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Original Article

Corrosion Properties of Ag-Au-Cu-Pd System Alloys Containing Indium

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Abstract

In this study, the corrosion resistance of Ag-Au-Cu-Pd system alloys consisting of 5 or 10 mass% indium was evaluated. Levels of element release and tarnish were determined and electrochemical measurements performed. Results were compared with those for commercial silver-palladium-gold alloy. In terms of electrochemical behavior, the transpassive potential of these experimental alloys was 168–248 mV. Experimental alloys with 25 mass% Au showed similar corrosion resistance to control gold-silver-palladium alloy. Amount of released elements was 14–130 $\mu\text{g}/\text{cm}^2$ at 7 days, which is in the allowable range for dental alloys. Addition of indium to Ag-Au-Cu-10mass%Pd system alloys was effective in increasing resistance to tarnish and alloys containing 10 mass% of indium showed a minimal decrease in L^* values after immersion. These findings indicate that 25Au-37.5Ag-15Cu-10Pd-2Zn-10In-0.5Ir alloy is applicable in dental practice.

Key words: Ag-Au-Cu-Pd system alloy—Corrosion resistance—Tarnish

Introduction

High carat gold alloys with superior corrosion resistance in an oral environment have been widely used as dental alloys, presenting adequate workability and mechanical properties. On the other hand, the gold-silver-palladium alloys covered by the national and social health insurance systems in Japan have also been used over a long period of time. However, palladium allergies have been reported

for alloys with a high palladium content^{1,11)}. Therefore, the development of alloys with a low palladium content is necessary. Alloys with silver as their main component are considered to have low sulfidation resistance, showing inferior corrosion resistance as well as a tendency to tarnish under oral conditions. Addition of palladium to alloys is quite effective in inhibiting tarnish and corrosion⁸⁾. Therefore, the Japanese Industrial Standard (JIS)³⁾ has required 20% or more of palladium content

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Table 1 Composition of experimental 10% palladium Ag-Au-Cu-Pd system alloys

Alloy code	Au	Ag	Cu	Pd	Zn	In	Ir
2500	25	47.5	15	10	2	0	0.5
2505	25	42.5	15	10	2	5	0.5
2510	25	37.5	15	10	2	10	0.5
2000	20	52.5	15	10	2	0	0.5
2005	20	47.5	15	10	2	5	0.5
2010	20	42.5	15	10	2	10	0.5
S12	12	51	14.5	20	Others		

(mass%)

in gold-silver-palladium alloys. To prevent tarnish and corrosion in alloys containing silver as their main component while reducing the amount of palladium content, an increase in gold or platinum content has been suggested by some reports^{5,13}. Nevertheless, 30 mass% or more of gold content is required in alloys with low palladium content to inhibit tarnish and corrosion. In this situation, increasing the amount of gold or platinum is not a suitable option if one takes into account the effects of price fluctuations in the metal markets.

On the other hand, addition of cadmium or indium to silver alloy was effective in preventing sulfidation by silver⁹. One study reported that indium was less allergenic than palladium¹². Accordingly, in the present study, 6 types of Ag-Au-Cu-Pd system alloy (Au: 20 or 25 mass%, Pd: 10 mass%) containing 5 or 10 mass% indium were produced for evaluation of corrosion and tarnish resistance. Potentiodynamic polarization behavior, tarnish and dissolution of metal elements was determined by immersion tests using sulfide solutions to evaluate the development of a new type of Ag-Au-Cu-Pd system alloy as well as clarify the effect of addition of indium to this alloy system.

Materials and Methods

1. Alloy preparation

As experimental alloys, 6 types of alloy (100 g each) consisting of 10 mass% palla-

dium, 15 mass% copper, 20 or 25 mass% gold, 5 or 10 mass% indium and 37.5–52.5 mass% silver were produced (Table 1). For fabrication of each alloy, commercially available 99.9% Cu, In, Ag and Zn (Ishifuku Metal Industry, Tokyo, Japan) and 99.99% Au (Ishifuku Metal Industry) were used. As a control, a gold-silver-palladium alloy containing 12% gold (Kinpara S12 (S12): 51Ag-20Pd-14.5Cu-12.0Au and others, mass%, Ishifuku Metal Industry) was tested.

2. Corrosion and tarnish test

1) Electrochemical measurement

Plate type specimens (14 × 14 × 1 mm) were cast with 6 types of experimental alloy and one control alloy. Each specimen was polished using 600 grit waterproof abrasive paper and then ultrasonically cleaned in acetone and distilled water. As a testing solution, 0.9% aqueous NaCl solution (pH=6) was used. Using the Potentiostat Model 273A & Corrosion software M352C (PARC, Oak Ridge, Tennessee, USA) and an electrolytic cell stored in a thermostatic chamber at 37°C, saturated calomel electrode (SCE) was used as a reference electrode. In addition, a platinum counter electrode was prepared. Each specimen was immersed in an electrolytic cell using a sample holder with 1 cm² of the surface area of the specimen exposed.

Potentiodynamic polarization was performed under the following conditions: potential range, between -1,000 mV and +300 mV; scanning rate, 0.33 mV/s. The

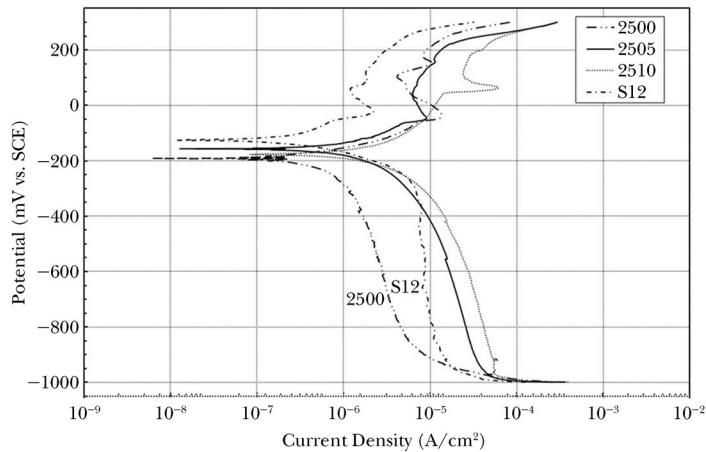


Fig. 1 Potentiodynamic polarization curves of experimental alloys containing 25% gold

relationship between potential and current density was plotted. Transpassive potential, passive current density and corrosion potential at the potentiodynamic polarization curves were determined according to ISO10271⁹⁾ and JIS T 6002⁴⁾.

2) Tarnish test

After casting experimental and control alloys into plates ($10 \times 10 \times 1$ mm), the specimens were embedded in epoxy resin. Thereafter, mirror polishing was performed using the standard metallographic procedure followed by ultrasonic cleaning with acetone and distilled water. The testing was conducted according to ISO8891. A cyclic dipping device (Nihon Void, Tokyo, Japan) was used to repeat specimen soaking in 0.1 mol/liter sodium sulfide hydrate solution ($\text{pH} \approx 12.5$; 10–15 sec) and air (45–50 sec) for 72 hr. Subsequently, differences in color were measured with a color meter (MCR-A, Minolta, Tokyo, Japan). Color difference (ΔE^*_{ab}) between at before and after cyclic immersion was determined using the following equation: $\Delta E^*_{ab} = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$

3) Static immersion test

After casting experimental and control alloys into plates ($10 \times 10 \times 1$ mm), the surfaces of the specimens were polished using 600 grit waterproof abrasive paper. The specimens

were ultrasonically cleaned in ethanol and distilled water. After hanging specimens by a nylon string in a sample bottle, they were stored in 4 ml aqueous solution ($\text{pH} \approx 2.3$) comprising 0.1 mol/liter lactic acid and 0.1 mol/liter NaCl for 7 days at 37°C using a thermostatic chamber following the method of ISO10271⁹⁾. Elements dissolved into the testing solution after 7 days immersion were analyzed by inductively coupled plasma-atomic emission spectroscopy (Vista-MPX, SII, Chiba, Japan). In this test, seven elements consisting of Au, Ag, Cu, Pd, Zn, In and Ir were analyzed. The lower detection limit of each element was 0.07 μg . The released quantity of each element was determined by obtaining the average of 3 specimens in each group.

3. Statistics

For the statistical analysis of released elements and color differences, a one-way analysis of variance (ANOVA) and the Scheffé multiple comparison test were conducted.

Results

1. Corrosion resistance and tarnish

The potentiodynamic polarization curves of the experimental alloys containing 25%

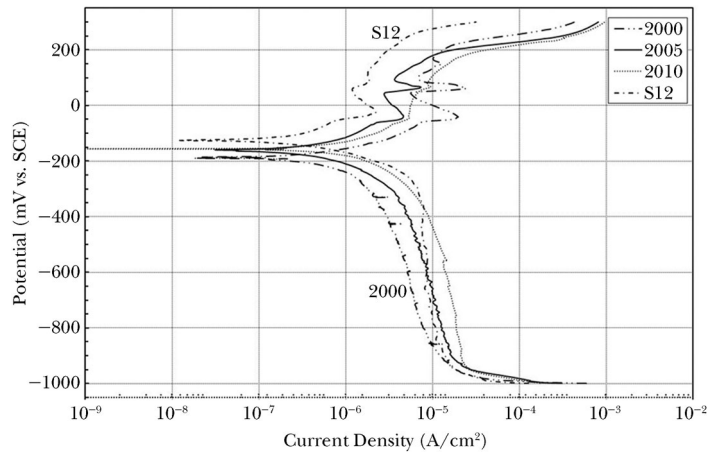


Fig. 2 Potentiodynamic polarization curves of experimental alloys containing 20% gold

gold (#2500, #2505, #2510) are shown in Fig. 1. In terms of corrosion potential, which ranged between -200 and -150 mV, the #2500 experimental alloy showed the minimal value at -200 mV; while #2505 exhibited the highest value at -150 mV. All the alloys in this group were passivated at around -50 to 0 mV. In terms of passive current densities at 100 mV, which ranged from 5 to $30 \mu\text{A}/\text{cm}^2$, #2510 exhibited the highest current density. Thereafter, a rapid increase in current densities at potentials of above 200 mV was recorded.

The potentiodynamic polarization curves of the experimental alloys containing 20% gold (#2000, #2005, #2010) are shown in Fig. 2. As with the experimental alloy containing 25% gold, corrosion potential ranged between -200 and -150 mV, with #2000 experimental alloy showing the minimal value at -200 mV, while #2010 showed the highest value at -150 mV. All the alloys in this group were passivated at around -50 to 0 mV. In terms of passive current densities at 100 mV, which ranged from 5 to $10 \mu\text{A}/\text{cm}^2$, #2010 showed the highest current density. A rapid increase in the current densities at a potential of between 150 and 200 mV was recorded.

The corrosion potential of S12 as a control at -100 mV was the highest value. It was passivated at a potential of around -30 mV;

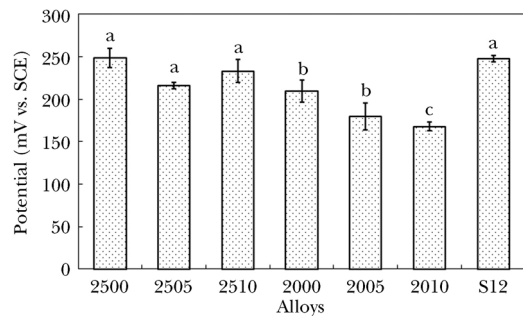


Fig. 3 Transpassive potentials of experimental alloys Same character indicates no significant difference, $p > 0.05$.

the passive current density at 100 mV was approximately $3 \mu\text{A}/\text{cm}^2$. A rapid increase in the current density at around 250 mV was observed.

The potentials with a rapid increase in current densities are presented as transpassive potentials in Fig. 3. The transpassive potentials of the experimental alloys ranged from 168 to 248 mV (vs. SCE). In this test, #2500 showed the highest value at 248 ± 11 mV, while #2010 showed the minimum value, 168 ± 5 mV. The transpassive potential of S12 as a control was 247 ± 4 mV.

The color values (L^*) of the experimental alloys at before and after immersion are

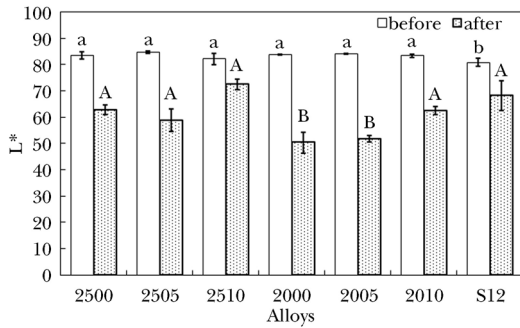


Fig. 4 L^* values of experimental alloys at before and after soaking

Same character indicates no significant difference, $p > 0.05$.

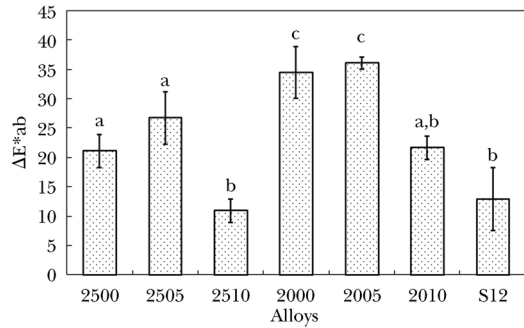


Fig. 5 Color difference (ΔE^*_{ab}) of experimental alloys in tarnish test

Same character indicates no significant difference, $p > 0.05$.

Table 2 Quantity of released elements and total amount of released elements after 7-day static immersion tests

Alloy code	Ag	Cu	Pd	Zn	In	Total amount
2500	0.87	12.20	—	1.54	—	14.61
2505	0.63	15.28	0.19	58.40	3.69	78.19
2510	0.64	18.89	0.19	43.31	6.13	69.16
2000	0.56	26.12	0.20	4.30	—	31.18
2005	0.61	29.71	0.20	5.28	4.48	40.28
2010	0.63	62.29	0.20	51.07	16.46	130.65
S12	0.66	2.95	0.20	0.51	0.16	4.48

—: below detection limit ($\mu\text{g}/\text{cm}^2/7\text{days}$)

shown in Fig. 4. Before immersion, L^* values of all testing materials ranged at almost the same level (80–84). The value of S12 (80) as a control was slightly lower than that of the other alloys. After immersion, L^* values of all testing materials ranged between 50 and 72, with #2510 and #2000 showing the maximum (72 ± 2) and minimum (50 ± 4) values, respectively. S12 as a control presented a relatively higher value (68 ± 6) than the experimental groups except #2510.

The color difference values (ΔE^*_{ab}) after immersion of the experimental alloys are shown in Fig. 5. ΔE^*_{ab} values ranged between 11 and 36. #2005 showed the highest value (36 ± 1); #2510 showed the minimum value (11 ± 2). The ΔE^*_{ab} value of S12 as a control (12 ± 5) was relatively lower.

The quantity of release for each element

and the total released amount from the experimental alloys are shown in Table 2. Dissolution of Ag, Cu, Pd, Zn and In from each experimental alloy was found, but release of Au and Ir was below the lower detection limit ($0.07 \mu\text{g}$). The minimum value of total dissolution ($14.61 \pm 10.15 \mu\text{g}/\text{cm}^2/7\text{days}$) was observed in #2500; the maximum value ($130.65 \pm 9.75 \mu\text{g}/\text{cm}^2/7\text{days}$) was found in #2010. The value of the control group (S12) was $4.47 \pm 1.53 \mu\text{g}/\text{cm}^2/7\text{days}$.

Discussion

1. Alloy composition

Studies regarding indium as an additive element in dental alloys have been conducted over a number of years. Indium is a relatively

low allergenic element among additive elements for dental alloys¹²⁾. Matsumoto⁶⁾ reported that addition of 20–30% indium to silver alloys improved resistance to tarnish. In the present study, the effects of addition of 5 or 10 mass% indium to Ag-Au-Cu-Pd system alloys were investigated in terms of resistance to corrosion and tarnish.

Yoshida *et al.*¹³⁾ and Matsumoto *et al.*⁵⁾ conducted studies on Ag-Au-Cu-Pd system alloys containing 5 mass% palladium, and found that 30–40 mass% gold was needed in addition to 5 mass% palladium to obtain a sufficient amount of resistance to corrosion and tarnish. The palladium content of commercially available gold-silver-palladium alloys adopted for national insurance is regulated to 20 mass%. In the present study, to reduce the amount of gold as much as possible, these amounts were fixed at 20 and 25 mass% and palladium content at 10 mass%.

2. Corrosion and tarnish resistance

Although each experimental alloy presented similar potentiodynamic polarization behavior, the experimental alloys with 25 or 20 mass% gold showed different levels of transpassive potential (Figs. 1, 2). A transpassive potential of more than 200 mV existed in the former, whereas less than 200 mV transpassive potential was found in the latter, indicating the influence of the gold content. On the other hand, a higher passive current density was found in the experimental alloys with 10% indium (#2510, #2010) than the alloys with 5% indium (#2505, #2005). This suggests that increase in indium content causes lowering of corrosion resistance. According to the comparison of potentiodynamic polarization curves against commercially available gold-silver-palladium alloy as a control, all the experimental alloys showed lower corrosion potentials, higher passive current density and either the same level or lower transpassive potentials. Thus, in terms of electrochemical behavior, the experimental alloys with 25 mass% Au showed similar corrosion resistance to control gold-silver-palladium alloy.

Tarnish resistance, as well as corrosion

resistance, is an important factor in dental alloys. Tarnish under oral conditions is a concern with alloys containing silver as their main component. The main reason for this phenomenon is considered to be sulfide products^{7,10)}. In our study, tarnish testing was conducted under severe conditions of cyclic exposure to sodium sulfide hydrate solution and air. The L* values of the experimental alloys before immersion (Fig. 3) were more than 80, presenting higher values than commercially available alloy. Light and white color alloys are preferable in terms of esthetics in restorations; however, the L* values of all the experimental alloys decreased after immersion. The value of the alloy with no indium (#2000), in particular, dropped to around 50. In contrast, alloys containing 10 mass% indium showed a minimal decrease in L* values after immersion, suggesting improvement in tarnish resistance due to the preventive effects of indium against sulfidation by silver.

Relative differences in discoloration can be compared quantitatively using ΔE^*_{ab} values. The ΔE^*_{ab} values of #2000 and #2005 alloys were more than 30, indicating considerable tarnish. Color differences in the experimental alloys with 25 mass% gold were smaller than in those with 20 mass% gold, indicating the effect of gold content in alloys. In addition, the ΔE^*_{ab} values of the experimental alloys with 10 mass% of indium were lower than those with 5 mass% indium. As with the aforementioned mechanism, this result indicates the preventive effects of indium against sulfidation by silver. Only experimental #2510 showed the same level of color difference with the control alloy (commercially available gold-silver-palladium alloy).

Large amounts of Cu, In and Zn were released in the solutions by the specimens in this study. Although the zinc content in all the experimental alloys was relatively low (2 mass%), released amounts of Zn were relatively high. This result agrees with those of previous reports showing that released amount of Zn was not in proportion to that of other alloy components¹⁴⁾; it is suggested that base metals

such as Cu, In and Zn on the specimen surfaces are selectively released in solutions. Released amounts of alloy elements from dental alloys should be kept as low as possible. The total released amount from dental alloys as determined by the ISO 22674 standard is $200 \mu\text{g}/\text{cm}^2/7$ days or less. The total released amounts in all the experimental alloys showed higher values than the control gold-silver-palladium alloy; however, all the values were within the limited range of the ISO standard. Therefore, the released amounts in the experimental alloys in the present study are considered to be within the allowable range for dental alloys.

In conclusion, addition of indium to Ag-Au-Cu-10mass%Pd system alloys is effective in increasing tarnish resistance. These findings suggest that 25Au-37.5Ag-15Cu-10Pd-2Zn-10In-0.5Ir alloy is applicable in dental practice from the viewpoint of corrosion and tarnish resistance.

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