Wear Corrosion Characteristics of Various Biomedical Materials in Quasi-Human Body Environment

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Abstract. In recent years, the demand for a biomedical material is increasing with the formation of the aged society with low birth rate, together with the lowering in joint disease patient's age. Especially, the demand for a total hip joint replacement has been increased. The main materials currently used for the total hip joint replacement were UHMWPE, alumina, zirconia, titanium alloys (mainly Ti-6Al-4V) and so on. Although these materials showed good biocompatibility, they had some problems such as generating of wear powder, causing brittle fracture, and having inferior corrosion resistance, respectively. Also, Ni-Ti was expected to apply to biomedical material for making best use of its shape-memory and super-elastic effects. However, wear corrosion characteristics of Ni-Ti in human body environment had not fully clarified yet. Therefore, in this research, authors evaluated wear and wear corrosion resistance of materials used in total hip joint replacement and also corrosion characteristics of metallic materials for biomedical use was evaluated. As a result, wear experiment showed that Y-TZP was best material and most suitable for total hip joint replacement. And results of wear corrosion experiment showed that Ni-Ti was charming inter-metallic material for biomedical use.

Introduction

In recent years, the demand for biomaterials is increasing with the formation of the aged society with a low birth rate. Especially, the requests for an artificial joint are increasing with joint disease patients, such as congenital dislocation, arthrosis deformans, chronic rheumatism, and osteoporosis[1]. In particular, an artificial hip joint occupies 60 percents of the demand for all artificial joints. Now the scale of market of an artificial hip joint is small about 50-60 billion yen in Japan. However, for the abovementioned reason, it is expected to expand at more than 10% growth rates. For an artificial hip joint, especially for stem and head, titanium alloy (mainly Ti-6Al-4V) has begun to use instead of stainless steel. Because titanium alloys has excellent corrosion resistance, biocompatibility and specific tensile strength compared with stainless steel[2]. Also, its elastic modules resembles to bone. Among various titanium alloys, nickel-titanium alloy was expected to apply to biomaterial, for example orthodontic wire in the realm of dentistry, and stent in the realm of surgery, for making best use of its shape-memory and super-elastic effects[3]. However, living body has some severe factors such as corrosion accelerating effect due to chloride ion, and wear and fatigue caused by the motion of human body. Therefore, most severe problems for metallic biomaterials are corrosion and wear resistances. There are some fears of toxic ion elution and soreness due to living body's necrosis caused by generated wear powder[4]. Intensive materials development for sliding parts of artificial hip joint has been conducted in these days. Now, titanium alloys are used for stem and head. At the same time, UHMWPE (ultra high molecular weight polythene) is used for cup material.[5] In recent years, ceramic materials such as alumina and zirconia are discussed to use for stem and head materials, because they have good characters of being inert to living body, superior corrosion resistance and high strength. However, ceramic materials and UHMWPE have inferior characters of brittle fracture and wear powder generation, respectively. Therefore in this research, authors evaluated corrosion resistance of titanium alloys which are used in artificial hip joint right now, and that of stainless steel that has a lot of results is using for artificial hip joint until now. At the same time, authors evaluated wear corrosion resistance of titanium alloys, alumina and zirconia through employing UHMWPE as a counter material. From these investigations, authors were intended to understand performances and problems of various biomaterials.

Experimental procedures

Polarization Measurement

Ni-Ti, Ti-6Al-4V and SUS316 wire materials whose diameter and length are 1 mm and 50 mm are used in this study. There materials were surface finished by acid pickling (hydrofluoric acid: nitric acid: ion exchanged water=1:4:5). Then, those wires were electropolished using a solution (ethanol: glycerin: perchloric acid=7:2:1). Finally, insulation of specimen was conducted with silicon except for the testing surface area of 1 cm^2. Chemical compositions of test specimens was indicated to Table 1.

Corrosion resistance of test specimens was evaluated through obtaining polarization curve by 3 electrodes electrochemical method in which working electrode was a test specimen, counter electrode was platinum-electrode and reference electrode was saturated calomel electrode. Electric connection between reference electrode cell and working electrode cell was maintained by salt bridge made of saturated KCl solution at 333K. Potentio-dynamic tests were conducted in quasi-human body environment, i.e., lactic Ringer's solution of 310K under the potential ranges from –1,000mV to +2,000mV for of Ni-Ti and SUS316, and from –1,000mV to +6,000mV for Ti-6Al-4V, respectively. Electrolytic composition of quasi-human body environment of lactated Ringer's solution and intercellular solution were indicated in Table 2. Detailed observations of surface morphology of test specimens were conducted by SEM .

Measurement of Specific Wear Amount and Friction Coefficient

As pin specimens relatively soft materials were applied to avoid digging out disk materials. Disk specimen size was selected to be 60×60×10mm. Because there are some fears of plate fracture due to the shortage of strength in case of applying thinner specimen and the degradation in the measurements accuracy in case of applying thicker specimens. The surface of plate specimen were polished to be Ra=0.05μm. On the contrary, pin type specimen sizes were selected to be ϕ 6×30mm, and the edges were rounded to be R=0.3 mm and roughness of pin test specimen surface was Ra=5μm. Disk specimens and ceramic pin specimens were ultrasonically cleaned using acetone and methanol referring to JIS R 1613[7]. They were dried 1 hour at 393K to remove water, and then they were naturally cooled in desiccator. After electrochemical testing specimens were cleaned and dried employing the same method. UHMWPE pin specimens were cleaned by distilled water, and they were dried 1 hour at 310K, then they were naturally cooled in desiccator. Combination of disk and pin materials and testing condition were shown in Table 3.

Wear tests were conducted by pin on disk type testing machine in quasi-human body environment of lactated Ringers solution at 310 K. Change in friction coefficient between pin and disk specimens was detected during wear testing. Also, weight of specimen was measured before and after wear test. And wear amount was calculated by using equation (1) referring to TR T 0003[6].

$$W = (W_1 - W_2) / P \cdot L \cdot \rho \qquad (1)$$

where W: Specific wear amount [mm^2／N] ,
W_1: Morality of before experiment [g]
W_2: Morality of after experiment [g],
L: Sliding distance [mm]
ρ: Density of specimen [g/mm3]
P : Load[N]$=p \times S$
p: Stress on wear surface [MPa]
S: Area of wear surface [mm^2]

Test conditions were determined as 6 rpm for disk sliding speed and 3 km for sliding distance referred to TR T 0003[6]. Environmental solution may eminently evaporate during testing, in consequence concentration change of ions is expected. And accelerating effect due to concentration change of ions in solution is worried about. Therefore, some amount of distilled water was dropped into solution during wear test to keep the concentrations of ions to be almost the same. Surface morphologies of all test specimens were observed by optical microscope, and that of Ti-6Al-4V disk specimen was observed by FE-SEM.

Table 1 Chemical Compositions of Test Specimens (wt%)

Elements	Ti	Ni	Al	V	Cr	Mn	N	C	Fe	Y	O	H	Mo
NiTi	55.6	44.4	—	—	—	—	—	—	—	—	—	—	—
Ti-6Al-4V	Bal	—	6.30	4.16	—	—	0.002	0.006	0.242	0.001	0.168	0.0044	—
SUS316	—	12.0	—	—	17.0	2.0	—	0.08	65.0	—	—	—	2.5

Table 2 Electrolytic Composition of Test Solution

Element [mEq/L]	Na$^+$	K$^+$	Ca^{2+}	Cl$^-$	Lactate$^-$
lactic Ringers Solution	130	4	3	109	28
Transcellular Solution	140	6	4	102	—

Table 3 Test Condition of Ti-6Al-4V Disk Specimen

Loading Stress [MPa]			**Disk Specimen**	**Pin Specimen**
2.5	**5.0**	**7.5**	**Ti-6Al-4V**	**UHMWPE**
---	**5.0**	**7.5**	**Ni-Ti**	**UHMWPE**
---	**5.0**	**7.5**	**SUS316L**	**UHMWPE**
---	**5.0**	**7.5**	$\mathbf{Al_2O_3}$	**UHMWPE**
---	**5.0**	**7.5**	$\mathbf{Al_2O_3}$	$\mathbf{Al_2O_3}$
---	**5.0**	**---**	$\mathbf{ZrO_2}$	**UHMWPE**
---	**5.0**	**---**	$\mathbf{ZrO_2}$	$\mathbf{ZrO_2}$

Results and discussions

Result of Polarization Measurement

Fig.1 showed results of polarization measurements obtained for Ni-Ti, Ti-6Al-4V and SUS316 specimens. Fig.2 showed surface morphologies of test specimens detected by SEM after testing. From the results shown in Fig.1, it was understood that SUS316 was in trans-passive state under the potential condition of 700[mV]. However, Ni-Ti and Ti-6Al-4V alloy were still in passive state. As a result, Ti alloys had better corrosion resistance compared with SUS316. In case of Ti alloys, first pitting potential (potential at $i=10\mu A/cm^{2)}$ of Ni-Ti and Ti-6Al-4V were obtained to be 1,175 mV and 2,000 mV, respectively. Ti-6Al-4V had better corrosion resistance compared with Ni-Ti, judging from the fact that the passive area of Ti-6Al-4V was wider than Ni-Ti. However, Ni-Ti alloy showed better corrosion resistance compared with Ti-6Al-4V under passive potential region from about 500 mV to 1000 mV. These facts imply that Ni-Ti alloy shows excellent corrosion resistance when it is used in not so severe environment. As shown in Fig.2, a little corrosion damages were recognized on Ti-6Al-4V and Ni-Ti specimens surface. On the other hand, clear corrosion damages such as pitting was detected on the surface of SUS316 specimen. From these results, difference in corrosion resistance between these materials shown in Fig.1 was confirmed.

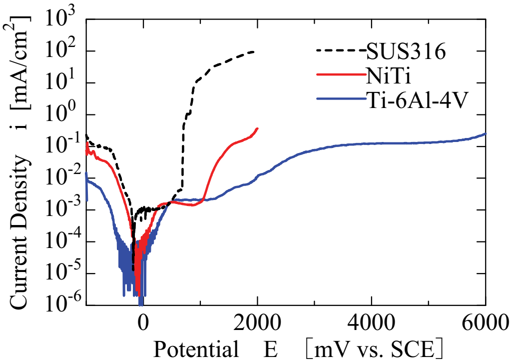
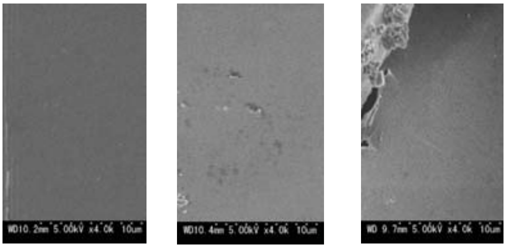


Fig.1 Results of Polarization Measurement



a) Ti-6Al-4V b) Ni-Ti c) SUS316

Fig.2 Surface Morphologies

Specific Wear Amount and Friction Coefficient

Specific wear amount was obtained from equation (1) and shown in Table 4. Moralities of Ni-Ti under loading stress of 5.0MPa and ZrO_2 under loading stress of 5.0 and 7.5MPa after experiment increased compared with that before experiment. Therefore, the specific wear amounts in these cases were considered to be zero. Also, friction coefficient during wear test was measured and shown in Fig.3 and 4. In Fig.5 surface morphologies of various specimens after wear corrosion test conducted under loading stress condition of p=5.0MPa were indicated. Proportional relationship between specific wear amount and loading stress was not recognized in the data shown in Table 4. Also, the specific wear amount of ceramic pin materials obtained under the same material coupling condition became extremely small compared with the case of using UHMWPE as a pin material. Friction coefficient of various metallic materials obtained under metals/UHMWPE coupling test condition became smaller compared with that of ceramic materials as show in Figure 3. However, the friction coefficient in case of ceramics/UHMWPE coupling wear test became smaller value compared with that obtained under ceramic/ceramic coupling test condition as shown in Figures 4.

Table 4 Specific Wear Amount Obtained under Various Testing Conditions

Loading Stress [MPa]	**Specific Wear Amount of Disk ×10^9 [mm^2/N]**		**Specific Wear Amount of Pin ×10^9 [mm^2/N]**	
2.5	**Ti-6Al-4V**	**32.7**	**UHMWPE**	**10.7**
5.0		**16.5**		**8.29**
7.5		**3.19**		**1.68**
5.0	**Ni-Ti**	**0**	**UHMWPE**	**5.46**
7.5		**0.653**		**9.10**
5.0	**SUS316L**	**1.44**	**UHMWPE**	**0**
7.5		**1.00**		**0**
5.0	**Al_2O_3**	**0.356**	**UHMWPE**	**6.46**
		0.365	**Al_2O_3**	**1.35**
7.5		**0.125**	**UHMWPE**	**7.13**
		0.344	**Al_2O_3**	**0.0988**
5.0	**ZrO_2**	**0**	**UHMWPE**	**1.68**
		0	**ZrO_2**	**0.0481**

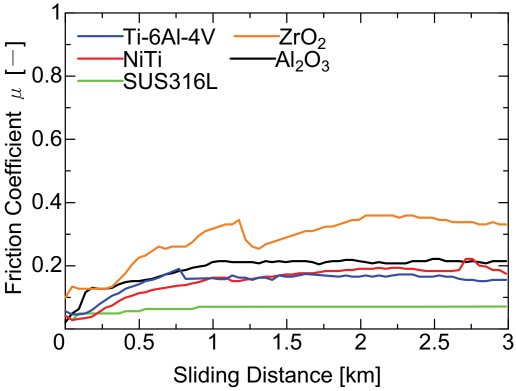


Fig. 3 Change of Friction Coefficient during Wear Corrosion Test: p=5.0MPa

In case of Al_2O_3, more smooth trace was recognized on the specimen surface after ware corrosion test conducted under Al_2O_3/Al_2O_3 combination as show in Fig. 6. As a result, it was made clear that in case of the same materials coupling ceramic wear the specific wear amount has been finally suppressed, however, further examinations of friction coefficient was requested. In the end of wear test, specific wear amount of Al_2O_3 was recognized to be larger than that of ZrO_2. Because, ZrO_2 has high strength and high toughness compared with those of Al_2O_3. For these reasons, ZrO_2 shows

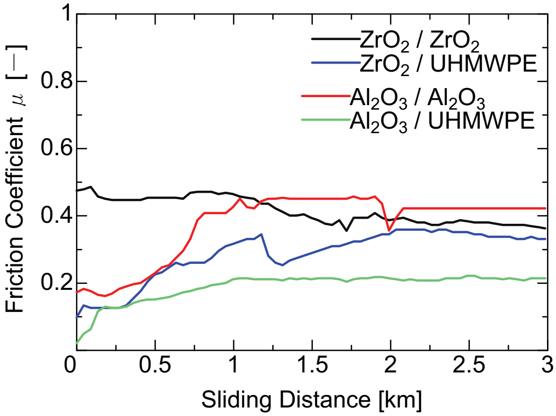
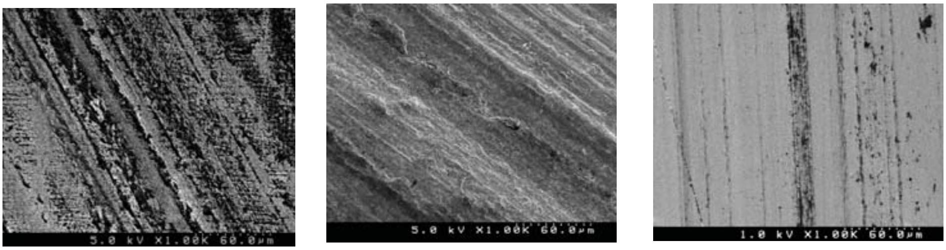
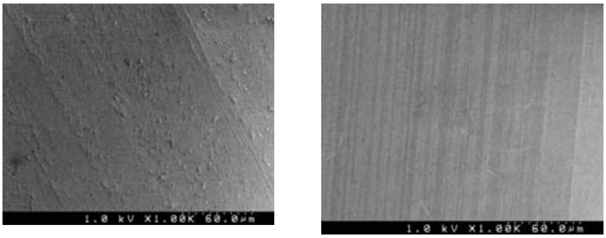


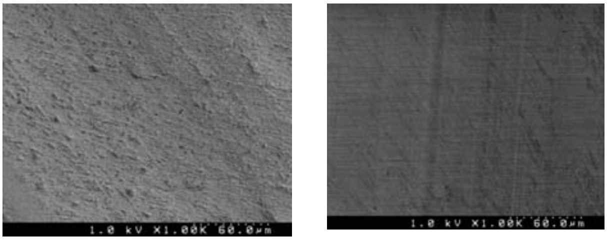
Fig. 4 Change of Friction Coefficient during Wear Corrosion Test: p=5.0MPa



a) Ni-Ti b) Ti-6Al-4V c) SUS316L

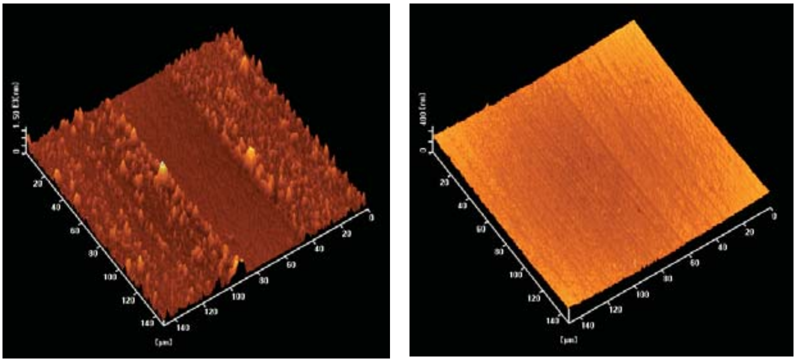


d) Al_2O_3 (vs. UHMWPE) e) Al_2O_3 (vs. Al_2O_3)



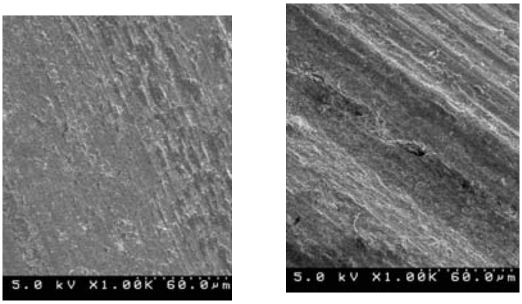
f) ZrO_2 (vs. UHMWPE) g) ZrO_2 (vs. ZrO_2)

Fig.5 Surface Morphologies Observed by FE-SEM, p=5.0MPa, Disk specimens, L=3 km



a) vs. UHMWPE b) vs. Al_2O_3

Fig.6 Three-dimension Images of Al_2O_3 Observed by AFM: p=5.0[MPa]

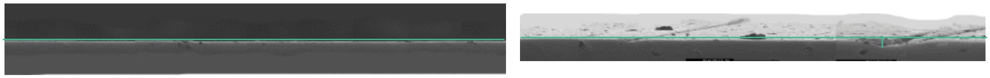


a) p=2.5 MPa b) p=5.0 MPa

Fig.7 Surface Morphologies after Wear Corrosion Test:Ti-6Al-4V Disk / UHMWPE, L=3 km

a) Ti-6Al-4V : p=2.5MPa Depth:13.6μm b) Ti-6Al-4V : p=5.0MPa Depth : 43.4μm

c) Ti-6Al-4V : p=7.5MPa Depth : 67.2[μm]



d) Ni-Ti : p=5.0MPa Depth : Unmeasurable e) Ni-Ti : p=7.5MPa Depth : 12.8μm

100μm

Fig.8 Two Dimensional Morphology of Ware Trace Observed by SEM: Metal/UHMWPE, L=3 km

excellent wear resisting character. From these viewpoints of high strength and better wear resisting properties of Ni-Ti alloy, it is expected that Ni-Ti alloy showed relatively smaller friction coefficient compared with Ti-6Al-4V. In fact, friction coefficient obtained under Ni-Ti/UHMWPE coupling condition coincided with above-mentioned expectation under stress condition of 5.0MPa, however, that value obtained under the stress revel of 7.5MPa became larger than that obtained underTi-6Al-4V/UHMWPE coupling condition. Then, authors have been conducted the same experiment again, as a result the same trend was recognized in experimental data. Therefore, it was necessary to examine the root cause of these behaviors through conducting various detailed analysis such as surface observation and qualitative chemical analysis. In Figures 7 surface morphologies of Ti-6Al-4V specimens observed by FE-SEM after wear testing under stress levels of 2.5 and 5.0MPa were indicated. These figures indicated that the more significant surface damages were recognized with the increase of loading stress. These characteristics were supported by cross-sectional observations of worn trace on specimen surface as shown in Fig. 8.

Conclusions

In this study, authors were intended to understand performances and problems of various biomaterials used under wear and corrosion condition in quasi-human body environment.

The results obtained were summarized as follows:

(1) In polarization measurement, Ti alloys had good corrosion resistance than SUS316. Especially in Ti alloy, Ti-6Al-4V had better corrosion resistance compared with Ni-Ti. However, particularly in passive area the passivation current density of Ni-Ti alloy became smaller than that of Ti-6Al-4V.

(2) Specific wear amount of biomedical metallic materials becomes larger than ceramic materials. Ti-6Al-4V showed inferior wear resistance compared with SUS316L and Ni-Ti alloy. Ni-Ti alloy showed superior wear corrosion resistance compared with other metallic bio materials. Therefore, Ni-Ti alloy has possibility to show good characteristic of passivation under wear corrosion condition. For this reason, Ni-Ti alloy has possibility to be used in living body as biomaterial under not so severe environment.

(3) Judging from the results of wear test, it was understood that friction coefficient increased and the more significant surface damages were recognized with the increase of loading stress. On the contrary, proportional relationship between specific wear amount and loading stress was not recognized. The friction coefficient in case of ceramics/UHMWPE coupling wear test became extremely suppressed compared with that obtained under ceramic/ceramic coupling test condition. However, flatness of wear trace of ceramic materials obtained under the same material coupling condition became extremely better compared with the case of using UHMWPE as a pin material. Among tested ceramics, ZrO_2 had better wear resistance than Al_2O_3.

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