Hardness and wear resistance of carbon nanotube reinforced Cu matrix nanocomposites

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Abstract

Carbon nanotube (CNT) reinforced Cu matrix (CNT/Cu) nanocomposites are fabricated by a novel fabrication process, named as molecular level process, which involves suspending CNTs in solvent by surface functionalization, mixing Cu ions with CNT suspension, drying, calcination and reduction. The molecular level process produces CNT/Cu nanocomposite powders, in which the CNTs are homogeneously implanted within Cu powders. The nanocomposite powders are consolidated into CNT/Cu nanocomposites by spark plasma sintering. The hardness and sliding wear resistance of CNT/Cu nanocomposite are enhanced by two and three times, respectively, compared to those of Cu matrix. The enhancement of hardness is due to the effect of homogeneous distribution of CNTs in Cu matrix, good bonding at CNT/Cu interfaces and high relative density of nanocomposites. The dispersed CNTs in Cu-matrix nanocomposite gives significantly enhanced wear resistance by retarding the peeling of Cu grains during sliding wear process.

Keywords: Carbon nanotube; Copper; Nanocomposite; Molecular level process; Wear resistance

1. Introduction

Several researches have shown that the carbon nanotube (CNT) can considerably enhance the mechanical and conductive properties of polymer and ceramic matrix during last decade [1–3]. In CNT/polymer nanocomposites, the addition of carbon nanotube as reinforcement improves the strength of the polymer matrix by several times [4,5]. Although there are some doubt on evaluation method for fracture toughness [6], Zhan et al. [7] showed remarkable enhancement of fracture toughness in CNT/alumina nanocomposite. Ning et al. [8] and Mo et al. [9] introduced sol–gel process for CNT/SiO₂ and CNT/Al₂O₃ nanocomposites which show the enhancement of fracture strength, hardness and fracture toughness. However, compared to CNT/polymer and CNT/ceramic nanocomposites, CNT/metal nanocomposites attract less attention due to their inferior mechanical properties than expected. Even though several researchers have fabricated CNT/metal nanocomposites by powder metallurgy process including mixing of CNTs with metal powders followed by hot pressing, the CNT/metal nanocomposites have failed to show anticipated enhancement of mechanical properties [10,11]. In previous researches on CNT/metal nanocomposites, inferior mechanical properties are mainly caused by agglomeration of CNTs and low relative density of the nanocomposite ranged 85–95%. Recently, Cha et al. [12] developed the molecular level process for homogeneous dispersion of CNTs in metal matrix and used spark plasma sintering (SPS) process for highly densified CNT/metal nanocomposites. Although most investigations have focused on fabrication process and mechanical properties, very few studies have been reported on wear properties of CNT/metal nanocomposites.

In this study, CNT/Cu nanocomposites are fabricated by molecular level process followed by spark plasma sintering process and the microstructure, hardness and wear resistance of CNT/Cu nanocomposites are characterized.

2. Experimental procedures

2.1. Fabrication of CNT/Cu nanocomposite powders by molecular level mixing process

The schematic fabrication process steps for molecular level process of CNT/Cu nanocomposite are shown in Fig. 1. The
Fig. 1. Schematic fabrication process steps for molecular level process of CNT/Cu nanocomposites.

fabrication process for CNT/Cu nanocomposite powders consists of four steps [12]. As the first step, multi-wall carbon nanotubes (MWCNTs), with diameter of 10–40 nm and with length of a few micrometers, were purified and functionalized by acid treatment. There are several chemical methods for attaching functional groups on the CNT surfaces [13–16]. Once the functional groups are attached on the CNTs, the electrostatic repulsive force between CNTs overcomes the Van der Waals force to form a homogeneous suspension within a solvent. In second step, Cu acetate monohydrate \([\text{Cu(CH}_3\text{COO)}_2\cdot\text{H}_2\text{O}]\) was added to the CNT suspension and sonicated for 2 h then the CNT/Cu ion precursor was fabricated. In third step, the solution of CNT/Cu ion precursor was vaporized with magnetic stirring at 100 °C, and the vaporized CNT/Cu ion precursor powders were calcinated into CNT/CuO nanocomposite powders at 350 °C in air. Finally the CNT/CuO composite powders were reduced into CNT/Cu nanocomposite powders under hydrogen atmosphere.

2.2. Consolidation and characterization of CNT/Cu nanocomposite powders

The fabricated CNT/Cu nanocomposite powders were consolidated by spark plasma sintering, which enables the powders to be sintered by Joule heat and spark plasma generated by high pulsed electric current applied through the compact [17]. The CNT/Cu nanocomposite powders were sintered at 550 °C for 1 min in a vacuum of \(10^{-3}\) mbar with an applied pressure of 50 MPa. The heating rate up to the sintering temperature was maintained at 100 K/min. The sintered CNT/Cu nanocomposite has the cylindrical shape of 15 mm diameter and 3 mm height. Microstructure characterization of CNT/Cu nanocomposites was carried out using high-resolution scanning electron microscopy (HRSEM) and transmission electron microscopy (TEM). The volume fraction of CNTs was determined by analyzing the carbon contents using an Elemental Analyzer (EA1110-FI)SONS) and a C/S analyzer (ELTRA CS800). Vickers hardness tests were performed to evaluate the hardness of CNT/Cu nanocomposites. Pin-on-disk type wear tests were performed to evaluate the wear resistance under dry sliding condition [18]. The wear tests were carried out at a sliding speed of 150 rpm, at applied load 30 N and rotating distance of 1 km using a rotating disk made by SKD 61 tool steel.

3. Results and discussion

The nanocomposite powders fabricated by the molecular level process gives homogeneously dispersed CNTs within Cu powders as shown in Fig. 2. The most important feature of this process is mixing CNTs with Cu ions in molecular level. That is, the CNTs are embedded or implanted within Cu powders rather than attached on the surface of Cu powders. The morphologies
Table 1
Relative densities of CNT/Cu nanocomposites with vol.% of CNTs

<table>
<thead>
<tr>
<th>Volume percent of CNT (%)</th>
<th>Measured density (g/cm³)</th>
<th>Theoretical density (g/cm³)</th>
<th>Relative density (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>8.79</td>
<td>8.90</td>
<td>99.2</td>
</tr>
<tr>
<td>5</td>
<td>8.45</td>
<td>8.53</td>
<td>99.0</td>
</tr>
<tr>
<td>10</td>
<td>8.08</td>
<td>8.17</td>
<td>98.9</td>
</tr>
</tbody>
</table>

of the CNT/CuO and CNT/Cu nanocomposite powders show an ideal composite microstructure, which displays morphologies of CNTs implanted in the powders (Fig. 2(a) and (b)). The fabricated CNT/Cu nanocomposite powders are consolidated into bulk CNT/Cu nanocomposite with full densification (above 99%) as shown in Table 1 by spark plasma sintering process. The photos of consolidated pure Cu and CNT/Cu nanocomposite specimens are displayed in Fig. 3(a) and the surface morphology of etched 5 vol.% CNT/Cu nanocomposite is shown in Fig. 3(b). The microstructure of consolidated CNT/Cu nanocomposites shows homogeneous distribution of carbon nanotubes within the Cu matrix. Particularly, the TEM images (Fig. 3(c)) shows that the carbon nanotubes form a three-dimensional network within Cu grain.

The hardness of the CNT/Cu nanocomposites measured by Vickers hardness test is shown in Fig. 4(a). A considerable enhancement of hardness is observed by addition of CNTs in
Cu matrix. The hardness increases almost linearly with increasing the CNT volume fraction up to 10%. When the 10 vol.% of CNTs are reinforced, the hardness of CNT/Cu nanocomposites is 1.1 GPa, which is about 1.8 times higher than that of Cu without CNTs. In previous researches, when the CNT/metal or CNT/ceramic nanocomposites are fabricated by molecular level process, the chemical bonding formed between the CNTs and the matrix ions provides homogeneous distribution of CNTs as well as high interfacial strength \[12,19\]. Therefore, it is confirmed that such remarkable enhancement of hardness by CNT reinforcement is originated from the high interfacial strength at CNT/Cu interface, the homogeneous distribution of CNTs within Cu matrix and attained high relative densities. Thus, based on this result, it can be shown that the improvement of mechanical properties of CNT reinforced nanocomposites is expected when the external load can be shared by homogeneously distributed CNTs through the load transfer from matrix to CNTs by sound interfacial strength at CNT/matrix.

Fig. 4(b) shows the wear loss and wear rate of CNT/Cu nanocomposites evaluated by pin-on-disk wear test. Under dry sliding wear condition, the wear loss of CNT/Cu nanocomposites is reduced to 1/3 compared to those of pure Cu matrix. This result means that this nanocomposite shows three times higher wear resistance by addition of CNTs. The microstructures of the worn surface of pure Cu and CNT/Cu nanocomposite were shown in Fig. 5(a) and (c). The worn surface of the CNT/Cu nanocomposite shows almost clear surface morphology as shown in Fig. 5(c), while that of the pure Cu shows flaked microstructure as shown in Fig. 5(a).

When the surface of pure Cu flakes away during the wear process, the worn chips are formed by peeling of Cu grains (Fig. 5(b)) near the worn surface. However, in case of CNT/Cu nanocomposite, the Cu grains are not easily peeled from the worn surface by the pinning of homogeneously implanted CNTs across Cu grains as observed in TEM images (Fig. 5(d)) of CNT/Cu nanocomposites. At the same time, the CNTs exposed to the worn surface during wear process can act as a lubricating carbon film owing to its low friction coefficient \[10\]. Therefore, the wear loss of CNT/Cu nanocomposites is remarkably decreased with increasing volume fraction of CNTs due to the effect of homogeneous distribution of CNTs in Cu matrix and low friction coefficient of exposed CNTs on the worn surface.

4. Conclusion

The CNT/Cu nanocomposite with homogeneously dispersed CNTs within Cu matrix can be fabricated by means of a novel process named as the molecular level process. The hardness and wear resistance of fabricated CNT/Cu nanocomposite were significantly increased with increasing the volume fraction of CNTs. The remarkable enhancement of hardness is originated from the homogeneously distributed CNTs in Cu matrix, high interfacial strength at CNT/Cu interfaces and high relative density of nanocomposites. The dispersed CNTs in Cu-matrix nanocomposite provides considerably enhanced wear resistance.
by retarding the peeling of Cu grains during sliding wear process. It is concluded that the homogeneous distribution of CNTs with sound interface in Cu matrix is an important technological issue to enhance the mechanical behavior and wear resistance of CNT/Cu nanocomposite.

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References