Development of Low-Cost Manufacturing Process and Effects of Adding Small Amounts of Ta, O, and N on the Physical and Mechanical Properties of Highly Biocompatible Ti Alloys

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Zirconium (Zr), niobium (Nb), and tantalum (Ta) are important alloying elements of titanium (Ti) alloys for attaining superior biocompatibility. To develop low-cost manufacturing processes, we examined the effects of melting methods, Ta addition using a Ti-Ta mother alloy, and the addition of small amounts of oxygen (O) and nitrogen (N) on the continuous-hot-rolling, physical, and mechanical properties of biocompatible Ti alloys as well as their microstructure. Seven Ti-Zr-based alloys containing Zr, Nb, and Ta were subjected to vacuum arc melting, induction skull melting (ISM), and levitation induction melting. The use of Ti-30 mass% Ta mother alloy (hereafter, % represents mass%) was effective for melting the biocompatible Ti alloys. ISM was found to be a promising advanced method for biocompatible Ti alloys. A fine granular α -phase structure (approximately 1 μm), high strength, and excellent ductility were obtained in the continuous hot-rolling process. The Ti-Zr-based alloys were strengthened by adding small amounts of N and O. The observed mechanical properties were superior to those of artificial hip stems made of Ti-6Al-4V alloy. The Ti-Zr-based alloys started to melt at approximately 1620°C. The β -transus temperature (T_β) was in the range from 805 to 850°C. The microstructure was predicted using the temperature difference (ΔT) from T_β . The specific heat constant (C_p) and thermal conductivity (W) increased with increasing temperature up to T_β then decreased above T_β . The machinability of Ti-Zr-based alloy was similar to that of Ti-6Al-4V alloy. [doi:10.2320/matertrans.ME201917]

(Received February 6, 2019; Accepted April 18, 2019; Published June 21, 2019)

Keywords: biomedical titanium alloy, melting technology, mother alloy, continuous hot rolling, microstructure, tensile property, fatigue property, physical property

1. Introduction

Orthopedic implants require biomechanical compatibility as well as biological safety. Therefore, many types of metallic orthopedic device are used worldwide. The development of orthopedic implants optimized for each patient's needs or skeletal structure (custom-made orthopedic implants) has been made possible owing to advances in fabrication techniques.¹⁾ Along with the rapid progress of three-dimensional (3D) layer manufacturing technologies in the medical field, the development of orthopedic implants customized to the skeletal structure and symptoms of each patient is now possible.

To obtain regulatory approval for orthopedic devices produced by 3D layer manufacturing in Japan, evaluation of the fatigue properties of the base metal and the durability of the orthopedic devices is desired.²⁾ Reentry, Ids Co., Ltd. (Suita, Osaka, Japan), a dental material supplier, acquired Pharmaceutical Affairs Approval for the use of SP2 cobalt (Co)-chromium (Cr)-molybdenum (Mo) alloy (Co-25%Cr-5%Mo-5%W) powder as a dental material for 3D layer manufacturing from the Japanese Ministry of Health, Labour and Welfare on April 27, 2018 (Approval No.: 23000BZX00121000).³⁾ Co-25Cr-5Mo-5W alloy (Hereafter, alloy compositions are expressed in mass%) satisfies Japanese Industrial Standard (JIS) T 6121 and JIS T 6115 for dental materials.^{4,5)}

As the metallic materials for orthopedics, stainless steels,⁶⁾ Co-Cr-Mo alloys,⁷⁾ commercially pure titanium (C.P. Ti),⁸⁾ and Ti alloys^{9,10)} have been used and standardized in JIS. Implantable C.P. Ti is classified into five grades in JIS T 7401-1,⁸⁾ namely, extra low interstitial (ELI) grade ($O \leq$

0.1% , $Fe \leq 0.1\%$), grade 1 ($O \leq 0.18\%$, $Fe \leq 0.2\%$), grade 2 ($O \leq 0.25\%$, $Fe \leq 0.3\%$), grade 3 ($O \leq 0.35\%$, $Fe \leq 0.3\%$), and grade 4 ($O \leq 0.4\%$, $Fe \leq 0.5\%$). As the grade of C.P. Ti increases, the amount of trace elements such as O and iron (Fe) increases.⁸⁾ Among Ti alloys, Ti-6Al-4V alloy⁹⁾ is widely used in the medical field. Ti-6Al-4V alloy is an α (alpha)- β (beta)-type Ti alloy having a mixed structure comprising the α -phase (hexagonal-close-packed structure, hcp) and β -phase (body-centered-cubic structure, bcc). The tensile and fatigue strengths of C.P. Ti can be increased by increasing the amounts of trace elements such as O and Fe, whereas the fatigue strength of C.P. Ti grade 4 (C.P. Ti G 4) can be made similar to that of Ti-6Al-4V alloy by 20% cold working.¹¹⁾ Adding a small amount of other metal elements improves the quality of Ti alloys. Ti alloys have higher corrosion resistance and biocompatibility than C.P. Ti G 4 owing to the addition of Mo, Zr, Nb, Ta, and so forth.¹²⁾ Ti-15Zr-4Nb-(1 to 4)Ta alloy, designated as a Ti-Zr-based (α - β -type) alloy, has been developed in Japan as a highly biocompatible alloy for long-term biomedical applications¹³⁾ and is standardized in JIS T 7401-4.¹⁰⁾

The main Ti-melting techniques include vacuum arc remelting (VAR), electron beam melting (EBM), induction skull melting (ISM), and levitation induction melting (LIM). Advances in VAR, ISM, and LIM techniques in the medical field have made it possible to melt biocompatible Ti alloys containing refractory Nb and Ta metals. Ta, having high specific gravity and a high melting point, easily segregates at the bottom of a Ti alloy ingot. Therefore, for Ti alloys to which Ta is added, a melting method that minimizes this segregation is required. Although a VAR melting technique using fine Ta powder with a particle size of 2.5 μm or smaller has been developed, the manufacturing cost is higher than that of conventional Ti-6Al-4V alloy.¹¹⁾ As another method

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of minimizing the segregation of Ta, it is important to develop a Ti–Ta mother alloy and a melting technique using the mother alloy. There have been no reports on the manufacture of biomedical Ti alloys using a Ti–Ta mother alloy.

When 30%Ta is added to Ti, the melting point of Ti–Ta alloy decreases from 3000 to 1725°C,¹⁴⁾ which is close to the melting point of Ti (1670°C). Thus, among the Ti–Zr-based alloys containing Ta, Ti–30Ta mother alloy is useful for uniformly dissolving Ta in manufacturing. Also, to develop a low-cost manufacturing process for Ti–Zr-based alloys, we focused on the process of forging ingots and billets, and the continuous hot-rolling process as well as the melting method. In all these processes, it is important to improve the material yield and reduce the number of processes. In the continuous hot-rolling process used in this study, round bars can be hot-rolled from billets in 4–8 minutes. Moreover, the yield of the material can be improved by hot-forging various implants from rods with compared to manufacturing implants by cutting. Therefore, it is important to examine the micro-structural changes and mechanical properties of Ti–Zr-based alloys subjected to the continuous hot-rolling process.

In this study, to develop a lower-cost manufacturing process for biocompatible Ti alloys, we examined the effects of melting methods and Ta addition using Ti–30Ta mother alloy on the continuous-hot-rolling, physical, and mechanical properties of Ti–Zr-based alloys as well as their micro-structure. In addition, the effects of adding of small amounts of O and N on these properties were examined. Moreover, the properties of these alloys and their machinability with cutting tools were compared with those of Ti–6Al–4V alloy.

2. Materials and Methods

2.1 Alloy specimens

2.1.1 Melting methods for Ti–Zr-based alloys

Seven different Ti–15Zr–4Nb–(0–4) Ta (Ti–Zr based) alloys (JIS T 7401-4) for medical implants were melted by the following four methods: (1) VAR using Nb and Ta powders, (2) VAR using Ti–Ta mother alloy, (3) ISM, and (4) LIM. These seven Ti–Zr-based alloys are α - β -type Ti alloys.

In VAR using Nb and Ta powders, Ti–15Zr–4Nb–4Ta–0.3O–0.1N (Ti-15-4-4-0.3-0.1N, hereafter referred to as Ti-Zr A), Ti–15Zr–4Nb–1Ta–0.3O–0.1N (Ti-15-4-1-0.3O-0.1N, hereafter referred to as Ti-Zr B), and Ta-free Ti–15Zr–4Nb–0.3O–0.1N (Ti-15-4-0.3O-0.1N, hereafter referred to as Ti-Zr C) alloys were melted. Vacuum arc remelting (VAR) using Nb and Ta powders is shown as a representative example. Sponge Ti (aircraft grade, mild sponge M100A, purity $\geq 99.6\%$) and Zr (nuclear grade, purity $\geq 99.5\%$), Ti powder (particle diameter $\leq 150\ \mu\text{m}$, purity $\geq 99.7\%$), Nb powder (particle diameter $\leq 44\ \mu\text{m}$, purity $\geq 99.7\%$), Ta powder (particle diameter $\leq 2.5\ \mu\text{m}$, purity $\geq 99.6\%$), NbN powder (N $\geq 11\%$, particle diameter: 4–7 μm , purity $\geq 99\%$), and TiO₂ powder (particle diameter: 0.2 μm , purity $\geq 98\%$) were used for VAR. The amounts of N and O were adjusted on the basis of the amounts of NbN and TiO₂ powders, respectively.

The sponges and powders formulated with the target alloy compositions were compressed into 300-mm-diameter and

25 kg briquettes with a 4000 ton press. Mixed powders with Ta:Ti = 2:3 and Nb:Ti = 1:1 (mass ratios) were placed at the center of each briquette. Fifty briquettes were plasma-welded in an Ar atmosphere by horizontal rotation stacking (diameter, 300 mm; length, 3.5 m). Each welded briquette (Ti electrode) was vacuum-arc-melted in a 1000 kg melting furnace. The conditions for the primary melting in vacuum were as follows. Ti–Zr-based alloy was deposited on a starting (stub) material (C.P. Ti grade 2). The initial melting current was set to 6 kA. The melting rate was set to 8–10 kg/min. The constant and final melting currents were 12 kA $\pm$ 20% and 9 kA, respectively. To homogenize of the primary ingot, it was remelted. The secondary electrode (primary ingot) subjected to remelting was 400 mm in diameter and 1.6 m in length. The remelting conditions in vacuum were as follows. The constant melting current and melting rate were 17 kA $\pm$ 20% and 13–18 kg/min, respectively. The upper and lower ends of the remelted ingot (diameter, 480 mm; length, 1.1 m; weight, 1000 kg) were cut, and the oxide scale and scratches on the ingot surface were ground with a grinder. The absence of scratches on the surface of the polished ingot was confirmed by a color check. Moreover, the surface of the polished ingot was inspected for internal defects by supersonic flaw detection. For Ti–Zr A, Ti–Zr B, and Ti–Zr C, the same raw materials and melting equipment were used.

In VAR using the Ti–Ta mother alloy, Ti–30Ta mother alloy was used to uniformly dissolve Ta. Ti–15Zr–4Nb–1Ta–0.3O (Ti-15-4-1-0.3O, hereafter referred to as Ti-Zr D) alloy was melted. To manufacture the Ti–Ta mother alloy, sponge Ti (aircraft grade, purity $\geq 99.9\%$) was press-molded in a mold (width, 100 mm; height, 50 mm; length, 380 mm). Small Ta plates (purity $\geq 99.9\%$) were lined up on the press-molded sponge Ti. More pressed sponge Ti was placed on the Ta plates and further press molded. That is, the Ta plates were placed between the upper and lower pressed sponge Ti. The press-molded sponge Ti (Ti electrode consisting of two pieces, each of width 100 mm, height 105 mm, and length 380 mm) was triple-melted by side feed melting using an electron beam (EB) furnace (power, 70 kW). For homogenization, the Ti–30Ta alloy ingot (diameter, 120 mm; length, 255 mm) was remelted in the EB furnace. Then, the Ti–30Ta mother alloy (21 kg) was chipped for VAR. The Ta, Fe, Cr, Ni, O, and N concentrations of the chipped Ti–30Ta alloy were 30.1, 0.012, 0.002, 0.014, 0.034, and $<0.003\%$, respectively.

To manufacture a Ti–Zr D electrode, the Ti–30Ta mother alloy was molded into briquettes blended with the alloy composition using sponge Ti (purity $\geq 99.9\%$), sponge Zr (purity $\geq 99.9\%$), and Ti–53Nb alloy chips (Nb, 53.0%; Cr $< 0.05\%$; Ni $< 0.025\%$; O:0.52%; N, 0.042%). Then, they were vacuum-arc-melted twice in vacuum. The melting currents of the primary and secondary melting in vacuum were 15 and 20 kA, respectively. The weight of the remelted Ti–Zr D ingot (diameter, 410 mm; length, 330 mm) was approximately 200 kg. For comparison, a Ti–15Zr–4Nb–0.3O alloy ingot (about 200 kg, Ti-15-4-0.3O, hereafter referred to as Ti-Zr E) without Ti–Ta mother alloy added was also vacuum-arc-melted with the same raw materials and melting equipment with as those for Ti-Zr D.

For comparison with VAR, the Ti-15Zr-4Nb-1Ta-0.3O alloys were melted by ISM and LIM. In the ISM process, small corner blocks of C.P. Ti (purity $\geq 99.3\%$), small corner blocks of C.P. Ti oxidized at 1000°C for 2 h in air, Ti chips (purity $\geq 99.3\%$), sponge Zr (nuclear grade; size, 0.8–35 mm; purity $\geq 99.5\%$), Nb powder (particle diameter $\leq 74\ \mu\text{m}$, purity $\geq 99.9\%$), and Ta powder (particle diameter $\leq 150\ \mu\text{m}$, purity $\geq 99.9\%$) were used. Ti-Nb-Ta briquettes (diameter, 50 mm; weight, 300 g) were each compressed with 94 g of Ti chips, 150 g of Nb powder, and 56 g of Ta powder using a 40 ton press. The Nb and Ta powders were placed at the center of the briquettes with the Ti chips so that the Nb and Ta powders did not fall off from the briquettes. Sixty Ti-Nb-Ta briquettes were compressed. Fifty Zr briquettes (600 g/briquette) were also compressed with sponge Zr using a 40 ton press. The C.P. Ti block, oxidized C.P. Ti block, Zr briquettes, and Ti-Nb-Ta briquettes were placed in a water-cooled Cu crucible in accordance with the target alloy composition. Then, the mixture was high-frequency-melted (skull-melted) in vacuum. The Ti-Zr-based alloy ingot was lowered and repeatedly melted while after each addition of briquette. A Ti-15Zr-4Nb-1Ta-0.3O (Ti-15-4-1-0.3O, hereafter referred to as Ti-Zr F) alloy ingot with a diameter of 196 mm and a weight of about 150 kg was melted. In this ISM, the Ti-Zr F alloy was not remelted.

Finally, a Ti-15Zr-4Nb-1Ta-0.3%O alloy ingot (500 kg, Ti-Zr G) was melted in a levitation induction furnace. In LIM, sponge Ti (purity $\geq 99.3\%$) and Zr (purity $\geq 99.5\%$), Nb (purity $\geq 99.9\%$), and Ta (purity $\geq 99.9\%$) plates were used as raw materials. The LIM ingot was vacuum-arc-melted to rehomogenize it.

2.1.2 Forging of Ti-Zr-based alloys

The seven Ti-Zr-based alloy ingots were homogenized at approximately 1200°C for more than 6 h and β -forged at the same temperature to form a 300-mm-square billet. After reheating the billet to 1200°C, it was β -forged into a 230-mm-square billet. Then, it was β -forged again, while controlling the grain growth of the β -phase, at 1000 to 1100°C to make the β -phase as small as possible relative to the size of the billet and the forging ratio. The forging ratio (cross section before forging/cross section after forging) in β -forging was more than 3. Afterwards, the billet was α - β -forged to obtain the α - and β -structures by decoupling the fine β -phase. Billets (100 mm square) were manufactured by α - β -forging at 800–850°C under atmospheric conditions using a 1200 ton forging machine. To prevent the edge of the billet from cracking caused by heat loss, the forging time was minimized by adjusting the forging reduction and forging width/speed. The reheating of the ingot and forging were repeated once or twice to optimize the ingot size and microstructure. Between the β - and α - β -forgings, the billet surface was ground with a grinder to prevent cracking caused by the oxide scale formed on the ingot surface.

Figure 1(a) shows the Ti-Zr A alloy ingot and α - β -forged billet (100 mm square). The other Ti-Zr-based alloys were similarly manufactured as α - β -forged billets. Table 1 shows the chemical compositions of the seven Ti-Zr-based alloys used in this study. Note that no Ta was added to the Ti-Zr C and Ti-Zr F alloys.

Fig. 1 (a) Ti-Zr A alloy ingot and 100-mm-square billet after β - and α - β -forgings. (b) Schematic illustration of continuous hot rolling of Ti-Zr-based alloy to obtain rod specimens.

Table 1 Chemical compositions (mass%) and T_β values of the seven Ti-Zr based alloys C. P. Ti, and Ti-6Al-4V alloy used.

Alloy	Zr	Nb	Ta	Pd	Fe	O	N	H	C	Ti	$T_\beta / ^\circ\text{C}$
Ti-15-4-4-0.3O -0.1N (Ti-Zr A)	16.55	4.0	3.9	<0.01	0.04	0.28	0.09	0.0012	0.007	Bal.	835
Ti-15-4-1-0.3O -0.1N (Ti-Zr B)	17.24	3.97	1.67	0.02	0.036	0.29	0.096	0.0027	0.011	Bal.	850
Ti-15-4-0.3O -0.1N (Ti-Zr C)	16.10	3.90	0.17	<0.01	0.026	0.254	0.080	0.0010	0.010	Bal.	850
Ti-15-4-1-0.3O (Ti-Zr D)	15.07	3.92	1.05	0.003	0.03	0.30	0.003	0.003	0.002	Bal.	823
Ti-15-4-0.3O (Ti-Zr E)	17.1	4.2	-	<0.01	0.026	0.28	<0.01	<0.001	<0.01	Bal.	805
Ti-15-4-1-0.3O (Ti-Zr F)	16.36	3.27	0.94	-	0.09	0.26	0.005	0.008	0.015	Bal.	-
Ti-15-4-1-0.3O (Ti-Zr G)	16.6	4.0	1.5	<0.02	0.04	0.33	<0.01	<0.001	<0.01	Bal.	810

	Al	V	Fe	O	N	H	C
C.P. Ti Grade 2	-	-	0.043	0.108	0.004	0.0049	0.002
C.P. Ti Grade 3	-	-	0.12	0.18	0.004	0.0034	0.009
C.P. Ti Grade 4	-	-	0.197	0.275	0.003	0.0069	0.011
Ti-6Al-4V	6.4	4.4	0.10	0.07	0.02	0.0027	0.025

2.1.3 Hot-rolling test of fabricated rods

A continuous hot-rolling test was conducted with 100-mm-square $\times$ 1-m-long Ti-Zr-based alloy billets. Figure 1(b) shows a schematic illustration of the continuous hot-rolling process for the rod billets. After maintaining them at T_β -50°C for 2 h, the billets were hot-rolled continuously in the α - β temperature region (below T_β) at a low rolling speed to prevent an increase in the internal temperature of the rolling rod. Here, T_β represents the β -transus temperature.

In the rough rolling, the rolling rolls were reciprocated to reduce the rhombus-shaped rod after 90° rotation. By reciprocating hot rolling 8–10 times while rotating by 90° after each hot rolling, we gradually reduced the rhombus-shaped rod. In the intermediate rolling, rhombus-shaped rods were changed to angular rods. The cross section of the rods was reduced by repeatedly forming plate (rectangle) rods from the angular rods. In the finish rolling, the plate rods were hot-rolled to form oval (elliptical) rods. Finally, the oval rods were hot-rolled to form circular rods by performing 2 to

4 passes. The diameter of the rods after continuous hot rolling was 52, 37, 32, 31, 27, 24, 18, 17, 12, 11, or 10 mm. To remove a bend formed during hot-rolling, the hot-rolled rods were corrected at 400°C. After correcting, all the hot-rolled Ti rods were annealed at 700°C for 2 h. Then, the oxide film on the hot-rolled Ti rods after annealing was removed by peeling. Since there were a large number of billets, hot-rolling tests for the systematic investigation of the effects of the diameter of the hot-rolled rods on the microstructure, and the mechanical and physical properties were conducted using a large number of melted Ti-Zr A and Ti-Zr B ingots. The diameters of the hot-rolled for Ti-Zr C, Ti-Zr D, Ti-Zr E, and Ti-Zr G rods were 27 and 24 mm and those of the hot-rolled Ti-Zr F rods were 27 and 18 mm.

To investigate the effects of hot rolling on the tensile properties and fatigue strength, the microstructure of each hot-rolled Ti-Zr-based alloy was analyzed by optical microscopy, scanning electron microscopy (SEM), and transmission electron microscopy (TEM, Hitachi H-800; acceleration voltage, 200 kV). TEM observations were performed using disc-shaped specimens of 3 mm diameter, which were prepared by electrolytic polishing with 94% methanol+6% perchloric acid solution. The volume fraction, grain size, and aspect ratio of the α -phase after hot rolling were measured by image analysis using three traced SEM images and their average values were calculated.

2.2 Evaluation of physical properties

To investigate the effect of adding small amounts of Ta, O, and N on the physical properties of Ti-Zr-based alloys, the melting points of four typical Ti-Zr-based alloys (Ti-Zr A, Ti-Zr B, Ti-Zr E, and Ti-Zr G) were measured by differential thermal analysis (DTA). C.P. Ti G 2, C.P. Ti G 4, and Ti-6Al-4V (hereafter referred to as Ti-6-4) alloy were used for comparison with these typical alloys whose chemical compositions are shown in Table 1. Test specimens of 3 mm diameter and 1.5 mm height were cut from the Ti-Zr-based alloys and the Ti materials used for comparison. Heat flows in DTA were measured at a heating rate of 10°C/min in Ar at a flow rate of 200 mL/min.

The density (ρ), specific heat constant (C_p) at a constant pressure, thermal conductivity (W), and average linear expansion coefficient (L) were measured using the Ti-Zr-based and Ti-6-4 alloys and Co-28Cr-6Mo alloy which Ti-free material for comparison. Details of the microstructure and mechanical properties of this alloy are given in the literature.¹⁵⁾ ρ , C_p , and L were measured in accordance with JIS Z 8807,¹⁶⁾ JIS R 1611,¹⁷⁾ and JIS Z 2285,¹⁸⁾ respectively. ρ was measured by weighing in a liquid in accordance with JIS Z 8807. C_p was measured using a test specimen of 5 mm diameter and 1 mm height by differential scanning calorimetry (DSC) at room temperature (20°C) and from 100 to 1000°C at intervals of 100°C in Ar at a flow rate of 200 mL/min. W was calculated as $C_p \times$ thermal diffusivity (m^2/s) $\times \rho$ at room temperature in accordance with JIS R 1611. Thermal diffusivity was measured using test specimens of 10 mm diameter and 1 mm height by the laser flash method in accordance with JIS R 1611. L was measured using test specimens of 3 mm diameter and 15 mm length at a heating rate of 5°C/min in Ar at a flow rate of 100 mL/min and

calculated from the slope at each temperature in the range from 30 to 1250°C.

The Vickers hardness (Hv) of the Ti-Zr A, Ti-Zr B, Ti-6-4, and Co-28Cr-6Mo alloys, C.P. Ti G 4, and high-N stainless steel was measured. The high-N stainless steel (Fe-22Cr-2Mo-10Ni-0.3N-3Mn-0.5Nb) was used to compare the workability at high temperatures, and details of its microstructure and mechanical properties are given in the literature.¹⁹⁾ Hv was measured at room temperature (23°C) and from 100 to 1000°C at intervals of 100°C. It was measured at a load of 500 g up to 700°C and a load of 100 g at temperatures of 800°C and above. The holding time at each temperature was 5 min. Hv at room temperature was measured at a load of 1 kg.

2.3 Measurement of β -transus temperature

The test specimens subjected to heat treatment were prepared from α - β -forged Ti-Zr-based alloy billets. The test specimens were heat-treated at 850, 845, 840, 835, 830, 825, 820, 815, 810, 805, 800, 795, 790, 780, 770, 760, 750, 740, 730, 720, 700, 660, 650, 600, and 500°C for 1 h followed by water quenching. For comparison, some Ti-Zr-based alloys were furnace-cooled. The heat-treated specimens were embedded in resin and polished to a mirrorlike finish with 200 to 4200 grit waterproof emery paper and OP-S suspension. Then, each sample was etched with nitric acid solution containing 10 vol% H_2O_2 and 3 vol% hydrogen fluoride for microstructural observation.

The microstructures of the Ti-Zr-based alloys were analyzed by optical microscopy and SEM to investigate the changes in the α (hcp crystal)- and β (bcc crystal)-matrix structures. Three SEM images were taken from each Ti-Zr-based alloy after etching for image analysis. The SEM images of the heat-treated Ti-Zr-based alloys were analyzed by transparency tracing, and all the phases except the α -phase were blackened out for image analysis. The volume fractions of the α - and β -phases were measured by image analysis using the three traced SEM images. The average volume fractions of the α - and β -phases were then calculated.

2.4 Mechanical tests

2.4.1 Room-temperature tensile tests

To estimate the mechanical properties of the seven Ti-Zr-based and Ti-6-4 alloys, tensile tests were conducted at room temperature. Figure 2 shows the dimensions of each mechanical test specimen used for room-temperature tensile and fatigue tests. Figure 2(a) shows the uniform rod specimen used for the tensile test. Three test specimens were cut from the center of each annealed Ti-Zr-based alloy rod with their longitudinal direction (L-direction) parallel to the rolling direction and from a 30 mm Ti-6-4 alloy rod annealed at 700°C for 2 h. Tensile test specimens of 5 mm diameter and 25 mm gauge length (GL) were pulled at a crosshead speed of 0.5% of the GL/min until the proof stress reached 0.2%. The crosshead speed was then changed and maintained at 3 mm/min until the specimen fractured. The 0.2% proof stress ($\sigma_{0.2\%PS}$), ultimate tensile strength (σ_{UTS}), total elongation (T.E.), and reduction in area (R.A.) were measured. The mean and standard deviation were calculated from the results of the three specimens.

Fig. 2 Dimensions of specimens used for room-temperature tensile and fatigue tests: (a) tensile test; (b) hourglass-shaped-rod fatigue test; (c) miniature tensile test; (d) miniature hourglass-shaped-rod fatigue test.

2.4.2 Fatigue tests

To investigate the effect of hot rolling on fatigue strength, fatigue tests were conducted in accordance with JIS T 0309.²⁰⁾ Figure 2(b) shows the hourglass-shaped rod specimen used for fatigue tests cut from each Ti–Zr-based alloy rod annealed at 700°C for 2 h after continuous hot rolling and from a 30 mm Ti–6–4 alloy rod annealed at 700°C for 2 h. The fatigue test specimens were machined with their longitudinal direction parallel to the hot-rolling direction. To remove the inner strain generated on the surfaces of the specimens during the manufacturing process, the specimen surfaces were fully ground using 600 grit waterproof emery paper in the direction parallel to the test specimen.

The fatigue tests were carried out using an electrohydraulic servo testing machine with a sine wave at a stress ratio R (minimum cyclic stress ($\sigma_{\min}$)/(maximum cyclic stress ($\sigma_{\max}$))) of 0.1 and a frequency of 10 Hz in air. To obtain profiles of the relationship between $\sigma_{\max}$ and the number of cycles to failure N (S–N curves), the specimens were cycled at various constant maximum cyclic loads up to $N = 10^7$ cycles, at which the specimens remained unbroken. The fatigue strengths at 10^7 cycles (fatigue limit, σ_{FS}) were measured from S–N curves.

2.4.3 Comparative tests with implant devices used in clinical settings

The tensile and fatigue properties of artificial hip joint stems made of Ti–6–4 alloy, which are widely used in clinical setting, were also investigated for comparison with those of the present Ti–Zr-based alloys in this study. The cementless total hip stems used were a Zimmer VerSysHA/TCP Fiber Metal MidCoat colorless stem (65-7645-012-00, stem Z),

Fig. 3 Method of evaluating machinability using cutting tool. (a) Method of evaluating cutting resistance during steady flank wear of cutting tool. (b) Method of evaluating flank wear of cutting tool tip and definitions of corner wear (VB_C), flank wear (VB), and boundary wear (VB_N).

a DePuy S-ROM stem (900533210, stem D), a Smith & Nephew stem plus a femoral component (7130-5412, stem N), and a Stryker Osteonics Super Secure-Fit HA stem (J6054-0812; Ti–6–4, stem S). Miniature tensile uniform rod specimens (gauge length, 15 mm; diameter, 3 mm) and fatigue specimens (hourglass-shaped rod specimens: minimum diameter, 3 mm) were cut from each cementless stem, as shown Figs. 2(c) and (d), respectively. Tensile tests were conducted at a crosshead speed of 0.5% of the GL/min until the proof stress reached 0.2%. The crosshead speed was then changed and maintained at 3 mm/min until the specimen fractured. The fatigue tests with miniature fatigue test specimens were conducted under the same conditions as those in 2.4.2.

2.5 Machinability evaluation tests

The machinability of Ti–Zr A and Ti–6–4 alloys was estimated from the cutting resistance and the amount of wear of a cutting tool, as shown in Fig. 3. Cutting tests were conducted using specimens of 50 and 30 mm diameters and a cutting tool (tip: NTN-ZM3DCGT11T302RS, holder: NTN SDJCR1616X11N) in water-soluble cutting oil at a cutting speed of 80 m/min, a tool feed rate of 0.2 mm/rev, and a cutting depth of 0.5 mm. The main partial cutting force (F_t), tool feed force (F_m), and normal (thrust) force (F_s) during the flank wear of the tool tip were measured. Their resultant force (F_r) was defined as the cutting resistance. The changes in the corner wear (VB_C), flank wear (VB), and boundary wear (VB_N) during the flank wear of the cutting tool were measured as a function of cutting time. Ti–Zr A, having high Ta, N, and O contents, was used to evaluate machinability. To ensure a sufficient amount of cutting, we selected rods with diameters of 50 and 30 mm.

3. Results and Discussion

3.1 Physical properties of Ti–Zr-based alloys

Figure 4 shows the peaks of C.P. Ti G 2, C.P. Ti G 4, the three typical Ti–Zr-based alloys and Ti–6–4 alloy measured by DTA. The Ti–Zr-based alloys started to melt at approximately

Fig. 4 Melting points of C.P. Ti G 2, C.P. Ti G 4, Ti-6Al-4V, and three Ti-Zr-based alloys measured by DTA.

Fig. 5 Changes in (a) specific heat constant (C_p), (b) thermal conductivity (W), and (c) average linear expansion coefficient (L) of Co-28Cr-6Mo, Ti-Zr-based, and Ti-6Al-4V alloys as a function of heat treatment temperature.

1620°C, which was lower than the temperatures for C.P. Ti G 2, C.P. Ti G 4, and Ti-6-4 alloy. The liquidus (melting starting) temperatures of C.P. Ti G 2, C.P. Ti G 4, and the Ti-6-4, Ti-Zr A, Ti-Zr B, Ti-Zr E, and Ti-Zr G alloys were 1663 ± 1 , 1665 ± 3 , 1653 ± 1 , 1626 ± 1 , 1621 ± 5 , 1620 ± 2 , and 1627 ± 2 , respectively. The liquidus temperatures of C.P. Ti G 2, C.P. Ti G 4, and Ti-6Al-4V alloy obtained by DTA were close to the liquidus temperatures (1665 ± 5 , 1660 ± 10 , and $1655 \pm 15^\circ\text{C}$) of C.P. Ti G 2, C.P. Ti G 4, and Ti-6Al-4V alloy reported in the literature,²¹⁾ respectively.

Figures 5(a), (b), and (c) show the changes in the specific heat constant (C_p), thermal conductivity (W), and average linear expansion coefficient (L) as a function of temperature, respectively. For comparison, these changes for Co-28Cr-

Fig. 6 Temperature dependence of Vickers hardness (Hv) of high-N stainless, Co-28Cr-6Mo, C.P. Ti grade 4, Ti-Zr A, Ti-Zr B, and Ti-6Al-4V alloys.

6Mo alloy are also shown in Fig. 5. The error bars represent standard deviations. To examine the effects of adding small amounts of Ta, O, and N on these properties, we selected the four Ti-Zr-based alloys. C_p and W increased with increasing temperature up to T_β and then decreased above T_β . The change in L with increasing temperature for the Ti-Zr-based alloys, except at approximately T_β , was smaller than that for the Co-28Cr-6Mo alloy. The effect of adding a small amount of Ta on these properties was small.

Figure 6 shows the temperature dependence of Hv. Hv of C.P. Ti G 4 and the Ti-Zr A, Ti-Zr-B, and Ti-6-4 alloys tended to be lower than that of the high-N stainless steel and Co-28Cr-6Mo alloy in the temperature range from 400 to 1000°C. However, it was found that the difference in Hv was almost eliminated at 1000°C. Here, Ti-Zr A and Ti-Zr B, which have high Ta, O, and N contents, were used as representative Ti-Zr-based alloys. From these results, it is considered that the Ti-Zr based and Ti-6-4 alloys are easier to die-forge at high temperatures than the stainless steel and Co-28Cr-6Mo alloy.

3.2 β -transus temperature of Ti-Zr-based alloys

Figure 7(a) shows optical micrographs of Ti-Zr A after solution treatment at 800, 820, and 835°C for 1 h followed by cooling in water. The microstructure of the Ti-Zr A treated with the solution below T_β consisted of an α' -martensite (hcp) phase containing a primary α (hcp)-phase. This α' -martensite was formed by a martensitic transformation from the bcc phase to the hcp phase induced by water cooling. The volume fraction of the α -phase increased with decreasing solution treatment temperature. On the other hand, that of the β -phase, which is stable at high temperatures, decreased with decreasing solution treatment temperature. Similar results were obtained for other Ti-Zr-based alloys.

Figures 7(b) and (c) show the change in the volume fraction of the α -phase as functions of the solution treatment temperature and the temperature difference (ΔT) between T_β and the solution treatment temperature, respectively. The results for the Ti-6Al-4V alloy shown in Figs. 7(b) and (c) are cited from the literature.²²⁾ The results shown by circles (○) in Figs. 7(b) and (c) were also literature values measured

Fig. 7 (a) Optical micrographs of Ti-Zr A after solution treatment at 800, 820, and 835°C for 1 h followed by cooling in water. Change in volume fraction of α -phase for Ti-Zr-based and Ti-6Al-4V alloys as functions of (b) solution treatment temperature and (c) difference (ΔT) between T_β and solution treatment temperature.

for Ti-16Zr-4Nb-4Ta-0.2O-0.04N alloy (Ti-16-4-4-0.2O, T_β : 810°C) with lower O and N contents than Ti-Zr A.¹¹⁾ The volume fractions of the α -phase for the furnace-cooled (F.C.) Ti-Zr B and Ti-16-4-4-0.2O alloys are shown in Fig. 7(b). The T_β values of the Ti-Zr-based alloys were much lower than that of the Ti-6Al-4V alloy (T_β : 995 ± 15°C).²¹⁾ The volume fraction of the β -phase was close to 100 vol% at solution treatment temperatures of 805 to 850°C. The changes in the volume fraction of the α -phase as a function of ΔT from T_β were almost the same for the Ti-Zr-based and Ti-6Al-4V alloys, as shown in Fig. 7(c). Thus, the microstructural changes of (α - β)-type Ti alloys at each temperature can be predicted using ΔT from T_β .

In Figs. 7(b) and (c), the changes in volume fraction for Ti-Zr D indicated by squares ($\square$) and for Ti-Zr E indicated by inverted triangles (∇) are away from the curve in the temperature range from 700 to 800°C. The volume fraction of the α -phase for the furnace-cooled (F.C.) Ti-Zr-based alloy was close to that for the Ti-6Al-4V alloy.

3.3 Tensile properties and microstructure of hot-rolled Ti-Zr-based alloys

Figure 8 shows the tensile properties of the continuously hot-rolled Ti-Zr based alloy rods as a function of the rod diameter. High strength and excellent ductility were obtained for each rod diameter (10 to 52 mm). The Ti-Zr based alloys can be strengthened by combining hot rolling and adding small amounts of N and O.

Figure 9 shows the microstructures of the hot-rolled Ti-Zr B (rod diameter, 11 mm), Ti-Zr D (27 mm), Ti-Zr F (18 mm), and Ti-Zr G (27 mm) alloy rods. According to the optical micrographs of a longitudinal (L) section parallel to the rolling direction and a transverse (T) section perpendicular to the rolling direction, two-phase equiaxed fine grains of the α - and β -phases were produced. As clearly shown in Figs. 9(c)–(f), a similar optical microstructure was obtained even when the melting method was different. Ti-Zr-based alloy rods manufactured by other melting methods also showed a similar optical microstructure.

Fig. 8 (a) Effects of rod diameter on mechanical properties ($\sigma_{0.2\%PS}$, σ_{UTS} , T.E., and R.A.) and (b) room-temperature Vickers hardness (Hv) of hot-rolled Ti-Zr A and Ti-Zr B alloys.

Fig. 9 Optical micrographs of hot-rolled Ti-Zr-based alloy rods. (a), (b) Ti-Zr B (11 mm rod), (c), (d) Ti-Zr D (27 mm rod), (e) Ti-Zr F (18 mm rod), and (f) Ti-Zr G (27 mm rod) alloy rods. (a), (c) Longitudinal (L) sections parallel to the rolling direction and (b), (d), (e), (f) transverse (T) sections perpendicular to the rolling direction.

Figure 10 shows TEM images of the hot-rolled Ti-Zr B (rod diameter, 17 mm) and Ti-Zr G (27 mm) alloy rods. Electron beam diffraction analysis confirmed the existence of the β -phase at the grain boundaries of the α -phase, as shown in Figs. 10(a), (b), and (c). In the energy dispersive X-ray spectroscopy (EDS) analysis of the α - and β -phases, the amounts of Nb and Ta were higher in the β -phase than in the

Fig. 10 TEM images of transverse sections of hot-rolled (a) Ti-Zr B (17 mm rod) and (f) Ti-Zr G (27 mm rod) alloy rods; (b), (c) electron beam diffraction patterns; (d), (e) EDS patterns.

Fig. 11 SEM images of transverse sections of hot-rolled Ti-Zr A alloy rods. (a) 52 mm rod, (b) 37 mm rod, (c) 32 mm rod, and (d) 18 mm rod.

α -phase, as shown in Figs. 10(d) and (e). Similar TEM images of Ti-Zr-based alloy rods manufactured by the other melting methods were examined and no inclusions were observed.

SEM observation was performed to examine the microstructural change with the diameter of the hot-rolled Ti-Zr A rods. Ti-Zr A with high Ta, O, and N contents, was used as a typical alloy in the SEM observation. The β -phase appears white in the SEM image shown in Fig. 11. The microstructures of all other Ti-Zr-based alloy rods were similar to this microstructure. As the rod diameter decreased, the grain diameters of the β - and α -phases tended to decrease.

Fig. 12 Effects of rod diameter on volume fraction of β -phase, grain diameter, and aspect ratio of α -phase for hot-rolled Ti-Zr A.

Fig. 13 SEM images of the fracture surface of the Ti-Zr B alloy (18 mm rod) after the tensile test. (b) Magnification of square area in (a), and (c) magnification of square area in (b).

Figure 12 shows the effects of the rod diameter on the volume fraction of the β -phase, the grain diameter, and aspect ratio of the α -phase obtained by the analysis of SEM images. The grain diameter of the α -phase was approximately 1 μ m and the aspect ratio of the α -phase was in the range from 2 to 3. The effects of the rod diameter on the volume fraction of the β -phase, the grain diameter, and aspect ratio of the α -phase were small.

Figure 13 shows SEM images of the fracture surface of Ti-Zr B after the tensile test. Dimples were observed on all fracture surfaces. A magnification of the square area in Fig. 13(a) is shown in Fig. 13(b), and a magnification of the square area in Fig. 13(b) is shown in Fig. 13(c). Similar fracture surfaces were observed on the other hot-rolled Ti-Zr-based alloys. The dimples tended to be finer in the Ti-Zr-based alloys having higher strength.

Table 2 summarizes the tensile properties (mean $\pm$ standard deviation) of the seven hot-rolled Ti-Zr-based

Table 2 Tensile properties (0.2% proof stress, $\sigma_{0.2\%PS}$; ultimate tensile strength, σ_{UTS} ; elongation, T.E.; and reduction of area, R.A.), fatigue strength at 10^7 cycles (σ_{FS}), and fatigue ratios (σ_{FS}/σ_{UTS}) of Ti-Zr-based alloys, Ti-6Al-4V alloy used for a rod and various stems.

Ti Alloy	$\sigma_{0.2\%PS}$ / MPa	σ_{UTS} / MPa	T. E. (%)	R. A. (%)	σ_{FS} / MPa	$\sigma_{FS} / \sigma_{UTS}$
Ti-Zr A	941 $\pm$ 1	1025 $\pm$ 1	20 $\pm$ 1	49 $\pm$ 3	870	0.85
Ti-Zr B	978 $\pm$ 1	1062 $\pm$ 1	20 $\pm$ 1	55 $\pm$ 1	865	0.81
Ti-Zr C	858 $\pm$ 2	920 $\pm$ 1	21 $\pm$ 1	60 $\pm$ 1	730	0.79
Ti-Zr D	801 $\pm$ 1	889 $\pm$ 1	23 $\pm$ 1	62 $\pm$ 1	705	0.79
Ti-Zr E	788 $\pm$ 1	859 $\pm$ 1	23 $\pm$ 1	64 $\pm$ 1	695	0.81
Ti-Zr F	897 $\pm$ 2	931 $\pm$ 5	21 $\pm$ 3	54 $\pm$ 1	740	0.79
Ti-Zr G	832 $\pm$ 2	924 $\pm$ 3	21 $\pm$ 1	59 $\pm$ 1	690	0.75
Ti-6Al-4V	849 $\pm$ 1	936 $\pm$ 1	16 $\pm$ 1	42 $\pm$ 3	700	0.75
Stem Z	798 $\pm$ 1	844 $\pm$ 1	24 $\pm$ 1	43 $\pm$ 2	685	0.81
Stem D	843 $\pm$ 3	899 $\pm$ 1	22 $\pm$ 1	40 $\pm$ 3	780	0.87
Stem N	855 $\pm$ 27	945 $\pm$ 10	21 $\pm$ 5	25 $\pm$ 4	735	0.78
Stem S	910 $\pm$ 30	949 $\pm$ 19	21 $\pm$ 2	49 $\pm$ 6	740	0.78

alloys (rod diameter: 18–27 mm), the Ti-6-4 alloy rod (30 mm), and the test specimens cut from the four types of artificial hip stem. The tensile properties of the continuously hot-rolled Ti-Zr-based alloys were superior to those of the Ti-6-4 alloy and the artificial hip stems.

3.4 Fatigue properties of hot-rolled Ti-Zr-based alloys

Figures 14(a) and (b) show the S-N curves obtained using the seven types of continuously hot-rolled Ti-Zr-based alloy rods (rod diameter, 18–24 mm). We selected the optimum rod diameter for manufacturing artificial hip stems by hot

Fig. 14 S-N curves of Ti-Zr-based alloy rods obtained by tension-to-tension fatigue test with sine wave. (a) S-N curves of Ti-Zr-based alloy rods melted using VAR with Nb and Ta powders or using VAR with mother alloy. (b) S-N curves of Ti-Zr-based alloy rod melted by ISM and LIF.

Fig. 15 S-N curves of Ti-6Al-4V alloy specimens cut from four types of artificial hip stems and Ti-6Al-4V alloy 30 mm rod.

forging. The fatigue strengths (σ_{FS}) of Ti-Zr A and Ti-Zr B alloy rods subjected to VAR with Nb and Ta powders at 10^7 cycles were approximately 870 and 865 MPa, respectively, as shown in Fig. 14(a). On the other hand, σ_{FS} value for the Ti-Zr C rod was approximately 730 MPa. The σ_{FS} values of the Ti-Zr D rod subjected to VAR with the Ti-30Ta mother alloy and the Ti-Zr E rod not containing Ta were 705 and 695 MPa, respectively. The σ_{FS} values of Ti-Zr F and Ti-Zr G subjected to ISM and LIF were approximately 740 and 690 MPa, respectively, as shown in Fig. 14(b). In particular, it was found that σ_{FS} for the Ti-Zr-based alloys was increased by adding small amounts of N and O.

Figure 15 shows the S-N curves of the specimens cut from the four types of artificial hip stem and from a 30 mm Ti-6-4 alloy rod. The σ_{FS} values of these specimens were between 685 and 780 MPa. The σ_{FS} values of Ti-6-4 alloy rod were approximately 700 MPa.

The fatigue strength of these Ti alloys and the ratios of the fatigue strength at 10^7 cycles to the ultimate tensile strength (σ_{FS}/σ_{UTS}) are also shown in Table 2. The ratios for all the Ti-Zr-based alloys were higher than 70%. It was thus demonstrated that a relatively high fatigue strength can be achieved by hot rolling, which produces a microstructure consisting of a fine α - β -phase. These results showed that the use of Ti-30Ta mother alloy was effective for the Ti-Zr-based alloys containing Ta and that the addition of O was also useful for strengthening the Ti-Zr-based alloys. ISM is also a promising melting method for highly biocompatible Ti alloys containing large amounts of Nb and Ta.

3.5 Machinability of Ti-Zr-based alloy

Table 3 shows the main partial cutting force (F_t), tool feed force (F_m), normal (thrust) force (F_s), and cutting resistance (F_r) during the flank wear of the tool tips. Also, Table 3 shows the cutting forces in the steady state during flank wear. The cutting resistance of Ti-Zr A was close to that of Ti-6-4 alloy.

Figures 16(a), (b), and (c) respectively show the changes in the corner wear (VB_C), flank wear (VB), and boundary wear (VB_N) of the cutting tools as a function of cutting time. The tool wear of Ti-Zr A was similar to that of Ti-6-4 alloy. Thus, the machinabilities of the Ti-Zr-based and Ti-6-4 alloys were similar. For comparison, the machinability of the solution-aged Ti-Zr A alloy¹¹⁾ is shown in Fig. 16. It was

Table 3 Cutting flank wear resistances (Fr) of the tool tips of Ti–Zr-based and Ti–6Al–4V alloys with 30 and 50 mm diameters.

Alloy	F_t / N	F_m / N	F_s / N	Fr / N
Ti–Zr A (30 mm)	224	80	50	242
Ti–6Al–4V (30 mm)	219	80	50	238
Ti–Zr A (50 mm)	215	129	66	259
Ti–6Al–4V (50 mm)	219	64	46	232
Ti–Zr A (50 mm) S.T. + Aging	249	282	142	401

Fig. 16 Changes in (a) corner wear (VB_C), (b) flank wear (VB), and (c) boundary wear (VB_N) of the cutting tools for Ti–Zr A 50 mm rods as a function of cutting time.

found that the tool wear was markedly greater than that for the annealed Ti–Zr A alloy.

4. Conclusions

To develop low-cost manufacturing processes for biocompatible Ti–Zr-based alloys, the effects of melting methods, Ta addition using Ti–30 mass% Ta mother alloy, and the combined addition of O and N on the continuous-hot-rolling conditions, physical properties, microstructure, room-temperature tensile properties, fatigue strength, and machinability of highly biocompatible Ti–Zr-based alloys were investigated. In the investigation of the melting methods, seven Ti–Zr-based alloys containing Zr, Nb, and Ta were subjected to VAR, ISM, and LIM.

The melting point, specific heat constant (C_p), thermal conductivity (W), average linear expansion coefficient (L), Vickers hardness (H_v), and β -transus temperature (T_β) of the biocompatible Ti–Zr-based alloys were measured. The Ti–Zr-based alloys started to melt at approximately 1620°C, which was lower than the melting temperatures of C.P. Ti G 2, C.P. Ti G 4, and Ti–6Al–4V alloy. C_p and W increased with increasing temperature up to T_β then decreased above T_β . T_β was in the range from 805 to 850°C for the seven Ti–Zr-based alloys. The change in L with increasing temperature was small for the Ti–Zr-based alloys.

The microstructural changes of the (α – β)-type Ti alloys at each temperature were predicted using the temperature difference (ΔT) from T_β . High strength and excellent ductility were obtained for each Ti–Zr-based alloy rod diameter (12 to 50 mm) in the continuous hot-rolling process. A fine equiaxed α -phase structure (grain diameter, approximately 1 μ m) containing a fine β -phase at the grain boundaries of the α -phase was observed. The Ti–Zr-based alloys were strengthened by adding trace amounts of N and O. It was found that relatively high tensile strength and fatigue strength can be achieved by hot rolling.

These tensile properties were superior to those of artificial stems. The machinability of cutting tools was similar for the Ti–Zr-based and Ti–6Al–4V alloys. The use of Ti–30% Ta mother alloy was effective for the Ti–Zr-based alloys containing Ta, and the addition of O was also useful for strengthening the Ti–Zr-based alloy without Ta. ISM was found to be a promising method for biocompatible Ti alloys.

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