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ORIGINAL ARTICLE

Hardness and microstructure of Ti-15Mo-5Zr-3Al alloy for dental casting

MAMIKO KOCHI[1], HIROYASU KOIZUMI[2,3], MAHOKO MURAKAMI[2], HISAJI KIKUCHI[4,5], HIDEO MATSUMURA[2,3] & TAKAYUKI YONEYAMA[4,5]

[1]*Division of Applied Oral Sciences,* [2]*Department of Fixed Prosthodontics,* [3]*Division of Advanced Dental Treatment, Dental Research Center,* [4]*Department of Dental Materials, and* [5]*Division of Biomaterials Science, Dental Research Center, Nihon University School of Dentistry, Chiyoda-ku, Tokyo, Japan*

Abstract

Objective. The hardness and microstructures of Ti-15Mo-5Zr-3Al alloy castings were investigated for application to dental cast prostheses. ***Materials and methods.*** Cast specimens of Ti-15Mo-5Zr-3Al alloy, Ti-6Al-7Nb alloy and CP Ti were prepared using a centrifugal-type casting machine and a magnesia-based investment material. The hardness of the cross-sections of the cast specimens were measured. The microstructure of the castings was observed using an optical microscope and was then analyzed by X-ray diffractometry. ***Results and conclusions.*** The hardness of Ti-15Mo-5Zr-3Al alloy at the inner part of the castings was 361 Hv, while the hardnesses of Ti-6Al-7Nb alloy and CP Ti were 384 and 269 Hv, respectively. The thickness of the surface hardened layer for Ti-15Mo-5Zr-3Al alloy was thinner than those for Ti-6Al-7Nb alloy and CP Ti. The microstructure of the Ti-15Mo-5Zr-3Al alloy casting was confirmed to be β phase.

Key Words: *castability, hardness, microstructure, titanium alloy, titanium*

Introduction

Titanium and its alloys became one of the major metallic biomaterials [1–4]. The reasons for this widespread application in the medical field are outstanding biocompatibility, excellent corrosion resistance and desirable mechanical properties, including high specific strength. In particular, β-type titanium alloys with low elastic modulus have been investigated extensively [1,4–6]. The crystal structure of titanium is hexagonal α-phase at room temperature and changes to cubic β-phase at 882°C. This β-phase shows high ductility as well as low elastic modulus' however, it can only be stabilized at room temperature by the addition of other elements [7], such as Mo, V, Nb and Ta. Among many compositions of β-type titanium alloys investigated for biomedical application, four alloys have been registered in international standards: Ti-13Nb-13Zr (ASTM F 1713), Ti-12Mo-6Zr-2Fe (ASTM F1813), Ti-15Mo (ASTM F2066) and Ti-15Mo-5Zr-3Al (ISO 5832-14) alloys.

Ti-15Mo-5Zr-3Al alloy is one of the β-type titanium alloys and was reported to show excellent corrosion resistance [8] and biocompatibility [7,9], comparable to pure titanium. Due to its superior mechanical and biological properties, Ti-15Mo-5Zr-3Al alloy has been clinically introduced and used as an orthopedic implant material [9].

In dentistry, titanium has been used as a material for dental implants and prostheses. Generally, most of the metallic parts of dental prostheses, including fixed and removable partial dentures, are constructed by a precision casting method using a lost-wax technique, although a precision milling method with CAD/CAM systems has been clinically introduced recently. Due to its high melting temperature and reactivity with oxygen, as compared with conventional dental casting alloys, special casting machines and mold materials are used for the dental casting of titanium [10–13]. Although dental casting systems for titanium have been successfully developed and applied clinically, unalloyed pure titanium has some disadvantages in

Correspondence: Hiroyasu Koizumi, Department of Fixed Prosthodontics, Nihon University School of Dentistry, 1-8-13, Kanda-Surugadai, Chiyoda-ku, Tokyo 101-8310, Japan. Tel: +81-3-3219-8145. Fax: +81-3-3219-8351. E-mail: koizumi@dent.nihon-u.ac.jp

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clinical application, such as low mechanical strength [14], difficulty in polishing [15,16] and poor wear resistance [17]. As such, biomedical α/β-type Ti-6Al-7Nb alloy was introduced as a dental casting alloy [14,17,18] and has been applied clinically in various dental prostheses [19,20].

Since β-type titanium alloys show good ductility of cubic β-phase and flexibility due to low elastic modulus, they could show fracture resistance and applications of large undercut in dental prostheses. With respect to β-type titanium alloy castings, the properties of Ti-Zr alloy [21], Ti-Mo alloy [22] and Ti-Nb based alloys [23] have been reported. However, basic properties of Ti-15Mo-5Zr-3Al alloy showing superior mechanical and biological properties have not been reported as a dental casting alloy.

The aim of this study was to investigate the hardness and microstructure of Ti-15Mo-5Zr-3Al alloy for application to dental cast prostheses.

Materials and methods

Cast specimen preparation

In the present study, the hardness of Ti-15Mo-5Zr-3Al alloy (Kobe Steel, Kobe, Japan) was investigated for the purpose of comparison with Ti-6Al-7Nb alloy (T-Alloy Tough; GC, Tokyo, Japan) and grade 3 commercially pure titanium (CP Ti, T-Alloy H; GC), which are used clinically as dental casting metals. The properties of these metals are summarized in Table I.

The casting ring was a hog-backed ring (ST ring; Selec, Osaka, Japan). The mold was constructed using a magnesia-based investment material (Selevest CB; Selec) according the manufacturer's instructions (water/powder ratio: 0.20). Two hours after the wax pattern was invested, the mold was heated up to 850°C in an electric furnace (KDF-S80; Denken, Kyoto, Japan) at a heating rate of 6°C/min and was maintained at this temperature for 1 h. The mold was then cooled to 120°C inside the furnace. Each metal ingot (30 g) was placed in a dental casting machine (Ticast Super R; Selec) and the melting/casting chamber was evacuated to 7×10^{-2} Pa. The metal ingot was then arc-melted (210 A, electrode distance 6 mm) for 60 s at a pressure of 2.8×10^{4} Pa in a high-purity argon atmosphere and then centrifugally cast into the mold. These casting conditions were set according to the manufacturer's instructions for titanium and titanium alloys. The resulting castings were bench-cooled without removing the mold from the casting. The castings were cleaned by a ultrasonic cleaner and air-abraded with 50–70-μm-grain alumina (Hi Aluminas; Shofu) for 30 s (Jet Blast II; J. Morita MFG, Osaka, Japan) at 0.2 MPa.

Hardness test

In order to evaluate the surface reacted layer of the cast specimen with the mold material, a hardness measurement on the transverse cross-section of the specimen was conducted using a microhardness tester (HM-101; Akashi, Yokohama, Japan). The size of the cast specimens was 6 mm in diameter and 5 mm in height. The specimens were embedded in epoxy resin (Epo-thin; Buehler, Lake Bluff, IL) and then wet-ground with a series of silicon carbide papers (#800–2000, WetorDry Tri-M-ite; 3M, St. Paul, MN). Five specimens were tested for each condition. Hardness measurement was carried out from the surface of the specimen toward the center at an interval of 50 μm and measurements were conducted five times at each position. The Vickers hardness number was determined by applying a load of 0.98 N for 15 s. The bulk hardness values were measured at a distance of approximately 400 μm from the surface [24] and were analyzed through Kruskal-Wallis test (SPSS) and Steel-Dwass multiple comparison test (Kyplot 5.0). P-values of less than 0.05 were considered to be statistically significant.

Microscopic observation

The specimen size was 6 mm in diameter and 5 mm in height. All specimens were embedded in epoxy resin (Epo-thin) and then wet-ground with silicon carbide papers. The ground specimens were then polished with felt buff and a diamond suspension (0.25 μm, Metadi; Buehler). After polishing, the cast specimens were treated with a corrosive solution of 1% hydrofluoric acid and 13% nitric acid for 8 s. The microstructures of the surface reacted layer and the inner bulk part were observed using an optical microscope (Optiphot; Nikon, Tokyo, Japan) at ×100 magnification.

Table I. Metals used in this study.

Metal	Manufacturer	Lot number	Composition (mass%)
Ti-15Mo-5Zr-3Al	Kobe Steel Ltd.	AC7552	Ti:87.0, Mo:15.0, Zr:5.0, Al:3.0
Ti-6Al-7Nb	GC Corp.	0702261	Ti:86.5, Nb:7.0, Al:6.0, Fe+Ta:0.5
CP Ti	GC Corp.	070611	Ti: > 99.2, Fe: < 0.30

X-ray diffractometry

Cast specimens were constructed from Ti-15Mo-5Zr-3Al alloy, Ti-6Al-7Nb alloy and CP Ti. Five specimens were prepared for each metal and the specimen size was 6 mm in diameter and 5 mm in height. The top surface of the specimen was ground to remove the reacted layer. X-ray diffraction (XRD) patterns of the three metals were obtained with Ni-filtered Cu Kα radiation using an X-ray diffractometer (Miniflex II; Rigaku, Tokyo, Japan) operated at 30 kV and 15 mA. The central part of the specimen was used for detection. The scan rate was 2.0°/min and the range of 2θ was between 3–110°. Peak analysis was performed using analytical software (PDXL ver.1.0.7.1; Rigaku) and the index of the International Centre for Diffraction Data (ICDD; Newton Square, PA).

Results

Hardness

The results of the bulk hardness number, i.e. the hardness of the inner part at a depth of 300–500 μm, are summarized in Table II. Ti-6Al-7Nb alloy exhibited the highest bulk hardness (384 Hv, category a), followed by Ti-15Mo-5Zr-3Al alloy (361 Hv, category b) and CP Ti (269 Hv, category c) in that order. Changes in the hardness of the cross-sections from the surface to a depth of 600 μm for the metal castings are summarized in Figure 1. Figure 1A shows the hardness of the Ti-15Mo-5Zr-3Al alloy castings. The hardness in the surface layer of approximately 150 μm in thickness increased from the bulk hardness. Figure 1B shows the hardness of the Ti-6Al-7Nb alloy castings, in which the hardness in the surface layer of approximately 200 μm in thickness increased from the bulk hardness. Figure 1C shows the hardness of the CP Ti castings, in which the hardness in the surface layer of approximately 250 μm in thickness increased from the bulk hardness.

Microstructures and constituent phases

Figure 2 shows the microstructures of the surface area of the castings obtained by optical microscopy. In each micrograph, the surface layer reacted with the mold was observed, which consisted of coarse acicular crystals. Below the surface layer, large grains of β phase were observed for Ti-15Mo-5Zr-3Al alloy (Figure 2A), whereas fine acicular structures were

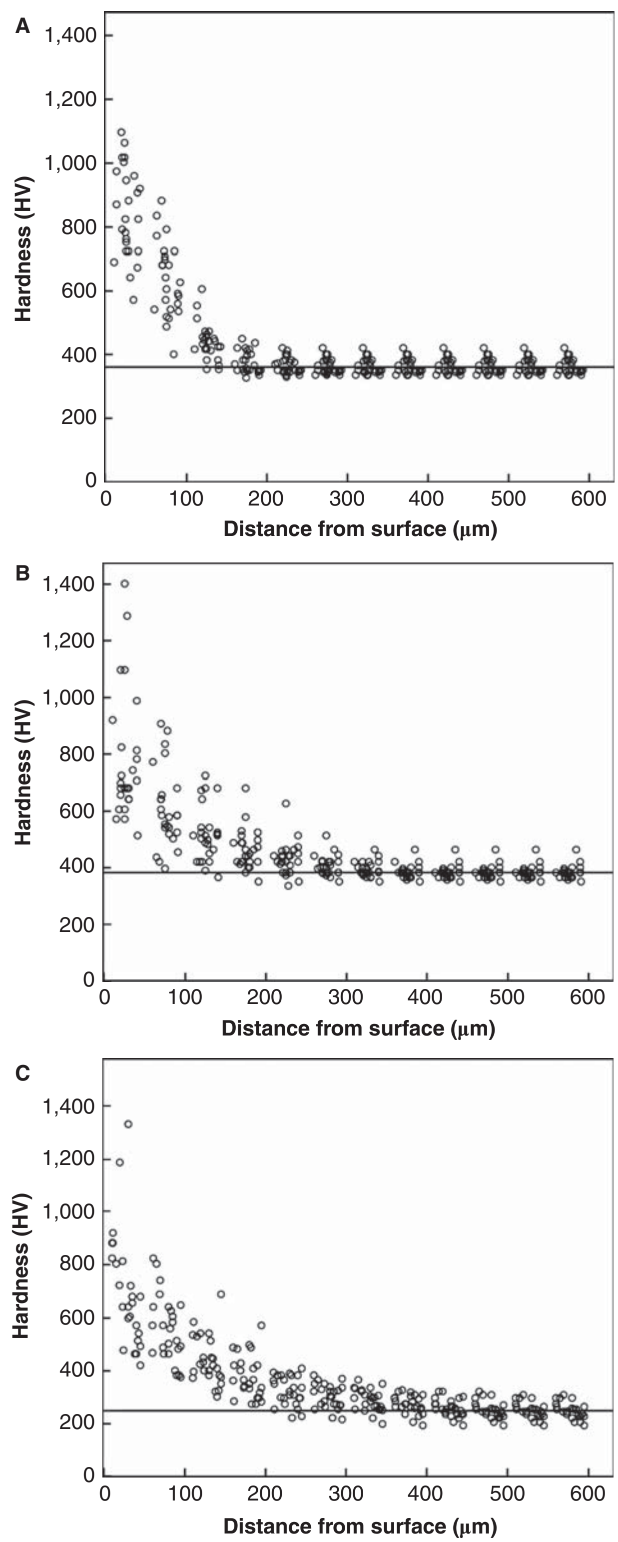

Figure 1. Changes in microhardness of the castings: (A) Ti-15Mo-5Zr-3Al alloy, (B) Ti-6Al-7Nb alloy and (C) CP Ti. The horizontal lines in the graphs show the mean bulk hardness (Table II).

Table II. Hardness of the inner part of the castings (H_V).

Metal	Mean (SD)	Median	IQR	Category
Ti-15Mo-5Zr-3Al	361 (24)	351	37	b
Ti-6Al-7Nb	384 (23)	383	21	a
CP Ti	269 (35)	264	51	c

$n = 5$; SD, standard deviation; IQR, Interquartile range.
Statistic category, different letters indicate that they are statistically different ($p < 0.05$).

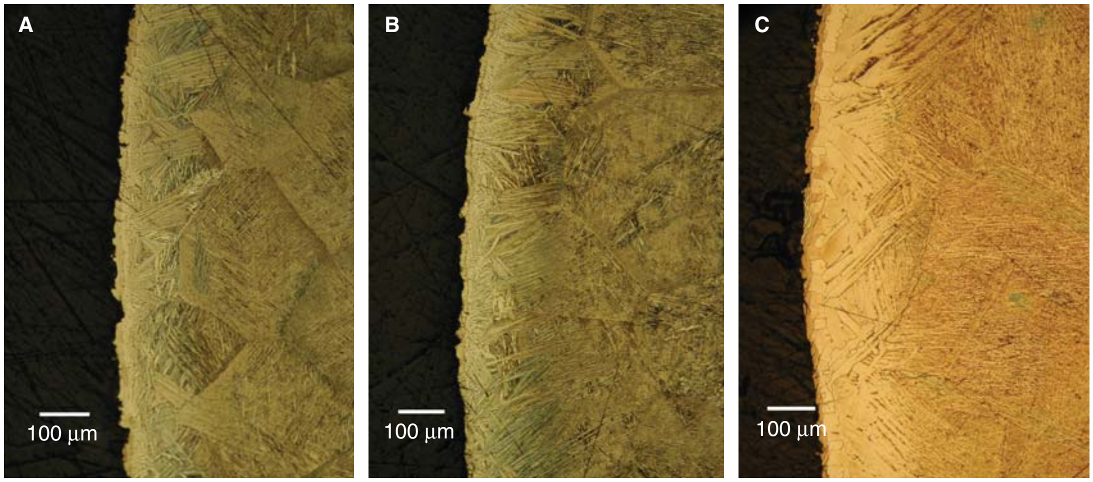

Figure 2. Microstructures of the castings: (A) Ti-15Mo-5Zr-3Al alloy, (B) Ti-6Al-7Nb alloy and (C) CP Ti.

observed for CP Ti (Figure 2C). The inner part below the surface layer for Ti-6Al-7Nb alloy exhibited a microstructure of acicular crystals precipitated in β phase grains (Figure 2B).

Figure 3 shows the XRD patterns of Ti-15Mo-5Zr-3Al alloy, Ti-6Al-7Nb alloy and CP Ti castings. Ti-15Mo-5Zr-3Al alloy castings consisted of only body-centered cubic (bcc) β phase. The main specific peaks for Ti-15Mo-5Zr-3Al alloy existed at 38.6°, 56.0°, 70.3°, 83.5° and 96.2° (Figure 3A). For Ti-6Al-7Nb alloy castings, hexagonal α and β phases were detected and the main specific peaks were at 38.7°, 55.6°, 70.3°, 83.5° and 96.0° (Figure 3B). Only α phase was detected for CP Ti castings. Specific peaks of α phase existed at 34.6°, 37.9°, 39.6°, 52.5°, 62.4°, 70.1°, 75.7°, 76.9° and 101.9°, whereas unknown peaks existed at 20.4°, 92.3°, 105.4° and 108.7° (Figure 3C).

Discussion

The hardness at the surface layer was higher than the bulk hardness for the all metal castings. The main reason for this increase in hardness is the formation of a surface layer reacted with oxygen and other substitutional elements in the mold [10–12]. As shown in Figure 1, the thickness of the hardened layer was different among the three metals. The thickness of the hardened layer for Ti-15Mo-5Zr-3Al alloy was estimated to be 150 μm, whereas those for Ti-6Al-7Nb alloy and CP Ti were 200 and 250 μm, respectively. This tendency of the thickness of the surface reacted layer was also observed in the microscopic observation of the microstructures (Figure 2). According to a previous paper describing the relation between the thickness of surface reacted layer and the marginal adaptation of fixed dental prostheses, the thinner reacted layer exhibited better marginal adaptation [12]. This indicates that the thin surface reacted layer of Ti-15Mo-5Zr-3Al alloy may result in good marginal adaptation of cast dental prostheses.

Ti-6Al-7Nb alloy exhibited the highest bulk hardness, followed by Ti-15Mo-5Zr-3Al alloy and CP Ti. Since the hardness value is defined in terms of the size of indentation marks, the hardness value is affected by the resultant indentation depth after the unloading process [25]. Therefore, the hardness value correlates with yield strength [26], flow stress [27] and elastic modulus.

Ti-6Al-7Nb alloy was reported to exhibit higher hardness than CP Ti in castings due to the presence of a refined two-phase structure of α and β phases [18]. In the present study, these α and β phases were detected through XRD analysis of Ti-6Al-7Nb alloy castings and microstructure observation revealed a two-phase structure with acicular α crystals in β phase grains. With respect to the Ti-Mo binary alloys, β phase alloys containing 10% or more molybdenum were reported to exhibit high hardness [22]. In the present study, although Ti-15Mo-5Zr-3Al alloy included 3% aluminum, which is an α phase stabilizer for titanium, in the composition, only β phase was detected by XRD analysis. Therefore, it was confirmed that Ti-15Mo-5Zr-3Al alloy consisted of dominant β phase structure after dental casting.

Conclusions

The hardness and microstructures of Ti-15Mo-5Zr-3Al alloy dental castings were investigated and compared with those of Ti-6Al-7Nb alloy and CP-Ti for application in dental prostheses.

The bulk hardness of Ti-15Mo-5Zr-3Al alloy at the inner part of the castings was 361 Hv, whereas those of Ti-6Al-7Nb alloy and CP Ti were 384 and 269 Hv, respectively. The thickness of the surface hardened layer for Ti-15Mo-5Zr-3Al alloy, which was estimated to be 150 μm, was thinner than those

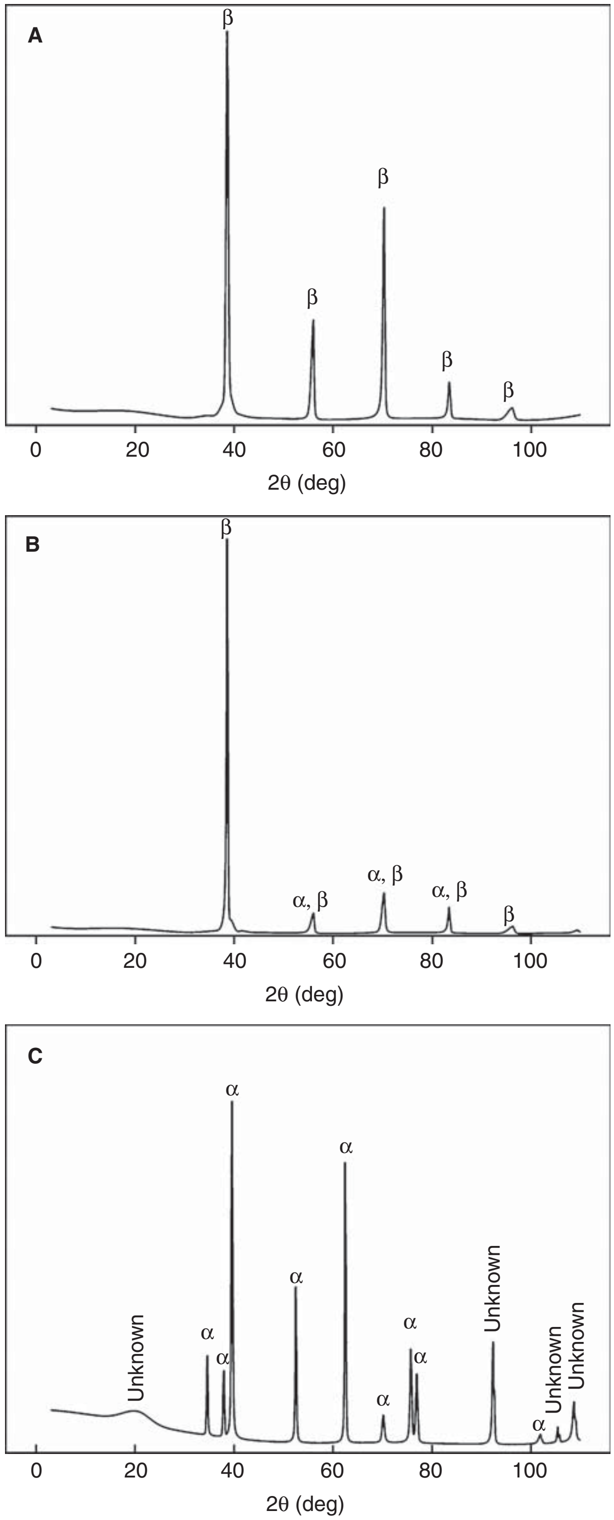

Figure 3. X-ray diffractogram of the castings: (A) Ti-15Mo-5Zr-3Al alloy, (B) Ti-6Al-7Nb alloy and (C) CP Ti.

for Ti-6Al-7Nb alloy and CP Ti. Microscopic observation revealed that the surface reacted layer consisted of coarse acicular crystals for the three metals tested. Below the surface layer, a large β grains phase was observed for Ti-15Mo-5Zr-3Al alloy, whereas fine acicular structures of the α phase were observed for Ti-6Al-7Nb alloy and CP Ti. The microstructure of Ti-15Mo-5Zr-3Al alloy was confirmed to be β phase structure after dental casting by XRD analysis.

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