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Friction behavior of network-structured CNT coating on pure titanium plate

Junko Umeda[a,*], Bunshi Fugetsu[b], Erika Nishida[c], Hirofumi Miyaji[c], Katsuyoshi Kondoh[a]

[a] Joining and Welding Research Institute, Osaka University, Osaka 567-0047, Japan
[b] Graduate School of Environmental Science, Hokkaido University, Sapporo 060-0810, Japan
[c] Department of Periodontology and Endodontology, Hokkaido University Graduate School of Dental Medicine, Sapporo 060-8586, Japan

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ABSTRACT

Friction behavior of the network-structured CNTs coated pure Ti plate was evaluated by ball-on-disk wear test using SUS304 ball specimen under dry condition. The friction coefficient was significantly low and stable compared to the as-received Ti plate with no coating film. CNTs coating film had two important roles; self-lubrication and bearing effects to reduce the friction coefficient and carbon solid-solution hardening to improve the abrasive wear property of Ti plate. The annealing treatment at higher temperature (1123 K) was more effective to reduce the friction coefficient than that at lower temperature (973 K) because the Ti plate surface was uniformly covered with CNTs film even after sliding wear test. This is due to TiC interlayer formation via a reaction between Ti plate and carbon elements originated from CNTs during annealing. As a result, a strong interface bonding between CNTs film and Ti plate surface was obtained by higher temperature annealing treatment, and obstructed the detachment of CNTs film during wear test.

1. Introduction

Carbon nanotube (CNT) has not only high mechanical strength but also excellent 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 reinforced with CNTs. The results indicated that CNTs have been effective to reduce both wear loss and friction coefficient of the composite materials [2–4]. On the other hand, titanium (Ti) and its alloy have been used in automotive, aeronautics and chemical industries due to their remarkable mechanical properties and excellent corrosion resistance. They have, however, poor tribological properties in contact with other metal materials or itself due to their high reactivity [5]. The surface modification treatments using carbon materials for the Ti matrix have been developed to improve the wear resistance; for example, a laser cladding process to form titanium carbide (TiC) using Ti–CNTs mixture powders [6], in situ formed TiC dispersoids via reaction between Ti and CNTs [7] and diamond-like carbon (DLC) surface coating [8]. In particular, a free energy of TiC formation is a large negative value compared to the other metal carbides [9]. Then, TiC phases are easily synthesized from Ti–C system, and the thermally stable TiC compounds are obtained on Ti substrate surface. These studies revealed the coatings onto Ti materials have significantly improved tribological properties by TiC hard phases dispersion and low friction coefficient of carbon elements.

In use of CNTs as raw materials, the main problem is to prevent their segregation and to uniformly disperse them into or onto the materials. This is because their agglomeration easily occurs due to the strong attractive or repulsive van der Waals forces between carbon atoms at the most-surface layer of CNTs [10,11]. The wet process using the zwitterionic surfactant solution is one of the effective methods to completely resolve CNT bundles with no damage and disperse individual CNTs in the solution [12]. The metal powders such as magnesium (Mg) and aluminum (Al) are dipped into this solution containing un-bundled CNTs to prepare their composite powders uniformly coated with CNTs [13,14]. This wet process is simple and valuable in comparison with the above previous techniques which are generally applied under high temperature processing. In this study, CNTs coated at relatively low temperatures to improve the interfacial coherence and metallurgical bonding of the MWCNTs film to Ti substrate.

In this study, the network-structured CNT coating film was formed on the pure Ti substrate surface by using the above CNT

* Corresponding author.
E-mail address: umedaj@jwri.osaka-u.ac.jp (J. Umeda).

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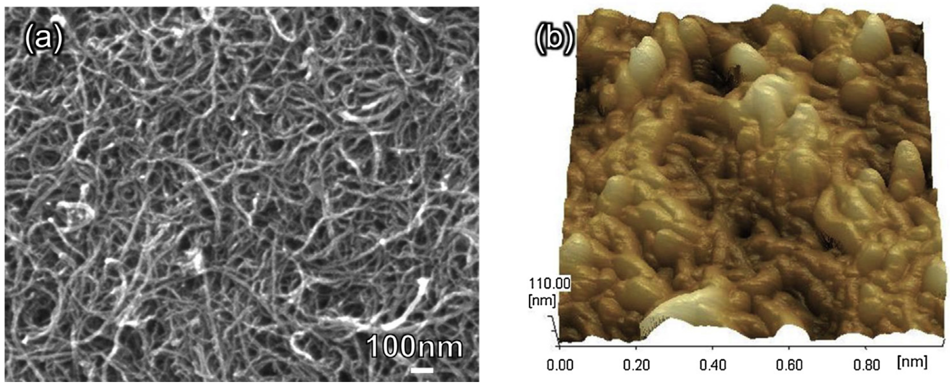


Fig. 1. Surface morphology of network-structured MWCNTs film on pure Ti plate after annealing at 1123 K observed by SEM (a) and AFM (b).

dispersed solution, and the effects of heat treatment conditions after CNTs coating on the microstructural and mechanical properties at the interface between CNT film and Ti substrate, and the tribological behavior of the CNTs films by wear test under dry conditions were investigated. In particular, the local microstructure evaluation to understand TiC formation effect at the interface after heat treatment on the adhesion of CNTs film to the substrate was carried out.

2. Experimental details

A commercial pure Ti plate, ASTM Gr 2, was employed as a substrate, and multi-wall carbon nanotubes (MWCNTs), having 9 nm mean diameter and 1.5 μm average length, were used as starting materials. The isopropyl alcohol (IPA) based zwitterionic surfactant solution with concentration of 1.0 wt% CNTs was prepared according to the previous study [13]. Ti plate was dipped into this solution, and subsequently annealed at 973 K and 1123 K for 1.8 ks in a vacuum furnace to completely remove IPA solution elements and solid zwitterionic surfactants [13]. Microstructure analysis on CNTs and Ti plate surface was carried out by using X-ray diffraction (XRD, SHIMADZU, XRD-6100), optical microscope (OLYMPUS, DSX-500), scanning electron microscope (SEM, JEOL, JSM-6500F) equipped with energy dispersive X-ray spectrometer (EDS, JEOL, JED-2300), transmission electronic microscopy (TEM, JEOL, JEM-2010), and atomic force microscopy (AFM, SHIMADZU, SPM-9600). Fig. 1 shows an example of microstructure analysis on CNTs coating film of Ti plate surface (after annealed at 1123 K) by SEM and AFM. The network-structure consisting of un-bundled individual CNTs was formed on the plate. Micro-hardness test was conducted by using Vickers micro-hardness tester (SHIMADZU, HMV-2T) with a loading weight of 0.025 N for 15 s. Ra of as-received original Ti plate was 0.08 μm, by using a profile meter (Tokyo Seimitsu, Surfcom1400D). In additionally, Ra of the MWCNTs film coating substrates after annealing was 2.4 at 1123 K and 2.6 at 973 K, respectively. CNTs coated Ti plate and as-received original Ti plate were served to ball-on-disk wear test equipment (RHESCA Co. Ltd., FPR-2100) under dry sliding conditions at ambient temperature to investigate their tribological behavior. SUS304 stainless steel ball with 4.76 mm diameter and 160–178 Hv micro-hardness was used as a counterpart material. The sliding speed was 31.4 mm/s, and the applied constant load from the SUS304 ball was controlled at 9.8 N in 3.6 ks. The friction radius and sliding distance of this wear test were 5 mm and 113 m, respectively. Then, the friction coefficient between the Ti plate surface and SUS304 ball was automatically calculated during wear test. Wear tracks and cross sectional view of CNTs film of each specimen after wear test were investigated by optical microscope and SEM–EDS.

3. Results and discussion

3.1. Microstructure analysis of CNTs film after annealing

As shown in Fig. 2, XRD profiles of as-received pure Ti plate, CNTs coated Ti plate after annealing 973 K and 1123 K in vacuum. 1123 K annealed specimen clearly indicates TiC diffraction peaks, which are never detected in the original as-received Ti plate. The patterns in the narrow scanning range ($2\theta = 33–43^\circ$) also shows a small but clear peaks of TiC in the 973 K annealed specimen. It means that TiC formation via reaction between CNTs and Ti plate was performed during vacuum heat treatment because the Gibbs' standard free energy of TiC formation is −172 kJ/mol at 1073 K [15]. In addition, Carbon atoms originated in CNTs would diffuse into α-Ti during annealing treatment at 973–1123 K. As shown in the XRD profiles of the annealed specimens at 973 K and 1123 K in Fig. 2(a), α-Ti peaks obviously shifted to a lower diffraction angle, compared to the original Ti plate. That is, a few carbon atoms originated from CNTs dissolved into α-Ti crystal during annealing, and resulted in the enlarged lattices of α-Ti. It means that carbon solid solution into α-Ti occurred because the carbon solubility is limited as about 0.5 wt% at 1273 K. In particular, when the annealing at 1123 K was employed, not only the carbon solution but also TiC layer formation occurred at the interface between the CNTs coating film and Ti substrate as shown in Fig. 3.

Fig. 4 reveals SEM–EDS line scan analysis on the above CNTs coated Ti plates after annealing treatment. In case of the specimen annealed at 973 K (a), carbon (C) and Ti profiles from the outermost surface are constant. The concentrated C elements, however, are clearly detected at the near surface area (about 1.5 μm depth) area in case of 1123 K annealing (b), and the Ti concentration obviously decreases at the same area. In addition, the higher temperature annealing treatment accelerates the diffusion and solid solution of carbon atoms into pure Ti material as shown in Fig. 4(c), and results in the formation of TiC layer at the interface between CNTs film and Ti plate.

3.2. Micro-hardness distribution at near surface of Ti plate

Fig. 5 shows micro-hardness profiles from the outermost surface of Ti plates. CNTs coated Ti specimen with 1123 K annealing treatment reveals extremely high values (473 Hv) compared to the other specimens. In addition, the hardness gradually decreases in the inside direction due to the solid-solution strengthening by carbon diffusion under higher temperature annealing treatment as mentioned in Fig. 4(c). In case of 973 K annealed specimen, a small increment of micro-hardness at the near surface area (137 Hv) was detected, comparing the original Ti plate (115 Hv). This is also due

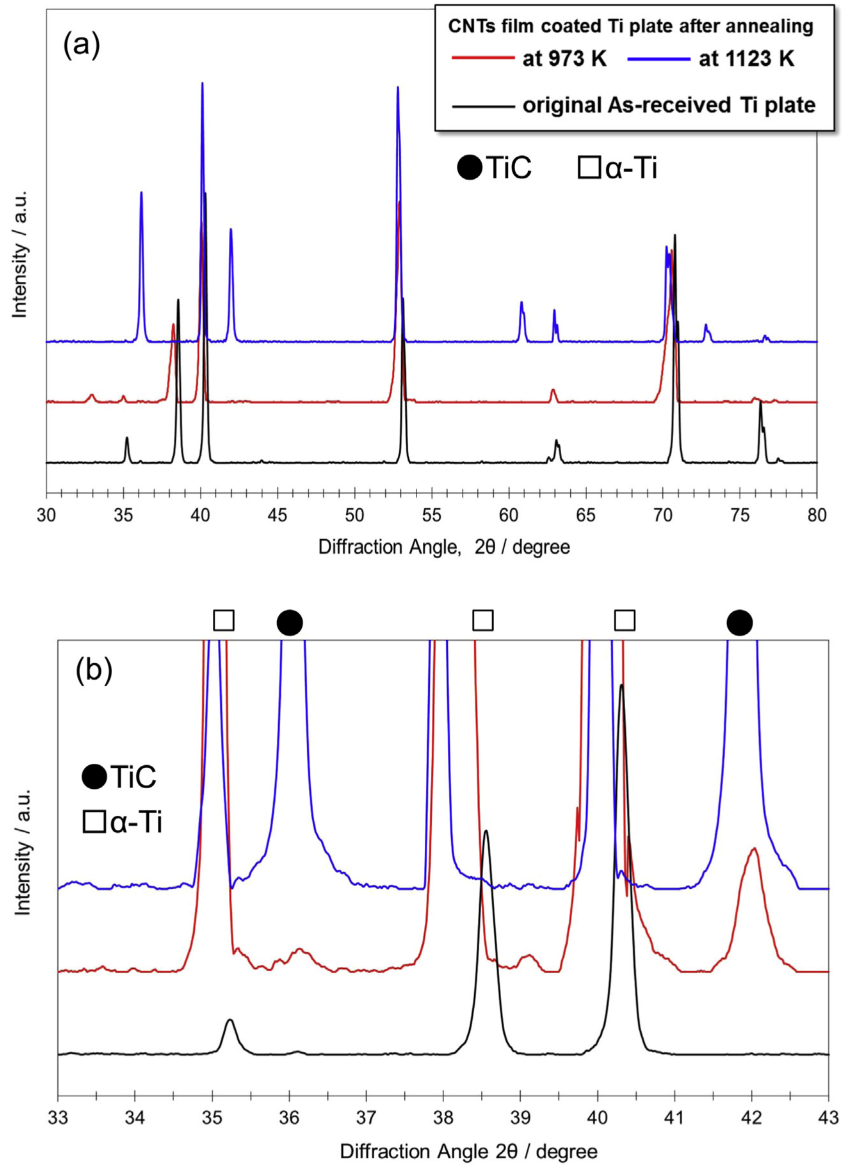


Fig. 2. XRD profiles of as-received pure Ti plate, CNTs coated Ti plate after annealing at 973 K and 1123 K in wide (a) and narrow (b) scanning range.

to a very small amount of carbon solid-solution into Ti crystal under lower temperature heat treatment.

3.3. Friction and wear properties of CNTs coating film on Ti plate

The friction coefficient evolution of the original and CNTs coated Ti plate specimens by using ball-on-disk wear test is shown in Fig. 6. As shown in the original Ti plate (a), the friction coefficient is significantly large (average value; 0.95) and the remarkable variation during wear test is observed because of the typical severe abrasive and adhesive wear damages between the metal ball and disk specimens. Particularly, a large variation of the friction coefficient would be caused by “stick-slip” sliding phenomenon in the adhesive wear. On the other hand, two specimens coated with CNTs

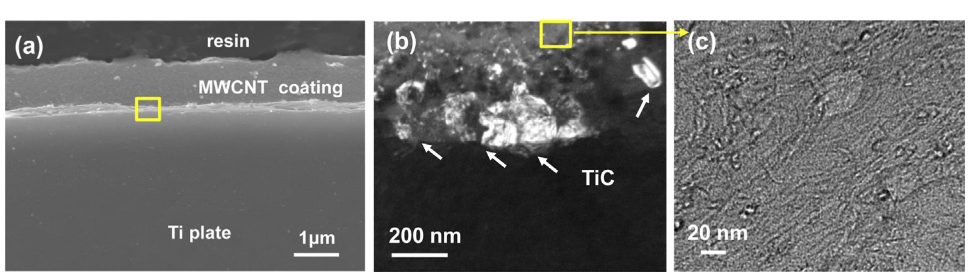


Fig. 3. SEM observation on the cross-section of MWCNTs film coated Ti plate annealed at 1123 K (a). Dark field of TEM observation on the cross-section of MWCNTs film coated Ti plate annealed at 1123 K (b) and high resolution TEM image of MWCNTs film on Ti plate annealed at 1123 K (c).

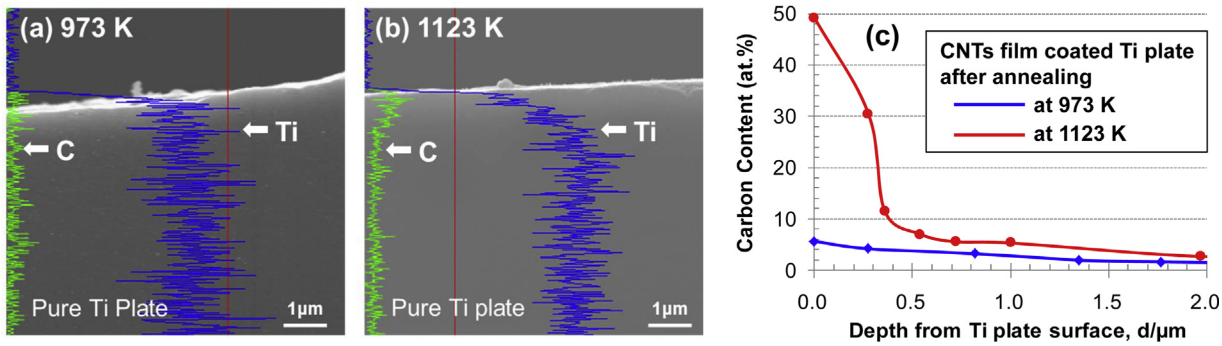


Fig. 4. SEM–EDS line scan analysis on CNTs coated Ti plate after annealing at 973 K (a) and 1123 K (b), and carbon content distribution at near outermost surface (c).

film shown in (b) and (c) reveal the low and stable friction coefficient compared to the original specimen with no coating film. It means the CNTs coating film contributes to a mild sliding phenomenon under dry sliding condition. In particular, 0.19 average value of CNTs coated Ti plate after annealing at 1123 K suggests a formation of very stable lubricant films at the contacting interface between the ball and plate specimens.

To clarify wear behavior of each specimen, the wear track observation on Ti plate and SUS304 ball was carefully carried out by using optical microscope and SEM–EDS. The surface morphology observation results are summarized in Fig. 7. As-received original Ti specimen (a-1) shows severe damages and a lot of wear debris at the wear track. The maximum wear depth of the Ti plate surface is 7.0 μm. This is due to an abrasive wear phenomenon because the micro-hardness of SUS304 ball (160–178 Hv) is much larger than that of pure Ti plate (115 Hv) and digs up Ti specimen as wear debris. In addition, the active Ti material easily sticks to the counter materials (SUS304), and results in an adhesion wear phenomenon. EDS analysis in (a-2) obviously indicates both Fe elements on Ti plate and Ti elements on SUS304 ball. In case of Ti plate with CNTs films after annealed at 973 K (b-1), the smooth sliding surface is observed at the wear track. EDS analysis result, however, means the remained CNTs coating film on the wear track is very limited, and CNTs transfer to the contacting area of SUS304 ball. Furthermore, Fe and Cr elements originated from SUS304 ball are never detected at the wear tracks of Ti plate, and a very small amount of Ti elements are found at SUS304 ball surface as shown in Fig. 7(b-2). That is, the main wear mechanism of this specimen is an abrasive phenomenon, not adhesive behavior. As shown in Fig. 7(c-1), CNTs coated Ti plate annealed at 1123 K obviously shows the remained CNTs film at the wear track, and a few CNTs transfer to the contacting area of SUS304 ball. The maximum wear depth of the Ti plate is 1.5 μm. This is because severe abrasive damages of the Ti plate surface contacting with SUS304 ball specimen is completely obstructed because of both the CNTs coating film and surface hardening due to carbon solid-solution shown in Fig. 5, and results in very small and stable friction coefficient as previously shown in Fig. 6. When comparing the wear track width of the specimen (a) with no coating film, that of the specimens (b) and (c) is much small. This is also because of the mild abrasive wear behavior due to the self-lubricant [16–18] and bearing effects [19–21] of the network-structured CNTs coating film existing at the sliding interface.

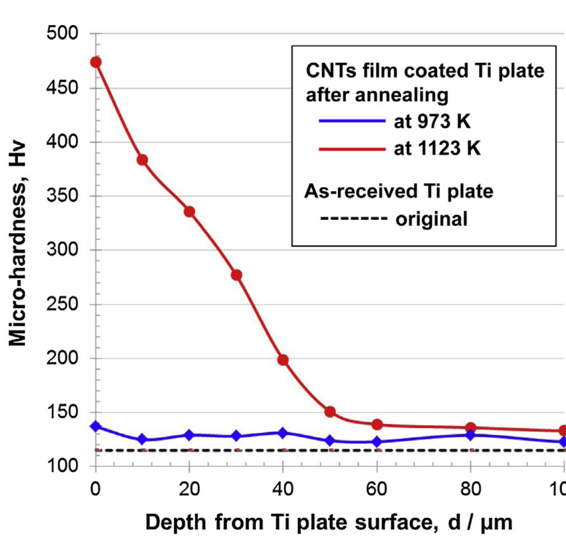


Fig. 5. Micro-hardness distribution from outermost surface of as-received Ti plate and with CNTs film after annealing at 973 K and 1123 K.

Fig. 8 shows the detail observation results at the wear tracks of each Ti plate surface. In case of as-received Ti plate (a), a lot of fine debris with 0.2–1 μm diameter and abrasive wear damages by contacting with SUS304 ball are obviously observed on the wear track. As shown in (a-1), EDS point analysis on the debris (point 001 and 002) dispersed at the wear track indicates the debris contains Fe and Cr elements originated from SUS304 ball specimen because the severe abrasive wear phenomenon takes place in both pure Ti plate and SUS304 ball specimens. As shown in CNTs coating films on Ti plate after annealing at 973 K (b), the coating films are locally detached from the Ti plate surface and some debris are observed at the wear track. As shown in (b-2), the debris (point 01) contains a very small amount of Fe and Cr elements (Fe; 0.70 at.%, Cr; 0.19 at.%). It suggests that the mild abrasive wear behavior occurs due to the existence of CNTs films as solid lubricant layers at the dry sliding interface. On the other hand, the network-structured CNTs film completely remains on the wear track of Ti plate in use of the annealing treatment at 1123 K (c), and no debris is also observed at the sliding track. Therefore, as shown in Fig. 6, the friction coefficient of the Ti specimen (c) completely coated with the CNTs film is much low and stable compared to the specimen (b) with the local coating film. The surface morphology difference of CNTs coating films between (b) and (c) Ti plate specimens depends on the affinity of CNTs film with Ti plate surface. With increase in the annealing temperature, the acceleration of solid-state diffusion of the carbon atoms originated from CNTs into Ti becomes more active, and results in the formation of TiC interfacial layer having an important role to strongly bond the CNTs to the Ti plate. Then, the CNTs coated Ti specimen annealed at 1123 K shows no detachment of CNTs after wear test shown in Fig. 8(c).

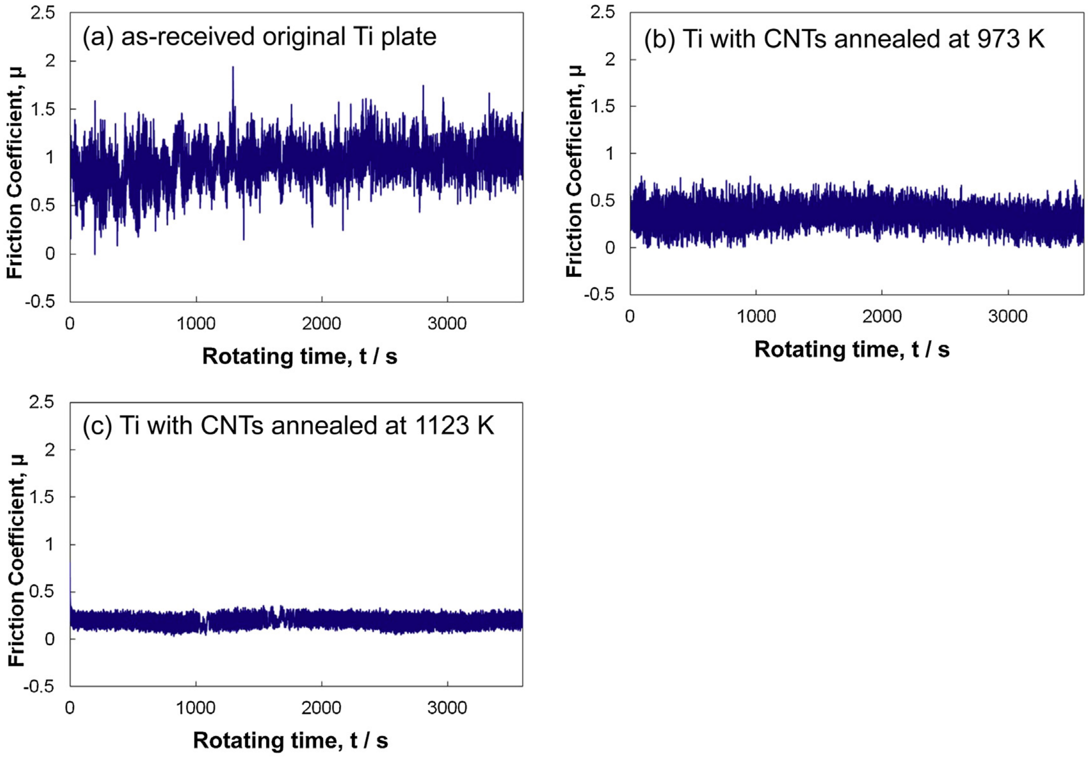


Fig. 6. Friction coefficient changes of as-received Ti plate (a) and with CNTs film after annealing at 973 K (b) and 1123 K (c) by using ball-on-disk wear test under dry sliding condition.

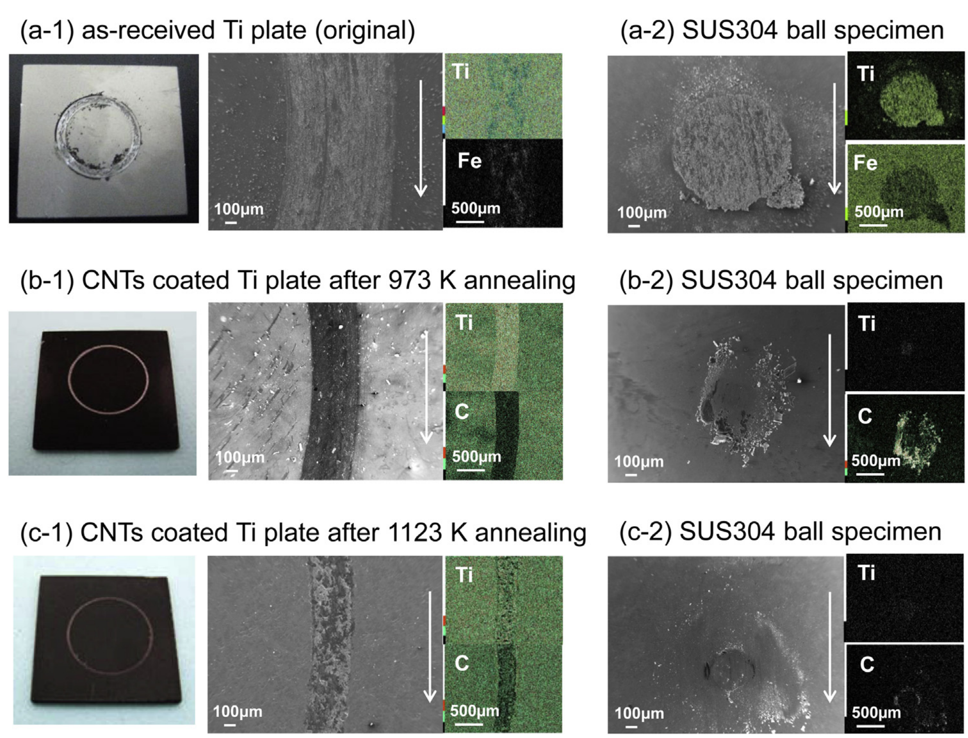
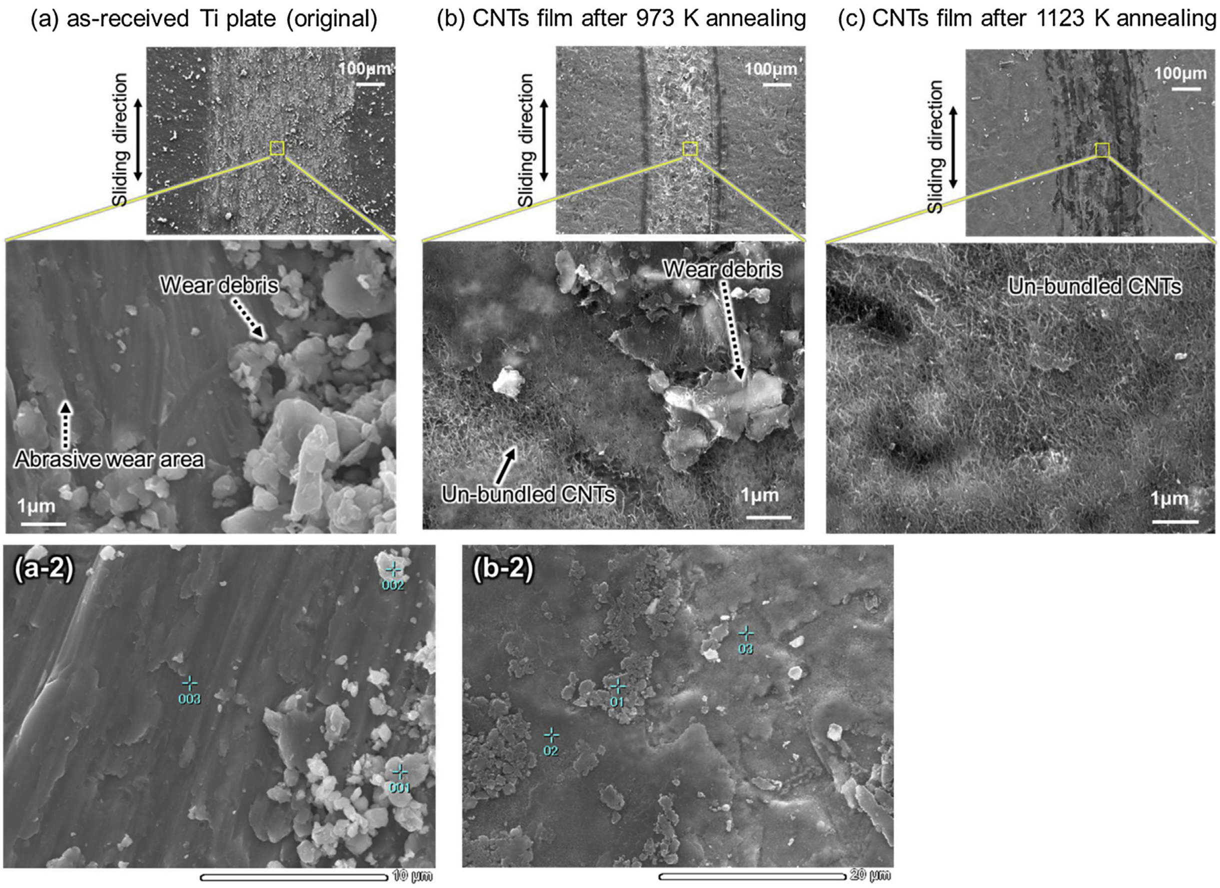


Fig. 7. Surface morphology observation on wear tracks of Ti plate and SUS304 ball using original Ti (a), Ti with CNTs film after annealing at 973 K (b) and 1123 K (c).



at.%	Ti	Fe	Cr
01	89.94	7.45	2.61
02	70.65	22.47	6.88
03	99.41	0.59	0

at.%	Ti	C	Fe	Cr
01	55.49	43.62	0.70	0.19
02	53.24	46.76	0.00	0.00
03	93.69	6.31	0.00	0.00

Fig. 8. Detail observation on wear tracks of Ti plates after wear test by SEM, and EDS point analysis on wear tracks of Ti plate and debris dispersed at sliding surface; as-received Ti plate (a-2) and CNTs coated Ti plate after annealing at 973 K (b-2).

4. Conclusions

A severe abrasive wear phenomenon occurred and a lot of debris was observed at the wear track when as-received Ti plate with no coating film was employed under dry sliding condition. In case of the network-structured CNTs film coated on Ti plate specimens, a very low and stable friction coefficient was obtained. The average value of the friction coefficient was 0.19 of CNTs coated Ti plate after annealing at 1123 K, in contrast a value of no coating film on Ti plate was 0.95. CNTs film existing at the interface between the Ti plate and SUS304 ball specimens contributed to a formation of mild sliding conditions because of their self-lubricant and bearing effects. In addition, micro-hardness increment of the outermost surface of CNTs coated Ti plate caused by carbon solid-solution strengthening was also effective to obstruct the abrasive wear phenomenon by SUS304 ball and to reduce the wear loss. SEM–EDS analysis clarified that CNTs films completely existed on the Ti plate surface and no film was detached from the surface after wear test due to its strong bonding to Ti plate via carbon solid-state diffusion and formation of TiC interfacial layer by higher temperature annealing treatment. The frictional behavior of the MWCNTs films formed on the Ti plates after annealing was attributable not only to the specimens bearing effect and self-lubrication but also to TiC formation at the interface between the MWCNTs film and the Ti plate, which was significantly effective in improving the interfacial bonding strength.

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