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Tribological behavior of powder metallurgy Ti composites reinforced with multi-wall carbon

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***Abstract*— The friction and wear behavior of multi-wall carbon nanotubes (MWCNTs) reinforced pure Ti matrix composites fabricated by powder metallurgy (PM) process was evaluated under dry sliding conditions. Individual MWCNTs were uniformly coated on Ti powder surface by immersing Ti powders into the solution suspended with 3.0 wt% un-bundled MWCNTs. After heat treatment at 873 K for 3.6 ks of MWCNTs/Ti composite powders to completely remove the zwitterionic surfactant elements, they were elementally mixed with pure Ti powders by ratios of 0, 20, 50 and 100 in wt%. Spark plasma sintering process and hot compression were applied to each mixed powder to be consolidated and to obtain the full-dense Ti composite plate specimen. Some of MWCNTs were reacted with Ti powder matrix, and resulted in formation of TiC hard particles. The disk specimens were machined from PM Ti composites, and the ball-on-disk wear test was carried out at the rotational speed of 120 rpm (sliding velocity; 62.8 mm/s) with an applied load of 0.98 N, where 304 stainless steel ball was employed as a counter material. With increase in the MWCNTs content of the specimen, Vicker's micro-hardness of Ti composite remarkably increased, and a friction coefficient gradually decreased due to obstruct the adhesive wear phenomenon at the sliding surface between Ti matrix and SUS304 material by both MWCNTs and TiC dispersoids of the composites.**

Keywords*— *Powder metallurgy; Ti; MWCNTs; composite; friction coefficient; TiC; adhesive and abrasive wear

I. INTRODUCTION

Since the first observed multi-wall carbon nanotubes (MWCNTs) reported by S. Iijima [1], MWCNTs have been interested in various research fields due to their excellent properties [2-3], especially, significant improvement of mechanical properties. The previous studies indicated that MWCNTs reinforced metal matrix composites strongly enhanced the yield strength, tensile strength and hardness [4-13]. Regarding the improvement of tribological properties by using MWCNTs, for example the network-structured nanotubes films coated on Ti substrate successfully showed a low and stable friction coefficient under a dry sliding condition [14]. However, there are a few reports on the tribological behavior of metal matrix composites reinforced MWCNTs for structural application [15-17]. Cumings and Zettle [18] revealed the slip phenomenon of MWCNT that the outer and inner shell nanotube could be eased to extract with out damages. This possibly leads to the materials design of low friction bearing applications in nanoscale. Regarding to the application in higher scale levels, the previous study [16] showed MWCNTs addition to the commercial Ti-6Al-4V alloy was not effective to improve the friction behavior and then their wear resistance decreased due to some dandled of nanotubes in the matrix. In this study, the wet coating process of MWCNTs on pure Ti powder surface was employed to uniformly disperse un-bundled MWCNTs in the matrix of the Ti composites. The wear behavior of MWCNTs reinforced pure Ti matrix composites was investigated under dry sliding conditions. The dependence of friction coefficient changes on MWCNTs content of the Ti composites was evaluated in detail.

II. EXPERIMENTAL PROCEDURE

A. *Specimen preparation*

Commercial pure Ti powder produced by hydride-dehydride (HDH) process [19, 20], having a mean particle size of 28.3 μm, was used as the matrix raw material. The chemical compositions of raw Ti powder were Fe; 0.03, Si; 0.01 Mg <0.001, Cl <0.002, O; 0.21, N; 0.02, H; 0.04, C <0.01 in wt%. A small amount of hydrogen was contributed to form titanium hydride (TiH_x) compounds in raw Ti powder. Multi-wall carbon nanotubes (Nanocyl S.A.) with an average diameter of about 9.5 nm and length of about 1.5 μm were used as the reinforcement. The wet process to prepare MWCNTs coated pure Ti composite powders was applied in this study [8, 11] as follows: the zwitterionic surfactant solution with 3.0 wt% of MWCNTs was employed in the experiment. The zwitterionic surfactant composes both hydrophobic and hydrophilic functional group which overcomes the van der Waals force between MWCNTs effectively [21]. Therefore, MWCNTs were individually dispersed in the zwitterionic surfactant solution. Ti powders were immersed into this aqueous MWCNT/zwitterionic solution and subsequently dried in the furnace at 373 K for 10.8 ks. To eliminate the solid zwitterionic substance and prevent the oxidation of Ti powder surface, the dried Ti powders were heated by the horizontal tube furnace at 873 K for 3.6 ks under mixed hydrogen and argon (H_2/Ar) gas atmosphere. MWCNTs/Ti composite powders were elementally mixed with un-coated raw pure Ti powders in weight ratios of 0, 20, 50 and 100 wt% to control CNTs content of the starting materials.

Each elemental mixture powder was named as 0C, 20C, 50C and 100C, respectively. They were consolidated by spark plasma sintering (SPS, Syntech Co. SPS-103S) process at 1073K for 1.8 ks under vacuum atmosphere, where an applied pressure was 30 MPa. The sintered Ti composite billets were heated at 1273 K for 180 s under Ar gas atmosphere, and followed by hot-compression process in the closed die at 673 K, where the compression pressure and holding time were 600 MPa and 10s, respectively. These hot-compression billets were machined to coin-shape specimens with 40 mm diameter and 10 mm height, which were used as disk specimens in ball-on-disk wear test. The surface roughness, Ra was controlled lower than 0.1 μm by polishing treatment.

B. *Materials characterization*

A density of each hot-compressed billet was determined by Archimedes method. Hardness of each Ti composite material was measured by Vicker's micro-hardness tester (Mitsutoyo) with 0.025 N applied. Wear sliding surfaces were investigated by optical microscope and scanning electron microscopy (SEM, Hitachi SU-70) equipped with Energy dispersive X-ray spectrometry (EDS). Intermetallic formation of MWCNTs/Ti composites and microstructures of wear tracks and debris were characterized by locally selected area micro-X-ray diffractometer (XRD, Bruker-D8) using Co*Kα*1 radiation (wavelength 1.78897 Ǻ)

C. *Ball-on-disk wear test*

A Friction test was carried out by using a ball-on-disk wear test machine (RHESCA Co Ltd., FPR-2100 model) under air atmosphere, where 304 stainless steel (304SUS) ball with 4.76 mm diameter was used as a counter specimen. The rotation speed of 120 rpm with track radius of 5 mm (equivalent to a surface sliding speed of 62.83 mm/s) and the normal applied load of 0.98 N were decided in this study. The total wear test time was 300 s because it was important to understand the role of MWCNTs/TiC dispersoids on the improvement of the initial wear behavior of CNTs/Ti composite materials. The frictional torque between the ball and disk specimens during wear test was automatically recorded by PC, and a friction coefficient was calculated from the measurement.

III. RESULTS AND DISCUSSION

A. *Materials characterization*

The morphology of un-bundled MWCNTs coated Ti composite powders via the above wet process after heat treatment to eliminate the solid zwitterionic substance was shown in Fig.1. By close observation of the marker in Fig. 1(a), individual MWCNTs were uniformly dispersed on the Ti powder surface and their network structures were formed as shown in Fig. 1(b). This is an ideal morphology of the starting powder used in preparation of CNTs/Ti composite materials. The measured density of each composite was listed in Table 1.

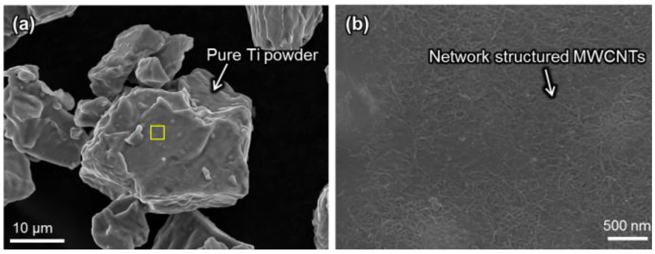

Fig.1 SEM observation on pure Ti powder surface coated with un-bundled MWCNTs (a) and uniformly dispersed MWCNTs with network structure on Ti powder surface (b).

Table 1 Carbon content, relative densities, micro-hardness and surface roughness of each specimen.

Sample	Carbon content	Density[1]	Calculated density[2]	Relative density	Surface roughness, Ra	Surface hardness	Bulk hardness	
	(wt.%)	(g·cm^{-3})	(g·cm^{-3})	(%)	μm	(Hv 0.025)	(Hv 0.025)	(HRC)
0C	0.012	4.507	4.509	99.96	0.102	431	262	24.3
20C	0.024	4.433	4.508	98.34	0.055	497	299	29.6
50C	0.084	4.350	4.503	96.61	0.075	504	352	35.7
100C	0.346	4.326	4.482	96.52	0.091	535	363	36.9

[1] Archimedes method, [2] Rule of mixture; using: ρ Ti = 4.51 g·cm^{-3} and ρ MWCNTs = 1.6 g·cm^{-3}

Regarding to the density, the theoretical value for each Ti composite composition was calculated by the rule of mixture. In these results, the hot-compressed pure Ti matrix composites indicated the remained MWCNTs and in-situ formed TiC particle during SPS [8] in their microstructures. The calculation was carried out under the assumption of no reaction between Ti and MWCNTs because the volume fraction of the remained MWCNTs and TiC compounds could not measured exactly. The assumption also neglected the effect of a small amount of TiH_x compounds due to no significant difference in the theoretical density between TiH_x of 4.50 [22] and Ti of 4.51 g·cm^{-3} [23]. With increase in the CNTs content, the relative density showed a little decrease because the compactability of CNTs/Ti composite sintered billet becomes poor due to the increase of the amount of in-situ formed TiC hard particle in the matrix. It is obvious, however, the effect of pores less than 1~3% on the friction behavior was neglected. The hardness of each composite specimen was measured by Vicker's micro-hardness tester as shown in Fig 2.

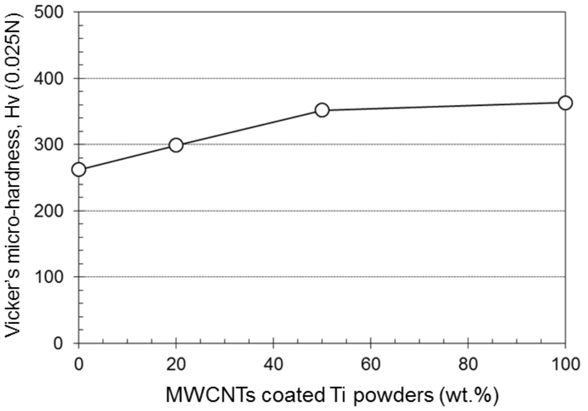

Fig.2 Dependence of PM Ti composites on amount of MWNCTs coated Ti composite powders.

The enchantment of micro-hardness was directly increased by increasing the amount of additive MWCNTs. Regarding to the effect of TiH$_x$ compounds, the previous work showed that the hardness of TiHx was about 30% higher than that of pure Ti matrix [24], that is, TiHx compounds are not significantly effective on micro-hardness measurement of Ti composites. Therefore, 28% large difference in the micro-hardness between 0C (pure Ti) and 100C specimens was mainly due to raw MWCNTs and in-situ formed TiC dispersoids compared to TiHx compounds.

B. Tribological properties

Changes in friction coefficient of each Ti composite and the dependence of the kinetic friction coefficient on CNTs content were shown in Fig. 3 and Fig. 4, respectively..

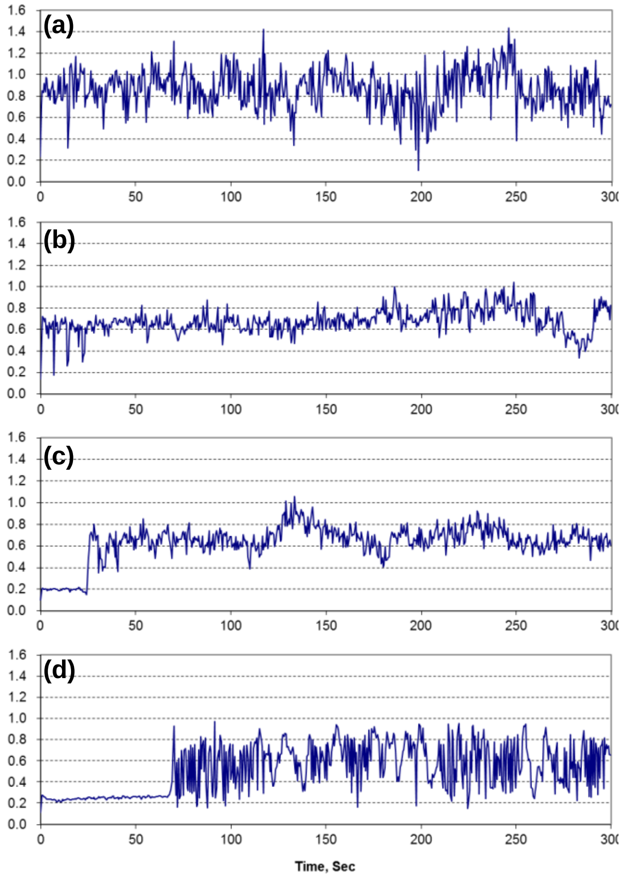

Fig.3 Friction coefficient profiles of 0C (pure Ti) (a), 20C (b), 50C (c) and 100C (d) PM Ti composite specimens under applied load of 0.98N.

In Fig. 3(a), the profile of pure Ti material contains a large variation, for example the maximum value was over 1.4. It means the sticking phenomenon often occurred at the contacting interface between Ti disk and SUS304 ball specimens in sliding. When MWCNTs were contained in the disk specimen as shown in (b)~(d), its variation obviously decreased and the maximum friction coefficient was less than 1.0. In addition, with increase in the CNTs content, the initial period with very low friction coefficient about 0.2 was observed, and it became much longer in case of 100C specimen (d). It suggested that the smooth and stable sliding condition was formed at the contacting interface between the disk and ball specimens by increment of MWCNTs content

Furthermore, the kinetic friction coefficient gradually decreased with increase in MWCNTs content of the disk specimens as shown in Fig. 4. It indicates MWCNTs dispersed in the Ti matrix have some lubricant roles effective to reduce the friction torque at the sliding surface. The wear loss of each disk specimen was calculated to measure the weight changes before and after wear test. The average value of three test results was 0.36 (0C), 0.20 (20C), 0.18 (50C) and 0.05 (100C) mg. This tendency corresponds well to the kinetic friction coefficient dependence shown in Fig. 4, that is, the wear resistance of pure Ti material was improved by addition of MWCNT reinforcements.

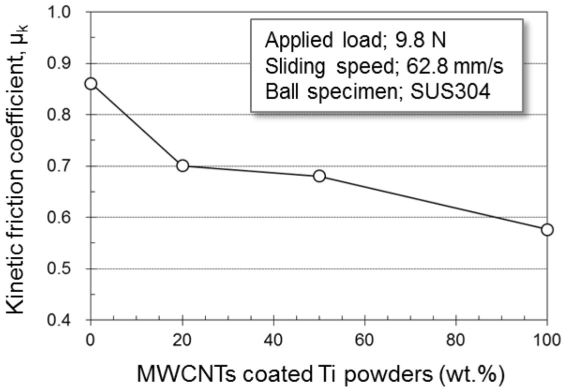

Fig. 4 Kinetic friction coefficient (μ_k) of PM Ti composites with different content of MWCNTs/Ti composite powders.

SEM analysis was carried out on the sliding tracks of each disk specimen. As shown in Fig. 5, pure Ti material (a) revealed severely damaged area, in particular typical adhesive wear phenomenon on the sliding surface. Very few wear debris was observed because pure Ti matrix is very reactive and much softer than the counter material of SUS304 steel, and then pure Ti debris are easily stuck on the sliding surfaces. In comparing the sliding surface morphologies shown in Fig. 5(b)~(d), the adhesive wear behavior transfer to the abrasive wear with increase in the MWCNTs content of Ti composites. In addition, the total area of the seizure debris gradually decreased and the sliding area showed smooth surfaces. This is because the increment of micro-hardness by MWCNTs and in-situ formed TiC hard particle dispersoids was effective to obstruct the adhesive wear phenomena, and resulted in smoothly sliding conditions. TiC fine particle dispersion also has an important role to obstruct the direct contact of Ti matrix to SUS304 counter material surface in sliding wear test

As shown in Fig. 6(a), the wear debris exists on the sliding track of 100C specimen, and plastically deformed as a plate. High magnification observation photo shown in Fig. 6(b) reveals the remained original MWNCTs and their deformed thin film in the debris are surrounded by both in-situ formed TiC compounds and Ti particles. MWCNTs and their thin films could be considered to the solid lubricating layers resulting in decrease of the friction coefficient. This is one reason why a friction coefficient of MWCNTs/Ti composites was improved as shown in Fig. 3(c), (d) and Fig. 4. EDS-point analysis was applied to the sliding surface (marker 1) and the debris (marker 2). As shown in Fig. 6(c) at marker 1, Ti was mainly observed, and a small intensity of Cr, Al, Si and Fe elements was also detected. On the other hand, EDS analysis result at the marker 2 corresponding to the debris indicated the elements of Fe, Cr, Ni, Al and Si originated from 304 stainless steel counter ball were obviously detected as shown in Fig. 6(d). The other elements such as Na and Ca resulted from the zwitterionic solution and impurities of MWCNTs themselves.

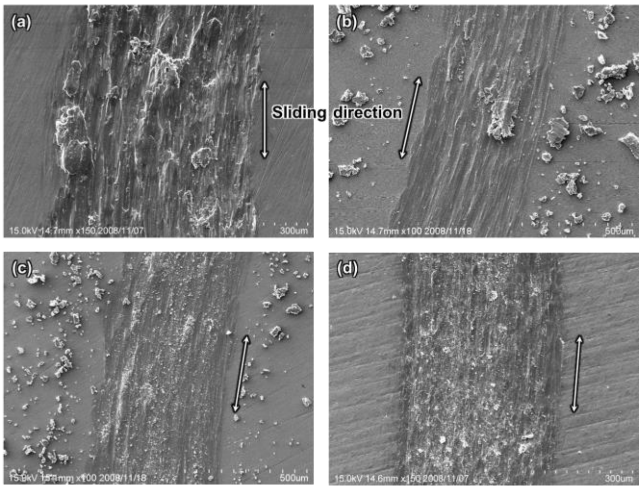

Fig.5 SEM observation on sliding surface of 0C (pure Ti) (a), 20C (b), 50C (c) and 100C (d) PM Ti composite specimens under applied load of 0.98N.

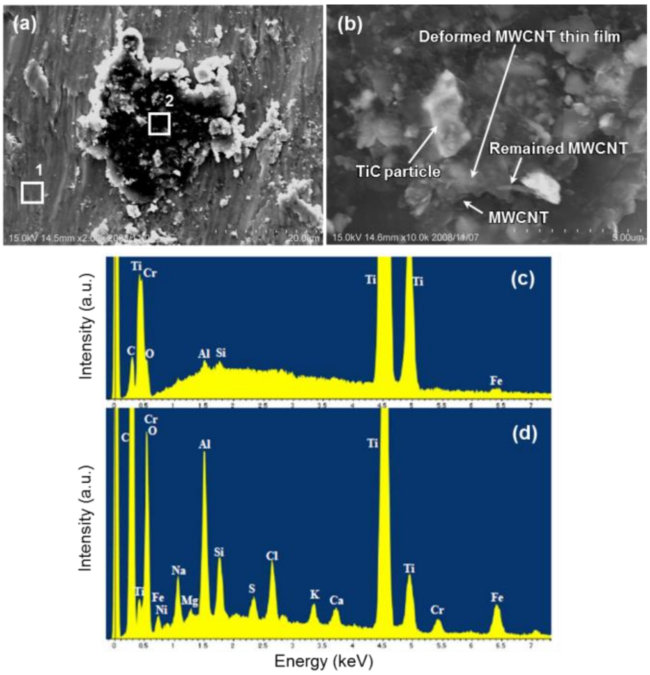

Fig. 6 SEM-EDS results on sliding surface of 100C specimen. Overview of sliding surface (a), high magnification around marker No.2 (b), EDS results of marker No.1 (c) and marker No.2 (d).

Figure 7 reveals micro-XRD profiles of the sliding surface of 0C (a) and 100C (b) specimens. Structure and phase confirmation at each surface were characterized by locally selected XRD analysis. In case of 0C (pure Ti) specimen, the only Ti peak was detected, and the XRD profile of 100C specimen showed three phases consisting of Ti, TiC and TiHx.

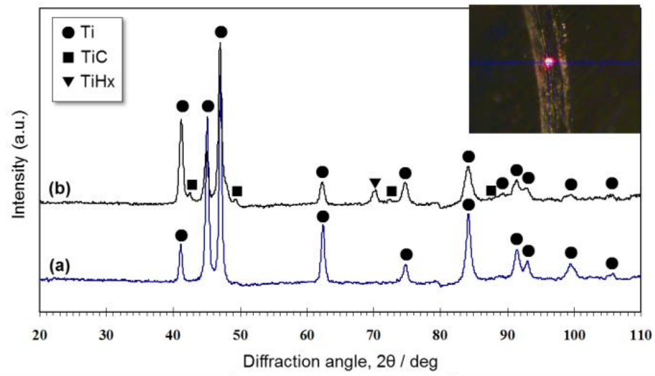

Fig. 7 Micro-XRD profiles on sliding surface of 0C (a) and 100C (b) Ti composites.

As mentioned above, TiC was formed via reaction between MWCNTs and Ti matrix during SPS process. TiHx compounds originated from raw Ti powders are thermally decomposed at 700 K in atmosphere [25]. Accroding to the friction coefficient profile in Fig. 3(a), 0C (pure Ti) specimen showed very high values and the sticking behavior obviously occurred. It means the temperature of pure Ti disk was over 700 K by severe sliding condition, and resulted in the decomposition of TiHx compounds during sliding and contacting to the counter material surface. As a result, no tribochemical reaction at the sliding surfaces was characterized in the initial stage of the ball-on-disk wear test under dry sliding conditions used in this study.

IV. CONCLUSIONS

The remarkable enhancement of hardness had resulted from the homogeneous distribution of MWCNTs and in-situ formed TiC hard particles in Ti matrix. The remained MWCNTs showed their good self-lubricating properties resulting in lowering of friction coefficient, and both MWCNTs and TiC dispersoids were effective to obstruct the sticking phenomena between Ti composite disk and SUS304 ball specimens during sliding wear test. As a result, the wear type obviously transferred from the adhesive to the abrasive phenomena with increase in the MWCNTs content of PM Ti composite materials.

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