Corrosion Resistance of Dental Alloys in Pseudo-Oral Environment

Yoshimitsu Okazaki¹ and Emiko Nishimura²

¹Mechanical Engineering Laboratory, National Institute of Advanced Industrial Science and Technology, Ministry of Economy, Trade and Industry, Tsukuba 305-8564, Japan

²Japanese Industrial Standards Center, National Institute of Advanced, Ministry of Economy, Trade and Industry, Tsukuba 305-0044, Japan

The corrosion resistance of dental alloys was investigated by taking anodic polarization measurements in 1 mass%-lactic acid, artificial saliva, and cell-culture medium solutions. The role of alloying elements in the passive film that formed on the dental alloys by the anodic polarization was examined using X-ray photoelectron spectroscopy. The quantity of metals released from the dental alloy into the 1% lactic acid solution at each anodic potential was compared. In the anodic polarization curves for the Au and Au–Ag–Pd alloys, the current density tended to decrease with higher Au content. In the Ag alloy, the current density sharply increased in the 1 mass%-lactic acid solution. On the other hand, the passivity zone was slightly seen in the artificial saliva and Eagle's medium solutions. Amalgam had a low open-circuit potential, and a passivation peak was seen. The peaks of the Au4f and Ag3d orbital were high in the surface of the passive film formed on the Au and Au–Ag–Pd alloys by anodic polarization in the artificial saliva solution. SnO₂ and In₂O₃ peaks were observed in the passive film formed on the Ag alloy. SnO₂ and CuO peaks were seen in the passive film on amalgam surface. In the Au and Au–Ag–Pd alloys, Cu was released most in the low potential region less than 1.0 or 0.5 V vs. SCE, respectively. For the Ag alloys, Zn release was most, and Ag, Sn and In were also released. In amalgam, Sn release increased with higher anodic potentials. Cu release also increased at potentials over 0 V. Ag and Hg release increased from potentials over 0.5 V. Considering that the electrode potential measured in the pseudo-oral environment is a maximum of 0.2 V, it is important to examine the effect of Cu and Ag releases for the Au and the Au–Ag–Pd alloys, Zn release for the Ag alloy, and Sn and Cu releases for amalgam.

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1. Introduction

The portion of the population over 65 years of age could reach 25% early in the 21st century in Japan. Metallic materials will be increasingly used in dental treatments that typically include implants such as artificial roots and cast prostheses. The precious metal alloys (Au, Au–Ag–Pd, Ag), and Ni–Cr, Co–Cr and Ti alloys will be used to make the inlays, crowns, bridges, dentures and other prostheses. These prostheses need to have excellent mechanical properties and corrosion resistance. Recently, the development of dental alloys with high corrosion resistance and less metal release was also expected for sufferers of metallic allergies. The stronger and more stable the passive film that forms on the surface of a prosthesis, the better the corrosion resistance and the less the release of metal ions from the surfaces. As such, research on the behavior of metal ions released in the pseudo-oral environment is more important.^{1–9)}

To investigate corrosion resistance in the pseudo-oral environment, anodic polarization curves in artificial saliva, 1% lactic acid and cell-culture medium solutions were measured with precious metal alloys (Au, Au–Ag–Pd, Ag) and amalgam. The chemical state of the alloy elements in the passive film that formed on the dental alloy surface in the anodic polarization tests was analyzed using X-ray photoelectron spectroscopy. Additionally, to examine the behavior of metal ion release, the quantities of metal released at each potential in the anodic polarization tests were measured using inductively coupled plasma-mass spectrometry.

2. Experimental Methods

2.1 Specimens and centrifugal casting

Two commercial gold alloys, three Ag–Au–Cu alloys, three Ag alloys and one amalgam alloy were used in this investigation (Table 1). Test specimens, 10 mm × 10 mm × 5 mm thick, were cast in a centrifugal casting machine by using gypsum-based investment which was pre-heated to 973 K. The mold was bench-cooled to room temperature after casting. The specimens were all as cast. Test cast specimens were ground and sandblasted with Al₂O₃. The amalgam was mixed to make the same size block with an amalgam mixer. The chemical compositions of these cast materials are shown in Table 1.

2.2 Anodic polarization test

The anodic polarization test was performed in accordance with the JIS T 0302 standard. The surfaces of the centrifugally cast block specimens, except for 1 cm², were coated with epoxy resin. The exposed surface was polished with waterproof emery paper up to 600 grit under running water and then cleaned in an ultrasonic bath of ethanol for 5 min. Anodic polarization tests were conducted independently in 1 mass%-lactic acid solutions (pH = 2.5), artificial saliva (Saliveht®; pH = 5.7) and Eagle's medium¹⁰⁾ (pH = 8.3) containing calf serum (10 vol%). The testing solutions (400 mL) were bubbled with high-purity nitrogen gas at a rate of 3.33×10^6 m³/s (200 cm³/min) for 0.6 ks (O₂ < 0.1 ppm). After each specimen was initially held at –0.8 V for 300 s, anodic polarization tests were conducted from –1 V to a maximum of 2 V at a sweep rate of 3.33×10^4 V/s (20 mV/min) with a small amount of high-purity nitrogen gas flowing over

Table 1 Chemical compositions (mass%) of materials used.

Alloys		Au	Ag	Pd	Cu	In	Sn	Zn	Hg	Pt
Au alloy	NC-20K	82.7	7.96	1.00	6.86	—	—	0.48	—	—
	NC-18K	74.6	4.73	1.94	17.0	—	—	0.97	—	—
Au–Ag–Pd alloy	New palla gold	12.1	55.8	19.9	9.91	—	—	1.42	—	—
	New palla 20	20.0	40.6	20.0	17.9	—	—	0.96	—	—
	New palla gold solder	15.1	36.4	14.8	17.0	—	—	16.0	—	—
Ag alloy	Super silver	—	73.2	—	—	2.00	8.79	15.9	—	—
	Alloy silver	—	70.4	0.36	—	24.1	—	5.18	—	—
	Success E	—	70.3	—	—	23.8	—	5.91	—	0.073
Amalgam	Spherical-D Capsule	—	33.3	—	6.95	—	14.9	—	44.7	—

the solution surface. A platinum electrode and a saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. Measurements were repeated three times at 37°C.

2.3 Analysis of passive film

The effects of the alloying elements on the passive films were examined by X-ray photoelectron spectroscopy (XPS). The sample surfaces were finished by buff-cleaning using a high-quality SiO₂ (OP-S) suspension after polishing them with up to 4200 grit waterproof emery paper under running water. Anodic polarization tests in 1 mass%-lactic acid or artificial saliva solutions were carried out at a sweep rate of 3.33×10^4 V/s from -1 V to the following potential (vs. SCE): 0.650 V or 0.540 V for Au (NC-20K®) alloy, 0.375 V or 0.210 V for Au–Ag–Pd (New Palla Gold®) alloy, 0.180 V or -0.042 V for Ag (Super Silver®) alloy, 0.050 V or 0.300 V for amalgam, respectively. The conditions of the XPS measurement (ESCALAB220i-XL, manufactured by VG Scientific Ltd.) were an X-ray source of monochromated-Al K α , tube voltage: 10 kV, tube current: 13 mA, and measurement diameter: 600 μ m. The scan number of wide-scan and Multi-Reason Scan (MRS) was 5 and 20, respectively.

The depth profile was measured with an Auger electron microscope (JAMP-7100 manufactured by JOEL Ltd.). Measurement conditions were as follows: acceleration voltage: 5 kV, incident current: 500 nA, Ar⁺ sputtering voltage: 3 kV, measurement diameter: 50 μ m and sputtering rate of SiO₂/Si: 0.033 nm/s (2 nm/min).

2.4 Measurement of metal concentration by ICP-MS

A 2-mL sample was taken from the measurement solutions at each potential in the anodic polarization test into a Falcon centrifugal tube that was cleaned with 5% nitric acid and ultra-pure water. The metal concentrations released into the measurement solutions by anodic polarization were measured using an inductively coupled plasma-mass spectrometer (ICP-MS).

Perfluoro alkoxyl alkane (PFA) flasks were cleaned with pure water after use and filled with a 5 mass%-nitric acid solution and carefully plugged to exclude air. The flasks were emptied before use and cleaned inside and outside with a 5%-nitric acid solution and ultra-pure water (18.3 M Ω). The micro-pipette tips used for sampling were cleaned by same method. A Yokogawa analytical systems HP 4500 spectrometer with an auto-sampler (CETAC ASX 500) was used. The

Table 2 Operating conditions for ICP-MS using an auto-sampler.

Plasma conditions	
Radiofrequency (R.F.) power	1.2 kW
Plasma gas (Ar) flow rate	15 L/min
Auxiliary gas (Ar) flow rate	1 L/min
Carrier gas (Ar) flow rate	1.1 L/min
Sampling distance	5 mm
Auto sampler conditions	
Rinsing solution	3% HNO ₃ , Ultra-pure water
Rinsing rate by peristaltic pump	0.5 s ⁻¹ (2 mL/min)
Rinsing time	180 s
Exchange rate of sampling solution	0.5 s ⁻¹ (2 mL/min)
Exchange times for sampling solution	120 s
Stabilization time for peristaltic pump	60 s
Sample up take rate by peristaltic pump	0.12 s ⁻¹ (0.48 mL/min)
Data acquisition	
Peak jumping mode	
Number of points per peak	3
Number of repetitions	6
Integration time (s)	1

measurement conditions using the auto-sampler are shown in Table 2.

The isotopic mass numbers used to measure the metal concentrations were Au: 197; Ag: 107; Pd: 106; Cu: 63; Zn: 64; In: 115; Sn: 120 and Hg: 202 so as to minimize the influence of the matrix. The single-element standard solutions (SPEX CertiPrep, Inc., 1000 μ g/mL) were diluted for the Au, Ag, Pd, Cu, Zn, In and Hg standard solutions. Ultra-high-purity nitric acid (TAMAPURE-AA-10, Tama Chemicals Co., Ltd.) was used to prepare the measurement solutions. The internal standard solution was 1 μ g/L Co. The working curves were established in concentrations of 6 points and above, and exhibited linearity of the correlation factor (r) = 0.999 or above. All ICP-MS measurements were taken in a clean room (class 10000) and the measurement solutions were prepared in a clean bench (class 100). The mass axis and intensity were adjusted with a tuning solution containing 10 μ g/L of Li, Y, Ce, and Tl. The limits of analysis for the metallic elements under these conditions were all below 0.05 μ g/L.

3. Results and Discussion

3.1 Anodic polarization curves

Figure 1 shows the anodic polarization curves measured

Fig. 1 Comparison of anodic polarization curves for dental-cast alloys in 1 mass%-lactic acid solution. (a) Au and Au-Ag-Pd, (b) Ag alloy and amalgam.

Fig. 2 Comparison of anodic polarization curves for dental-cast alloys in artificial saliva and Eagle's medium solutions. (a) a artificial saliva, (b) Eagle's medium.

in the 1 mass%-lactic acid solution at 37°C. As shown in Fig. 1(a), passivation peaks were seen in the Au and Au-Ag-Pd alloys. The current density tended to decrease at higher Au content. As shown in Fig. 1(b), in the case of

Fig. 3 XPS wide-scanning spectra for surface of passive film formed on Au (a) and Au-Ag-Pd (b) alloys by anodic polarization in artificial saliva solution at 37°C.

the Ag alloys the passivation peak was not observed, and the current density markedly increased. Amalgam had a low open-circuit potential (corrosion potential) and a passivation peak was also observed. Figure 2 compares the anodic polarization curves measured in the artificial saliva and Eagle's medium solutions. The open-circuit potential decreased in the order of Au (83Au-8Ag-7Cu), Au-Ag-Pd (12Au-56Ag-20Pd-10Cu), Ag (73Ag-9Sn-16Zn-2In) and amalgam (33Ag-7Cu-15Sn-45Hg). In the Ag alloy a small passivation peak was seen unlike in the 1% lactic acid solution as shown in Fig. 2(b).

3.2 XPS analysis of passive film

Figures 3 and 4 show the wide-scanning spectra of the passive film that formed on the dental alloys in the anodic polarization tests in the artificial saliva solution. In the Au alloy surface, peaks of binding energy for Au4f, Au4d, Au4p, Au4s, Ag3d, Ag3p, Ag3s, Cu2p, O1s, C1s orbital were observed. The Au4f peak was high but the O1s peak was low. For the Au-Ag-Pd alloy, the Ag3d peak was high as shown in Fig. 3(b). In the case of the Ag alloy surfaces, Ag3d, Ag3p, Sn3d, Sn3p, Zn2p, Zn3p, Zn3s, In3d, O1s, C1s peaks were observed as shown in Fig. 4(a). In the amalgam surfaces, Sn3d, Sn3p, Hg4d, Hg4f, Ag3d, Ag3p, Cu2p peaks were observed, and the Sn3d peak was high.

Figures 5 and 6 show the depth profiling of the oxide film that formed on the Ag alloy and amalgam surfaces. Figure 5 shows the results in the artificial saliva solution. In the Ag alloys, the intensity of Au is scaled down one-half of that of actual intensity as shown in Fig. 5(a). The intensity of O decreased and Ag increased at longer sputtering times. The Sn intensity was high in the amalgam surfaces. The Hg intensity

Fig. 4 XPS wide-scanning spectra for surface of passive film formed on Ag (a) and amalgam (b) alloys by anodic polarization in artificial saliva solution at 37°C.

Fig. 5 Sputtering profiles in passive film formed on Ag (a) and amalgam (b) alloys by anodic polarization in artificial saliva solution at 37°C.

Fig. 6 Sputtering profiles in passive film formed on Ag (a) and amalgam (b) alloys by anodic polarization in 1 mass%-lactic acid solution at 37°C.

at the passive film surface was low. Figure 6 shows the results in the 1 mass%-lactic acid solution. The tendency was nearly similar to that obtained with the artificial saliva solution.

Table 3 summarizes the binding energy of the alloy elements obtained by MRS. The binding energy of metal measured in the artificial saliva solution was nearly the same as that in the 1% lactic acid solution. SnO_2 and In_2O_3 ¹¹⁾ peaks were observed in the passive film formed on the Ag alloy. SnO_2 and CuO peaks were seen in the passive film on amalgam surface.

3.3 Release of Metallic ions in anodic polarization

The metal concentrations in the 1 mass%-lactic acid solution sampled at each potential in the anodic polarization test were measured with ICP-MS. The metal concentration of the solution before inserting the specimens was used as a blank concentration, and the amount of metal released into the 1 mass%-lactic acid solution at each anodic potential (vs. SCE) was estimated. The results are shown in Figs. 7 and 8. In the Au alloys, the Cu release was the highest, and slightly increased at potentials over 1.0 V. The Ag release slightly increased in the high-potential region. The Au release was the lowest. For the Au-Ag-Pd alloys, the Cu release was largest at potentials lower than 0.6 V. The increase of the Ag release was small up to 0.6 V and then markedly increased thereafter. Pd release increased from approximately 0.7 V. In the Ag

Table 3 Comparison of binding energy for alloy elements in the surface of passive film formed on dental-cast alloys by anodic polarization in artificial saliva and the 1% lactic acid solutions.

Alloy	Solution	Au		Ag		Cu		Pd				
		4f _{7/2}	4f _{5/2}	3d _{5/2}	3d _{3/2}	2p _{3/2}	2p _{2/1}	3d _{5/2}	3d _{3/2}			
Au alloy	Artificial saliva	83.9	87.5	368.0	374.0	932.5	952.2	335.2	340.5			
	1 mass% lactic acid	83.9	87.6	368.0	374.0	932.5	952.3	335.2	340.4			
Au–Ag–Pd alloy	Artificial saliva	83.8	87.5	368.1	374.1	932.5	952.3	335.2	340.5			
	1 mass% lactic acid	83.8	87.5	368.0	374.1	932.5	952.2	335.2	340.5			
		O		C								
		1S		1S								
Au alloy	Artificial saliva	531.1	532.7	284.6	286.1	287.6	288.9					
	1 mass% lactic acid	530.7	532.4	284.5	286.0	287.6						
Au–Ag–Pd alloy	Artificial saliva	530.9	532.7	284.9	286.5	288.0	289.1					
	1 mass% lactic acid	531.6	532.3	284.7	286.1	287.9	289.0					
Alloy	Solution	Ag		Sn				Cu		Zn 2p	Hg	
		3d _{5/2}	3d _{3/2}	3d _{5/2}		3d _{3/2}		2p _{3/2} CuO	2p _{2/1} CuO		4f _{7/2}	4f _{5/2}
Ag alloy	Artificial saliva	368.5	374.5	485.2	487.1	493.7	495.6			1022.6		
	1 mass% lactic acid	368.4	374.4	485.2	487.1	493.7	495.4			1022.4		
Amalgam	Artificial saliva	368.5	374.6	485.2	487.1	493.7	495.6	933.4	953.2		100.0	104.1
	1 mass% lactic acid	368.6	374.6	485.1	487.0	493.7	495.4	933.5	953.3		100.0	104.0
		In				O				C 1S		
		3d _{5/2}		3d _{3/2}		1S						
		In	In ₂ O ₃	In	In ₂ O ₃							
Ag alloy	Artificial saliva	444.0	444.5	451.7	453.0	530.7	532.3	285.1	286.6		288.1	289.3
	1 mass% lactic acid	444.1	445.3	451.6	452.9	531.0	532.9	285.2	286.6		288.1	289.1
Amalgam	Artificial saliva					530.8	532.0	285.2	286.7			288.9
	1 mass% lactic acid					530.8	532.3	533.5	285.3	286.6	287.5	289.1

alloys, the Zn release was the largest, and Ag, Sn and In releases were observed as shown in Fig. 8(a). For amalgam, Sn, Cu, Ag and Hg releases were as shown in Fig. 8(b). Sn release tended to increase with higher potentials. Cu release increased at potentials over 0 V. Ag and Hg release sharply increased from potentials over 0.5 V.

Considering that the electrode potential measured in a pseudo-oral environment is a maximum of 0.2 V,¹²⁾ it is important to examine the effects of Cu and Ag releases for the Au and Au–Ag–Pd alloys, Zn release for the Ag alloy, and Sn and Cu releases for amalgam.

4. Conclusions

The anodic polarization curves of the Au, Au–Ag–Pd and Ag alloys and amalgam were compared in the artificial saliva, 1% lactic and cell-culture medium solutions. The effect of the alloy elements in the passive film that formed on the alloy surface was analyzed by X-ray photoelectron spectroscopy. The quantity of metal released at each potential was also compared. The following conclusions were drawn:

(1) For the Au and Au–Ag–Pd alloys, passivation peaks were observed in the 1 mass%-lactic acid solution. The current density tended to decrease with higher Au content. On the other hand, for the Ag alloy, passivation peaks were not observed, and the current density sharply increased. Amal-

gam had a low open-circuit potential, and a passivation peak was seen. For the Ag alloy, the passivity zone was seen slightly in the artificial saliva and Eagle's medium solutions.

(2) The peaks of the Au4f and Ag3d orbital were high in the surface of the passive film that formed on the Au and Au–Ag–Pd alloys in the anodic polarization test with the artificial saliva solution. SnO₂ and In₂O₃ peaks were observed in the passive film formed on the Ag alloy. SnO₂ and CuO peaks were seen in the passive film on amalgam surface.

(3) The metal concentrations released at each potential (vs. SCE) into the 1 mass%-lactic acid solution were compared. For the Au and Au–Ag–Pd alloys, Cu was released most in the low potential region less than 1.0 or 0.6 V, respectively. The Au release was also the least. For the Ag alloys, the Zn release was the most, and Ag, Sn and In also released in significant amounts. Their releases increased from approximately 0.4 V. Amalgam released Sn, Cu, Ag and Hg. Sn release increased with higher potentials. Cu release also increased at potentials over 0 V. Ag and Hg release increased at potentials over 0.5 V. Considering that the electrode potential measured in a pseudo-oral environment is a maximum of 0.2 V, it is clearly important to examine the effect of the Cu and Ag releases for the Au and Au–Ag–Pd alloys, the Zn release for the Ag alloy, and the Sn and Cu releases for amalgam.

Fig. 7 Change in amount of metal released from Au (a) and Au-Ag-Pd (b) alloy into 1 mass%-lactic acid solution as a function of anodic potentials.

Fig. 8 Change in amount of metal released from Ag (a) alloy and amalgam (b) into 1 mass%-lactic acid solution as a function of anodic potentials.

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