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Corrosion of Dental Au-Ag-Cu-Pd Alloys in 0.9 % Sodium Chloride Solution

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Two Au-Ag-Cu-Pd dental casting alloys (Au:12% and 20%) used. The test solutions used 0.9 % NaCl solution (isotonic sodium chloride solution), 0.9 % NaCl solution containing 1 % lactic acid, and 0.9 % NaCl solution containing 1 % lactic acid and 0.1 mol dm^{-3} Na_2S. The surface of two samples in three sample solutions was not natural discoloration during one year. The alloy containing 12 % gold was easily alloyed and the composition was uniform comparing with the alloy containing 20 % gold. The rest potentials have not a little effect after three months. The kinds of metals could not definitely from the oxidation and reduction waves of metal on the cyclic voltammograms. The dissolutions of gold and palladium were 12 % Au sample in the 0.9 % NaCl solution containing 1 % lactic acid and 0.1 mol dm^{-3} Na_2S. The pH of solution had an affect on dissolution of copper, and sulfur ion had an affect on dissolution of silver. The copper dissolved amount from 20 % gold sample was about 26 times comparing with that of 12 % gold sample in the 0.9 % solution containing 1 % lactic acid. Corrosion products were silver chloride and copper chloride in NaCl solution, and silver sulfide and copper sulfide in NaCl solution containing Na_2S.

Keywords : *dental alloy, NaCl solution, rest potential, polarization curve*

1. Introduction

Many dental alloys were the high corrosion resistance. Dental alloys were determined noble metal alloys (Au, Pd-Ag, Pd-Cu, Au-Ag-Pd, Ag-Zn, Ag-Sn-Zn, amalgam) and based metal alloys (Co-Cr, Ni-Cr, Ti and its alloy, stainless steel). Dissolving ion was little.[1] The necessity of valuation of corrosion resistance and safety for the biotissue is rising. It is important to know the kinds of ions and its elution amount from dental alloy such present state is reflected. The quantitative analysis of the elution ion becomes a standard in the corrosion test of dental alloy in ISO and JIS. The elution ions are the reality and high index of which the corrosion amount of dental alloy. In recent years, the interest of metal allergy is high, and elution ion of the dental alloy is noticed. Some alloys are widely used as dental casting alloys for inlay, crowns and bridge. Some Au-Ag-Cu-Pd alloys have good mechanical properties. However these alloys have some problems to corrosion resistance.[2)-8)] Recently, electrochemical technique used to study the corrosion of dental alloys.[6)-18)] The metal products rusted readily, because these products immersed in salvia in mouth at all times, and exposed to acid or alkaline foods. The metal products tarnished, and are dissolved as corrosion. The some metal ions dissolved exhibited toxicity to living body. Natural discoloration in the course of time had known with Na_2S. In generally, Na_2S solution used for corrosion resistance test.

In this study, the corrosion behavior of two Au-Ag-Cu-Pd alloys in three test solutions was determined using electrochemical technique. .

2. Experimental

The test specimens made by casting. The composition and mechanically property are shown in Table 1. The exposed area of test specimens used was 0.8 cm x 1.3 cm (thickness, 0.05 cm). One side of each specimen was sealed with a teflon adhesive tape. The exposed plane was polished with # 2000 emery paper before testing. The specimen degreases with acetone before testing. A specimen placed in a 100 cm^3 of test solution in Erlenmeyer flask with plug, and maintained at 310 k throughout the

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Table 1. Composition and mechanically property

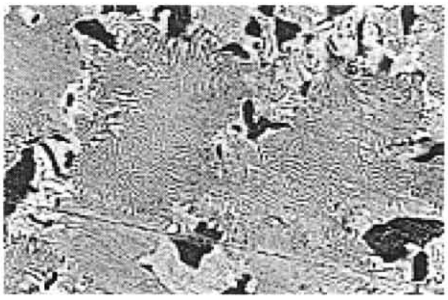
Sample composition (%)					Density (g/cm^3)	Melting point(k)	Tensile strength (MPa/mm^2)	Elongation (%)	Hardness (Hv)
Au	Pd	Ag	Cu	others					
12	20	46	20	2	11.5	1203	804	3	288
20	20	42.5	15	2.5	12.1	1233	833	4	300

experiment. After one year, specimen was removed, concentration of elution metal ions in the test solution were determined by using of inductively coupled plasma (ICP) analysis. Rest potential measured in the interval week during a period of one year. Cyclic voltammogram measured during potential sweep method with potentiostat (Hokuto Denko, Model HR-101B) and function generator (Hokuto Denko, Model HB-104). Sweep rate was 20 mV/s. Reference electrode used saturated Ag/AgCl. Corrosion products were determined with X-ray diffraction analysis after measuring of anodic polarization curves.

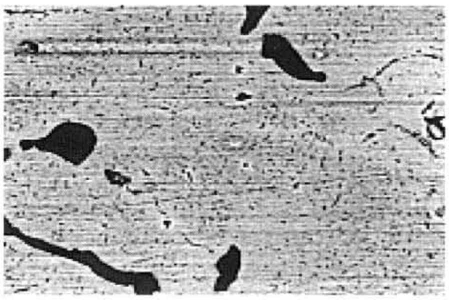
3. Rsults and discussion

3.1 Back scattered electron image

Fig. 1 shows the surface of alloys. The surface showed construction in a picture. It is whitely shown as the atomic weight increases. The alloy containing 12 % Au was easily alloyed and the composition was uniform comparing with the alloy containing 20 % Au.



12%Au sample



20%Au sample

Fig. 1. Black scattered electron image Magnification: x1500

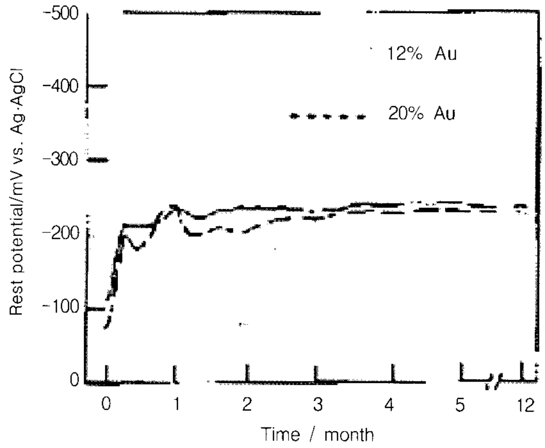


Fig. 2. Rest potential in 0.9 % NaCl solution

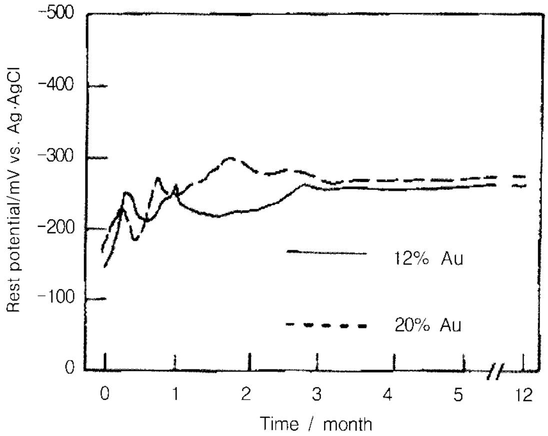


Fig. 3. Rest potential in 0.9 % solution containing 1% lactic acid

3.2 Rest potential

The rest potential is shown in Fig. 2 ~ 4. The continuous line indicated 12% gold. The dotted line indicated 20% gold. The rest potentials of two samples tended to be almost same. Rest potentials increased to noble direction until about one month in the 0.9 % NaCl solution. In the 0.9 % NaCl solution containing 1 % lactic acid, rest potentials increased to noble direction during a period of

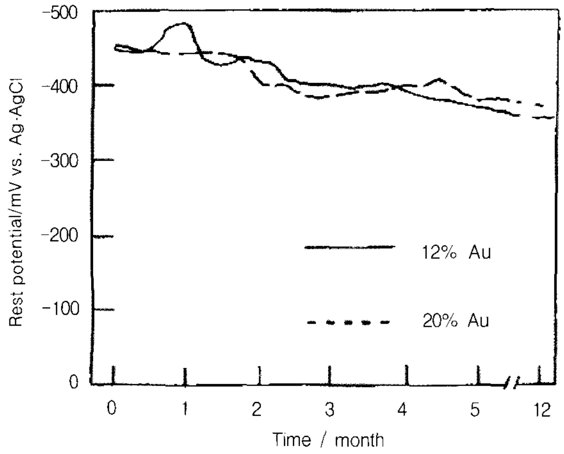


Fig. 4. Rest potential in 0.9 % solution containing 1% lactic acid and 0.1 mol dm^{-3}

about three months, formation and destruction of the corrosion product have been generated, because the potential vibrated. Thereafter potentials were stabilized. In the 0.9 %NaCl solution containing 1 % lactic acid and 0.1 mol dm^{-3} Na_2S, rest potentials were shifted to based direction during a period of about one year. This potential was differed other solutions. It was estimated that the formation and disconnect of metal sulfides or chlorides on surface were occurred. Surface of two samples in three test solutions was not natural discoloration during one year. The corrosion products could be not determined, cyclic voltammetry technique was tried.

3.3 Cyclic voltammogram

The cyclic voltammograms are shown in Fig. 5~7. The voltammograms were differed. In the 0.9 % NaCl solution, the 12 % Au sample showed one oxidation peak at about -510 mV and one reduction peak at -1350 mV vs. Ag/AgCl. The 20 % Au sample showed one oxidation peak at -470 mV and three reduction peaks at -800, -1400 and -1660 mV vs. Ag/AgCl. In the 0.9% NaCl solution containing 1% lactic acid, the 12% Au sample indicated one oxidation peak at -500 mV and three reduction peaks at -800, -1300 and -1650 mV vs. Ag/AgCl. The 20% Au ample showed one oxidation peak at -600 mV and two reduction peaks at -1250 and -1650 mV vs. Ag/AgCl. In the 0.9 % solution containing 1 % lactic acid and 1 mol dm^{-3} Na_2S, the 12 % Au sample showed two oxidation peaks at 300 and 400 mV vs. Ag/AgCl, and two reduction peaks at 0 and -250 mV vs. Ag/AgCl. The 20 % Au sample showed two small oxidation peaks at 300 and 400 mV and two reduction peaks at 0 and -250 mV vs. Ag/AgCl. The kinds of metals could be not definitely from the oxidation and reduction waves of metals. It was estimated

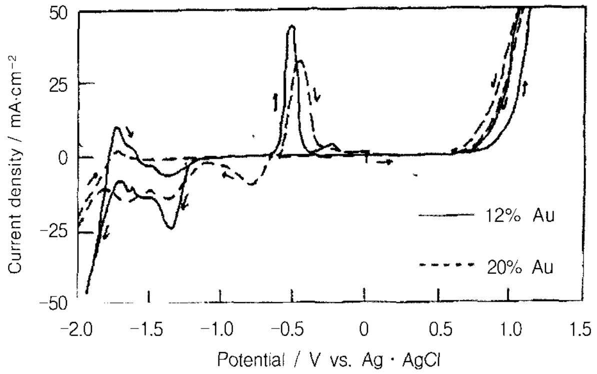


Fig. 5. Cyclic voltammogram in the 0.9 % NaCl solution

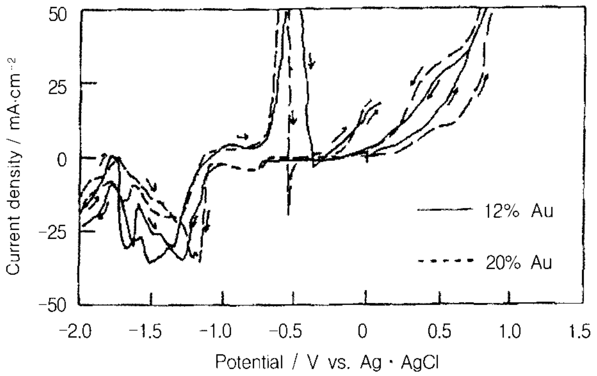


Fig. 6. Cyclic voltammogram in the 0.9% NaCl solution containing 1% lactic acid.

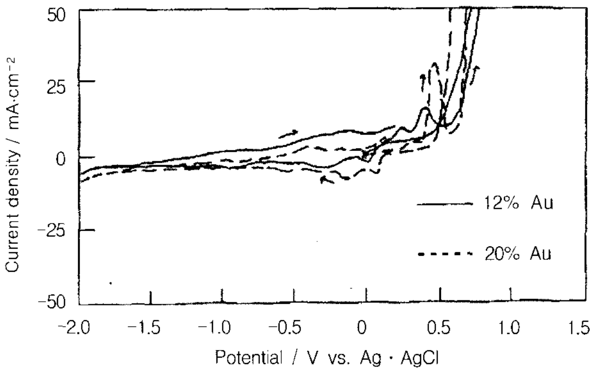


Fig. 7. Cyclic voltamogram in 0.9% NaCl solution containing 1% lactic acid and 0.1 moldm^{-3}

that silver and copper chloride or sulfide were mainly corrosion products.

3.4 Dissolution amount

Dissolution amounts is shown in Table 2. Ag and Cu in two samples dissolved in all test solutions. The pH (4-9)

Table 2. Dissolution amounts of after one year

Sample Au content	Test solution	Dissolution amount (μg/cm^2)			
		Au	Pd	Ag	Cu
12	A	·	·	1.6	3.2
20	A	·	·	0.53	0.53
12	B	·	·	1.1	6.4
20	B	·	·	1.6	170
12	C	2.6	5.3	3.7	3.7
20	C	·	·	2.6	2.6

Test solution:A;0.9 % NaCl solution, B;0.9 % NaCl solution containing 1 wt% lactic acid, C;0.9% solution containing 1 % lactic acid and 0.1 mol/dm^3 Na_2S

of test solution had not little effects. Au and Pd in 12 % Au sample was dissolved in the 0.9 % NaCl solution containing 1 % lactic acid and 0.1 mol dm^{-3} Na_2S. The copper dissolved amount in 20 % Au sample was about 26 times comparing with that of 12 % Au sample in the 0.9 % NaCl solution containing 1 % lactic acid. It was estimated that major products were silver and copper chloride or sulfide. The surface of two samples in three test solution was not natural discoloration during one year.

References

1. Y. Takada, *Zairyoto - Kankyo*, **49**, 454 (2000).
2. L. Niemi and I. Holland, *J. Den. Res.*, **63**, 1014 (1984).
3. B. Grosgogeat, M. Lissac, J. Brugirard, F. Dalard and L. Reclaru, *J. Den. Res.*, **74**, 938 (1995).
4. M. Ohta, T. Shiraishi, M.. Nakagawa and S. Matsuya, *J. Mat. Sci.*, **29**, 2083 (1994).
5. C. Mulders, M. Darwish and R. Holze, *J. Oral. Rehabili*, **23**, 825 (1996).
6. N. K. Sarker, D. W. Berzins, and A. Prasad, *Den. Mater.*, **16**, 374 (2000).
7. D. W. Berzins, I. Kawashima, R. Graves, and N. K. Sarkar, *Den. Mater.*, **16**, 266 (2000).
8. Z. Cai, S. G. Vermilyea, and W. A. Brantly: *Dental Materials*, **15**, 202 (1999).
9. J. Brugirard, R. Bargain, J. C. Dupuy, H. Mazille, and G. Monnier, *J. Dent. Res.* **52**, 828 (1973).
10. N. K. Sarkar, R. A. Fuys, and J. W. Stanford, *J. Den. Res.*, **58**, 1572 (1979).
11. R. I. Holland, R. B. Jorgensen, and H. Hero, *Den.Mater.*, **2**, 143 (1986).
12. R. I. Holland, *Scand. J. Den. Res.*, **99**, 75 (1991).
13. C. Bessing, M. Bergman, and A. Thoren, *Den. Mater.*, **3**, 153 (1987).
14. J. G. Gerstorfer and H. Weber, *Den. Mater.*, **3**, 289 (1987).
15. R. I. Holland, *Dent. Mater.* **8**, 241 (1992).
16. Grosgogeat, M. Lissac, J. Brugirard, J. Dalard, and L. Reclaru, *J. Den. Res.*, **74**, 938 (1995).