Corrosion Resistance, Mechanical Properties, Corrosion Fatigue Strength and Biocompatibility of New Ti Alloy without V for Medical Implants

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Corrosion resistance due to wear changes with the materials used as disk and pin, frictional load, potential zone and with the pH of the solution. A new Ti-15%Zr-4%Nb-4%Ta alloy containing 0.2%Pd showed an excellent wear access corrosion properties compared to other Ti alloys. The addition of Y.

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The population of persons over 65 years of age is increasing every year in Japan, and the use of artificial body implants is increasing accordingly. Along with various implant materials such as Co-Cr alloy and SUS316L stainless, the use of Ti-6%Al-4%V ELI alloy as a body implant alloy is increasing. β type Ti-15%Mo-5%Zr-3%Al and α + β type Ti-6%Al-2%Nb-1%Ta alloys have been developed for artificial hip joints by Kobe Steel Ltd. in Japan and are clinically used as artificial hip joints for cement and cementless types, respectively. For cementless artificial hip joints made of Ti-6%Al-2%Nb-1%Ta alloy, a part of the neck in the stem surface was improved with titanium plasma spray coating in combination with a bottom coating of apatite-wollastonite containing glass-ceramic to obtain a stable bone contact sooner after implantation. Hydroxyapatite-coated artificial hip joints made of Ti-6%Al-4%V ELI alloy have also been developed using an inert-gas shielded arc spray technique with titanium powder in combination with hydroxyapatite-coating by Kyocera Corporation. The effects of various metallic concentrations on the relative growth ratios for cultured cells were examined using extracted mediums with various metallic particles. Ti, Zr, Nb and Ta show low cytotoxicity. As α + β type alloys for medical implants not containing V, Ti-5%Al-2.5%Fe and Ti-6%Al-7%Nb alloys are specified by ISO 5832-10 and 5832-11 standards. A near β type alloy, Ti-13%Nb-13%Zr alloy, is also specified in ASTM F 1713-96 standard. β type alloys having a slightly lower Young’s modulus than that of α + β type alloy, such as Ti-12%Mo-6%Zr-2%Fe, Ti-15%Mo-3%Nb-3%Al, and Ti-29%Nb-13%Ta-5%Zr alloys, are also being developed for medical implants. Ti-13%Nb-13%Zr alloy is reported to possess a higher adhesion of osteoblasts and a lower bacterial adhesion than pure Ti and Ti-6%Al-4%V alloy. Our group has reported on the effects of Zr, Nb, Ta and Pd on corrosion resistance in a physiological saline solution, mechanical properties and biocompatibility with cultured cells (cytocompatibility). Corrosion resistance has been improved by adding Zr, Nb, Ta and Pd because the resultant ZrO2, Nb2O5, Ta2O5 and PdO strengthen the TiO2 passive film formed on new alloy. The room-temperature mechanical strength of the annealed (973 K - 7.2 ks) alloy was increased by adding Zr and small quantities of oxygen and nitrogen. As a consequence, Ti-15%Zr-4%Nb-4%Ta-0.2%Pd alloy

1. INTRODUCTION
showed excellent corrosion resistance, mechanical properties and biocompatibility compared to Ti-6%Al-4%V ELI alloy. Wear-accelerated corrosion of Ti alloys in the biological environment using cyclic polarization measurement from 0 to 5 V has been reported\(^\text{15}\). \(\alpha + \beta\) type Ti-6%Al-4%V and Ti-6%Al-7%Nb alloys possessed the best combination of corrosion and wear resistance, although commercially pure Ti and the near \(\beta\) type (Ti-13%Nb-13%Zr) and \(\beta\) type (Ti-15%Mo) alloys displayed excellent corrosion resistance. In this work, the corrosion resistance in a physiological saline solution, the mechanical properties and the biocompatibility using cultured cells and rat tibia implantation for Ti alloys were examined. The effect of heat treatment for new Ti alloy, namely, Ti-15%Zr-4%Nb-4%Ta containing 0.2%Pd, 0.2%O and 0.05%N, on mechanical properties and corrosion fatigue properties were also investigated. The fatigue test was carried out under a tension-to-tension mode with a sine wave at a stress ratio of 0.1 and at a frequencies of 2 Hz and 10 Hz in Eagle's medium solution using a corrosion-fatigue cell with 90%N\(_2\)+5%CO\(_2\)+5%O\(_2\) gas bubbling. Further, the effect of the wave shape on corrosion-fatigue strength was examined using a sine wave and load profile estimated by an analysis of forces and actions of the human hip joint.

2. MATERIALS AND EXPERIMENTAL METHOD

2.1. ALLOY SPECIMENS AND HEAT TREATMENTS

The new Ti-15%Zr-4%Nb-4%Ta containing 0.2%Pd, 0.2%O, 0.05%N (hereafter called Ti-15%Zr-4%Nb-4%Ta), pure Ti grade 2, Ti-6%Al-4%V ELI, Ti-6%Al-2%Nb-1%Ta and \(\beta\) type Ti-15%Mo-5%Zr-3%Al alloys were melted by vacuum arc melting. In the case of \(\alpha + \beta\) type alloys, after \(\beta\) and \(\alpha - \beta\) forging, the alloys were annealed for 7.2 ks at 973 K. For \(\beta\) type alloy, solution treatment was carried out at 1058 K for 1.8 ks and then quenched in water. Moreover, to determine the optimum solution treatment and aging conditions for the Ti-15%Zr-4%Nb-4%Ta alloy, alloy specimens 17 mm in diameter and 10 mm in thickness were cut after \(\alpha - \beta\) forging. These specimens were kept in a range of 1028 to 1073 K (755 to 800°C) for 3.6 ks and then water cooled. The solution treated specimens were aged in a range of 623 to 723 K for 18 to 54 ks (5 to 15 h) and then air cooled. Table 1 shows the chemical composition of these materials. For comparison, the chemical composition of Co-Cr alloy and SUS316L stainless steel is also shown in Table 1.

<table>
<thead>
<tr>
<th>Table 1 Chemical composition (mass%) of materials used.</th>
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<tr>
<td>Cr</td>
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<tr>
<td>SUS316L</td>
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<td>Co-Cr alloy</td>
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2.2. ANODIC POLARIZATION TESTS UNDER STATIC AND FRICTIONAL CONDITIONS

When the current density measured by anodic polarization testing is low, the corrosion resistance of an alloy is excellent. Several block specimens of 10 mm x 10 mm x 5 mm in thickness were cut from the sample alloys under static condition. The surfaces of the specimens, except for 1 cm\(^2\), were coated with epoxy resin and then polished with waterproof emery paper up to 4600 under running water and ultrasonically cleaned in ethanol. The anodic polarization tests were conducted independently in 1 mass% lactic acid (pH=2.5) and Eagle’s MEM (Minimum Essential Medium: mainly composed of NaCl : 6.8 g, C\(_6\)H\(_{12}\)O\(_6\) : 1 g, KCl : 0.4 g, CaCl\(_2\) : 0.2 g, NaH\(_2\)PO\(_4\) : 0.115 g, containing various inorganic salts and kanamycin, etc. in 1 dm\(^3\) of pure water) containing 10% fetal bovine serum, 7.5%NaHCO\(_3\) (2.3 vol%), and 3%L-glutamine (1 vol%) (hereafter called Eagle’s medium solution, pH=8.2-8.8) solutions. The testing solution was bubbled with high-purity nitrogen gas at a rate of 3.33 x 10\(^4\) m\(^3\)/s (200 cm\(^3\)/min) for 0.6 ks (10 min). The specimen was initially held at -1 V for 300 s. An anodic polarization test was carried out from -1 V to a maximum of 5 V at a sweep rate of 6.67 x 10\(^4\) V/s (40 mV/min) under a small amount of high-purity nitrogen gas flowing to the solution surface.

The micromotion between the bone and the implant gives rise to metallic ion release. This results in the loosening of the stem and thus giving rise to pain. The effect of frictional load on the anodic polarization
properties in 1 mass% lactic acid and Eagle's medium solutions was investigated. A polarization cell to measure the anodic polarization curves under the frictional condition is shown in Fig. 1. The specimen electrode is reciprocally moved by a cam in the contact with apatite ceramics. The applied load was displayed digitally by the load cell and the frictional load was adjusted with screws. To maintain the testing solution at 310 K, hot water was circulated around the cell. The reciprocal speed was varied by changing the gears and the ratio of teeth in the gear box. The cell is made of teflon, and the holder to fix the ceramics is made of polychlorotrifluoro ethylene (PCTFE, Daiflon). A test specimen 10 mm in diameter and 10 mm in thickness was prepared out of sample alloy. After connecting the test specimen to a platinum wire by lug terminal and screw, they were inserted into daiflon, and the specimen surface, except for 0.8 cm², was covered with epoxy resin. Thereafter, the specimen surface was polished with waterproof emery paper up to #600 under running water, followed by ultrasonic cleaning in ethanol. The reciprocal distance was 5 mm, apatite and alumina ceramics were used for the friction specimen to simulate bone tissue, and the data collecting interval was 2 s, the reciprocal speed at $10^{-3}$ to $10^{-2}$ m/s (0.1 to 1 Hz), and the frictional load was up to 59 N. However, because the frictional area in this test was less than 10% of the surface area, the measuring area was assumed to be a constant area of 0.8 cm².

After setting the specimen electrode and the friction specimen in the polarization cell, the testing solution was deaerated with high-purity nitrogen at a rate of $1.67 \times 10^{-6}$ m³/s for 0.6 ks. The specimen was initially held at -1.5 V for 300 s. An anodic polarization test was then carried out from -1.5 V to 5 V at a sweep rate of $6.67 \times 10^{-4}$ V/s (40 mV/min) with a small amount of high-purity nitrogen gas flowing to the solution surface. Moreover, during the anodic polarization test, measurement was performed by adjusting the screws to minimize frictional load fluctuation (to a maximum 40% of the mean frictional load).

2.3. TENSILE TEST AND MICROSTRUCTURE OBSERVATION

Tensile testing was conducted with test specimens 6 mm in diameter and 22 mm in gage length at room temperature at a crosshead speed of $8.33 \times 10^{-4}$ m/s (0.5 mm/min). After etching the test specimen in HF: HNO₃ : H₂O at a ratio of 15 : 20 : 65 cm³ containing 10%H₂O₂, the microstructure was observed with an optical microscope, a scanning electron microscope (SEM) and a transmission electron microscope (TEM). The sample specimen for TEM observation was prepared by electrolytic polishing (35 to 55 V, 40 to 100 mA) in a mixture of 95% acetic anhydride and 5% perchloric acid solutions.

2.4. CORROSION FATIGUE TEST IN PYSHIOLOGICAL SOLUTION

The fatigue test specimen with the shape and dimensions shown in Fig. 2 was cut from the sample alloys. The corrosion fatigue test was carried out in Eagle's medium solution. To remove the inner strain in the surface of the alloy caused in the manufacturing process, the surface of the test specimen was fully finished with #600 waterproof emery paper in the direction parallel to the test specimen. The test specimen was fitted up in a cell (polyethylene, inside...
MEM solution. Alloy plates (33 mm in diameter and 1 mm in height) containing Eagle's medium for MC3T3-E1 cells. The cells were then counted using a Coulter counter. The number of cells in each dish in the control was estimated using the following formula: (average number of cells per dish after 4 d incubation) / (average and standard deviation values of the relative growth ratio were estimated using more than 5 dishes. Metallic ions are released from Ti-6%Al-4%V alloy implants in vivo. Figure 3 shows the MTS model 858 Mini Bionix equipment, cell and the hip joint load profile used in the test. (a) 858 Mini Bionix, (b) Physiological saline solution cell, (c) Hip joint load profile.

2.5. CYTOCOMPATIBILITY

Two types of cells, namely, L929 cells derived from murine fibroblastic tissue and murine osteoblast-like MC3T3-E1 cells were used. The culture medium for the L929 cells was prepared by adding 7.5% NaHCO₃ solution (2.3 vol%), fetal bovine serum (10 vol%), and 3% L-Glutamine solution (1 vol%) to the Eagle's MEM solution. For the MC3T3-E1 cells, the culture medium was prepared by adding fetal bovine serum (10 vol%) and 7.5% NaHCO₃ solution (2.4 vol%) to α-MEM solution. Alloy plates (33 mm in diameter and 1 mm in height) were cut from the sample alloys. The surfaces of the plates were then polished with waterproof emery paper up to #1000 under running water and ultrasonically cleaned in ethanol. All the plates were sterilized in an autoclave at 394 K (121 °C) for 1.8 ks. The plates were then placed in a culture dish 35 mm in diameter. 2.8 ml medium solution and 0.2 ml cell suspension containing 3.0x10⁴ L929 and 5.0x10⁴ MC3T3-E1 cells were separately seeded on these plates. These dishes were then incubated for 345.6 ks (4 d) under a 95%air-5%CO₂ atmosphere at 310 K (37 °C). After incubation, the cells were completely separated by pipetting using trypsin (0.1 mass%, 3 mL) and electrolyte (balanced electrolyte solution, 3 mL) and transferred into a Coulter cup containing 3 mL Eagle's medium for L929 cells or α-medium for MC3T3-E1 cells. The cells were then counted using a Coulter counter. The number of cells in each dish in 0.5 mL of medium containing trypsin and electrolyte was counted four times and the average number of cells in each dish was estimated. The Ti-6%Al-4%V ELI alloy plate was the control. The relative growth ratios of the L929 and MC3T3-E1 cells were estimated using the following formula: (average number of cells per dish after 4 d incubation) / (average number of cells in the control). The average and standard deviation values of the relative growth ratio were estimated using more than 5 dishes. Metallic ions are released from Ti-6%Al-4%V alloy implants inside the human body. To accelerate the release of metallic ions, wear tests were carried out using Ti-15%Zr-4%Nb-4%Ta alloys, pure Ti grade 2 and Ti-6%Al-4%V ELI alloy disks (5 mm in thickness and 70 mm in diameter) against these alloys and apatite ceramics pin (20 mm in length and 9 mm in diameter) in Eagle's MEM solution (pH: 4.3) not containing fetal bovine serum and 7.5% NaHCO₃ solution. The wear tests were carried out under a load of 9.8 N, a rotation diameter of 27 mm, a rotation speed of 0.2 m/s up to 10⁷ cycles. The experiment was carried in a cell made of polycarbonate material. After wear testing, Eagle's MEM solution was centrifuged at 50 000 g for 0.9 ks, and the supernatant was filtered with 0.2, 0.1, 0.05, 0.025, and, finally, a 0.015 μm membrane using a vacuum pump to remove wear particles. Thereafter, Eagle's medium was prepared by adding fetal bovine serum (10 vol%), 7.5% NaHCO₃ solution (2.3 vol%), and 3% L-Glutamine solution (1 vol%) to this Eagle's MEM solution. 3.0x10⁴ L929 and 5.0x10⁴ MC3T3-E1 cells were seeded using this worn Eagle's medium and α-medium containing worn Eagle's medium, respectively. The metallic concentration in this worn medium was analyzed by ICP-MS (inductively coupled plasma mass spectrometer). Eagle's medium without bearing and α-medium not containing the worn Eagle's medium were used as control for L929 and MC3T3-E1 cells, respectively.

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2.6. CHEMICAL ANALYSIS OF METALLIC ELEMENTS IN MEDIUM BY ICP-MS

Perfluoro alkoxyl alkane (PFA) flasks were cleaned with ultra-pure water (18.3 MΩ) after use and filled with a 5 mass% nitric acid solution and carefully plugged to exclude air. The flask was emptied before use, and cleaned inside and outside with a 5% nitric acid solution and ultra-pure water. A Yokogawa Analytical Systems HP4500 spectrometer with auto sampler (CETAC ASX500) was used in this study.

The mass axis and intensity were adjusted with a tuning solution containing 10 mass ppb Li, Y, Ce, and Ti. The typical measurement conditions for plasma and the autosampler are as follows: frequency: 27.1 MHz, radio-frequency (R.F.) power: 1.2 kW, plasma gas (Ar) flow rate: 15 dm³/min, auxiliary gas (Ar) flow rate: 1.0 dm³/min, carrier gas (Ar) flow rate: 1.1 dm³/min, sampling distance: 5 mm, rinsing rate by peristaltic pump with 3% nitric acid and ultra-pure water: 0.5 s⁻¹ (2x10⁻⁵ dm³/min), rinsing time: 180 s, exchanging rate by peristaltic pump for sampling solution: 0.5 s⁻¹, exchange time for sampling solution: 120 s, stabilization time for peristaltic pump: 60 s, simple uptake rate: 4.8x10⁴ dm³/min (peristaltic pump speed: 0.12 s⁻¹).

The isotopic mass numbers used for measurement of Ti, Al and V concentrations are Ti: 49 and 50, Al: 27 and V: 51, respectively. The integration time for the mass number is 1 to 3 s. The micro-pipette tips for sampling were cleaned with a 5% nitric acid solution and ultra-pure water before use. The single-element standard solutions (SPEX CertiPrep, Inc., 1000 mass ppm) were diluted to use as the Ti, Al and V standard solutions. Ultra-high-purity nitric acid (TAMAPURE-AA-10) was used for preparing measurement solutions. The 0.5 mass ppb Cobalt or Indium were used as the internal standard solution. The working curves were established in the concentration of 5 points and above. All ICP-MS measurements were taken in a clean room (class 10000) and the measurement solutions prepared in a clean bench (class 100).

The internal standard method is effective for correcting equipment fluctuation in long-term measurements. A standard solution was added to the Eagle's and α-medium solutions so that they contained 100 mass ppb of Ti, Al and V concentrations. The medium solution was diluted with 1% nitric acid solution from 2 to 500 times to compare Ti, Al and V concentrations determined by ICP-MS. The result is shown in Fig. 4. Twice dilution may result in damage to the instrument since the medium solution contains a high level of salts. So, the Ti, Al, and V concentrations in the Eagle's and α-medium solutions are approximately measurable when the medium solution is diluted by 5 to 50 times. Ti, Al and V standard solutions were added to the Eagle's medium to obtain various concentrations. These medium solutions were then diluted to 25 times with 1 mass% nitric acid solutions. Figure 5 shows comparisons of Ti, Al and V concentrations measured by ICP-MS. The determination for Ti, Al and V concentrations at roughly more than 1 mass ppb was possible by directly diluting Eagle's and α-medium solutions from 10 to 40 times with 1 mass% nitric acid solutions. However, these concentrations were changed by the existence of hydrochloric and sulfuric acid solutions, and use of the Pyrex glass flask.

![Fig. 4 Effect of dilution for Eagle's medium (a) and α-medium (b) containing 100 mass ppb Ti, Al and V on the metallic concentration measured by ICP-MS using Co as internal standard.](image)

![Fig. 5 Comparison of the metallic concentrations measured with ⁴⁹Ti, ²⁷Al and ⁵¹V using Co as internal standard.](image)

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2.7. RAT TIBIA IMPLANTATION

Six-week-old male Wistar rats which were fed for more than 1 week and weighed 104~124 g were used. Implant specimens 2.0 mm in diameter and 1.5 mm in height for Ti-15%Zr-4%Nb-4%Ta and Ti-6%Al-4%V ELI alloys were cut from the sample alloy by considering the size of tibia. The edges of the column were then cut (C 0.1) and the surface was polished with waterproof emery paper. After pentobarbital sodium solution (nbutal solution) was intraabdominally injected in a dose of 25 mg/kg, the site 10 mm below the knee joint on right and left sides was shaved, sterilized and incised with a scalpel. The bone surface was exposed and isolated to the bone membrane. For the implant cavity, a hole 2 mm in diameter and 2 mm deep was formed perpendicular to the longer axis of the cortical bone with an infusion of sterile physiological saline. For this, round dental burs 1 mm (#3) and 2 mm (#8) in diameter were used in turn using a micromotor for implant surgery rotating at low speed. The Ti-15%Zr-4%Nb-4%Ta and Ti-6%Al-4%V ELI alloys were then implanted into the bone marrow of the left and right sides of the tibia, respectively, and the wound was sutured. Tibias on the right and left sides were extracted from 5 rats for the preparation of decalcified tissue (n=3) and undecalcified tissue (n=2) samples after death by an intraabdominal administration of pentobarbital sodium solution 6, 12, 24 and 48 weeks after implantation.

The procedure for the preparation of decalcified tissue sample is shown in Fig. 6 (a). Bone tissue was fixed with a 10% neutral formalin solution and decalcified with a 10% formic acid formalin solution. After decalcifying, bone tissue was cut with a blade parallel to the longer axis of tibia and so as if to divide the vertical axis of the Ti alloy implant into two. Then, the Ti alloy implant was removed. The bone tissue that was cut into two was dehydrated and defatted with 70-100% alcohol and 100% acetone. After embedding with paraffin wax, embedded specimen were sliced to a thickness of 4 µm using a micro cutting machine. These sliced sections were stained with Hematoxylin Eosin stain (H. E. stain) and Azan Malloy stain (A. M. stain). The structural changes of new bone tissues were observed with an optical microscope. The procedure for the preparation of undecalcified tissue sample is also shown in Fig. 6 (a). Bone tissues were fixed as above. Tissues embedded in resin were cut to a thickness of 100 µm parallel to the long axis of the tibia so as to divide the vertical axis of the Ti alloy implant into two with a diamond blade. The sliced resin block was then polished to a thickness of 40 µm with waterproof emery paper from #600 to #1000, followed by staining with H. E. stain. After H. E. staining, the structural changes of new bone tissues were observed. Furthermore, for the measurement method of thickness for new bone tissue as shown in Fig. 6 (b), the thickness of new bone tissue at 10 sites formed in medullary was measured with decalcified and undecalcified optical micrographs for the central part of the Ti alloy implant. Changes in thickness in new bone tissues were statistically analyzed with Student's t-test.

![Fig. 6 Schematic diagram of the preparation of the microscopic sections (a) and measuring points for bone contact thickness (b).](image_url)
3. RESULTS AND DISCUSSION

3.1. CORROSION RESISTANCE

Figure 7 shows anodic polarization curves measured in 1 mass% lactic acid and Eagle's medium solutions at 310 K. A passivation peak for pure Ti grade 2 and Ti alloys is not observed and the polarization curve immediately enters the passivity zone. The current density in the potential region of 1 V and over increases as the potential increases, and increases rapidly in the potential region of 2 V and over, except for β type Ti-15% Mo-5%Zr-3% Al alloy. Figure 8 shows the change in the width of the frictional area after anodic polarization test in the Eagle's medium solution. The widths of frictional area for the Ti alloys are larger than those of SUS316L stainless steel and the Co-Cr alloy. However, the effect is small when the mean frictional load is 20 N or more. Figure 9 shows comparisons of anodic polarization curves under a static condition and the mean frictional load of 49 N at a frequency of 1 Hz with apatite ceramics in the Eagle's medium solution at 310 K (37 °C). The current density was higher than that of static state and fluctuates by destruction and formation of passive film. In the cases of SUS316L stainless steel and the Co-Cr alloy, fluctuation of the current density is seen only in the passivity zone, but almost no fluctuation is seen in the active and transpassive zones.

As to the Ti alloy, fluctuations of the current density arising from friction are seen from the activity zone to the high potential region, increasing in fluctuation widths of current density (maximum-minimum current densities) and the mean current density (the mean value of maximum and minimum values). In the case of Ti-15%Zr-4%Nb-4%Ta alloy as shown in Fig. 9 (d), the fluctuation of the current density is small up to the high-potential zone. To examine the effect of pH, the anodic polarization test was conducted in a 1% lactic acid solution with a mean frictional load of 20 N. Figure 10 shows the result of the Ti-6%Al-4%V ELI and Ti-15%Zr-4%Nb-4%Ta alloys. There is a tendency for the current density to increase in comparison with the results of the Eagle's medium solution. Figure 11 shows the effect of reciprocal speed on anodic polarization curves of Ti-15%Zr-4%Nb-4%Ta alloy with a mean frictional load of 20 N. The effect of friction is small irrespective of increases in the reciprocal speed. Figure 12 shows changes in the corrosion potential due to friction of 1 Hz. The SUS316L stainless steel and the Co-Cr alloy show a small decrease in corrosion potential in spite of the increased frictional load. On the other hand, the Ti alloys show considerable decreases.

Fig. 7 Comparison of the anodic polarization curves for various implant alloys in deaerated 1 mass% lactic acid (a) and Eagle's medium (b) solutions under the static condition at 310 K.

Fig. 8 Change in the width of frictional area after anodic polarization with apatite ceramics in deaerated Eagle's medium solution at 310 K as a function of mean frictional load.
Fig. 9 Effect of kinetic frictional force of 49 N on the anodic polarization curves with apatite ceramics for various implant alloys in Eagle's medium solution at 310 K. (a) SUS316L stainless steel, (b) Co-Cr alloy, (c) Ti-6%Al-4%V ELI, (d) Ti-15%Zr-4%Nb-4%Ta alloy.

Fig. 10 Effect of kinetic frictional force of 20 N on the anodic polarization curves with apatite ceramics for Ti-6%Al-4%V ELI (a) and Ti-15%Zr-4%Nb-4%Ta (b) alloys in 1% lactic acid solution at 310 K.

Fig. 11 Effect of lateral reciprocal speed on the anodic polarization curves for Ti-15%Zr-4%Nb-4%Ta alloy in Eagle's medium solution at 310 K.
From this result, it is considered that under the frictional environment, the stressing zone turns anodic and its periphery cathodic, and corrosion tends to progress compared to the static environment. In order to compare the effect of friction among the alloys, the effect of friction was examined by dividing the mean value of the current density by a static value of current density at each potential. The results are shown in Fig. 13. The increase in the current density due to friction with the Co-Cr alloy is small compared to the Ti alloys. With respect to the Ti alloys, there is a tendency for the effect of friction to increase in the low potential region; in the high potential region, however, the effect of friction is small. Aluminum ceramic pin instead of apatite ceramic pin also show the same tendency.

![Graph](image1)

**Fig. 12** Change in the corrosion potential during friction with apatite ceramics in deaerated Eagle's medium at 310 K as a function of mean frictional load.

**Fig. 13** Change in the ratio of current density for friction to static conditions as a function of potential for apatite ceramics in Eagle's medium (a) and 1 mass% lactic acid (b) solutions.

### 3.2. MECHANICAL PROPERTIES

The Ti-15%Zr-4%Nb-4%Ta alloy specimens were kept in the 1028 to 1073 K (755 to 800 °C) for 3.6 ks, water cooled, then aged at 673K (400 °C) for 36 ks. Figure 14 shows changes in the 0.2% proof strength (\(\sigma_{0.2}\%PS\)), ultimate tensile strength (\(\sigma_{UTS}\)), total elongation (T.E.) and reduction of area (R.A.) of the new Ti alloy as a function of solution treatment temperature. The 0.2% proof strength, ultimate tensile strength, total elongation and reduction of area decrease with a higher solution treatment temperature. The reduction of area, in particular, decreases sharply with a lower vol% of \(\alpha\) phase as shown in Fig. 14. The Ti-15%Zr-4%Nb-4%Ta alloy was solution-treated at 1048 K (775 °C) for 3.6 ks and aged. Figures 15 (a) and (b) show changes in the 0.2% proof strength, ultimate tensile strength, total elongation and reduction of area as a function of aging temperature and aging time; respectively. Strength and ductility are affected very little by aging temperature and aging time. We assumed the optimum heat treatment conditions for the Ti-15%Zr-4%Nb-4%Ta to be aging at 673K for 29 ks (8 h) after solution treatment at 1048 K for 3.6 ks.

![Graph](image2)

**Fig. 14** Effect of solution-treating temperature for Ti-15%Zr-4%Nb-4%Ta alloy on the mechanical properties at room temperature and volume percentage of \(\alpha\) phase.

Figure 16 shows a comparison of the TEM microstructures for Ti alloys. Ti alloys annealed at 973K for 7.2 ks are mostly lath of \(\alpha^*\) martensite, while the solution-treated Ti-15%Zr-4%Nb-4%Ta alloy consists of the primary \(\alpha\) phase and \(\alpha^*\) martensite. Fine \(\alpha\) phase precipitate is due to aging after solution treating. A good
balance between strength and ductility is derived when the fine α phase is uniformly distributed by solution treatment and aging. Comparisons of the mechanical properties of Ti alloys at room temperature are summarized in Table 2.

![Graphs showing mechanical properties of Ti alloys](image)

**Fig. 15** Effect of aging temperature (a) and aging time (b) for Ti-15%Zr-4%Nb-4%Ta alloy after solution treatment at 1048 K for 3.6 ks on the mechanical properties at room temperature.

**Fig. 16** TEM micrographs for various Ti alloys after annealing at 973 K for 7.2 ks and solution treating plus aging. (a), (b) and (f) annealing, (c), solution treating at 1058 K for 1.8 ks, diffractions in bright field (d) and dark field (e) in (c), (g) and (h) S.T. plus aging.

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<td>80±0</td>
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<tr>
<td>Ti-15Zr-4Nb-4Ta</td>
<td>Annealing</td>
<td>877±7</td>
<td>881±4</td>
<td>27±4</td>
<td>59±1</td>
<td>100±1</td>
</tr>
<tr>
<td>Ti-6Al-7Nb*</td>
<td>Annealing</td>
<td>918±1</td>
<td>1026±3</td>
<td>14±0</td>
<td>51±1</td>
<td>97±1</td>
</tr>
</tbody>
</table>

*Minimum value in ISO Standard
3.3. CORROSION FATIGUE STRENGTH

Figure 17 (a) shows a comparison of the S-N curves obtained from the corrosion fatigue test with the sine wave in the Eagle's medium solution. The fatigue strength at the 10th cycle for β type alloy, which have comparatively high strength at room temperature, was lower than that of α + β type alloy annealed at 973 K. The number of cycles to failure for Ti-15%Zr-4%Nb-4%Ta alloy annealed at 973 K increased as maximum stress was decreased, and it was found that rupture stress at 10^8 cycles coincided at approximately 600 MPa. The fatigue strength of Ti-6%Al-4%V ELI alloy at the 10th cycle is also comparatively high. The fatigue strength of Ti-6%Al-2%Nb-1%Ta alloy at the 10th cycle was approximately 700 MPa. In the fatigue-fractured surface of α + β type alloys, fatigue cracks originated from stress concentration regions such as inclusions in the periphery of the fatigue test specimen. A number of fatigue cracks starting from the inclusion and a cleavage type fracture mode with river pattern were seen on the fracture surface of the β alloy. Comparison of S-N curves obtained from the corrosion fatigue test using a sine wave and human hip joint load profile after solution treatment plus aging is shown in Fig. 17 (b). The fatigue strength is higher than with annealed specimens. Also, the effect of frequency on fatigue strength at 2 Hz and 10 Hz were almost similar, and the fatigue strengths were the same for the sine wave and human hip joint load profile for Ti-15%Zr-4%Nb-4%Ta alloy.

3.4. CYTOCOMPATIBILITY FOR Ti ALLOYS

Figure 18 shows a comparison of Ti alloy plates for the relative growth ratios of L929 and MC3T3-E1 cells. The relative growth ratios of L929 and MC3T3-E1 cells for the Ti-15%Zr-4%Nb-4%Ta alloy are slightly higher than those of Ti-6%Al-4%V alloy (control). The change in the relative growth ratio of L929 cells as a function of wear cycles is shown in Fig. 19 (a) for the wear test with alloy disk against the apatite ceramics pin from 10^7 to 10^8 wear cycles. The relative growth ratio remained at 1 (non-cytotoxicity) for pure Ti grade 2 and Ti-15%Zr-4%Nb-4%Ta alloy. Figure 19 (b) shows the change in the relative growth ratio of MC3T3-E1 cells with α - medium containing worn Eagle's medium prepared for 4x10^7 and 10^8 cycles of wear in Eagle's MEM solution. The relative growth ratio of MC3T3-E1 cells sharply decreased in the case of Ti-6%Al-4%V ELI alloy at both 4x10^7 and 10^8 wear cycles, while the relative growth ratio remained at 1 for pure Ti grade 2 and Ti-15%Zr-4%Nb-4%Ta alloy. Figures 20 (a) and (b) show the changes in the concentrations of Ti, Al and V in Eagle's medium and α - medium solutions as a function of wear cycles and a volume percentage of worn Eagle's medium added to α - medium, respectively.

Figure 20 (a) shows that the concentrations of Ti and Al in the worn Eagle's medium solution were almost the same as the number of wear cycles increased, but the metallic concentration of V ions in the the wear tested
Eagle's medium solution gradually increased as the number of wear cycles increased from $10^4$ to $10^5$ cycles. The metallic concentration of Al in $\alpha$-medium gradually increased, but the V concentration increased sharply. The effect of V concentration on cell viability obtained by the extraction of metallic particles in Eagle's and $\alpha$-medium is summarized in Fig. 21. A good coincidence between Fig. 20 and Fig. 21 for the V ion concentration was observed. The various metallic concentrations for the Ti-15%Zr-4%Nb-4%Ta alloy in Eagle's medium after $10^5$ wear cycles were very low ($\text{Ti} < 0.01$, Zr : 0.004, Nb : 0.001, Ta : 0.0004 and Pd : 0.01 mass ppm). The pH of the Eagle's MEM solution increases as the wear cycles increase due to wear of the alloy disk against the apatite ceramics pin. Based on these results, it is thought that as the number of wear cycle increases, pH increases and so the release of V ions increases in the case of wear of the alloy disk against the apatite ceramics pin. However, as the effect of Al concentration on cell viability depends on surface roughness, surface treatment, strength of the Al oxide film and extracting condition with Al particles, we suggest that further research is needed on the cytotoxicity of Al.

Fig. 19 Change in the relative growth ratio of L929 cells with the number of wear cycles in Eagle's medium solution (a) and the volume percentage of worn Eagle's medium for alloy disk against apatite ceramics in $\alpha$-medium.

Fig. 20 Change in the metallic concentration in Eagle's medium as a function of number of wear cycles (a) and with the volume percentage of worn Eagle's medium for Ti-6%Al-4%V ELI disk against apatite ceramics pin in Eagle's MEM solution at $10^5$ wear cycles in $\alpha$-medium (b).

Fig. 21 Effects of Ti,Zr,Nb,Ta concentration (a) and V concentration (b) on the relative growth ratios of L929 and MC3T3-E1 cells.
3.5. RATIO TIBIA IMPLANTATION FOR TI ALLOYS

Representative undecalcified tissue specimens for Ti-15%Zr-4%Nb-4%Ta and Ti-6%Al-4%V ELI alloys after 7.3 Ms (12 weeks) implantation are shown in Fig. 22. Inflammatory cells and foreign body tissue response were not observed. Decalcified tissue specimens stained with H.E. are shown in Figs. 23 and 24. From these results, it is clear that new bone is formed around the alloy implant in the case of both Ti alloys. It can also be seen that no strange bone formation was observed.

Fig. 22 Optical micrographs of undecalcified sections of new Ti (a) and Ti-6%Al-4%V ELI (b) alloys stained with H. E. stain after 7.3 Ms (12 weeks) implantation.

Fig. 23 Optical micrographs of decalcified sections of Ti-6%Al-4%V ELI alloy stained with H. E. stain after 3.6-29 Ms (6-48 weeks) implantation.
Fig. 24 Optical micrographs of decalcified sections of Ti-15%Zr-4%Nb-4%Ta alloy stained with H. E. stain after 3.6-29 Ms (6-48 weeks) implantation.

In addition, representative decalcified tissue samples at 29 Ms (48 weeks) are shown in Fig. 25. Since the A.M. stain is stained blue, new bone tissue with mature calcification formed at 29 Ms after implantation.

Fig. 25 Optical micrographs of decalcified sections of new Ti (a) and Ti-6%Al-4%V ELI (b) alloys stained with A. M. stain after 29 Ms (48 weeks) implantation.
A comparison of the thickness of new bone tissues is shown in Fig. 26. In both alloys, the thickness of new bone tissue tended to increase from 3.6 Ms (6 weeks) to 14.5 Ms (24 weeks) and was almost unchanged after 14.5 Ms. The results of the statistical significant difference test showed no significant difference in the thickness of new bone tissues with p<0.05 among 3.6, 7.3, 14.5 and 29 Ms (6, 12, 24, 48 weeks) for both alloys.

4. CONCLUSION

(1) The current density in the high potential region is very low for the new Ti-15%Zr-4%Nb-4%Ta alloy, thus which shows considerably high corrosion resistance. The current density becomes higher during friction than during static conditions. The fluctuation width was observed in the passivity zone for Co-Cr alloy. However, in the case of Ti alloys, the fluctuation width was observed in both activity and passivity zones. Among the Ti alloys, during friction against apatite ceramics, the current density was low for the new Ti alloy in the high potential region, and the fluctuation width of the current density was narrow compared to other Ti alloys. The effect of the lateral speed was also negligible for the new Ti alloy compared to other Ti alloys. For corrosion resistance during wear conditions, change of the materials used as disk and pin, frictional load, potential zone and the pH of the solution, the new Ti alloy showed excellent wear corrosion properties compared to other Ti alloys.

(2) As the solution treatment temperature increased, the ductility of the new Ti alloy decreased. After solution treatment, the mechanical strength did not change much as the aging time and the aging temperature were increased. The addition of O and N to the new Ti alloys and heat treatment substantially increased the ultimate tensile strength to 1000 MPa, and total elongation was more than 10 %. The fatigue strength of $\beta$ type Ti-15%Mo-5%Zr-3%Al alloy at 10$^7$ cycles was lower than that of $\alpha + \beta$ type alloys. The fatigue strengths of Ti-15%Zr-4%Nb and Ti-6%Al-2%Nb-1%Ta alloys annealed at 973 K for 7.2 ks at 10$^7$ cycles were about 600 and 700 MPa, respectively. The fatigue strength of solution-treated and aged new Ti alloy at 10$^7$ cycles was 950 MPa. The effect of at 2 Hz and 10 Hz frequencies on the fatigue strength was almost the same. Further, the fatigue strength was almost the same for the sintered and bone hip joint load profile.

(3) The relative growth ratio of L929 and MC3T3-E1 cells for the new Ti alloys was slightly higher than that of Ti-6%Al-4%V ELI alloy plate. In the case of wear test in Eagle's MEM solution, the relative growth ratio remained at 1 for pure Ti grade 2 and Ti-15%Zr-4%Nb-4%Ta alloy. On the contrary, the relative growth ratio of L929 cells steeply decreased from 3x10$^4$ number of wear cycles and almost became equal to 0 at 10$^7$ wear cycles for the Ti-6%Al-4%V ELI alloy disk against the apatite ceramics pin. The pH of the Eagle's MEM solution increases as the wear cycles increase for the wear of the alloy disk against the apatite ceramics pin. As the number of wear cycles increases, pH increases and so the release of V ions increases.

(4) The new Ti alloy implant has a similar new bone tissue formation rate to Ti-6%Al-4%V ELI alloy when implanted in rat tibia. The mean thickness of the newly formed bone around the new Ti and Ti-6%Al-4%V ELI alloy implants continuously increased up to 14.5 Ms (24 weeks), and change in the mean thickness thereafter, until 29 Ms (48 weeks) were very small.

REFERENCES


