

Corrosion Resistance of Dental Ti-Ag Alloys in NaCl Solution

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The purpose of this study was to evaluate the corrosion resistance of experimental dental Ti-Ag alloys in 0.9% NaCl solution. Open-circuit potential (OCP) measurement and elution tests of the alloys with 5–30% Ag were performed. The amounts of both Ti and Ag ions released from the alloys with Ag \leq 20% were below the detection limit. A very small amount of Ti ions was released from some of the 22.5% Ag specimens and some of the 25% Ag specimens. The time for the Ti-Ag alloys with 5–25% Ag to become the stable potential was earlier than that for titanium, and the OCP of the alloys was higher than that of titanium. These results indicated that the corrosion resistance of the alloys with 5–25% Ag was equivalent to that of titanium. On the other hand, it was suggested that the precipitation of TiAg deteriorated the corrosion resistance of Ti-Ag alloys because TiAg dissolved preferentially in the NaCl solution. Ti-Ag alloys with 5–25% Ag can be used not only as dental restorative materials but also as dental implant materials. [doi:10.2320/matertrans.M2009355]

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1. Introduction

Among various dental metals, titanium has a reputation for excellent biocompatibility, good corrosion resistance, and high specific tensile strength and has been used for dental implants or metal base dentures. However, titanium has some problems, such as poor machinability and insufficient strength for some dental applications that require comparatively high strength.¹⁾ As part of our studies developing a new dental titanium alloy with enhanced machinability and mechanical properties, we prepared experimental Ti-Ag alloys and investigated their properties.^{2–5)} The machinability of the Ti-Ag alloys with 20 and 30 mass% Ag was superior to that of titanium (hereafter, “mass%” will be referred to as “%”).^{2,3)} The strength and hardness of the alloys with 5–20% Ag became higher as the Ag concentration increased.⁴⁾ The bond strengths between the alloys with 10–20% Ag and dental porcelain were found to be above the minimum value required by ISO 9693 specifications.⁶⁾ On immersion in simulated body fluid, calcium phosphates, which enhance biocompatibility and facilitate osseointegration, were spontaneously formed on the Ti-Ag alloys with 20% and 25% Ag.⁷⁾ From these studies, Ti-Ag alloys were found to have a potential as dental alloys.

Dental alloys should have good corrosion resistance, since they are used in the human mouth. Although titanium has good corrosion resistance, alloying may reduce its corrosion resistance, especially when the alloying gives rise to the precipitation of intermetallic compounds such as Ti-Ag system. In a previous study, anodic polarization tests were performed in a 0.9% NaCl solution to characterize the relationship between the corrosion resistance and microstructures of Ti-Ag alloys with 5–40% Ag.⁸⁾ Ti-Ag alloys with up to 17.5% Ag, which formed a single α titanium structure, had excellent corrosion resistance, similar to that of titanium. The Ti-Ag alloys with 20–25% Ag contained α titanium and Ti₂Ag. The Ti₂Ag on the specimen surfaces dissolved preferentially at 0.29 V vs. NHE (hereafter, “V vs. NHE” will be referred to as “V”). However, the 20–25% Ag alloys passivated again immediately after the preferential dissolution. The Ti-Ag alloys with 27.5–30% Ag contained

α titanium and Ti₂Ag, or α titanium, Ti₂Ag, and TiAg, and they showed a breakdown potential of about 0.21 V. The 27.5–30% Ag alloys did not passivate again after the breakdown. Ti-40%Ag consisted of α titanium, Ti₂Ag, and TiAg and corroded remarkably. TiAg dissolved at 0.09 V. From the results of the anodic polarization test, we concluded that alloys with up to 25% Ag can be used for dental applications.

The quantitative determination of dissolved ions is essential in corrosion tests specified in ISO, ASTM, or JIS.^{9–11)} The level of dissolved ions is considered to be the most direct index of corrosion that would exert an immediate effect on living tissue.¹²⁾ In recent years, metal ions released from dental alloys have been considered to be a cause of metal allergy.¹³⁾ Among the elements that have been used in the dental alloys, titanium and silver pose the lowest risk of metal allergies.¹⁴⁾ Moreover, it has been reported that the Ti-25%Ag alloy is not mutagenic and imposes minimal risks associated with cytotoxicity.¹⁵⁾ Nevertheless, the amount of ions released from the Ti-Ag alloy should be as low as possible. In addition to anodic polarization tests, it is necessary to examine the corrosion resistance of the Ti-Ag alloys in terms of the amount of released ions. Open-circuit potential (OCP) measurement of alloys is also important in order to determine the dynamic equilibrium potential of the alloys in an electrolyte solution.

In the present study, a series of Ti-Ag alloys with 5–30% Ag was prepared, and OCP measurement and elution tests of the alloys were performed in a 0.9% NaCl solution. The purpose of this study was to evaluate the corrosion resistance of the experimental dental Ti-Ag alloys in terms of the OCP and the amount of released ions.

2. Materials and Methods

2.1 Preparation of specimens

The equilibrium phase diagram of Ti-Ag system¹⁶⁾ are shown in Fig. 1. Experimental Ti-Ag alloys with 5, 10, 17.5, 20, 22.5, 25, 27.5, and 30% Ag were examined in the present study. The desired amounts of titanium sponge (>99.8%, grade S-90, OSAKA Titanium technologies Co., Ltd.,

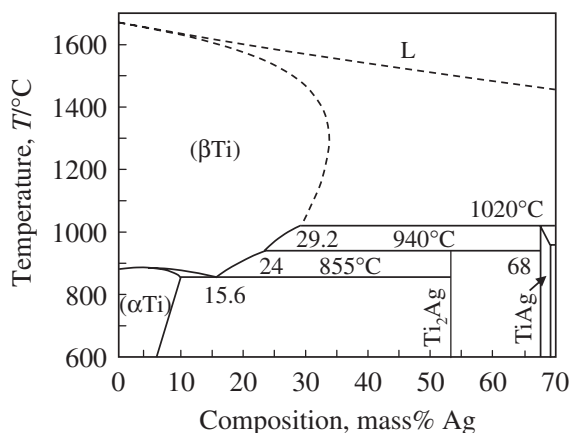


Fig. 1 Equilibrium phase diagram for Ti-Ag system.¹⁶⁾

Amagasaki, Japan) and pure silver (>99.99%, Ishifuku Metal Industry Co., Ltd., 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. Titanium ingots were made from the titanium sponge in the same way.

Ingots of each Ti-Ag alloy and titanium were cast into plates 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. All the surfaces of the cast plates were abraded to a depth of 300 μm using silicon carbide abrasive paper to remove the hardened surface layer on the castings. These polished plates were then cut into square specimens (8.0 mm × 8.0 mm × 2.2 mm) for the OCP measurement and rectangular specimens (15 mm × 10.0 mm × 1.9 mm) for the elution test. Each specimen surface was polished using 180–800 grit silicon carbide abrasive paper, ultrasonically cleaned with distilled water for 60 s, and finally rinsed with ethanol.

2.2 Open-circuit potential measurement

Immediately after cleaning, the OCPs of the alloys were measured against a Ag/AgCl electrode in 300 ml of the 0.9% NaCl solution with saturated dissolved oxygen at 37°C for 259.2 ks (= 72 h) ($n = 3$). These OCPs were then converted to potentials measured against a normal hydrogen electrode (NHE). The potentials immediately after immersion and at 259.2 ks after immersion were statistically analyzed by one-way ANOVA and the Tukey HSD test at a significance level of $\alpha = 0.05$. After the measurement, the specimen surfaces were observed using an optical microscope.

2.3 Elution test

Each specimen was immersed in 10 ml of the 0.9% NaCl solution with saturated dissolved oxygen at 37°C for 604.8 ks (= 7 days). After each specimen was extracted from the solution, the ions released in the solution were analyzed qualitatively and quantitatively using inductively coupled plasma (ICP) spectrometry (IRIS-AP, Japan Jarrel Ash Co., Ltd., Japan) ($n = 5$). The amount of released ions was calculated in terms of the mass per unit area ($\mu\text{g}\cdot\text{cm}^{-2}$). The results were statistically analyzed by one-way ANOVA

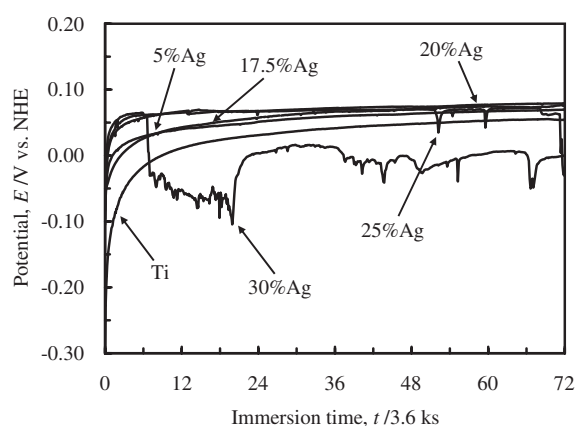


Fig. 2 Open-circuit potentials of Ti-Ag alloys and titanium in 0.9% NaCl solution with saturated dissolved oxygen at 37°C.

and the Tukey HSD test at a significance level of $\alpha = 0.05$. Selected specimen surfaces were observed using a scanning electron microscope (SEM) (JSM-6060, JEOL, Tokyo, Japan) before and after the elution test.

3. Results

3.1 Open-circuit potentials

The changes in the OCPs of the Ti-Ag alloys and titanium in the NaCl solution are shown in Fig. 2. The OCPs of all of Ti-Ag alloys immediately after immersion were significantly higher than that of titanium ($p < 0.05$). There was no significant difference in the potential among the Ti-Ag alloys ($p > 0.05$). The Ti-Ag alloys with 5–20% Ag and titanium became passive, and their potentials rose and then leveled off. The time for the Ti-Ag alloys to become the stable potential was earlier than that for titanium. The OCPs of the Ti-Ag alloys at 259.2 ks after immersion appeared to be higher (i.e., nobler) than that of titanium. The potentials of 17.5% Ag and 20% Ag were significantly higher than that of titanium ($p < 0.05$).

The 22.5% Ag and 25% Ag specimens showed two types of OCP behavior. Two or three samples out of five samples showed almost the same OCP behavior as that of the 20% Ag specimens. In contrast, the remaining samples out of five samples showed several sets of abrupt OCP drop and recovery to the original level. The potential just before the abrupt drop was about 0.07 V. Preferential dissolution of an intermetallic compound was observed on the surfaces of specimens in which the abrupt drop of potential occurred. In both cases, the mean OCP value was similar to that of the 20% Ag specimen. The OCP curves of the 27.5% Ag specimen were similar to those of the 30% Ag specimen. The potential increased to 0.08 V immediately after the immersion and abruptly dropped to about -0.05 V at 21.6 ks. Then, the potential showed a lot of noises for a while and rapidly increased but not to the original level. Subsequently, several sets of potential drop and recovery were observed. The mean OCP values of the 27.5% Ag and 30% Ag specimens were lower than that of the 20% Ag specimen. Corroded surfaces and a corrosion product were observed in all 27.5% Ag specimens and all 30% Ag specimens after the test.

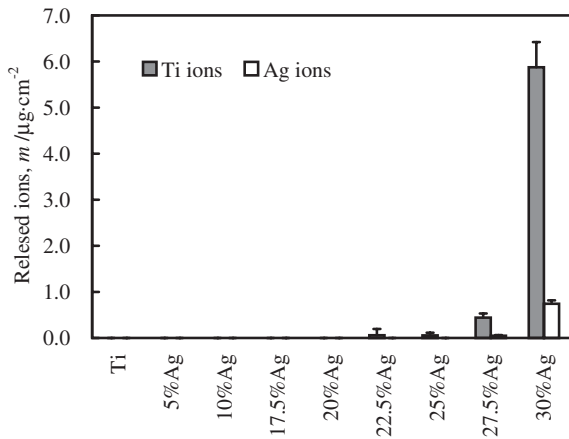


Fig. 3 Ions released from Ti-Ag alloys and titanium in 0.9% NaCl solution with saturated dissolved oxygen at 37°C for 604.8 ks.

Table 1 Detection limit and quantification limit.

Ions	Detection limit (μg·cm ⁻²)	Quantification limit (μg·cm ⁻²)
Ti	0.0030	0.014
Ag	0.014	0.063

3.2 Released ions

The amount of ions released from the Ti-Ag alloys and titanium in the NaCl solution for 604.8 ks is shown in Fig. 3. The detection and quantification limits of the ICP used in this study are shown in Table 1. Ti and Ag ions were not detected from Ti-Ag alloys with Ag ≤ 20%. In case of the 22.5% Ag and 25% Ag specimens, a very small amount of Ti ions was detected from two or three samples out of five samples, but the amount of Ag ions released from all the 22.5% Ag specimens and all the 25% Ag specimens was below the detection limit. The amounts of Ti ions released from 22.5% Ag and 25% Ag were 0.061 μg·cm⁻² and 0.057 μg·cm⁻², respectively. There was no significant difference in the amount of ions released from each alloy ($p > 0.05$). Both Ti and Ag ions were detected from all 27.5% Ag and 30% Ag specimens. The amount of Ag ions released from 27.5% Ag was below the quantification limit. The total amounts of ions released from 27.5% Ag and 30% Ag were about 0.49 μg·cm⁻² and 6.6 μg·cm⁻², respectively. The total amounts of ions released from the Ti-Ag alloys significantly increased as the concentration of Ag increased in the 25–30% Ag range ($p < 0.05$).

3.3 Microstructures before and after the elution test

Intermetallic compounds were not observed in Ti-Ag alloys with up to 17.5% Ag. A few needle-like intermetallic compounds were observed in the 20% Ag. The amount of intermetallic compounds increased along the grain boundaries with an increase in the Ag concentration. In addition to the needle-like intermetallic compounds, non-needle-like intermetallic compounds were observed in some of the 22.5% Ag specimens and some of the 25% Ag specimens; these non-needle-like intermetallic compounds were clearly observed in the 27.5% Ag and the 30% Ag. Microstructures of

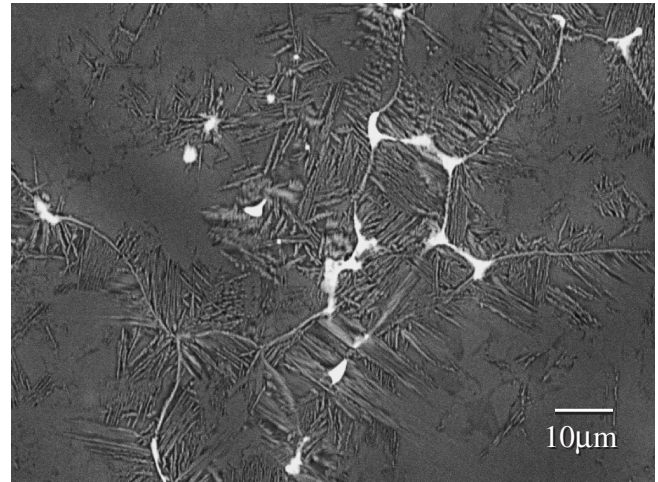


Fig. 4 Microstructures of Ti-30%Ag alloy.

the Ti-30%Ag alloy are shown in Fig. 4. Most of the non-needle-like intermetallic compounds were present in the grain boundaries.

No structural changes were observed in the alloys with 5–20% Ag and titanium after the elution test. Among the 22.5% Ag specimens and 25% Ag specimens, those specimens from which no released ions were detected showed no structural changes, but those from which released ions were detected showed slight structural changes. The surface structures of the Ti-25%Ag alloy changed by the elution test are shown in Fig. 5. Preferential dissolution of only a part of the non-needle-like intermetallic compounds was observed. The dissolved area was surrounded by the remaining intermetallic compounds. The microstructures of the corroded Ti-30%Ag alloy after the elution test are shown in Fig. 6. Intergranular corrosion and elimination of a part of grains were observed in the 27.5% Ag specimen and 30% Ag specimen.

4. Discussion

4.1 Alloy phases of Ti-Ag alloys

Cast Ti-Ag alloys with up to 17.5% Ag showed a typical single α titanium structure. In our previous study,⁸⁾ we reported that when the Ti-Ag alloys were cast and then bench-cooled, the eutectoid reaction in them did not occur or occurred only slightly, and Ti₂Ag of the cast Ti-Ag alloys was precipitated along grain boundary while the alloys were cooled to the eutectoid temperature. The needle-like intermetallic compounds observed in the alloys with Ag ≥ 20% were Ti₂Ag. We also reported that the amount of Ti₂Ag increased with an increase in the Ag concentration in the Ti-Ag alloys with Ag ≥ 20%, and then, in addition to Ti₂Ag, TiAg also precipitated.⁸⁾ According to the Ti-Ag equilibrium phase diagrams (Fig. 1), at room temperature, TiAg in the cast Ti-Ag alloy should be concentrated in the grain boundaries. It was suggested that TiAg was included in the non-needle-like intermetallic compounds.

4.2 Corrosion behavior of Ti-Ag alloys with up to 17.5% Ag

The OCP of the Ti-Ag alloys with up to 17.5% Ag was

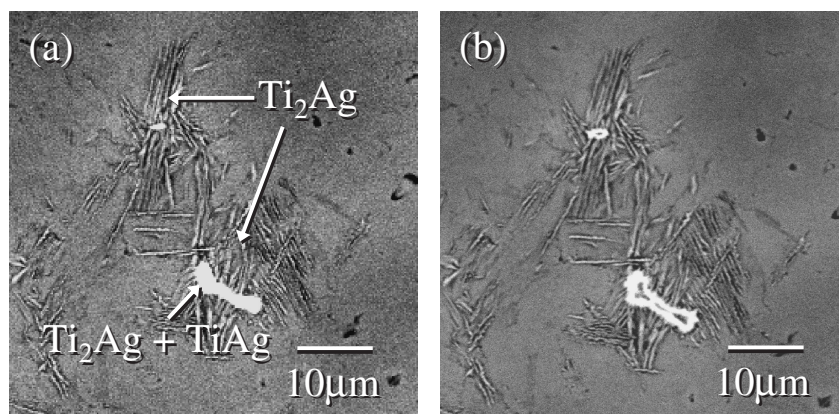


Fig. 5 Changes in the surface structure of the Ti-25%Ag alloy in elution test. (a) before immersion, (b) after immersion.

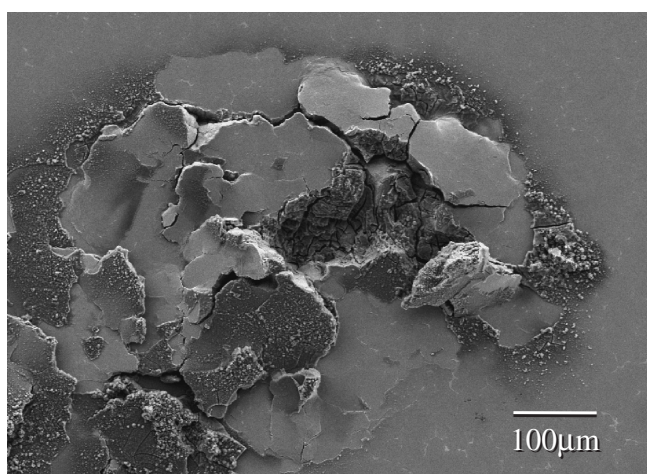


Fig. 6 Microstructures of corroded Ti-30%Ag alloy after elution test.

higher than that of titanium, and the time until the potential becomes stable after immersion was shorter for the alloys than for titanium. It was supposed that the presence of Ag in the Ti-Ag alloy increased the potentials of titanium, and the increased potentials promoted formation of the passive film. These results showed that the α phase of the Ti-Ag alloy formed a stable passivation film more quickly than titanium. Ti and Ag ions released from the α phase in Ti-Ag alloys were below the detection limit. Regardless of the Ag content, the α phase released virtually no ions in the NaCl solution, which was similar to the case of titanium. The OCP and amount of released ions, as well as the anodic polarization test, revealed that the α phase in the Ti-Ag alloys had excellent corrosion resistance that was equivalent to or higher than that of titanium in the NaCl solution.

4.3 Corrosion behavior of Ti-Ag alloys with 20–25% Ag

The 20–25% Ag structures included Ti_2Ag or Ti_2Ag and TiAg. A very small amount of ions was detected from some of the 22.5% Ag specimens and some of the 25% Ag specimens, and preferential dissolution of the intermetallic compounds was observed. The OCP for some specimens of the 22.5% Ag and 25% Ag dropped abruptly at about 0.07 V and shifted toward a less noble side. The dissolved intermetallic compounds were probably TiAg, because the

dissolution potential of TiAg in 0.9% NaCl solution obtained by the anodic polarization test was 0.09 V,⁸⁾ close to 0.07 V. The OCP of the Ti-Ag alloys was far lower than the dissolution potential of Ti_2Ag (0.29 V) in 0.9% NaCl solution obtained by the anodic polarization test. TiAg dissolved preferentially in the NaCl solution, but Ti_2Ag did not.

According to the Ti-Ag equilibrium phase diagrams (Fig. 1), at room temperature, TiAg in the cast Ti-Ag alloy should be surrounded by Ti_2Ag precipitated due to the peritectoid reaction, which is $(\beta Ti) + TiAg \rightarrow Ti_2Ag$ at 940°C. As shown in Fig. 5, the dissolution of only a core of the non-needle-like intermetallic compounds was observed in the Ti-25%Ag specimen after the test. The dissolved intermetallic compounds were TiAg, and the remaining intermetallic compounds were Ti_2Ag .

4.4 Corrosion behavior of Ti-Ag alloys with 27.5–30% Ag

In the OCP measurement, the potential of all the 27.5% Ag and 30% Ag specimens fell drastically at the dissolution potential of TiAg. In the elution test, the ions were released from all 27.5% Ag and 30% Ag specimens. However, TiAg could not be identified in 27.5% Ag and 30% Ag by X-ray diffraction in previous studies.^{8,17)} These results revealed that a small amount of TiAg existed in the cast Ti-Ag alloys with 27.5% Ag and 30% Ag, but the amount of TiAg was too small to be detected by X-ray diffraction. All 30% Ag alloy specimen surfaces showed remarkable corrosion. In this case, TiAg probably dissolved preferentially; then, intergranular corrosion occurred and the α phase was eliminated.

4.5 Total amount of ions released from Ti-Ag alloys

The total amount of ions released from 22.5% Ag and 25% Ag alloys was very small (approximately $0.06 \mu\text{g}\cdot\text{cm}^{-2}$). The amount released from 27.5% Ag (approximately $0.49 \mu\text{g}\cdot\text{cm}^{-2}$) was approximately 1/6 or less than that released from dental gold alloys (type 2 or type 4) (more than $3 \mu\text{g}\cdot\text{cm}^{-2}$) and dental base metal casting alloys (Co-Cr alloy) (approximately $3.5 \mu\text{g}\cdot\text{cm}^{-2}$) by the elution test under the same conditions.¹²⁾ Even if compared with the amount from the Ti-6Al-4V (approximately $2 \mu\text{g}\cdot\text{cm}^{-2}$) alloy and JIS SUS316L stainless steel ($1.8 \mu\text{g}\cdot\text{cm}^{-2}$),^{12,18)} the amount from 27.5% Ag was approximately 1/3 or less. Therefore, Ti-Ag alloys with up to 27.5% Ag have potential as not only dental

restorative materials but also dental implant materials in terms of the metal ion elution amount. Unlike Ti-6Al-4V or SUS316L, Ti-Ag alloys contain neither vanadium nor nickel, which present safety concerns.

5. Conclusion

Ti-Ag alloys with up to 27.5% Ag were found to have potential as both dental restorative materials and dental implant materials. For safer use as dental implant materials, the amount of Ag addition to the Ti-Ag alloys should be 25% or less, since 22.5% Ag and 25% Ag alloys passivated again if TiAg preferentially dissolved.

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