Mechanical Property, Fatigue Strength and Clinical Trial of Dental Cast Ti–15Zr–4Nb–4Ta Alloy

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The mechanical properties and fatigues strength of Ti–15Zr–4Nb–4Ta castings were compared with those of Co–Cr–Mo and Ti–6Al–7Nb castings, which have been clinically used in Japan. The mechanical properties of buffed and chemically polished dental castings were almost the same. The mean tensile strength (\(\sigma_{0.2}\)) and total elongation (TE) of the buffed Ti–15Zr–4Nb–4Ta castings were 832 ± 41 MPa, 964 ± 69 MPa and 7 ± 3%, respectively. The \(\sigma_{0.2}\), \(\sigma_{UTS}\) and TE of the buffed Ti–6Al–7Nb castings were 873 ± 30 MPa, 982 ± 27 MPa and 11 ± 4%, respectively. The \(\sigma_{0.2}\), \(\sigma_{UTS}\) and TE of the buffed Co–Cr–Mo castings were 589 ± 23 MPa, 773 ± 19 MPa and 10 ± 2%, respectively. The fatigue strength of the alloy castings at 1 × 10\(^{7}\) cycles was lower than that of the Co–Cr–Mo castings. The fatigue strengths of the Ti–Al–7Nb and Ti–15Zr–4Ta–4Nb castings at 1 × 10\(^{7}\) cycles were approximately 100 and 80 MPa, respectively. Clinical trials were carried out for complete and partial dentures made of the Ti–15Zr–4Nb–4Ta alloy. Clinical observation was conducted over a one year period for patients wearing complete or partial dentures. During the clinical observation, all five patients felt comfortable with the dentures, and fracture of the clasp was not observed.

\textbf{Keywords:} titanium alloy, dental casting, mechanical properties, fatigue strength, dental prostheses, clinical observation

1. Introduction

Ti, Zr, Nb and Ta exhibit excellent biocompatibility, and belong to the loose connective vascularized (vital) group with regards to tissue reaction.\textsuperscript{1} Our research group previously reported on the effects of Zr, Nb, Ta and Pd on the mechanical properties of Ti alloys and the biocompatibilities of these alloys with cultured cells, and on the corrosion resistance of Ti alloys, as determined using anodic polarization tests in synthetic body fluids.\textsuperscript{2–14} The mechanical strength at room temperature of this new Ti–Zr–Nb–Ta alloy annealed at 700°C for 2 h is increased by adding Zr and small quantities of oxygen and nitrogen.\textsuperscript{5,10} The anodic polarization property of the Ti alloy is improved when Zr, Nb, Ta and Pd are added, because the resultant ZrO\(_2\), Nb\(_2\)O\(_5\), Ta\(_2\)O\(_5\) and PdO strengthen the TiO\(_2\) passive film formed on the Ti alloy. The anodic polarization property under friction is also excellent.\textsuperscript{15} The relative growth ratios of the L929 and MC3T3-E1 cells are estimated using the following formula: (average number of cells per dish after 4 days of incubation)/(average number of cells in the control). The relative growth ratios of the L929 (1.09 ± 0.04) and MC3T3-E1 (1.08 ± 0.02) cells reacted with the Ti–15Zr–4Nb–4Ta alloy are slightly higher than those of the L929 and MC3T3-E1 cells with the Ti–6Al–4V alloy (1.0).\textsuperscript{12,13} The Ti alloy disk is worn with an apatite ceramic pin in Eagle’s medium, and the wear powder is sterilized in ethanol and added to the culture medium.\textsuperscript{16} The growth ratios of the L929 and MC3T3-E1 cells with the Ti–6Al–4V alloy wear powder relative to those of the control cells are lower than those of the L929 and MC3T3-E1 cells with the Ti–15Zr–4Nb–4Ta alloy wear powder. The concentration of V released from the wear powder into the medium increases with an increasing amount of wear powder. For the Ti–15Zr–4Nb–4Ta wear powder, the maximum Ti concentration released from the wear powder roughly agrees with the results obtained using high-purity Ti particles.\textsuperscript{16} In contrast, for Zr, Nb and Ta, the maximum metal concentrations released from the wear powders are much lower than those obtained using high-purity metal particles. In vitro and in vivo, the concentrations of Ti and alloying elements (Zr, Nb and Ta) released from the Ti–15Zr–4Nb–4Ta alloy are much lower than those of Ti, Al and V released from the Ti–6Al–4V extralow interstitial alloy.\textsuperscript{17,18} The fatigue strength of the Ti–15Zr–4Ta–4Nb alloy annealed at 700°C for 2 h is approximately 600 MPa in Eagle’s medium at 1 × 10\(^{6}\) cycles, and the fatigue strength of the Ti–15Zr–4Ta–4Nb alloy aged after solution treatment increased to 800 MPa in Eagle’s medium.\textsuperscript{19} Ti–15Zr–4Nb–4Ta alloy with its excellent mechanical properties, corrosion resistance and fatigue strength and cytocompatibility can be used for medical purposes.

Advances in precision dental casting technology have made it possible to fabricate Ti prostheses. The Ti utilized in dental prostheses is mostly commercially available pure Ti. In this study, the mechanical properties and fatigue strengths of the Co–Cr–Mo and Ti–6Al–7Nb castings, which have been clinically used, and Ti–15Zr–4Nb–4Ta castings at room temperature were investigated. The various complete and partial dentures were fabricated with the Ti–15Zr–4Nb–4Ta alloy. In addition, five patients who wore the dentures cast with the Ti–15Zr–4Nb–4Ta alloy were clinically observed over a one year period.

2. Materials and Methods

2.1 Alloy specimens

The Ti–15Zr–4Nb–4Ta alloy specified in JIS T 7401-4 for surgical implants was subjected to vacuum-arc melting. Cast ingots were \(\beta\)-forged into rod specimens 45 mm in diameter after soaking at 1050°C for 4 h and then \(\alpha\)-\(\beta\)-forged at 750°C.
After forging, the oxidized surface layer formed was removed. Then rod specimens, 42 mm in diameter and 13 mm in height, were cut from the forged alloy. The chemical composition of the Ti–15Zr–4Nb–4Ta alloy is shown in Table 1.

### 2.2 Dental casting

The Ti–15Zr–4Nb–4Ta alloy was cast using an arc-melting suction-and-pressure-type casting machine (manufactured by Wada Precision Dental Laboratories Co., Ltd.) into a phosphate-bounded Al₂O₃/LiAlSiO investment (GC Co., T-invest) in an Ar atmosphere. The T-invest mold was heated at 750°C for 1 h and reheated at 1050°C for 1 h. The rod specimens in the melting chamber were heated in an Ar atmosphere and arc-melted after vacuum deaeration. The melting time was 60 s. The melted specimens were cast into the T-invest mold preheated to 150°C. The argon pressure for dental casting was 0.2 MPa (2 kgf/cm²). After casting, sprues were removed with a carbide bar, and then the specimens were sandblasted with white alundum. The surface of the castings after sandblasting was chemically polished with a mixture of nitric acid and hydrofluoric acid (HF:HNO₃:H₂O = 1:2:5). In some cases, the cast surface was finished by water buffing after chemical polishing.

For comparison, the Co–Cr–Mo (ISO 5832-4) and Ti–6Al–7Nb (ISO 5832-11) alloys were cast under clinical conditions. The surface of the Co–Cr–Mo castings was electropolished or buffed. The surface of the Ti–6Al–7Nb castings was chemically polished or buffed.

### 2.3 Mechanical tests

Mechanical test specimens 3 mm in diameter and 12 mm in gauge length (Fig. 1) were cast. After casting, sprues were removed using a carbide bar. The surface layer of each specimen was then removed using white alundum. After sandblasting, the surface of the castings was chemically polished with a mixture of nitric acid and hydrofluoric acid. Moreover, the surface of some part of the chemically polished castings was finished by water buffing. The mechanical test at room temperature was performed at a crosshead speed of 0.5 mm/min for each casting (n = 6).

### 2.4 Fatigue test

Specimens of the same dimensions used in the mechanical test were used in the fatigue test. Test conditions were set so as to load a sine wave with a stress ratio (R = (minimum tensile stress)/(maximum tensile stress)) of 0.1, a frequency of 10 Hz, and a maximum of 10⁷ cycles in air.

### 2.5 Fabrication of dental prostheses

Metal plates for complete and partial dentures were cast using the Ti–15Zr–4Nb–4Ta alloy. After sandblasting with white alundum, the surface of the castings was chemically polished with a mixture of nitric acid and hydrofluoric acid. The final surface was finished by water buffing and inspected for internal defects, such as blowholes and cavities, using X-ray photography (tube voltage: 60 kV, tube current: 30 mA, irradiation time: 0.1 s).

### 2.6 Clinical trial

Patients visiting The Department of Prosthetic Dentistry, Nihon University Dental Hospital, Matsudo, gave sufficiently informed consent regarding the use of Ti alloy dentures. Five patients were requested to have dentures cast with the Ti–15Zr–4Nb–4Ta alloy. The complete and partial dentures were fabricated with metal plates so as to satisfactorily adjust the dentures to the mucous membrane. Three patients had complete dentures and two patients had partial dentures. Moreover, a denture with a metal plate made of the Co–Cr–Mo alloy was prepared for use in case the Ti alloy denture fractured.

### 3. Experimental Results

#### 3.1 Mechanical properties

Table 2 shows a comparison of the mechanical properties (average and standard deviation values) of the buffed and chemically polished two types of Ti alloys and Co–Cr–Mo castings. The mechanical properties of the buffed and chemically polished castings were almost the same. The 0.2% proof strength (σ₀.₂%/PS), ultimate tensile strength (σ₁/UTS), and total elongation (TE) of the buffed Ti–15Zr–4Nb–4Ta castings were 832 ± 41 MPa, 964 ± 69 MPa, and 7 ± 3%, respectively. The σ₀.₂%/PS, σ₁/UTS, and TE of the Ti–6Al–7Nb castings were 872 ± 31 MPa, 980 ± 29 MPa, and 29 ± 4%

<table>
<thead>
<tr>
<th>Titanium Alloy</th>
<th>Zr</th>
<th>Nb</th>
<th>Ta</th>
<th>Pd</th>
<th>Fe</th>
<th>O</th>
<th>N</th>
<th>H</th>
<th>C</th>
<th>Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti–15Zr–4Nb–4Ta</td>
<td>15.24</td>
<td>3.90</td>
<td>3.92</td>
<td>0.22</td>
<td>0.022</td>
<td>0.162</td>
<td>0.048</td>
<td>0.011</td>
<td>0.002</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

Table 1 Chemical composition (mass%) of materials.

Table 2 Comparison of mechanical properties (average and standard deviation values) of dental castings at room temperature.

<table>
<thead>
<tr>
<th></th>
<th>σ₀.₂%/PS/MPa</th>
<th>σ₁/UTS/MPa</th>
<th>T. E. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti–15Zr–4Nb–4Ta</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chemically polished</td>
<td>834 ± 24</td>
<td>953 ± 71</td>
<td>9.3 ± 4.0</td>
</tr>
<tr>
<td>Finished by water buffing</td>
<td>832 ± 41</td>
<td>964 ± 69</td>
<td>6.5 ± 3.4</td>
</tr>
<tr>
<td>Ti–6Al–7Nb</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chemically polished</td>
<td>873 ± 17</td>
<td>987 ± 9</td>
<td>9.2 ± 3.4</td>
</tr>
<tr>
<td>Finished by water buffing</td>
<td>872 ± 31</td>
<td>980 ± 29</td>
<td>10.6 ± 4.5</td>
</tr>
<tr>
<td>Co–Cr–Mo</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electropolished</td>
<td>620 ± 25</td>
<td>805 ± 19</td>
<td>10.7 ± 4.6</td>
</tr>
<tr>
<td>Finished by water buffing</td>
<td>589 ± 23</td>
<td>772 ± 19</td>
<td>9.8 ± 2.1</td>
</tr>
</tbody>
</table>

![Fig. 1 Dimensions of specimens for mechanical and fatigue tests.](image-url)
patients. The dentures were satisfactorily compatible with the mucous membrane, and all the patients felt comfortable wearing the dentures. No surface imprint was observed when the dentures were removed. None of the patients complained of a metallic taste from the dentures.

4. Discussion

The demand for Ti prostheses is increasing particularly for patients with allergies. The Co–Cr–Mo alloy has a specific gravity of 8.2, while the Ti–15Zr–4Nb–4Ta alloy has a smaller specific gravity of 5.0. Ti materials are thus advantageous for the fabrication of lightweight prostheses. The mechanical properties of the Co–Cr–Mo dental castings for metal plates, bars and clasps are established in the JIS T 6115 standard. The minimum values of $\sigma_{0.2\%PS}$, $\sigma_{UTS}$ and TE for Co–Cr–Mo castings in this JIS standard are specified as 500 MPa, 685 MPa and 3%, respectively. Commercially available pure Ti grade 2 lacks the necessary ultimate tensile strength, but both the Ti alloys and Co-Cr-Mo alloy used in this study meet these specifications.

To compare the dental casting properties of the Ti–15Zr–4Nb–4Ta alloy with those of commercially available pure Ti grade 2 and Ti–6Al–V alloy, the micro-Vickers hardness, tensile property at room temperature, concentration of metal released from Ti castings, and experimental fabrication of metal plates, crowns and bridges using the Ti–15Zr–4Nb–4Ta alloy were also examined. At a depth of approximately 200 μm from the surface of the castings, a high-hardness layer is formed due to the reaction of Ti alloy with the dental investment. This high-hardness layer is chemically polished to a thickness of approximately 50 μm with a mixture of nitric acid and hydrofluoric acid. However, this high-hardness layer may cause a decrease in fatigue strength as shown in Fig. 2(b). The concentrations of Ti, Zr, Nb and Ta ions released the Ti–15Zr–4Nb–4Ta alloy into the artificial saliva and 1% lactic acid solution are smaller than those of Ti, Al and V ions released from the Ti–6Al–4V alloy, and the concentration of Ti ions released from the Ti–15Zr–4Nb–4Ta alloy into the 1% lactic acid solution is less than 20% that of the Ti ions released from the Ti–6Al–4V alloy. TiN is surface-coated on a partial denture made of Ti–15Zr–4Nb–4Ta alloy using a TiN ion plating apparatus. The effect of the TiN surface coating on the mechanical properties of the Ti–15Zr–4Nb–4Ta casting is negligible. The concentrations of Ti, Zr and Nb ions released into the artificial saliva from the TiN-coated Ti–15Zr–4Nb–4Ta casting are smaller than those released from the chemically polished Ti–15Zr–4Nb–4Ta casting.

The fatigue strengths of the Co–Cr–Mo and annealed Ti–15Zr–4Ta–4Nb and Ti–6Al–7Nb alloys are approximately 400 MPa, 600 MPa and 620 MPa in Eagle’s medium at 1 × 10^7 cycles. The ratios of the fatigue strengths of the Co–Cr–Mo, Ti–15Zr–4Ta–4Nb and Ti–6Al–7Nb castings (Fig. 2) to those of the Co–Cr–Mo and annealed Ti–15Zr–4Ta–4Nb and Ti–6Al–7Nb alloys mentioned above were estimated. The fatigue strength ratios for Co–Cr–Mo, Ti–6Al–7Nb and Ti–15Zr–4Ta–4Nb castings are approximately 0.4, 0.2 and 0.1, respectively. These low fatigue strength ratios may be caused by microblowholes created due to the

11 ± 5%, respectively. The $\sigma_{0.2\%PS}$, $\sigma_{UTS}$, and TE of the buffed Co–Cr–Mo castings were 589 ± 23 MPa, 772 ± 19 MPa, and 10 ± 2%, respectively.

3.2 Fatigue strength

Figure 2 show comparisons of the S-N curves with sine wave loading. The S-N curves of the buffered and chemically polished castings showed similar tendencies. The number of cycles to failure for the castings increased with decreasing maximum stress. The fatigue strength of the Co–Cr–Mo castings at 1 × 10^7 cycles was approximately 200 MPa, and higher than that of the Ti alloys. The fatigue strengths at 1 × 10^7 cycles for the Ti–6Al–7Nb and Ti–15Zr–4Nb–4Ta castings were approximately 100 and 60 MPa, respectively. The fatigue-fractured surfaces of the Co–Cr–Mo and Ti–15Zr–4Nb–4Ta castings are shown in Fig. 3. Fatigue cracks originated from the blowholes in the middle of all castings. Many cracks were visible on the fatigue-fractured surfaces.

3.3 Dental prostheses and clinical observation

Complete and partial dentures were fabricated using the Ti–15Zr–4Nb–4Ta alloy so as to snugly fit the oral cavity (Figs. 4 to 6). Blowholes or cavities could not be observed by X-ray inspection of the castings, as shown in Figs. 5(b), 6(c) and 6(d). The five patients who wore complete or partial dentures made of Ti–15Zr–4Nb–4Ta alloy were clinically observed over a one year period. Figure 7 shows photographs of the representative complete or partial dentures worn by the
reaction of Ti alloy with the dental investment during casting. The fatigue strength of the Ti–6Al–7Nb casting at $1 \times 10^6$ cycles was higher than that of the Ti–15Zr–4Ta–4Nb casting (Fig. 2). This Ti–15Zr–4Ta–4Nb casting is not as widely used as the Ti–6Al–7Nb alloy in dental casting. Therefore, the fatigue strength of the Ti–15Zr–4Ta–4Nb alloy might be improved by the further improvement of the dental-casting technique.

Clinical problems in the use of dental prostheses made of Ti–15Zr–4Nb–4Ta casting were not observed in any of the patients during their clinical observation. Fracture of the clasp was not observed. As the patients themselves felt comfortable wearing the dentures with the Ti–15Zr–4Nb–4Ta alloy, this alloy is considered satisfactory for use as

Fig. 3 SEM micrographs of surface fractured by fatigue test with sine wave at 10 Hz. (a), (b) Co–Cr–Mo alloy fractured at $3.8 \times 10^6$ cycles under 160 MPa. (c), (d) Ti–15Zr–4Nb–4Ta alloy fractured at $1.2 \times 10^6$ cycles under 100 MPa.

Fig. 4 Complete denture with metal plate made of Ti–15Zr–4Nb–4Ta alloy. (a and b) Upper complete dentures and (c) lower complete denture.
dental prostheses. The denture will be clinically observed when the patients revisit the hospital.

5. Conclusions

The mechanical properties and fatigue strength of the Ti–15Zr–4Nb–4Ta casting were compared with those of the Co–Cr–Mo and Ti–6Al–7Nb castings. The mechanical properties of buffed and chemically polished castings were almost identical. The 0.2% proof strength, ultimate tensile strength and total elongation are listed respectively as follows: Ti–15Zr–4Nb–4Ta casting: 832 ± 41 MPa, 964 ± 69 MPa and
7 ± 3%; Ti–6Al–7Nb casting: 873 ± 30 MPa, 982 ± 27 MPa and 11 ± 4%; Co–Cr–Mo casting: 589 ± 23 MPa, 773 ± 19 MPa and 10 ± 2%. The fatigue strengths of the Ti alloy castings at 1 × 10^7 cycles were much lower than that of the Co–Cr–Mo casting. The fatigue strengths of the Ti–6Al–7Nb and Ti–15Zr–4Nb–4Ta castings at 1 × 10^7 cycles were approximately 100 and 80 MPa, respectively. Complete and partial dentures were fabricated with the Ti–15Zr–4Nb–4Ta alloy. During the clinical observation, all five patients wearing complete and partial dentures felt comfortable, and clinical problems, such as fracture of the clasp, could not be observed.

REFERENCES