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Hardness and Wear Resistance of Carbon Nanotube Reinforced Aluminum-Copper Matrix Composites

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Recently, carbon nanotubes (CNTs) have been attracted to reinforcement of composite materials due to their extraordinary mechanical, thermal and electrical properties. Many researchers have attempted to develop CNT reinforced metal composites with various fabrication methods and have shown possibilities for structural and functional applications. Among them, CNT reinforced Al matrix composites have become very attractive due to their huge structural application in industry. In this study, CNT reinforced Al–Cu matrix composites with a microstructure of homogeneous dispersion of CNTs in the Al–Cu matrix are investigated. The CNT/Al–Cu composites are fabricated by mixing of CNT/Cu composite powders and Al powders by high energy ball mill process followed by hot extrusion process. The hardness and wear resistance of the CNT/Al–Cu composites are enhanced by 1.4 and 3 times, respectively, compared to those values for the Al–Cu matrix. This remarkable enhancement mainly originates from the homogeneous dispersion of CNTs in Al–Cu matrix and self-lubricant effect of CNTs.

Keywords: Carbon Nanotube Composites, Aluminum, Wear.

1. INTRODUCTION

Many researchers have shown interest in the excellent physical, mechanical, electrical and thermal properties of carbon nanotubes.[1,2] In addition to these properties, nanoscale size, high aspect ratio and low density have inspired interest in CNTs as reinforcement for metal matrix composites. Unfortunately, CNTs are highly entangled due to the Van der Waals force between each CNT; wettability between metal and CNTs is also poor. Thus, the critical issues of CNT/Metal composites are how to homogeneously disperse CNTs in a matrix and how to initiate strong interfacial bonding between CNTs and a metal matrix. Several researchers have attempted to fabricate CNT/Metal composites by conventional powder metallurgy process.[3–7] However, it was not possible to effectively disperse the CNTs in the metal matrix by means of conventional powder metallurgy processes such as ball milling and wet mixing of CNTs and metal powers with sonication, because they have not enough energy to break a strong aggreegation of CNTs. Thus the mechanical properties of composites were lower than expect. In our previous studies, we developed a novel fabrication process for CNT/Metal composites, which process shows homogenous dispersion of CNTs in the matrix and strong interfacial bonding between CNTs and the matrix. This process is called the "Molecular-level mixing process."[8–11] The possibility of CNTs as reinforcement of metal matrix nanocomposites was shown with the huge increase of the mechanical properties such; there was as much as a three times increase of both yield strength[8] and wear resistance.[13]

However, the molecular-level mixing process cannot be directly applied to CNT/Al composites due to the difficulty in the reduction of Al oxide to Al. Therefore, CNT/Al composites have mainly been studied in the conventional powder metallurgy process. Lee et al. fabricated CNT/Al composites by mixing of CNTs and

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Al powders in aqueous solution using sonication followed by spark plasma sintering, they also characterized the wear properties.[12] When 1 wt.% of CNTs was added, the wear resistance increased, but the wear resistance decreased when the weight % of the CNTs was above 2 due to the agglomeration of CNTs. Agarwal et al. showed a 40% increase of wear resistance for cold-sprayed 1 wt.% CNT/Al composites.[13] Bae et al. fabricated CNT/Al composites by high energy ball mill process in order to increase the dispersion of CNTs in the Al matrix. They showed an enhancement of strength[14] and wear resistance.[15] The wear resistance of 4.5 vol.% CNT/Al composite is 2 times higher than that of the Al matrix. However, the increase of wear properties is still lower than that of the CNT/Cu composites formed by a molecular-level mixing process. Homogeneous dispersion of CNTs; also good interfacial bonding with the matrix is still an unsolved problem in CNT/Al composites. In order to obtain high strengthening in the composite, good dispersion of CNTs and a good interface between the CNTs and the matrix are very important.[16]

In this study, we develop a new fabrication process to increase the dispersion of CNTs in Al the matrix. We fabricated CNT/Al–Cu composites by a combination of a high energy milling process and a molecular-level mixing process followed by the hot extrusion process. The microstructure, hardness and wear resistance were characterized.

2. EXPERIMENTAL DETAILS

Multi-walled CNTs (Hanwha Nanotech Corporation), with diameters of 10–15 nm and fabricated by thermal chemical vapor deposition, were functionalized by acid treatment. The CNTs were stirred for 10 h in a mixed solution of H_2SO_4 and HNO_3 at a 3:1 ratio in order to attach the functional groups on the surface of the CNTs. The functionalized CNTs were dispersed in water by sonication to form a CNT suspension and then, $Cu(CH_3COO)_2 \cdot H_2O$ (Aldrich) aqueous solution and 2 M NaOH aqueous solution were added to the CNT suspension. The mixed solution was heated to 80 °C to form CNT/CuO composite. This was followed by vacuum filtering. The CNT/CuO composite powders were reduced at 300 °C for 6 h under a hydrogen atmosphere to obtain the CNT/Cu composite powders. The contents of CNTs in the CNT/Cu composite powders were 63 and 75 vol.% for 2 and 4 vol.% CNT/Al–Cu composites, respectively, in order to adjust the weight % of the Cu in the Al matrix to a value of 4. For the fabrication of the Al–Cu matrix, Cu powders were also fabricated under the same conditions without CNTs.

The CNT/Cu composite powders and Al powders (Kojundo Chemical Laboratory Co. Ltd., 99.9% purity) with an average particle size of 3 μm were mixed into the CNT/Al–Cu composite powders using a planetary mill (Fritsch GmbH). The planetary milling was performed at a rotation speed of 200 rpm for 3 h under an argon atmosphere. A stainless jar and zirconia ball were used. The ball to powder ratio was 10:1. The Al-4wt% Cu alloy powders were fabricated by mixing of Al powders and Cu powders under same conditions.

The CNT/Al–Cu composite powders were consolidated to bulk CNT/Al–Cu composites by hot extrusion process. Before hot extrusion, the CNT/Al–Cu composite powders were put into a 6061Al alloy can and degassed at 400 °C for 1 h. After sealing, the CNT/Al–Cu composite powders were hot extruded into rods at 420 °C with an extrusion ratio of 20:1 and a ram speed of 2 mm/s. By varying the volume fraction of the CNTs, three kinds of CNT/Al–Cu composite powders were hot extruded, i.e., 2, 4 vol.% CNT/Al–Cu composites and Al-4 wt.% Cu alloy.

A scanning electron microscope (SEM, Philips XL-30S) and a transmission electron microscope (TEM, Tecnai G2 F39 S-Twin) were used for observation of the microstructure of the CNT/Al–Cu composites. The volume fraction of the CNTs in the CNT/Al–Cu composites was determined by analyzing the carbon contents with an element analyzer (ThermoQuest Elemental Analyzer EA1110-FISONS). Vickers hardness tests were performed to evaluate the hardness of the CNT/Al–Cu composites. The wear property of the CNT/Al–Cu composites was evaluated by pin-on-disk type wear tests under dry sliding condition. The wear tests were performed at a sliding speed of 150 rpm, an applied load of 30 N and a sliding distance of 1 km. A disk made with SKD 61 tool steel was used as counterpart.

3. RESULTS AND DISCUSSION

Our strategy to improve the dispersion of CNTs in the Al matrix is an application of a molecular-level mixing process to conventional high energy ball milling process. First, the CNT/Cu composite powders were fabricated by molecular-level mixing process. We attached Cu nanoparticles on the surface of CNTs to make the CNTs separate from each other (schematic illustration shown in Figure 1(a). The gaps between the agglomerated CNTs became larger and this will help the CNTs to more easily disperse in the Al matrix. An SEM image of the CNT/Cu composite powders is shown in Figure 1(b). Cu nanoparticles, with sizes of 10 to 50 nm, are found to homogeneously decorate the surface of the CNTs and to separate the CNTs from each other.

Figure 2(a) shows the microstructure of the 4 vol.% CNT/Al–Cu composite powders after the high energy ball mill process. The CNTs are shown to be well dispersed in the Al–Cu matrix without any agglomeration and the Cu nanoparticles are mechanically alloyed in the Al and form an Al–Cu alloy matrix. Although there was only 3 h of milling time, the CNTs are embedded and implanted within the Al powders rather than attached on the surface of the Al powders. However, in the case of using pristine

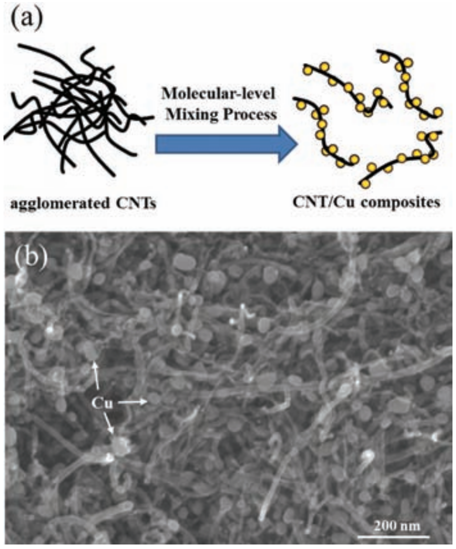

Figure 1. (a) Schematic illustration of CNT/Cu composite powders and (b) SEM micrograph of CNT/Cu composite powders.

CNTs instead of CNT/Cu composite powders, the CNTs are still agglomerated on the surface of the Al powders, as shown in Figure 2(b). This indicates that using CNT/Cu composite powders is more efficient than using pristine CNTs for the dispersion of CNTs in the Al matrix.

All the CNT/Al–Cu composites, after the hot extrusion process, show over 99% of relative density as shown in Table I. The microstructure with homogeneous dispersed CNTs in the Al–Cu matrix is shown in TEM image in Figure 3(a). Particularly, the CNTs are well bonded with the Al–Cu matrix without any defect or second phase such as Al_4C_3 (Fig. 3(b)).

Table I. Relative density of CNT/Al–Cu composites.

Volume fraction of CNT (%)	Relative density (%)
0	99.2
2	99.3
4	99.1

The hardness of the CNT/Al–Cu composites measured by Vickers hardness test is shown in Figure 4 and Table II. The hardness values increase almost linearly with increasing content of CNT. When 4 vol.% of CNTs are added, the hardness value of the CNT/Al–Cu composite corresponds to 142.6 HV, which is about 1.4 times higher than that of the Al–Cu matrix. This remarkable increase of hardness due to CNT reinforcement originates from the homogeneous dispersion of CNTs in the Al–Cu matrix and the high relative density. Our previous result, which investigated the strengthening mechanism of CNT reinforced Al matrix composite, shows that homogeneously dispersed CNTs without damage or reaction with Al matrix can improve the mechanical properties of compsites.[17, 18]

Figure 5 shows the wear properties of the CNT/Al–Cu composites evaluated by pin-on-disk wear test. The wear loss decreased linearly with the increasing content of CNTs and, in case of 4 vol.% CNT/Al–Cu composites, the wear loss is reduced to 1/3 compared to that of the Al–Cu matrix. The increase of wear properties is thought be due to the increase of hardness and the decrease of friction coefficient. This dramatic increase of wear resistance has not been reported yet in CNT reinforced Al matrix composites and clearly demonstrates the excellence of our fabrication process. The microstructures of the worn surface

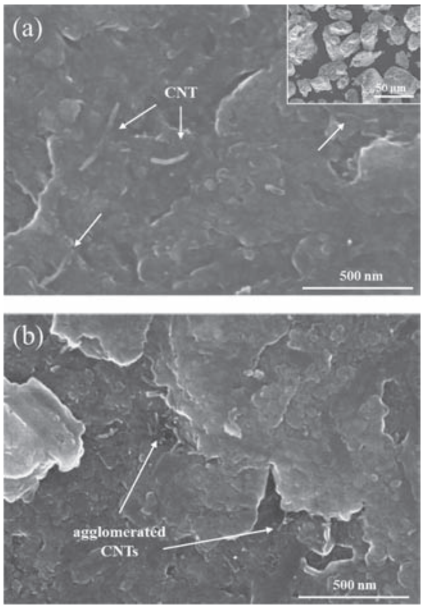

Figure 2. (a) SEM micrograph of CNT/Al–Cu composite powders and (b) SEM micrograph of CNT/Al powders from pristine CNTs.

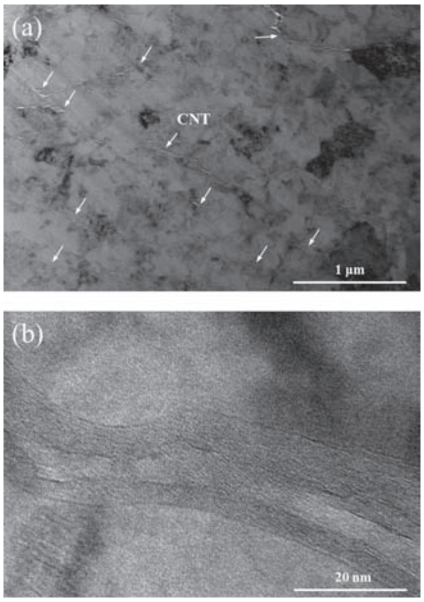

Figure 3. (a) TEM micrographs of 4 vol.% of hot extruded CNT/Al–Cu composites and (b) its high magnification image.

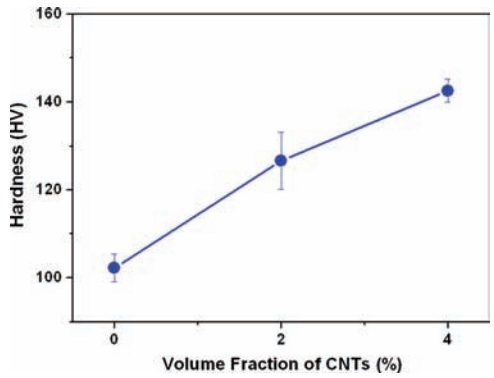

Figure 4. The variation of Vickers harness of CNT/Al–Cu composite with the volume faction of CNTs.

Table II. Hardness and wear loss of CNT/Al–Cu composites.

Volume fraction of CNTs (%)	Hardness (HV)	Wear loss (mg)
0	102.3 ± 3.1	2.96 ± 0.24
2	126.6 ± 6.5	1.73 ± 0.17
4	142.6 ± 2.6	1.01 ± 0.32

of the Al–Cu matrix and the CNT/Al–Cu composites are shown in Figure 6. The worn surface of the Al–Cu matrix shows a flaked microstructure; during the wear process, Al debris is easily formed by a delamination of Al grains,

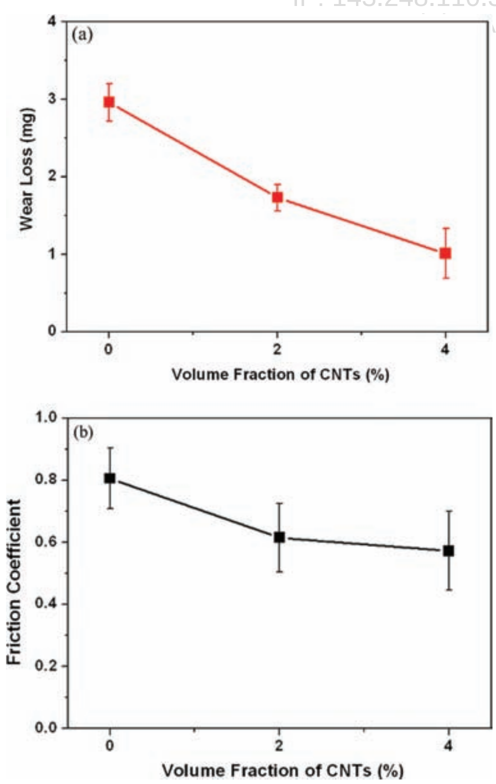

Figure 5. (a) The variation of wear loss of CNT/Al–Cu composite with the volume faction of CNTs and (b) the variation of friction coefficient of CNT/Al–Cu composites with the volume fraction of CNTs.

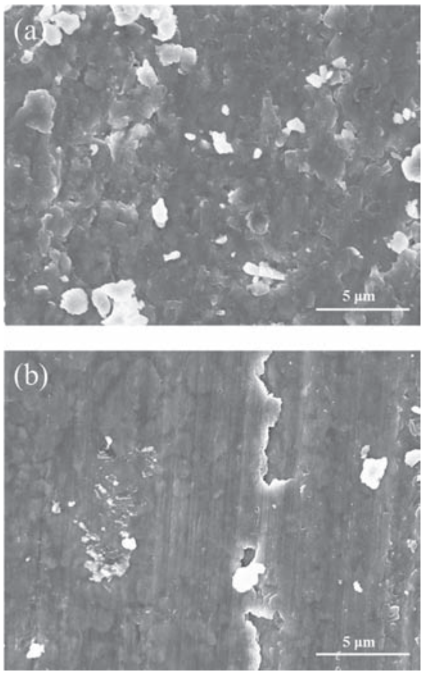

Figure 6. (a) SEM micrograph of worn surface of Al–Cu and (b) SEM micrograph of worn surface of CNT/Al–Cu composites.

which flakes away (Fig. 6(a)). However, the worn surface of the CNT/Al–Cu composite shows smooth and shallow grooves as can be seen in Figure 6(b). The Al grains are not easily delaminated from the worn surface due to the pinning of CNTs in the Al–Cu matrix with homogeneous dispersion. Moreover, the CNTs exposed to the worn surface during the wear process can act as a lubricating carbon film owing to their low friction coefficient.[11] Thus, the addition of CNTs enhances wear resistance due to not only the strengthening effect but also to the self-lubricating effect of CNTs.

4. CONCLUSION

CNT/Al–Cu composites powders with homogeneously dispersed CNTs in the Al–Cu matrix were fabricated by mixing CNT/Cu composite powders and Al powders by high energy ball mill process. Using CNT/Cu nanocomposite powders fabricated by a molecular-level mixing process is a very effective way to increase the dispersion of CNTs in the Al matrix by enlarging the gaps between the CNTs, which are strongly agglomerated in nature. The CNT/Al–Cu composites, which were hot extruded with full densification of the CNT/Al–Cu composite powders, show an increase of the hardness with the increasing volume fraction of CNTs due to the strengthening of the CNTs with homogeneous dispersion. The wear resistance of the CNT/Al–Cu composites significantly increased by 3 times compared to the values for the Al–Cu matrix. This considerable enhancement of wear resistance is due to the strengthening effect of CNTs and the self-lubricating effect of CNTs, which retard the delamination of Al grains during the wear process. From these results, the homogeneous dispersion of CNTs is thought to be a very important process that can effectively strengthen mechanical the properties of CNT/Al composites.

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