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.

**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.

**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, ASTM F136) 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 μm. Roughness measurements were carried out with the WykoNT9100 optical profiling system (Vecco 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°C. 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 10^6 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

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 μm. Roughness measurements were carried out with the WykoNT9100 optical profiling system (Vecco 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°C. 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 10^6 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) F: 9.8N (3.12MPa) (B) F: 196N (6.9MPa)

(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 16 mm. The pin heads were flat of 6
mm in diameter. The Ra of disc specimen was <0.02
µm, 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°C. 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/cm³). 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).

![Vickers hardness test scheme](image)

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
The wear volume of the Ti6Al4V was totally equal to that of the CoCrMo. The wear volume of the CNT-Ti64 was slightly larger than that of CNT-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 ($P<0.01$).

### 3.2 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. The average hardness of Ti6Al4V, SP700, CNT-Ti64, CNT-SP, and Ti64-FG: Fresh Green-Ti6Al4V was similar to that of the SP700 and both were higher than that of the CoCrMo. The hardness of Fresh Green-Ti6Al4V was $858 \pm 6.53$ HV0.25N which was extremely high (Fig. 6).

### 3.3 Hardness

The average hardness of Ti6Al4V, SP700, CNT-Ti64, CNT-SP, and Ti64-FG: Fresh Green-Ti6Al4V was similar to that of the SP700 and both were higher than that of the CoCrMo. The hardness of Fresh Green-Ti6Al4V was $858 \pm 6.53$ 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, and 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 25 percent 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.

Acknowledgment

The study was supported in part by Grants-in-Aid for scientific Research Grant Number 24592221. The study was supported in part from Teijin-nakashima medical Co. ltd. for the provision of UHMWPE. I wish to thank Dr. Takizawa at Nagano prefecture general industrial technology center for the provision of CNT testing material and thank Mr. Tanimoto at E&F Co. ltd. for helpful advices.

References


3) Tamai H, Suzuki M, Tsuncizumi Y, Tsukeoka T, Banks


