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Effect of chromium content on mechanical properties of casting Ti-Cr alloys

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The mechanical properties of a series of binary Ti-Cr alloys were investigated. Chromium content ranged from 5 to 20 mass%. Dumbbell- and disk-shaped specimens of each alloy were obtained by casting for mechanical testing and microstructural observation. Yield strength (YS) at 0.2%, tensile strength (TS), elongation (EL) and Vickers hardness (HV) were determined. The TS and YS of Ti-15Cr were similar to those of Ti-20Cr at approximately 880 or 900 MPa and higher than those of cp-Ti by nearly 55%. Among all Ti-Cr alloys, Ti-10Cr showed the lowest EL. At 50 µm below the surface, HV ranged from 370 to 420. Addition of 15 or 20 mass% chromium to titanium yielded sufficient strength and relatively high elongation values. Judging from the results of the mechanical properties, the suitability of Ti-Cr alloys with 15 or 20 mass% chromium for use in dental prostheses.

Keywords: Mechanical property, Titanium alloys, Titanium casting

INTRODUCTION

Titanium has seen increased use in fixed and removable prosthetics due to its excellent biocompatibility, high corrosion resistance and favorable mechanical properties. Despite these advantages, however, titanium and titanium alloys are inherently difficult to cast as they have a high melting point and show strong reactivity to elements such as oxygen at such temperatures. β-titanium alloys have been suggested as a solution to these problems as they offer certain benefits such as a lower melting temperature, solid-solution hardening and high ductility with a body-centered cubic structure.

In recent years, titanium implants and prostheses have come into wide use in clinical dentistry. However, some studies have noted pigmentation and discoloration occurring with titanium implants and denture bases. Recently, in other experiments on titanium alloys, we found that an experimental Ti-20Cr alloy containing 20 mass% chromium showed the least discoloration and superior corrosion resistance in a fluoride-containing saline solution. In addition, Takemoto et al. found that addition of chromium to titanium in the 5 to 20 mass% range was effective in enhancing resistance to corrosion by fluoride.

On the basis of the Ti-Cr phase diagram, the eutectoid composition is approximately 13.5 mass%. The Ti-5Cr and Ti-10Cr alloys correspond to the hypo-eutectoid compositions, whereas, the Ti-15Cr and Ti-20Cr alloys are in the hypereutectoid composition range. Alloying chromium to titanium had a marked effect on the mechanical properties of Ti-Cr systems, suggesting a potential advantage. However, the mechanical properties of casting Ti-Cr alloys have been still uncertain because the properties changed by processing methods, i.e. by using an investment materials.

The purpose of the present study was to evaluate the mechanical properties of a series of cast Ti-Cr alloys with a chromium content of up to 20 mass% with the aim of determining their suitability as titanium alloys for dental prostheses.

MATERIALS AND METHODS

Preparation of alloys

Experimental titanium alloys with a chromium content of 5, 10, 15, and 20 mass% (denoted as CR5, CR10, CR15, and CR20, respectively) were made by melting sponge titanium (>99.8 mass%, Osaka Titanium Technologies, Amagasaki, Japan) and pure chromium (99.99 mass%, Japan Metals & Chemicals Co., Ltd., Tokyo, Japan) in an argon-arc melting furnace (ACM-01, Diavac Limited, Yachiyo, Japan). To make homogeneous 30-g alloy buttons, the metal was turned over 6 times during melting. A single dumbbell-shaped acrylic pattern for tensile testing (15-mm gauge length and 3-mm diameter) and a disk-type wax pattern for hardness testing (14-mm diameter and 1.4-mm thickness) were directly attached to the sprue-former and invested in a mold ring with alumina/magnesia-based investment materials (Titavest CB, J. Morita, Kyoto, Japan). Each invested mold was burned out in accordance with the manufacturer’s recommendations by heating to 900°C at 15 °C/min and holding at this temperature for 50 min. The mold was then furnace-cooled to 650°C and subsequently placed in the casting machine.

An argon-arc melting/pressure difference casting unit (Cyclarc II, J. Morita, Kyoto, Japan) was used to fabricate cast specimens. For each casting, the casting chamber was filled with argon gas and pressure set at 0.03 MPa. To melt the buttons, an argon-arc was generated for 40 sec with an electric current at 150 A. After bench-cooling, the castings were divested and sandblasted with glass beads (80 micron, Jelenlko, Armonk, USA) from a distance of approximately 10 mm...
at a pressure of 0.5 MPa for 15 sec to remove any adhering investment using a sandblaster (Whirlwind, Jelenko, Armonk, USA). Castings in which no porosity was recognized in radiographs (DCX-100, Asahi Roentgen, Kyoto, Japan) were subjected to mechanical testing. Commercially pure titanium specimens (cp-Ti, JIS Grade 2, J. Morita, Kyoto, Japan) were also fabricated as a control.

**Mechanical properties**

Tensile tests (n=5) were performed at a crosshead speed of 0.5 mm/min at room temperature using a universal testing machine (Autograph AG-I, Shimadzu, Kyoto, Japan) equipped with a strain gauge extensometer. Yield strength (YS) at 0.2% offset, ultimate tensile strength (TS) and elongation (EL) to fracture were obtained from a stress-strain curve plot.

The Vickers microhardness (Hv) of each alloy was determined using a microhardness tester with a load of 2.94 N and 15 sec duration time (HMV-1, Shimadzu, Kyoto, Japan) on polished cross-sections of the casting disks. Measurements were made at 50 µm, 100 µm, and thereafter at 100 µm intervals up to 500 µm below the surface of the casts. Five specimens for each alloy were used and three indentations were made for each specimen at each location.

**Fractography and Metallography**

After tensile testing, surfaces were examined to determine fracture pattern under a scanning electron microscope (JSM 6340F, JEOL, Akishima, Japan). Metallographic observation was performed as follows: the cast disk was polished with abrasive paper and then in a slurry of suspended 0.05 µm colloidal silica; polished specimens were etched in Keller’s reagent; etched surfaces were observed under an optical microscope (Metaphot, Nikon, Tokyo, Japan).

**X-ray diffraction**

X-ray diffraction for phase analysis was performed for the cast specimens of each metal using Cu Kα radiation by using a diffractometer (RINT2500, Rigaku, Akishima, Japan) operating at 30 kV and 300 mA. The phases were identified by matching each characteristic peak with the JCPDS files.

**Statistical analyses**

The mechanical properties (YS, TS, EL, and Hv) were statistically analyzed using a one-way analysis of variance (ANOVA) at a significance level of \( p=0.05 \). Specimens were then compared using the Scheffé test at a significance level of \( p=0.05 \).

**RESULTS**

**Mechanical properties**

The results for YS and TS are shown in Fig. 1 and those for EL in Fig. 2. The YS and TS of titanium alloys with 10 mass% chromium (CR10) or more (CR15, CR20) were significantly greater (\( p<0.05 \)) than those of cp-Ti or titanium alloy with 5 mass% chromium (CR5). On the other hand, CR10 exhibited the lowest EL. The CR5, CR15, and CR20 specimens showed higher ductility. No statistically significant differences were observed in EL between cp-Ti and the various titanium alloys, except for with CR10.

The results of the hardness test for the Ti-Cr alloys are shown in Fig. 3. In all the alloys tested, hardness
at 50 µm below the surface ranged from 370 to 420. In CR5, CR15 and CR20, hardness gradually decreased with increase in depth up to 100–150 µm, after which it leveled off. In CR10, however, hardness gradually increased with increase in depth up to 100 µm.

**Fractography and Metallography**

Scanning electron micrographs of the typical fracture surfaces of the Ti-Cr alloy castings after tensile testing are shown in Fig. 4. All Ti-Cr alloys, except 10 mass% chromium, exhibited dimple-like structures in the center of the fractured surfaces. In CR10, the fractured surfaces consisted of dendrite structures (arrowhead) and cleavage-mode predominated in the center of the castings. The typical microstructure of each alloy casting is shown in Fig. 5. CR5 showed an acicular structure, with a large grain size of 200 µm. CR10 appeared to have an inhomogeneous microstructure. The fine acicular structure of CR15 was similar to that of CR20.

**X-ray diffraction**

The typical XRD patterns of the series of binary Ti-Cr alloys are shown in Fig. 6. α-Ti peaks were found for the CR5 and CR10 patterns. β-Ti peaks were found in the diffraction patterns of all Ti-Cr alloys. Apparently, more than 10 mass% chromium, the retained β was observed in the XRD patterns. The ω peak was found in CR10, this minimal broadened peak was identified as the likely ω-phase of the 2θ at 79.55 or 79.75°.

**DISCUSSION**

Alloying chromium to titanium offers a number of advantages such as increased mechanical strength, corrosion resistance to fluoride and a lower melting point. In the present study, we evaluated the mechanical properties of a series of Ti-Cr alloys with four different levels of chromium content ranging from 5 to 20 mass% in 5% increments. Titanium alloys with 10 mass% chromium or more showed a higher YS and TS than cp-Ti or titanium alloy with 5 mass% chromium. Among all Ti-Cr alloys, titanium alloys with 10 mass% chromium exhibited the highest strength. Some disagreement exists with regard to the relationship between chromium content and strength. Shimizu reported an increase in tensile strength of binary Ti-Cr alloys with an increase in chromium content ranging from 10–20 mass%, however, the strength was reduced addition of chromium further. Ikeda et al. reported that while the microstructure of binary Ti-Cr alloy fundamentally exhibited β-phase, when the chromium content ranged from 7–13 mass%, the alloy exhibited ω-phase, depending on cooling conditions, resulting in increased strength. We believe that one possible explanation for the disparity between our results and those of these earlier studies may lie in the casting process used. Although we used alumina/magnesia-based investment, Shimizu used a phosphate-bonded mold, which induces a reaction in the titanium alloy that results in highly...
brittle specimens. Therefore, they obtained a lower tensile strength at 10 mass% chromium content than the Ti-15Cr and Ti-20Cr.

The EL of each Ti-Cr alloy in this study was higher than that in an earlier study\textsuperscript{9}. Again, this may be explained by the use of a phosphate-bonded mold by Shimizu\textsuperscript{9}. These result suggested that one of the reason why difference of the reaction between the alloys and the molds in the present study, because of cast the alloys into phosphate-bonded mold. Furthermore, the diameter of their tensile test specimens was 2 mm, while that of this study was 3 mm. It is possible that the smaller diameter used in their study was the cause of the lower EL value obtained, even though the thickness of the reacted layer was similar to that in the present study. On the other hand, in this study, Ti-Cr alloy with 10 mass% chromium exhibited the lowest EL among all alloys tested. As described above, this agrees with the results of an earlier study\textsuperscript{9} showing lower ductility in Ti-Cr alloy with 10 mass% chromium than other Ti-Cr alloys. A decrease in ductility was also observed in the fractography. Cleaved grains, which are characteristic of decreased ductility, were observed in CR10. On the other hand, dimple ruptures, indicative of a typical ductile fracture, were observed in the fractured interior structures of CR15 and CR20.

Hardness near the surface in all the alloys was almost the same. In CR5, CR15, and CR20, hardness gradually decreased with increase in depth up to 100–150 µm, in the control specimens showed the same tendency in depth up to 200 µm. However, in CR10, hardness gradually increased with increase in depth up to 100 µm. Note that the interior hardness of CR10 was
the highest. The high hardness value of the interior of this particular alloy resulted from a fine martensitic microstructure. According to a previous report, addition of chromium to titanium causes a phase transition from $\alpha$-phase to $\beta$-phase. As described above, Ikeda et al.\textsuperscript{23,24} suggested that the development of $\alpha$-phase increased hardness and Koike et al.\textsuperscript{13} noted that $\alpha$-phase decreased ductility. The increase in hardness was probably caused by the solid-solution hardening of the $\alpha$-phase or the $\beta$-phase. In addition, the maximum in microhardness at 10 mass% chromium is believed to be a result of the strengthening/hardening effect of $\omega$-phase. This is in agreement with previous results using Ti-7Cr\textsuperscript{13,22}.

The yield strength, tensile strength, and elongation of the Ti-Cr alloys with 15 or 20 mass% chromium in this study (888–873, 905–898 MPa, and 12% each) get the better of those of hardened Type 4 gold-base alloys (493–825, 690–830 MPa, and 1–12%) and Co-Cr alloys (500–710, 650–870 MPa, and 2–12%)\textsuperscript{23-28}. Takemoto et al.\textsuperscript{17} reported the electrochemical corrosion behavior and dissolution behavior of binary Ti-Cr alloys with a chromium content of up to 20 mass% in fluoride-containing solutions. In that report, the corrosion resistance of Ti-Cr alloys increased with increase in chromium content.

From the viewpoint of mechanical properties and corrosion resistance, Ti-Cr alloys with 15 or 20 mass% chromium offer suitable materials for dental prostheses if other properties necessary for dental castings can be obtained.

CONCLUSIONS

We investigated the mechanical properties of a series of Ti-Cr alloys with a chromium content of up to 20 mass%. The results showed that chromium content affected mechanical properties. Addition of 15 or 20 mass% chromium to titanium yielded sufficient strength and relatively high elongation values. Such alloys offered improved mechanical properties, making them suitable as materials for dental prostheses.

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