Wear Behavior of Network-Structured Carbon Nanotube Coating on Titanium Substrate†

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Abstract

This study investigated the tribological property and wear behavior of pure titanium (Ti) plate coated with un-bundled multi-walled carbon nanotubes (MWCNTs). The network-structured MWCNT films were formed on Ti substrate, and their tribological properties were examined by the ball-on–disk wear test equipment under a dry sliding condition. SUS304 stainless steel ball was used as a counterpart material in this test. The mean friction coefficient of the Ti plate coated with MWCNTs was remarkably lower and stable compared to the as-received pure Ti plate without any coating films. SEM-EDS analysis showed the network-structured MWCNT films obviously remained after a wear test for 3.6 ks in sliding and no seizure phenomena with the SUS304 ball. The above excellent tribological performance was due to CNTs self-lubricant properties, their bearing effects and the strong metallurgical bonding between Ti plate and MWCNT films by annealing.

KEY WORDS: (Carbon nanotube coating), (Titanium), (Tribological property), (Friction)

1. Introduction

Carbon nanotube (CNT) has superior self-lubrication performance due to its high modulus as well as other carbon materials[1]. Previous studies have investigated CNTs tribological properties as lubricants on the surface of composites. The results indicated that CNTs have been effective to reduce both wear loss and friction coefficient of the composite materials[2-4]. Ti and Ti alloy have been used in automotive, aeronautics and chemical industries due to their remarkable mechanical properties and excellent corrosion resistance. On the other hand, they have poor tribological properties when in contact with other materials and itself due to their high reactivity[5]. The surface treatments for the Ti matrix have been explored to improve the wear resistance by various coatings, such as composite coating with CNTs[6], diamond-like carbon (DLC) surface coating[7], and CNTs coating[8]. The studies revealed the coatings onto Ti composites have improved tribological properties and their hardness.

In this study, un-bundled multi-walled carbon nanotubes (MWCNTs) have been employed on the pure Ti plate as the coating films. The tribological property and wear behavior of pure Ti plate coated with MWCNTs were investigated under dry sliding condition. The effects of MWCNTs on the friction coefficient and surface damages of Ti plate surface are also discussed. It is expected that CNTs confer a great self-lubricating ability on the sliding surface.

2. Experimental

A commercial pure Ti plate was employed as a substrate, and MWCNTs, having 9 nm diameters and 1.5 μm lengths, were used as starting materials. Isopropyl alcohol (IPA) based zwitterionic surfactant solution with concentration of 1.0 wt% MWCNTs was prepared in this study. The zwitterionic surfactant, consisted of both hydrophobic and hydrophilic groups, and played an important role to avoid the aggregation of CNTs due to van der Waals force between CNTs[9]. The independent MWCNTs were uniformly dispersed by using the zwitterionic surfactant solution. Ti plate was dipped into this solution, and subsequently annealed at 973 K and 1123 K for 30 min. by using a vacuum furnace to remove IPA solution. Hence, unbundled MWCNTs coated on Ti plate surface were obtained, and eliminated the solid zwitterionic surfactants. Microstructure changes were investigated by X-ray diffraction (XRD, SHIMADZU, XRD-6100), optical and scanning electron microscope (SEM, JEOL, JSM-6500F) equipped with energy dispersive X-ray spectrometer (EDS, JEOL, JED-2300). Micro-hardness test was conducted by using Vickers

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micro hardness tester (Shimadzu, HMV-2T) with loading weight of 0.025 N for 15 s. The Ti plates coated with un-bundled MWCNTs and as-received original Ti plate were examined by the ball-on–disk wear test equipment (RHESCA Co. Ltd., FPR-2100) under dry sliding conditions at ambient temperature to investigate their tribological properties. SUS304 stainless steel ball of 4.76 mm in diameter was used as a counterpart material. The sliding speed was 31.4 mm/s, and the applied load from the SUS304 ball was controlled at 0.98 N. The friction radius and sliding distance of this wear test were 5 mm and 113 m, respectively. Microstructures of wear track and cross sectional view of MWCNT films on the Ti plate surface were investigated by SEM-EDS.

3. Results and Discussion

Figure 1 shows the surface morphology of MWCNTs coated Ti plate after annealing at 1123 K. A film consisting of the network-structured MWCNTs is observed on the Ti plate surface, and moreover, no solid zwitterionic surfactant is detected on the surface except MWCNTs. This is an ideal morphology of network-structured CNTs coating film.

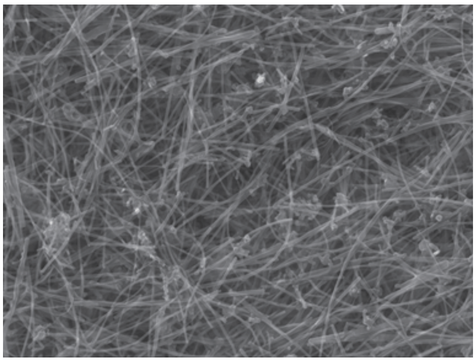

Fig.1 SEM image of coated MWCNTs on pure Ti plate annealed at 1123 K.

Figure 2 shows the XRD diffraction patterns of Ti plate with MWCNT films annealed at 1123 K (a) and 973 K (b), compared with the as-received original pure Ti plate (c). The only α-Ti (hcp) peaks are detected in the case of pure Ti plate (c) and MWCNTs annealed at 973 K (b). In the profile of the specimen annealed at 1123 K (a), titanium carbides (TiC) peaks are obviously detected. These results indicate that in-situ formation of TiCs occurred by the reaction of Ti plate and MWCNTs in annealing. The Gibb's standard free energy of TiC formation is -172 kJ/mol at 1073 K[10]. Thus, it is possible to form TiCs by the reaction of Ti plate with MWCNT film annealed at 1123 K. Furthermore, the above X-ray diffraction analysis of the MWCNTs coated Ti plates was confirmed that carbon atoms are dissolved into Ti plate by the α-Ti diffraction peaks being slightly shifted to lower angles.

Figure 3 indicates SEM-EDS analysis result of the cross-section of Ti plate with MWCNTs annealed at 1123 K. It is clearly observed that an in-situ formed TiC layer at the interface between the Ti substrate surface and MWCNT films, and that excellent metallurgical bonding at the interface is also obtained. The result of EDS line scan (red line) shows the contents of carbon (green line) and Ti (blue line). It shows that TiC is formed at the area where carbon and Ti intersect, and the carbon atoms originating from MWCNTs dissolve into Ti plate. The hardness test is applied to the surface and non-coated opposite side of the specimen annealed at 1123 K. The micro-hardness values of TiC layer and non-coated opposite side are 492 HV and 70 HV, respectively. It is also evident that the hardening is due mainly to the in-situ formed TiC layer at the interface between Ti substrate surface and MWCNT films by annealed at 1123 K.

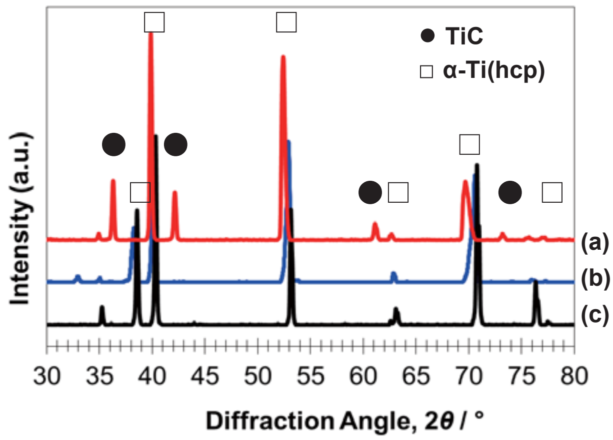

Fig.2 XRD patterns of pure Ti plate coated with MWCNTs annealed at 1123K (a), 973K (b), and as-received pure Ti plate (c).

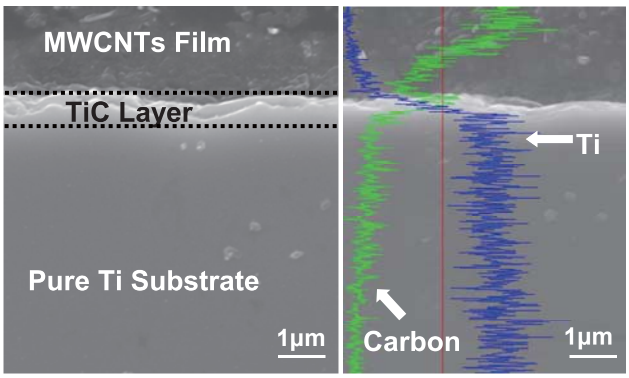

Fig. 3 SEM image of cross-section pure Ti plate coated with MWCNTs annealed at 1123K (a) and EDS line scan (b).

Figure 4 indicates changes in the friction coefficient of the Ti plate with MWCNTs annealed of 1123 K (a) and 973 K (b), and the as-received pure Ti plate (c). In the profile of the specimen annealed at 1123 K (a), the mean friction coefficient value is 0.20, while those values are 0.35 and 0.95 of the specimen annealed at 973 K (b) and the as-received pure Ti plate (c), respectively. The mean friction coefficient values drastically decrease with the Ti plate coated MWCNTs in contrast with pure Ti plate in which touched directly with the counter material. The result indicates the self-lubricant and bearing effects of the network-structured MWCNTs film caused such a low and stable friction coefficient.

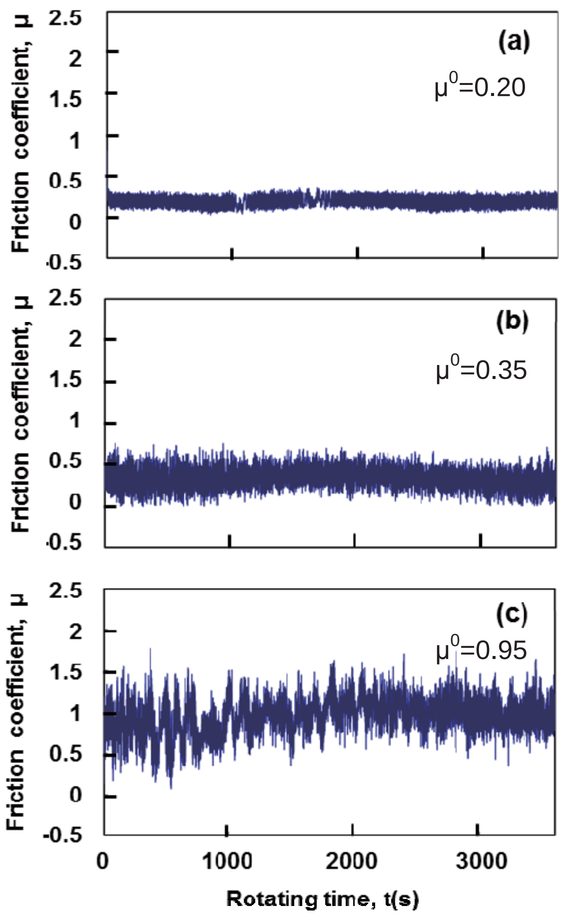

Fig. 4 Changes in friction coefficient of pure Ti plate coated with MWCNTs annealed at 1123K (a) and 973K (b), compared with as-received pure Ti plate (c).

To investigate the tribological behavior, SEM-EDS analysis is applied to the wear track of Ti plate surface. As shown in **Fig. 5**, the network-structured MWCNT films annealed at 973 K and 1123 K obviously remain on the wear track even after 3.6 ks in sliding. Especially, in the specimen annealed at 1123 K, TiC demonstrates the strong metallurgical bonding effect between Ti plate and MWCNT films. It also indicates no adhesion and stick-slip phenomenon on Ti plate surface coated with MWCNT films in contact with the SUS304 ball counterpart material. A few MWCNTs are detached from the plate surface, and then covered on both the wear track and the counterpart material surface. As a result, suitable lubricant films are formed at the sliding interface. Those results suggest the solid lubricant of network-structured MWCNT films and TiC hard dispersoids are effective in reducing the friction coefficient and obstructing the seizure phenomenon of the Ti plate surface under dry sliding conditions.

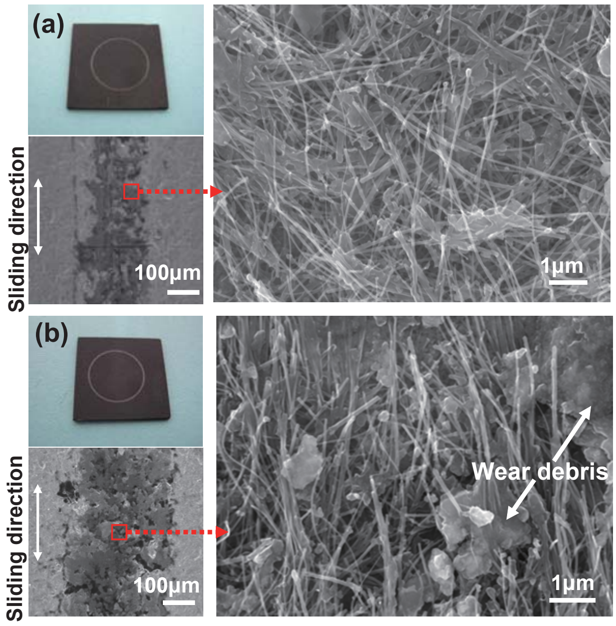

Fig.5 SEM-EDS analysis result of wear track of pure Ti plate coated with MWCNTs annealed at 1123 K (a) and 973 K (b).

4. Conclusion

The effects of MWCNTs coated Ti plate on the tribological properties have been examined under dry sliding conditions. MWCNT films revealed significantly lower and stable friction coefficients compared with pure Ti plate with no coating film. MWCNT films obviously remained on the wear tracks. The superior tribological performance was mainly due to the self-lubricating effect of network-structured MWCNTs coated on Ti plate surface, Ti plate hardening by carbon solid solution, and the defensive by hard TiC dispersoids. This study certainly suggests the possibility of improving tribological properties for Ti and Ti alloy.

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References

1) J. Cumings, A. Zettl, Low-friction nanoscale linear bearing realized from multiwall carbon nanotubes, Science 289 (2000) 602-604.
2) J. J. Hu, S. H. Jo, Z. F. Ren, A. A. Voevodin, J. S. Zabinski, Tribological behavior and graphitization of carbon nanotubes grown on 440C stainless steel, Tribology Letters 19 (2005) 119-125.
3) K. Miyoshi, K.W. Street Jr., R. L. V. Wal, R. Andrews, A. Sayir, Solid lubrication by multiwalled carbon nanotubes in air and in vacuum, Tribology Letters 19 (2005) 191-200.
4) G. Yamamoto, T. Hashida, K. Adachi, T. Takagi, Tribological Properties of Single-Walled Carbon Nanotube Solids, J. Nanosci. Nanotechnol. 8 (2008) 2665-0670.
5) K.G. Budinski, Tribological properties of titanium-alloys, Wear 151 (1991) 203–217.
6) M.M. Savalani, C.C. Ng, Q.H. Li, H.C. Man, In situ formation of titanium carbide using titanium and carbon-nanotube powders by laser cladding, Applied Surface Science 258 (2012) 3173-3177.
7) F. Platon, P. Fournier, S. Rouxel, Tribological behaviour of DLC coatings compared to different materials used in hip joint prostheses, Wear 250 (2001) 227–236.
8) K. Miyoshi, J. H. Sanders, C. H. Hager Jr., et al., Wear behavior of low-cost, lightweight TiC/Ti–6Al–4V composite under fretting: Effectiveness of solid-film lubricant counterparts, Tribology International 41 (2008) 24–33.
9) B. Fugetsu, W. Han, N. Endo, Y. Kamiya, T. Okuhara, Disassembling single-walled carbon nanotube bundles by dipole/dipole electrostatic interactions. Chem. Lett. 34 (2005) 1218-1219.
10) I. Barin, F. Sauert, E. Schultze-Rhonhof, W. S. Sheng, Thermochemical Data of Pure Substances, Part II (1989) 1528.