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Frictional and wear properties of cobalt/multiwalled carbon nanotube composite films formed by electrodeposition

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ABSTRACT

Carbon nanotubes (CNTs) have solid lubricity due to their unique structure, and as such, CNT composites are also expected to exhibit superior tribological properties. In this study, Co/CNT composite films were fabricated using a composite electrodeposition technique, and their tribological properties were investigated. Three different sizes of multiwalled carbon nanotubes (MWCNTs) were used as the CNTs in this study. The microstructures of the composite films were examined using scanning electron microscopy. Frictional and wear properties were examined using a ball-on-disk method without any lubricants at room temperature and at high temperatures (100–500 °C). The Co/MWCNT composite films had lower coefficients of friction than a cobalt film at room temperature. In contrast, the coefficients of friction of the Co/MWCNT composite film at high temperature became higher than that at room temperature and slightly lower than that of a cobalt film. These results are likely related to the formation of cobalt oxides on the surface and the heat dissipation of the MWCNTs.

1. Introduction

Carbon nanotubes (CNT) [1,2] have a unique structure (the highly preferred orientation of their graphitic basal planes is parallel to the axis [3]) and exhibit solid lubricity. Therefore, the tribological properties of CNT composites such as resin/CNT [4–8], ceramic/CNT [9–11] and metal/CNT [12] have been studied extensively. Metal/CNT composite coatings [13–17] are particularly promising as a friction abrasion resistant technology for a wide range of applications. We have previously reported the fabrication of metal/CNT composite films [18–21] and their superior frictional properties [22–24]. Previous research concerning the tribological properties of metal/CNT composite films has focused on room temperature frictional properties. Kedward et al. [25] reported that cobalt composite films, with WC, SiC, Cr_3C_2 and ZrB_2 as composite particles, exhibited superior wear resistance over nickel composite films, especially at high temperatures. Therefore, cobalt (Co)/CNT composite films are also expected to be attractive materials with improved frictional properties not only at room temperature, but also at high temperatures. However, there are no reports on the tribological properties of Co/CNT composite plating films.

In this study, Co/CNT composite films were fabricated using an electrodeposition technique, and the frictional and wear properties were evaluated at both room temperature and elevated temperatures.

2. Material and methods

2.1. Chemicals

Three different sized multiwalled CNTs (MWCNTs) were used in the present study. These commercially available MWCNTs included VGCF (Showa Denko Co., Ltd.), VGCF-S (Showa Denko Co., Ltd.) and MWNT-7 (Mitsui & Co., Ltd.), the specifications of which are given in Table 1. Special grade $CoSO_4 \cdot 7H_2O$, NaCl, NaOH and H_3BO_3 (Wako Pure Chemical Industries, Ltd.) and first-grade polyacrylic acid (PA5000; Wako Pure Chemical Industries, Ltd.; mean molecular weight of 5000) were used in this study. Pure water from a water purifier (RFP343RA, Advantec MFS, Inc.) was used in all the experiments.

2.2. Fabrication of Co/MWCNT composite films

A solution of 1.78 M $CoSO_4 \cdot 7H_2O$ + 0.26 M NaCl + 0.57 M H_3BO_3 [25] was used as the base plating bath. MWCNTs are hydrophobic and therefore were not uniformly dispersed in the base plating bath. A homogeneous dispersion of the MWCNTs was achieved by the addition of PA5000 to the base plating bath with stirring. The compositions of the composite plating baths are given in Table 2. The electrodeposition of the Co/MWCNT composite films and cobalt film was performed at 50 °C with agitation by bubbling air under galvanostatic conditions (2.5 A dm^{-2} for the Co/MWCNT composite films, 5 A dm^{-2} for the cobalt film) using a commercially available electrolytic cell (Model I, Yamamoto-Ms Co., Ltd.) with internal dimensions of 65 × 65 × 95 mm^3. The volume of the plating bath was 300 cm^3. Copper (B-60-P05, Yamamoto-Ms Co., Ltd.) and iron plates (B-60-P01, Yamamoto-Ms Co., Ltd.) with exposed

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Table 1
Specifications of the MWCNTs used in this work.

MWCNT	Diameter (nm)	Length (μm)
VGCF	100–150	10–15
VGCF-S	80	10–15
MWNT-7	60	10–15

surface areas of 10 cm^2 (3×3.33 cm) were used as cathodes for characterization of the microstructures and evaluation of the tribological properties, respectively. A cobalt plate (A-53-M1-P08-19, Yamamoto-Ms Co., Ltd.) was used as the anode. Electrodeposition performed with 900 C of electricity (90 C cm^{-2}) resulted in approximately 20 μm thick films.

2.3. CNT content of Co/MWCNT composite films

The content of MWCNTs in the composite films was determined by direct weighing. For the weight measurement, approximately >2 g of the Co/MWCNT composite film was electrodeposited (300 C cm^{-2}) on stainless steel substrates. After electrodeposition, the composite films were exfoliated from the stainless steel substrates and the cobalt matrix of the composite films was dissolved in nitric acid. The MWCNTs were filtrated from the nitric acid solution, dried and weighed. Measurements of the MWCNT content were carried out twice for each composite film and the mean value of the two measurements was used as the MWCNT content in the composite films. The MWCNT content was calculated in terms of mass%, volume% and as MWCNT number density. To calculate the volume%, the actual nanostructures of the MWCNTs were first analyzed using scanning transmission electron microscopy (STEM; HD-2300A, Hitachi). Each MWCNT had a cylindrical appearance and a hollow core with a diameter of 3–4 nm. Compared to the volume of an entire single MWCNT, that of the hollow core is negligible. Therefore, the volume% of MWCNTs in the composite film was calculated using the density of graphite (2.26 g cm^{-3}). To calculate the MWCNT number density (the number of MWCNTs per 1 g of composite film), each single MWCNT volume was calculated assuming a columnar shape of a single MWCNT using the dimensions given in Table 1. The mass of each single MWCNT was calculated using the density of graphite (2.26 g cm^{-3}), and the number of MWCNTs per 1 g of composite film was then calculated using the MWCNT mass% for the composite films.

2.4. Microstructure of Co/MWCNT composite films

The surface morphologies of the composite films were examined before and after the frictional tests using field emission-scanning electron microscopy (FE-SEM; JSM-7000 F, Jeol, Ltd.). A cross-sectional polisher (SM-09010 Jeol, Ltd.) was used to prepare cross-sectional samples for FE-SEM observations. The phase structures of the composite films were evaluated before and after frictional tests using X-ray diffraction analysis (XRD; XRD-6000, Shimadzu Seisakusho) with Cu K_α radiation.

2.5. Friction and wear properties of Co/MWCNT composite films

The frictional properties of the Co/MWCNT composite films were measured using a ball-on-disk-type friction test machine (High Temperature Tribometer THT1000, CSM Instruments Co.). An alumina ball (6 mm diameter, Hv = 1500) was used as the counter-surface. A test load of 2 N was used with a rotation speed of 1.0 cm s^{-1}, a 2-mm radius of rotation and 1000 rotations (the sliding distance was 12.56 m). Tests were conducted without the use of lubricants and under ambient conditions from room temperature to 500 °C. The wear volume was calculated from the cross-sectional areas of wear scars, which were measured using a roughness meter (Surtronic 25, Taylor Hobson Co.). The wear rate was calculated using the wear volume, the test load (2 N) and the sliding distance (12.56 m).

Table 2
Compositions of the plating baths.

Reagents	Cobalt	Co/VGCF	Co/VGCF-S	Co/MWNT-7
$CoSO_4 \cdot 7H_2O$	1.78 M	1.78 M	1.78 M	1.78 M
NaCl	0.26 M	0.26 M	0.26 M	0.26 M
H_3BO_3	0.57 M	0.57 M	0.57 M	0.57 M
PA5000		2×10^{-5} M	2×10^{-5} M	2×10^{-5} M
MWCNT		1.5 g dm^{-3}	0.8 g dm^{-3}	0.55 g dm^{-3}

3. Results and discussion

3.1. Surface and cross-sectional morphology of Co/MWCNT composite films

Fig. 1 shows surface and cross-sectional SEM images of the electrodeposited Co/MWCNT composite films. SEM images of a cobalt film are also shown (Fig. 1a, e) for comparison. Bare individual MWCNTs are distributed homogeneously on the surface of each Co/MWCNT composite film (Fig. 1b–d). The black areas in the cross-sectional SEM images are MWCNTs (Fig. 1f–h). There are no gaps and voids in the cross-sections of the films, which indicates that the composite films have compact structures. The MWCNTs are distributed individually and homogeneously throughout the composite films, so that the microstructure of the composite films in the depth direction is the same as that of the surface.

3.2. MWCNT content in composite films

The MWCNT content in the composite films are presented in Table 3. The order of MWCNT mass% and volume% for the Co/MWCNT composite films is Co/VGCF > Co/VGCF-S > Co/MWNT-7; the volume% (mass%) of the Co/VGCF composite film is approximately 3 times higher than the other composite films. However, the MWCNT number densities of the composite films are almost the same ($1.0–1.7 \times 10^{10}$).

3.3. Friction and wear properties of Co/MWCNT composite films

3.3.1. Friction and wear properties at room temperature

Fig. 2 shows the frictional behavior of the Co/MWCNT composite films at room temperature, in addition to that of a cobalt film for comparison. The cobalt film has a coefficient of friction of ca. 0.3 from the beginning to the end of the wear test. The coefficients of friction of the Co/MWCNT composite films are lower than that of the cobalt film. The coefficients of friction of the Co/MWNT-7 and Co/VGCF-S composite films increased gradually from the initial values of 0.15 and 0.16 to final values of 2.8 and 1.9, respectively. In contrast, the coefficient of friction of the Co/VGCF composite film remained constant at ca. 0.11 during the wear test. Thus, the order of lower coefficient of friction for the composite films with respect to the cobalt film is Co/VGCF > Co/VGCF-S > Co/MWNT-7, and the Co/VGCF composite film showed the lowest coefficient of friction. The MWCNT number densities of the composite films were almost the same, whereas the order for the MWCNT volume% in the composite films was Co/VGCF > Co/VGCF-S > Co/MWNT-7. Thus, the coefficients of friction may be related not to the number density, but to the volume% of MWCNTs in the composite films.

Although the type of MWCNTs may affect the frictional properties, the MWCNTs used in the present study are all graphitized, so that the effect on the coefficient of friction is considered to be negligible [23]. The contact area between the MWCNTs and the alumina counter surface increases with the volume% of MWCNTs, so that the contact area between the cobalt matrix and alumina counter surface decreases with increasing volume% of the MWCNTs, resulting in a lower coefficient of friction than the cobalt film. There have been many reports on coefficient of friction measurements for only MWCNTs [26–32]. Dickrell et al. [27] reported the coefficients of friction of vertically and transversely aligned MWCNTs to be 0.795 and 0.090, respectively, using a