Mechanical properties of dental Ti-Ag alloys with 22.5, 25, 27.5, and 30 mass% Ag

Masatoshi TAKAHASHI†, Masafumi KIKUCHI‡ and Yukyo TAKADA†

INTRODUCTION

The biocompatibility of Ti and its good corrosion resistance explain its wide use in dentures and dental implants. However, pure Ti lacks the strength required for dental prostheses such as clasps and bridges. As part of our research into new dental Ti alloys with enhanced mechanical properties, we prepared experimental Ti-Ag alloys containing up to 20 mass% Ag (hereafter, “%” stands for “mass%”) and investigated their properties. The strength and hardness of the alloys was found to increase with their Ag content, while their elongation at break decreased. The changes in the mechanical properties upon alloying were assigned to solid-solution strengthening of the α-titanium phase, to Ti2Ag precipitation, and to the formation of eutectic structures composed of α+Ti2Ag. The addition of Ag, at 25 mass% in particular, improves the mechanical properties of these alloys, making them suitable for high strength dental prostheses, such as implant-retained superstructures and narrow-diameter implants.

Keywords: Mechanical property, Titanium alloy, CAD/CAM, Dental implant, Ti-Ag alloy

The mechanical properties—tensile strength, yield strength, elongation after fracture, Vickers hardness, and Young’s modulus—and the phases of Ti-Ag alloys were investigated, as prepared with 22.5, 25, 27.5, and 30 mass% Ag. The tensile strength, yield strength, hardness, and Young’s modulus of the alloys increase with their Ag content up to 25 mass%, but their breaking elongation decreases. These changes in the mechanical properties are attributed to solid-solution strengthening of the α-titanium phase, to Ti2Ag precipitation, and to the formation of eutectic structures composed of α+Ti2Ag. The addition of Ag, at 25 mass% in particular, improves the mechanical properties of these alloys, making them suitable for high strength dental prostheses, such as implant-retained superstructures and narrow-diameter implants.

The yield strength (proof strength of 0.2% non-proportional extension) of the Ti-20%Ag alloy satisfied the standards for annealed type 4 dental casting alloys according to ANSI/ADA Specification No. 59, suggesting that this composition can be used for long-span bridges. Since the bond strength between Ti-Ag alloys with 10–20%Ag and porcelain was found to be above the minimum value specified in the ISO 9693 standard, they can also be used for porcelain-fused-to-metal crowns.

Because the machinability of Ti is poor, cutting, grinding, and polishing Ti dental prostheses is difficult. This poor machinability also poses a serious practical problem for the milling of Ti with dental CAD/CAM systems. The grindability (i.e., the ease of grinding and polishing) of Ti has been shown to improve on alloying with Ag, especially at 20% Ag. Furthermore, Ti-Ag alloys have been shown to be more machinable than Ti, in terms of the cutting force required for alloys containing 20% and 30% Ag, and in terms of tool life for the Ti-20%Ag composition. This improved machinability has been explained by the precipitated intermetallic compounds working as free-cutting additives in the free-cutting materials, as well as to the reduced breaking elongation of the alloys. These results reveal that compared with pure Ti, Ti-Ag alloys shorten the machining time, thereby extending tool life, and are therefore good candidates for dental CAD/CAM alloys.

Regarding bioactivity, Ti-Ag alloys with 20% and 25% Ag have been reported to inhibit artificial biofilm formation. Custom abutments made from Ti-20%Ag alloy may therefore prolong the life of dental prostheses by preventing biofilm infection. Similar to Ti furthermore, CaP have been shown to form spontaneously on Ti-20%Ag and Ti-25%Ag alloys immersed in simulated body fluid. The biocompatibility of Ti-Ag alloys makes them suitable for use as dental and orthopedic implants. Ti-Ag is therefore a promising dental machining alloy, especially for dental implant applications.

Although the intermetallic compounds that precipitate in Ti-Ag alloys improve their mechanical properties and/or machinability, they may also diminish their corrosion resistance. In cast Ti-Ag alloys, the alloy phases Ti2Ag and TiAg appear respectively at 20% and 27.5% Ag, and increase in concentration with the Ag content of the alloy. The corrosion resistance of these alloys has also been investigated. Anodic polarization tests demonstrate that the Ti-25%Ag alloy is suitable for dental applications, while elution tests (that quantify the ions released in solution) show that the corrosion resistance of this alloy is superior to that of Ti-6Al-4V. These studies reveal that the precipitation of Ti2Ag in the Ti-25%Ag alloy does not significantly degrade (in terms of dental applications) its corrosion resistance.

Dental prostheses, such as implant-retained superstructures, wide-span bridges, and clasps,
require higher-strength materials. Alloying with 20% Ag is favorable in this context, due to solid-solution strengthening and the formation of intermetallic compounds. Further strengthening can therefore be expected by increasing the Ag and thereby the intermetallic compound concentrations. Although the corrosion resistance of Ti-Ag alloys containing up to 25% Ag was shown to be sufficient\(^{14-16}\), the mechanical properties of these alloys have not been investigated to date. Here, in continuation of our previous study\(^3\), Ti-Ag alloys with Ag contents of up to 30% were prepared and evaluated in terms of their mechanical properties and microstructure.

**MATERIALS AND METHODS**

**Preparation of specimens**

Ti-Ag alloys with 22.5%, 25%, 27.5%, and 30% Ag were prepared. The desired amounts of Ti sponge (>99.8%, grade S-90, Osaka Titanium technologies, Amagasaki, Japan) and pure Ag (>99.9%, Hirano Seizaemon Shoten, Tokyo, Japan) were melted in an argon-arc melting furnace (TAM-4S, Tachibana Riko, Sendai, Japan) to form a 15 g ingot for each alloy, as in previous studies\(^3,8,14\).

The ingots of each Ti-Ag alloy were cast into testing specimens using a magnesia investment (Selevest CB, Selec, Osaka, Japan) in an argon gas-pressure dental casting machine (Castmatic-S, Iwatani, Osaka, Japan) at 200°C and then bench-cooled. The specimens for tensile tests were 3.0 mm in diameter and 15 mm in gauge length, while for the hardness tests, Young’s modulus tests, and X-ray diffraction experiments, 3.5 mm×8.5 mm×30.5 mm slabs were prepared. All the cast slabs were abraded to a depth of 250 µm using 180–800 grit SiC paper to remove their hardened surface layer.

**Tensile tests**

Tensile tests were carried out using a universal testing machine (DSS-2000, Shimadzu, Kyoto, Japan) at a crosshead speed of 0.5 mm•min\(^{-1}\) at room temperature (\(n=6\)). The ultimate tensile strength, yield strength (proof strength of 0.2% non-proportional extension), and the elongation after fracture were determined. The fractured surfaces were observed by scanning electron microscopy (SEM, JSM-6060, JEOL, Tokyo, Japan).

**Hardness tests**

The Vickers hardness of the specimens was determined using a micro Vickers hardness tester (HM-102, Mitutoyo, Kawasaki, Japan) with a 1.961 N load and a 30 s dwell time. Tests (\(n=9\)) were conducted at three randomly chosen points on each specimen.

**Measurement of Young’s modulus**

The Young’s modulus of the samples was measured (\(n=3\)) using the ultrasonic-pulse method, with an ultrasonic pulser/receiver (5800, Panametrics, Waltham, MA, USA) and ultrasonic transducers (M208 and V156, Panametrics), as described previously\(^{10}\).

**X-ray diffractometry**

X-ray diffraction (XRD) was performed at room temperature using Cu Kα radiation generated at 30 kV and 10 mA in an X-ray diffractometer (Miniflex CN2005, Rigaku, Tokyo, Japan). The peaks in the XRD patterns were indexed to an X-ray polycrystalline powder diffraction file (PDF-2, JCPDS-ICDD 2004).

**Statistical analysis**

The data obtained were submitted to one-way ANOVA and Scheffé’s statistical tests at a significance level of \(\alpha=0.05\), and compared with those obtained for pure Ti and Ti-Ag alloys with up to 20% Ag reported previously\(^3,0\).

**RESULTS**

**Tensile properties**

The tensile and yield strength of Ti-Ag alloys are plotted in Fig. 1 as a function of their Ag content, including the data for Ti and Ti-5–20%Ag alloys obtained in a previous study\(^3\). Both the tensile and yield strength increase with the Ag concentration, and are significantly higher (\(p<0.01\)) than for pure Ti in all alloys other than the Ti-5%Ag composition. The tensile and yield strengths increase markedly from 20% to 25% Ag and both peak at the latter concentration, at values of 694 MPa and 548 MPa, respectively. The difference in tensile strength between the 30% Ag alloy and pure Ti is not significant (\(p=0.05\)). This alloy was too brittle for yield strength tests.

The elongation after fracture of the Ti-Ag alloys is shown in Fig. 2 as a function of their Ag content, including as for Fig. 1 data from the previous study\(^3\). The elongations after fracture of the samples decreases as their Ag content increases, being significantly lower (\(p<0.01\)) than that of pure Ti for all alloys other than Ti-5%Ag. The decrease is more marked beyond 20% Ag. The specimens containing 25% and 27.5% Ag have breaking elongations of 3.3% and 2.4%, respectively. As mentioned above, the 30% Ag sample was very brittle, with a breaking elongation of ~0%.

**Fractography**

Figure 3 shows SEM images of typical fractured surfaces following tensile tests. Dimples, which are a feature of a ductile fracture, are visible for the 22.5–27.5% Ag samples (Figs. 3a–c). The dimpled area becomes smaller as the Ag concentration increases. A grain boundary fracture and/or a cleavage fracture are observed in the micrograph obtained for the 30% Ag alloy (Fig. 3d). Figures 3e–h reveal lamellar structures in the matrix grains for all Ti-Ag alloys. Microshrinkage, which was similar to that observed in the previous study\(^3\), was found in some specimens of these alloys.

**Hardness**

Figure 4 shows that the Vickers hardness of the Ti-Ag alloys increases with their Ag content, and is significantly higher (\(p<0.01\)) than that of pure Ti for all
compositions with more than 5% Ag. The 20% and 25% Ag alloys have a similar hardness (229–237), while that of the 30% Ag alloy is higher (264).

Young's modulus
Figure 5 reveals that the Young’s modulus of the Ti-Ag alloys decreases for Ag contents up to 20%, but increases thereafter. The Young’s modulus of the 20% Ag sample is significantly lower than that of Ti (p<0.01).

X-ray diffractometry
The XRD patterns obtained for the Ti-Ag alloys are displayed in Fig. 6. Peaks characteristic of α-titanium and of Ti2Ag are observed for all the alloys studied here. In contrast, no TiAg peaks are visible in any of the diffractograms. The number of matched Ti2Ag peaks tends to increase with the Ag content of the specimens.
DISCUSSION

In previous studies\textsuperscript{14-16} we found that the Ti\textsubscript{2}Ag and TiAg phases appeared at 20\% and 27.5\% Ag, respectively, and that the amount of both phases increased with the Ag concentration. We also reported that since a threshold concentration of intermetallic compounds has to be reached for the corresponding XRD peaks to be detected, those arising from the Ti\textsubscript{2}Ag and TiAg phases are only seen in the diffractograms from alloys with more than 22.5\% and 40\% Ag, respectively\textsuperscript{14,16}. The XRD results obtained support this interpretation. The increase in the strength of Ti-Ag alloys with up to 20\% Ag was mainly attributed to solid-solution strengthening\textsuperscript{30}. The greater increase observed here however for the Ti-Ag alloys with 20–25\% Ag is probably caused by Ti\textsubscript{2}Ag precipitation. The Ti-Ag system is eutectic with a eutectoid at 15.6\% Ag and 855°C\textsuperscript{17}. However, no microstructural evidence was found for the eutectic structure in fracture surfaces of the cast alloys with less than 20\% Ag\textsuperscript{14,16}. Since Ti-Ag alloys undergo a massive transformation from the β to the α phase, which depends on the cooling rate and composition\textsuperscript{15}, it is probable that little or no eutectic reaction occurs in Ti-Ag alloys with less than 20\% Ag when they are cast and then bench-cooled\textsuperscript{14}. On the other hand, lamellar structures, which may be regarded as eutectic structures composed of α+Ti\textsubscript{2}Ag phases, are found here at the fracture surfaces of the alloys containing more than 22.5\% Ag. This eutectic structure, as well as the Ti\textsubscript{2}Ag precipitation, probably contributes to the marked increase in strength of Ti-Ag alloys between 20\% and 25\% Ag. The increase in hardness could also be caused by solid-solution hardening, precipitated intermetallic compounds, and eutectic structures. The decrease in strength of the alloys above 25\% Ag is attributed to their embrittlement at higher Ag contents.

Although the increase in the concentration of intermetallic compounds leads to reduced breaking elongation for the Ti-Ag alloy with more than 20\% Ag, they remain ductile for Ag contents up to 27.5\%. The dimples revealed by SEM support a ductile fracture mechanism. Microshrinkage was found in some specimens, possibly due to the wide range of solidification temperatures for this system, as revealed by its equilibrium phase diagram\textsuperscript{18}. Since microshrinkage decreases the strength and breaking elongation of alloys, wrought Ti-Ag alloys may be preferable in this context.

A grain boundary and/or cleavage fractures are observed for the brittle 30\% Ag sample. This embrittlement is the result of large-scale intermetallic compound (Ti\textsubscript{2}Ag and TiAg) precipitation at the grain boundaries. Similar phenomena have been reported for other eutectic Ti alloys. Ti\textsubscript{2}Cu phase precipitates at Cu concentrations above 5\% in Ti-Cu alloys, which become brittle at 10\% Cu\textsuperscript{1,10}, while Ti-Au alloys become brittle at 40\% Au due to the precipitation of Ti\textsubscript{3}Au for Au contents above 30\%\textsuperscript{20,21}. Eutectic Ti alloys become brittle when the concentration or size of the intermetallic compounds becomes large. In our previous studies of Ti-Ag alloys, we found that the precipitated Ti\textsubscript{2}Ag particles were fine and well dispersed, while TiAg precipitation was concentrated at grain boundaries\textsuperscript{14-16}. This TiAg phase was furthermore found to diminish the corrosion resistance of the alloy because it dissolves preferentially at low potentials\textsuperscript{14-16}. Therefore, Ti-Ag alloys with up to 25\% Ag, in which only Ti\textsubscript{2}Ag precipitated, are good candidates for dental applications, both in terms of their corrosion resistance and breaking elongation.

Although the Young’s modulus decreases for Ag concentrations up to 20\% because Ag has a lower

![Fig. 5](image1.png) Young’s modulus of Ti-Ag alloys as a function of their Ag content.

![Fig. 6](image2.png) X-ray diffraction patterns obtained from Ti-Ag alloys with different Ag contents.
modulus than Ti, it increases thereafter due to the precipitation of intermetallic compounds\(^6\). The increase in both the Vickers hardness and Young's modulus of the alloys in going from 25% to 27.5% Ag is greater than from 20% to 25% Ag, suggesting that TiAg is harder and has a larger Young's modulus than Ti\(_2\)Ag. The yield strength, elongation after fracture, and Young's modulus of the Ti-25%Ag satisfy the ISO 22674 criteria for type 4 metallic materials\(^5\). The Ti-25%Ag alloy is therefore an appropriate material for implant-retained superstructures. Hardness is not one of the mechanical properties included in this ISO standard; it is noteworthy nonetheless that the Vickers hardness of Ti-25%Ag is similar to that of hardened type 4 dental gold casting alloys while being lower than that of Ti-6Al-4V\(^22\).

In recent years, narrow-diameter implants have been developed to reduce bone damage and achieve minimally invasive treatment, leading to push towards stronger implant materials to maintain the support they provide. The commercially pure (CP) grade 4 Ti and the Ti-6Al-4V alloy used for narrow-diameter implants contains Fe impurities, as well as Al and V for the latter\(^1\). Since these elements are known allergens and/or toxic, the development of safer alloys, such as Ti-3Al-2.5V, is desired. Our previous study\(^1,10,11\) demonstrated that the bioconductivity and biocompatibility of Ti-Ag alloys make them suitable for the fabrication of dental and orthopedic implants. Here, we show that the Ti-25%Ag alloy can be used for narrow-diameter implants, since its strength matches that of CP grade 4 Ti\(^12,22\).

Adding 20% and 30% Ag has been shown to improve the machinability of Ti-Ag alloys\(^8,10,11\). This is probably due to the dispersion throughout the matrix of precipitated intermetallic compounds, which may function as free-cutting additives for the free-cutting materials. Here, the enhanced machinability of the Ti-25%Ag is attributed to the precipitation of fine TiAg particles throughout the alloy. The properties characterized in this study for the Ti-25%Ag alloy demonstrate its attractiveness for CAD/CAM dental applications.

ACKNOWLEDGMENTS
The authors gratefully acknowledge the suggestions and advice received from Dr. Osamu OKUNO, Professor Emeritus of Tohoku University.

REFERENCES
1) ASM Committee on titanium and titanium alloys. Introduction to titanium and its alloys, Metals Handbook 9th ed Vol. 3 Properties and selection: Stainless steels, tool materials and special-purpose metals, ASM Int, Metals Park, 1980, p. 353-380.
2) ISO 22674. Dentistry —Metallic materials for fixed and removable restorations and appliances. ISO, Switzerland, 2006, p. 1-22.
3) Takahashi M, Kikuchi M, Takada Y, Okuno O. Mechanical properties and microstructures of dental cast Ti-Ag and Ti-Cu alloys. Dent Mater J 2002; 21: 270-280.
4) Kikuchi M, Takahashi M, Okuno O. Elastic moduli of cast Ti-Au, Ti-Ag, and Ti-Cu alloys. Dent Mater 2006; 22: 641-646.
5) ANSI/ADA Specification No. 5. Dental casting alloys. ADA, Illinois, 1997, p.1-12.
6) Yoda M, Kono T, Takada Y, Iijima K, Griggs J, Okuno O, Kimura K, Okabe T. Bond strength of binary titanium alloys to porcelain. Biomaterials 2001; 22: 1675-1681.
7) Chandler HE. Machining of reactive metals. Metals Handbook 9th ed. Vol. 16 Machining, ASM Int, Metals Park, 1989, p. 844-847.
8) Kikuchi M, Takahashi M, Okabe T, Okuno O. Grindability of dental cast Ti-Ag and Ti-Cu alloys. Dent Mater J 2003; 22: 191-205.
9) Kasahara H, Sato H, Kameyama Y, Sato H, Oyaizu Y, Shimpoo R, Tooe S, Takahashi M. Precision polishing of purity titanium and Ti-Ag alloys for dentistry. J Jpn Soc Abrasive Technol 2014; 58: 777-778.
10) Kikuchi M, Takahashi M, Okuno O. Machinability of experimental Ti-Ag alloys. Dent Mater J 2008; 27: 216-220.
11) Inagaki R, Yoda M, Kikuchi M, Kimura K, Okuno O. Machinability evaluation of a Ti-Ag alloy using a dental CAD/CAM. J Dent Res 2008; 87B: 1830.
12) Nakajo K, Takahashi M, Kikuchi M, Takada Y, Okuno O, Sasaki K, Takahashi N. Inhibitory effect of Ti-Ag alloy on artificial biofilm formation. Dent Mater J 2014; 33: 389-393.
13) Takahashi M, Kikuchi M, Hatori K, Orii Y, Sasaki K, Takada Y. Calcium phosphate formation on Ti-Ag alloys in simulated body fluid. J Biomech Sci Eng 2009; 4: 318-325.
14) Takahashi M, Kikuchi M, Takada Y, Okabe T, Okuno O. Electrochemical behavior of cast Ti-Ag alloys. Dent Mater J 2006; 25: 516-523.
15) Takahashi M, Kikuchi M, Takada Y, Okuno O. Corrosion resistance of dental Ti-Ag alloys in NaCl solution. Mater Trans 2010; 51: 762-766.
16) Takahashi M, Kikuchi M, Takada Y. Corrosion behavior of Ti-Ag alloys used in dentistry in lactic acid solution. Met Mater Int 2011; 17: 175-179.
17) Han MK, Hwang MJ, Won DH, Kim YS, Song HJ, Park YJ. Massive transformation in titanium-silver alloys and its effect on their mechanical properties and corrosion behavior. Materials 2014; 7: 6194-6206.
18) Murray JL, Bhansali KJ. The Ag-Ti system. Phase diagrams of binary titanium alloys, ASM Int, Materials Park, 1987, p. 6-11.
19) Kikuchi M, Takada Y, Kiyosue S, Yoda M, Woldu M, Cai Z, Okuno O, Okabe T. Mechanical properties and microstructures of cast Ti-Cu alloys. Dent Mater 2003; 19: 174-181.
20) Takahashi M, Kikuchi M, Takada Y, Okuno O, Okabe T. Corrosion behavior and microstructures of experimental cast Ti-Au alloys. Dent Mater J 2004; 23: 109-116.
21) Takahashi M, Kikuchi M, Okuno O. Mechanical properties and grindability of experimental Ti-Au alloys. Dent Mater J 2004; 23: 203-210.
22) O'Brien WJ. Tabulated values of physical and mechanical properties, Dental materials and their selection 3rd ed, Quintessence, Illinois, 2002, p. 309-385.