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〔 **Original Paper** 〕

# Wear characteristics of carbon nanotube reinforced titanium alloys

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**SUMMARY**

**Recently, carbon nanotube (CNT) reinforced titanium alloys and carbon-doped titanium oxide (Fresh Green) process of titanium alloys have been developed to achieve better mechanical property. The tribological behavior of them was examined in the study. A pin on disc tribometer was used to evaluate wear volume under metal on metal condition using Ti4.5Al3V2Mo2Fe (SP700), CNT SP700 and CoCrMo. Pin on disc tests were carried out to assess the tribological response of ultra-high molecular weight polyethylene to SP700, CNT SP700, Ti6Al4V, CNT Ti6AL4V, carbon-doped titanium oxide Ti6Al4V, and CoCrMo. In the metal on metal study, the addition of CNT to SP700 reduced wear volume less than the SP700 and the wear volume of the CNT SP700 was larger than that of the CoCrMo. In the metal on ultra-high molecular polyethylene study, the wear volume of the Ti6Al4V was totally equal to that of the CoCrMo. The wear volumes of CNT SP700 and CNT Ti6Al4V decreased to three fourths of that of the Ti6Al4V and the CoCrMo. The wear volume of the fresh green-Ti6Al4V decreased to one half of that of the Ti6Al4V and the CoCrMo. Hence, Fresh Green-Ti6Al4V might be a good candidate for sliding surface material.**

***Key words*: carbon nanotube, fresh green, pin on disc, titanium alloy, wear**

## Ⅰ. Introduction

Titanium alloys have been widely used in many industrial fields because they have excellent mechanical properties, higher specific strength than stainless steel and better corrosion resistance than stainless steel. Recently, automobile and aircraft industries have been eager to adopt lightweight devices to increase fuel economy. Therefore, the improvement to achieve higher mechanical strength has been expected with respect to titanium alloys. One of effective approaches is composite material. It has well known that in the addition of carbon to titanium alloys, the excessive carbon in titanium composition forms brittle titanium carbide and its mechanical strength is deteriorated. Carbon nanotube (CNT) has attracted many researchers as composite material or filler because of its extraordinary thermal conductivity, mechanical and electrical property. The use of CNT has limited to resin and lightweight metal

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*Abbreviations*: carbon nanotube: CNT, Ti-4.5Al-3V-2Mo-2Fe alloy: SP700, Ti-6Al-4V alloy: Ti6Al4V, Cobalt-28Chromium-6Molybdenum alloy: CoCrMo, carbon-doped titanium oxide: Fresh Green products due to the difficulty of dispersing CNT into base material. Anzawa et al. solved the problem using the silicon-coated multi-walled carbon nanotube to disperse CNT into titanium alloys uniformly. They developed a new process to manufacture CNT reinforced titanium matrix composites[1,2]. However, the addition of CNT over 1 wt% make titanium alloy fragile.

In orthopaedic field, titanium alloys has been applied to plates, screws, and intra-medullary nails without sliding surface. Hi-tech knee II artificial joint made of Ti6Al4V has been developed by the collaborative project of Teijin-nakashima medical Co. Ltd. (Okayama Japan) and our department. Its clinical results have been excellent over 20 years[3,4]. Thus, the purpose of study was to investigate the wear characteristic of CNT reinforced titanium alloys.

## Ⅱ. Materials and methods

Beta rich alpha-beta type titanium alloy (Ti-4.5Al-3V-2Mo-2Fe alloy, AMS4964) named SP700 was purchased from JFE steel corporation (Kawasaki, Japan). Ti-6Al-4V alloy (Ti6Al4V, ASTMF136) and Cobalt-28Chromium-6Molybdenum alloy (CoCrMo, ASTM F799) was purchased from Teijin-nakashima medical Co. Ltd.. CNT-reinforced SP700 and CNT-reinforced Ti6Al4V were provided from Nagano prefecture general industrial technology center (Nagano, Japan). The Ultra high-molecular weight polyethylene (UHMWPE) was provided from Teijin-Nakashima medical Co. Ltd.. The UHMWPE block was manufactured using direct compression molding method with GUR1050 powder.

Briefly, CNT titanium alloy was prepared as follows [1,2]. Firstly, multi-wall (Φ10～15 nm) CNT was produced with chemical vapor deposition method. Silicon coated CNT and titanium alloy powder was pre-mixed, hybridized and consolidated with a pulse electric current sintering machine. Sintered masses were hot-rolled or hot-extruded. Finally, solution and aging treatments were carried out.

### 2. 1 Pin on disc (metal on metal)

The disc samples were cut from 0.7 wt% CNT-SP700 plate, SP700 plate, and CoCrMo plate with a wire-cut spark machine. The size of disc sample was 40 mm x 40 mm and 5 mm in thickness. The pin specimens were machined from 0.7 wt% CNT-SP700 bar, SP700 bar and CoCrMo bar. The pin heads were flat of 2 mm in diameter and 3 mm in length. The surface roughness ($Ra$) of pins was $< 0.02\ \mu$m. Roughness measurements were carried out with the WykoNT9100 optical profiling system (Veecco Instrument, Inc., New York, USA).

Wear tests were conducted for each specimen (SP700, CNT-SP700, CoCrMo: n = 3) on a pin-on-disc apparatus (FRP-2100, RHSCA Corp., Tokyo, Japan)[5]. The lubricant containing distilled water, 25% bovine serum and 3% sodium azide was heated to 37 ± 2℃. The track radius for pins was 8 mm. The constant load compression of pin was 9.8 N; a contact stress of 3.12 MPa (Fig. 1A). The disc rotating speed was 20 mm/sec. The sliding distance was approximately 1.7 x $10^6$ mm. The apparatus stopped at every 4.32 x $10^5$ mm for measurement of wear. The wear of pins and discs were weighed and converted to volumetric values with densities (CoCrMo: 8.35 g/$cm^3$, SP700: 4.51 g/$cm^3$, CNT-SP700: 4.46 g/$cm^3$). The pin-on-disc apparatus measured the coefficient of friction per

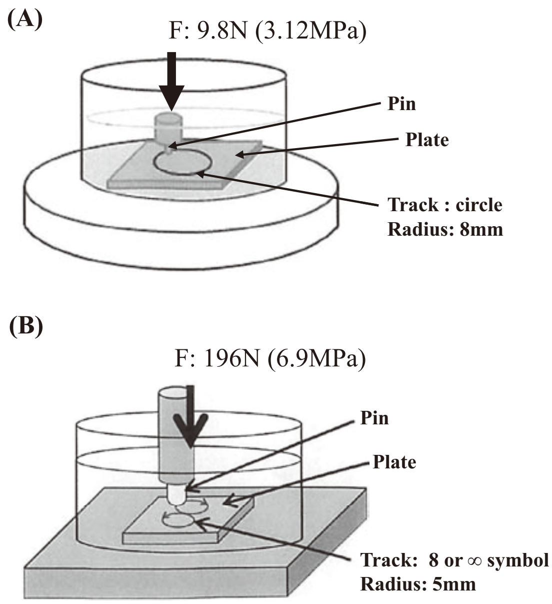



Fig. 1 Pin on disc test scheme
(A) Metal on metal (B) Metal on UHMWPE

second. The mean coefficient of friction in each pin and disc combination was calculated at every interval.

### 2. 2 Pin on disc (UHMWPE on metal)

The disc samples were cut from 0.7 wt% CNT-SP700 plate, SP700 plate, 0.9 wt% CNT-Ti6Al4V plate, Ti6Al4V plate and CoCrMo plate with a wire-cut spark machine. The disc sample was 40 mm x 40 mm and 5 mm in thickness. In addition, the carbon-doped titanium oxide layer (Fresh Green) was formed by oxidizing and carbonizing Ti6Al4V plate (Ofa Co. Ltd., Urayasu, Japan). Fresh Green layer was free from binders and the concentration of carbon and oxygen was gradually changing within the boundary area between Fresh Green layer and base Ti6Al4V[6]. The pin specimens were machined from UHMWPE in the form of diameter 10 mm and length 16mm. The pin heads were flat of 6 mm in diameter. The *Ra* of disc specimens was $<0.02$ $\mu$m, while that of Fresh Green Ti6Al4V was 0.109. Wear tests were carried out for each specimen (SP-700, CNT-SP700, Ti6Al4V, CNT-Ti6Al4V, Fresh Green-Ti6Al4V, CoCrMo: n = 3) on a pin-on-disc apparatus (two dimensional convex sliding fatigue tester, MS-tech Co. Ltd., Osaka, Japan). The lubricant containing distilled water, 25% bovine serum and 3% sodium azide was heated to 37 ± 2℃. The track for pins followed an 8 or ∞ symbol shape, each loop had a diameter of 10 mm. The constant load compression of pin was 196 N corresponding to a contact stress of 6.9 MPa (Fig. 1B). The disc rotating speed was 30 mm/sec. The total sliding distance was approximately 2.5 x $10^7$ mm. The apparatus stopped at 1.25 x $10^7$ mm for measurement of wear. The wear of pins and discs were weighed and converted to volumetric values with the density (UHMWPE: 0.934 g/cm$^3$). The control pin was also soaked in the lubricant during the test period. After 1.25 and 2.5 x $10^7$ mm of sliding, the specimens and the control were ultrasonically cleaned, dried and weighed with a microbalance (ME5, Sartorius stedim biotech, Goettingen, Germany). Any weight change of pin was compensated by the weight of water absorption in the control pin.

### 2. 3 Hardness testing

Vickers Hardness of each disc was measured using a micro hardness testing machine (HM-200, Mitsutoyo, Kawasaki, Japan). Testing was carried out to the surface in all cases with a load of 0.25N (Fig. 2).

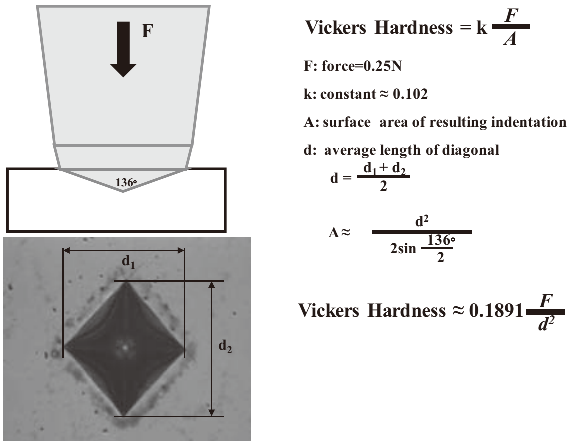



Fig. 2 Vickers test scheme

The lubricant containing distilled water, 25% bovine serum and 3% sodium azide was heated to 37 ± 2°C.

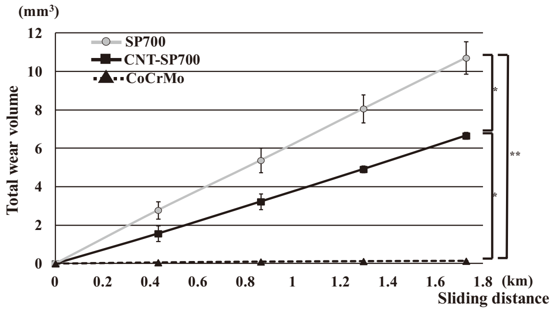
### 2. 4 Statistical analysis

Two groups were compared with Student's T test. *P*-values $<0.05$ was considered to represent a statistically significant for all the analyses. Data was expressed as mean ± standard deviation. The analyzing soft, Ekuseru-Toukei 2015 (Social Survey Research Information, Tokyo, Japan) was used on a computer.

## Ⅲ. Results

### 3. 1 Wear volume (metal on metal)

The wear volume of the CNT-SP700 pin and disc decreased to approximately 50% of that of the SP700 and that was much larger than that of the CoCrMo. The coefficient of friction of the CNT-SP700 was smaller than that of the SP700 and that was slightly larger than that of the CoCrMo (Fig. 3). The wear volume of the SP700 pin was much larger than that of the SP700 plate. In the CNT-SP700, the wear volume of the plate was larger than that of the pin (Fig. 4). In the SP700 and the CNT-SP700, the significance level for the wear volume of pin and plate was 0.0003 and that of the CoCrMo was 0.02. The coefficient of friction in the CNT-SP700




| Distance / Coefficent of friction | 0-0.432 (km) | 0.432-0.864 | 0.864-1.296 | 1.296-1.728 |
|---|---|---|---|---|
| SP700 | 0.33±0.06 | 0.40±0.06 | 0.36±0.01 | 0.37±0.02 |
| CNT-SP700 | 0.27±0.03 | 0.26±0.04 | 0.26±0.04 | 0.27±0.02 |
| CoCrMo | 0.28±0.05 | 0.25±0.09 | 0.20±0.03 | 0.25±0.02 |

Fig. 3 Total wear volume of pin and plate in SP700, CNT-SP700 and CoCrMo

Data are shown as mean ± S.D. n = 3, *$P < 0.01$, **$P < 0.001$ (Student's $t$-test)

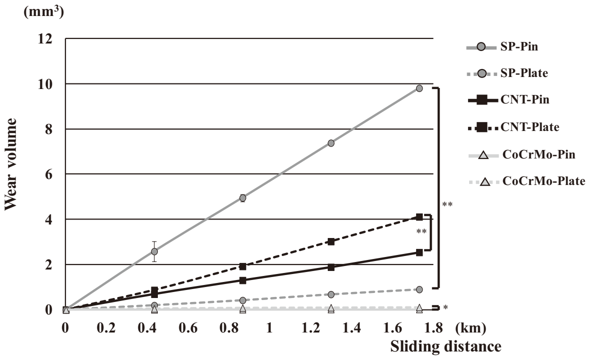



Fig. 4 Wear volume of pin and plate in SP700, CNT-SP700 and CoCrMo

*$P = 0.02$, **$P = 0.0003$ (Student's $t$-test)

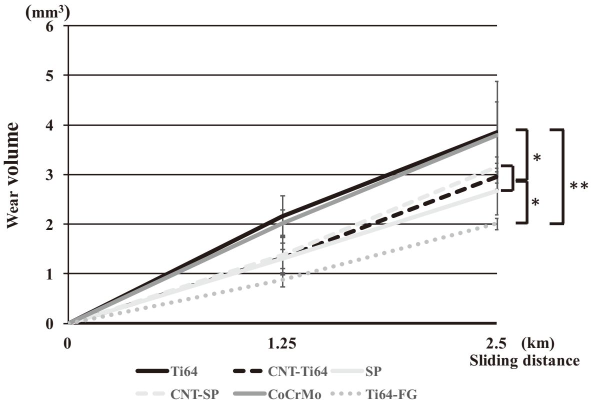



Fig. 5 Wear volume for pin of UHMWPE against Titanium alloys and CoCrMo

Ti64: Ti6Al4V, CNT-Ti64: CNT-Ti6Al4V, SP: SP700, CNT-SP: CNT-SP700, CoCrMo, and Ti64-FG: Fresh Green- Ti6Al4V *$P < 0.05$, **$P < 0.01$ (Student's $t$-test)

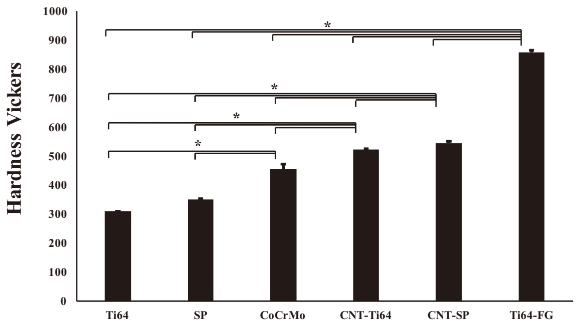



Fig. 6 Vickers Hardness of each plate

Ti64: Ti6Al4V, CNT-Ti64: CNT-Ti6Al4V, SP: SP700, CNT-SP: CNT-SP700, CoCrMo, and Ti64-FG: Fresh Green-Ti6Al4V $P < 0.001$ (Student's $t$-test)

was smaller than that in the SP700 and it is similar to that in the CoCrMo.

### 3. 2 Wear volume (metal on UHMWPE)

The wear volume of the Ti6Al4V was totally equal to that of the CoCrMo (Fig. 5). In the CNT-Ti6Al4V, the SP700 and the CNT-SP700, the wear volume decreased to three fourths of that of the Ti6Al4V and the CoCrMo ($P < 0.05$). The wear volume of the CNT-SP700 was slightly larger than that of CNT-Ti6Al4V. There was no difference between the wear volume of the SP700 and the CNT-SP700. The wear volume of the Fresh Green-Ti6Al4V decreased to one half of that of the Ti6Al4V and the CoCrMo ($P < 0.01$).

### 3. 3 Hardness

The average hardness of Ti6Al4V, SP700, CoCrMo, 0.9 wt% CNT-Ti6Al4V, and 0.7 wt% CNT-SP700 was 308 ± 1.78, 349.1 ± 2.36, 454 ± 18.7, 521.0 ± 3.0, and 543.1 ± 7.7 HV0.25N, respectively. The hardness of 0.9 wt% CNT-Ti6Al4V was similar to that of 0.7 wt% CNT-SP700 and both were higher than that of CoCrMo. The hardness of Fresh Green-Ti6Al4V was 858 ± 6.53 HV0.25N which was extremely high (Fig. 6).

## Ⅳ. Discussion

In total hip arthroplasty, the combination of the ball (CoCrMo) and socket (UHMWPE) are common[7]. The one of alternatives is metal on metal (CoCrMo) device. Metal on metal implants have been used because the polyethylene wear from UHMWPE socket can be avoided and the use of larger ball to decrease the risk of dislocation can be available[8].

With the addition of CNT to SP700, the Young's modulus reached to over 123 GPa[1,2]. Its hardness was 543 HV0.25N which was higher than that of CoCrMo. Therefore, the pin on disc test (metal on metal) was carried out under physiological condition. The wear volume of the CNT-SP700 was less than the SP700. The addition of CNT to SP700 decreased the difference between the pin and plate wear volume. However, the wear volume of the CNT-SP700 was large enough compared to that of the CoCrMo. The coefficient frictions of the CNT-SP700 and the CoCrMo were 0.26-0.27 and 0.20-0.28, respectively. The significance level for the wear volume of pin and plate was 0.0003 in the CNT-SP700, although that of the CoCrMo was 0.02. Anzawa reported that titanium carbide particles precipitated in grain boundary and it was a primary factor of strengthening in CNT-SP700 [1,9]. These mean the composition of CNT-SP700 isn't homogeneous, microscopically and it is the mixture of hard and soft area. The pin specimen was machined from 0.7 wt% CNT-SP700 bar, amd the disc sample was cut from 0.7 wt% CNT-SP700 plate. There is a possibility that the dispersing state of CNT might be different between the bar and the plate. It could cause larger wear volume in the CNT-SP700 than the CoCrMo.

Titanium alloys have been widely used in plates, screws, and implants due to high specific strength, relatively low modulus, good biocompatibility and corrosion resistance. Nevertheless, there is few device applied to sliding surfaces because of their poor wear resistance. Hi-tech knee II total knee joint made of Ti6Al4V has been clinically used since 1994 and has showed good results. Especially, there has been no revision of polyethylene wear over 1500 cases. The same wear volume of Ti6Al4V and CoCrMo in the pin on disc (metal on UHMWPE) tests supported the clinical data of Hi-tech knee II. The SP700, the CNT-SP700 and the CNT-Ti6Al4V reduced the wear volume by approximately 25percent and there are no differences among them. However, the Fresh Green-Ti6Al4V showed the approximately 50% decrease of wear volume. Its surface roughness is high ($Ra = 0.109$) and the improvement of its surface roughness might bring forth to further reduction of wear volume. More than a decade ago, oxidized zirconium was introduced to a bearing surface. Oxidized zirconium is ceramic-like material and its hardness is two times higher than that of CoCrMo. In vitro knee simulator study revealed that the wear volume for UHMWPE articulating with oxidized zirconium decreased by 85 percent, compared to that of CoCrMo[10,11]. The carbon-doped titanium oxide layer of Fresh Green Ti6Al4V is also ceramic-like material and its hardness is similar to that of oxidized zirconium. In addition, titanium alloy has good biocompatibility and less allergic.

There are some limitations in the study. The sliding distance is not enough in the pin on disc tests. SEM observation wasn't carried out with respect to the sliding surface. However, Fresh Green-Ti6Al4V might be a good candidate for sliding surface material.

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