mass%-CNT, is in a transition state of the electric conductivity. Considering the AT12C2 sample contains 12 vol.%-TiC, the electrical percolation formed CNT and TiC network in the Al$_2$O$_3$ matrix was estimated to occur at less than 1 vol.%-CNT content. It was thought that due to the agglomeration of CNTs and existence of pores in the sample respectively, more CNTs are needed to form the electrical percolation network.

**Oxidation resistance.** Morphological change of the sample after oxidation is shown in Fig. 4. A few micrometers white TiC particle is embedded in the grayish Al$_2$O$_3$ matrix on the polished sample before oxidation. On the oxidized samples, it can be seen

![Fig. 2 Fractured surface (a) and crack (b) of the AT12C3 sample.](image)

![Fig. 3 Electric conductivity of sintered samples.](image)

![Fig. 4 Morphology of the sample before and after non-isothermal oxidation at 1200°C.](image)
that several micrometers diameter grains, which agglomerate on the AT12C0 and AT12C3 sample, and are covered with the AT26C0 sample, appeared on the surfaces of these composites oxidized at 1200°C. Because oxidized grains were TiO₂ (rutile) detected by XRD, it can be attributed to the oxidation of TiC as a non-oxidized ceramics. During oxidation, TiC reacted with oxygen gas to produce not only TiO₂ but also carbon, which formed in circumstances of relative low partial pressure of oxygen of 10⁻³⁰ atm considering from the Ellingham diagrams [5]. In the initial stage of oxidation, formed TiO₂ was on the TiC particle of the sample surface, and then, the oxidation proceeded toward the inside of the sample. The TiO gas might be formed during reaction due to the relative low partial pressure in the inside of the sample. TiC oxidation forming TiO gas results in the formation of pores in the sample nearby surface. In fact, cross sectional observation of oxidized sample showed that there is porous structure as an oxidized region in depth with 20 or 30 µm (Fig. 5). Value of depth of oxidized region was plotted in Fig. 6. The AT12C0, AT12C1 and AT12C2 show almost the sample value in the ranging from 8 to 10 µm. It was found that despite having a lot of pores in the AT12C3 sample, it has a good oxidation resistance compare with the AT26C0 sample with small amount of pores. As the AT26C0 sample has TiC particle-percolated structure, oxidation is easy to proceed. In contrast, the AT12C3 sample shows isolated embedded TiC particle in Al₂O₃ matrix, TiC particles connect via small amount of CNT with small diameter, therefore, there is less progress on oxidation in the AT12C3 sample.

Summary
The CNT/Al₂O₃-TiC composite with 3 vol.% CNTs exhibited high mechanical properties and good electric conductivity, and the composite exhibited less progress on oxidation compared with the Al₂O₃-TiC composite with electric conductivity via TiC.

References