

The corrosion and tarnish behavior of new palladium-indium system alloys

HWA-SOO KIM

Division of Metals, Korea Institute of Science and Technology P.O. Box 131, Cheongryang, Seoul 136-791, Korea; Department of Metallurgical Engineering, Hanyang University, 17, Haengdang-dong, Seongdong-gu, Seoul 133-791 Korea

MAN-HYUNG DZO

Department of Metallurgical Engineering, Hanyang University, 17, Haengdang-dong, Seongdong-gu, Seoul 133-791 Korea

KYU-HWAN LEE, MYUNG-CHUL SHIN

Division of Metals, Korea Institute of Science and Technology P.O. Box 131, Cheongryang, Seoul 136-791, Korea

Emphasis on reduced costs has led to the greater use of economic alloys. Previous work has designed alloys with physical and mechanical properties similar to those of high gold alloys. Evaluation for the degree of corrosion and tarnish are to followed quantitatively by potentiodynamic and spectrophotometer analysis. In the view of the development in low nobility alloys, it is important that such testing be standardized to characterize the corrosion and tarnish properties of the compositions. But there are concerns with the long term chemical stability of these alloys, the resistance to corrosion and tarnish. Chemical stability is a complex problem involving alloy composition, nobility, microstructure and environment. © 2000 Kluwer Academic Publishers

1. Introduction

As prices of gold and precious metals have been recently going up, a lot of efforts are put it finding out alternative alloy elements with satisfactory properties, which can be available at a low price. Thus, new formulations are designed with properties similar to those found in high gold content alloys. Emphasis on cost has led to the greater use of palladium to maintain nobility by increasing the copper and silver. The color and corrosion property and tarnish resistance of palladium alloys are degraded due to the presence of Cu, Ag and etc [1–4]. The tarnish resistance is maintained when the composition of Pd exceeds 75%, but there are problems that the color becomes gray tone and a great amount of hydrogen pores are created by Pd, which is strong in absorption of hydrogen [5]. Long term durability as well as aesthetic appearance necessitates investigations of both corrosion and tarnish susceptibility of alloys. Although corrosion and tarnish are both of electrochemical character, there are many differences that set them apart in the various environments. Tarnish is defined as the visibly detectable discoloration of a metal caused by a thin adherent layer of insoluble reaction product, such as an oxide or a sulfide, induced by a chemical reaction between the metal and various environment. In contrast, corrosion involves the formation not only of insoluble reaction deposits but also of soluble products which would prove cytotoxic [5, 6]. The degree of tarnish was measured using a computerized spectrophotometer

(Cr-200, Minolta Japan). The CIELAB(International Commission on Illumination) uniform color scale was used to measure the color coordinates before and after tarnish exposure. The degree of tarnish is expressed in term of the composite color vector between the pre-exposure and post-exposure coordinates. Color information is expressed quantitatively as three parameters: ‘ L^* ’, indicating the light-dark relationship; ‘ a^* ’ giving the red-green values; and ‘ b^* ’, showing the yellow-blue component. The discoloration is expressed quantitatively by the value of ΔE^* calculated from the color vector formula [7].

$$\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$$

Corrosion is unwanted chemical reaction of metal with its environmental resulting in its continued degradation. Therefore corrosion of alloys is consequently important.

Corrosion rate, corrosion potential, breakdown potential of designed alloys were measured and compared to commercial Argenco Y^+ alloy. using potentiostat machine (Fig. 2) Experimental apparatus for the corrosion test were connected and controlled with IBM computer. In these days, the great interests are focused on the alternative gold alloy of Pd-In system which has a beautiful gold color. Pd-In has been reported as having a NiAl-type defect structure with Pd site vacancies at the composition in the excess of 50% In.



Figure 1 Spectrophotometer (cr-200. Minolta Japan).

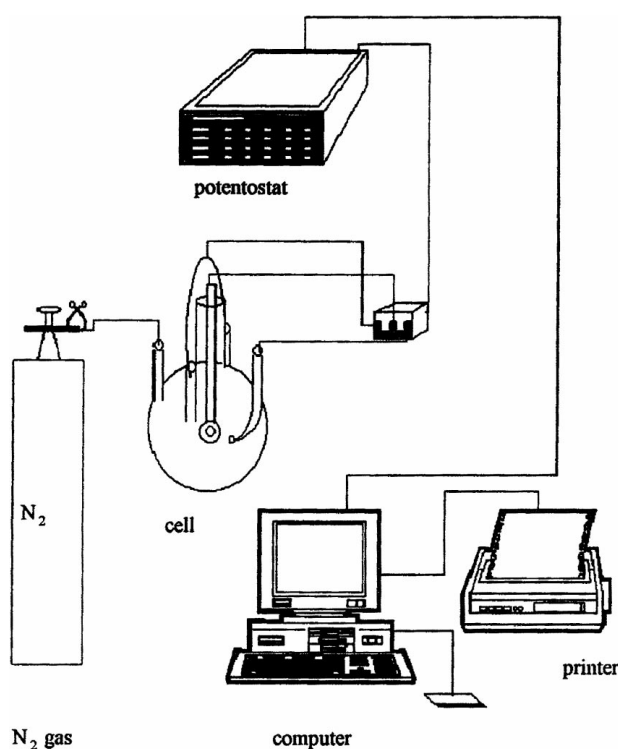


Figure 2 Experimental apparatus for corrosion test.

The results of hardness test confirm that constitutional vacancies begin to form at 49% In [8–11]. To obtain data for comparison with the results of studies using new designed alloys, the object of this research was the characterized electrochemical behavior of new designed Pd-In system alloys and commercial alloy by potentiodynamic polarization analysis and spectrophotometer in the 0.5%Na₂S solution and 22%(NH₄)₂S solution.

2. Experimental procedure

The alloys were obtained by vacuumed insertion of the specimens in composition as Table I and by vacuum arc melting method. The corrosion test specimens were cut in the dimension of 10 × 3 mm from each ingot manufactured as in Table I.

TABLE I Chemical compositions of Pd-In system alloys and commercial alloys (wt.%)

Specimen Code	Pd	In	Ag	Zn	Au	Cu	Nobility
A	40.0	29.0	26.0	2.0	1.0	2.0	41
B	40.0	29.0	25.0	2.0	2.0	2.0	42
C	40.0	29.0	23.0	2.0	3.0	3.0	43
Argenco Y ⁺	35.7	29.0	29	3.0	2.3	-	38

The tarnish test specimens were cast into round shapes (diameter 25.0 mm, thickness 1.2 mm) using lost wax investment casting technique and mounted in the epoxy resin. Both surfaces were polished by the silicon abrasive papers at first in the sequence of 120, 240, 320, 400 and 600 and were also consecutively polished by 6 μm diamond paste, successively 1 μm and 0.05 μm Al₂O₃. The corrosion tests were performed by potentiodynamic polarization method (Fig. 2) which has been used by Sakar *et al.* Potentiostat (EG & G MODEL 273, U.S.A.) equipped with programmable scanner was used in this study (10, 11). The corrosion specimens were corroded in the 0.5% Na₂S solution at 36.5°C. At this time, the applied potential was between -500 mV and +1000 mV and scan rate was 0.5 mV/sec. The Nitrogen gas is blown into the cell for 1 hr to eliminate the dissolved oxygen and the current densities at the anode specimen are measured as the function of constant applied voltage. Tarnish testing relied on controlled exposure time of the specimen to solutions in sulfur upon removal from the 0.5% Na₂S solution and immersed in constant temperature (36.5°C) bath and 22%(NH₄)₂S solution in constant temperature 60°C. Test duration of three days and 10 minute were determined for color measurement. XRD tests were performed by X-ray diffractometer (Phillips Co. Netherlands). Accelerating voltage was 25 kV and Cu and Ni were used for target and filter, respectively. The specimens finally polished by 0.05 μm were etched in the solution of KCN 10 g, (NH₄)₂S₂O₈ 10 g and H₂O 100 ml and maintained for 40–70 seconds. The corrosion test was stopped at near breakdown potential in the Potentiodynamic test. The OM and SEM

observed the region that showed the commencement of corrosion.

3. Results and discussion

3.1. Results of corrosion resistance tests

Differences in the tendency to dissolve among the individual compositions of alloys produce unique polarization behavior that is not seen in pure metal.

In the present study the reproducibility of polarization curves were satisfactory. The initial values of corrosion potential and of current density peaks were probably influenced by the primary occurrence of selective corrosion of complex alloys studied and also by the formation of surface layers that can show slightly different process [12–14]. The potentiodynamic polarization curve for each new designed alloy and commercial alloys Fig (3). As a result of the corrosion test between -500 mV and $+1000$ mV with potentiodynamic method the corrosion rate of 40Pd-29In-26Ag-2Zn-Au-2Cu(wt.%) was relatively admissible as shown Table II.

In case of comparison of the result obtained from the polarization curve of 40Pd-29In-26Ag-2Zn-Au-2Cu(wt.%) alloy and Argenco Y⁺ alloy. The 40Pd-29In-26Ag-2Zn-Au-2Cu(wt.%) alloy has fairly good corrosion rate, current density and passive breakdown potential. Therefore 40Pd-29In-26Ag-2Zn-Au-2Cu(wt.%) alloy is excellent in having higher corrosion resistance.

The corrosion resistance is expected to be due enriched Pd accumulate in the corrode surface. It was studied that alloy nobility dominated the measure the corrosion response. but microstructure also affected the corrosion resistance.

40Pd-29In-26Ag-2Zn-Au-2Cu(wt.%) and 40Pd-29In-25Ag-2Zn-2Au-2Cu(wt.%) alloys which can be

obtained by adding 2wt.%Cu Showed better corrosion resistance than 40Pd-29In-23Ag-2Zn-3Au-3Cu(wt.%) alloy which can be obtained by adding 3wt% Cu. Using the integrated corrosion current as rating basis, the nobility have the only important correlation. The amount of copper changes the rank ordering of the alloy beyond predicted the basis of nobility. This effect is very evident, where the corrosion value increases with roughly as show in Table II. The negative effect of copper on corrosion is evident. The Pd-In system alloy is brittle. This alloy is designed by multi regression analysis because of the elongation rate. For the increase of elongation rate. Copper was added. As the amount of copper is increased, I_{corr} and corrosion rate are increased and breakdown potential shows the tendency of decreasing as shown Table II. Also we can find out that the conventional Argenco Y⁺ alloy shows worse corrosion resistance than 40Pd-29In-26Ag-2Zn-Au-2Cu(wt.%) and 40Pd-29In-25Ag-2Zn-2Au-2Cu(wt.%) alloys and has dendrite structure inducing the corrosion of this alloy and hence large interdendrite region promotes corrosion.

3.2. Results of tarnish resistance tests

Data were collected for up to 3 days cumulative exposure time for the alloys in the 0.5% Na₂S solutions at 36°C and collected for 10 minutes exposure time in 22%(NH₄)₂S solution at 60°C. The exposure time, the amount of solution, volume of each sample and its mount, and solution temperature were all controlled during test. Tarnish is a complex phenomenon of compound formation on the alloy surface due to interaction with test environment [15, 16].

As indicated by the data in Table III and Fig. 3, the degree of tarnish varies with both the exposure time and alloy composition.

40Pd-29In-26Ag-2Zn-Au-2Cu(wt.%) alloy was the least susceptible to tarnish. The alloy ranking in the tarnish test illustrates that tarnish resistance of 40Pd-29In-26Ag-2Zn-Au-2Cu(wt.%) alloy and Argenco Y⁺ is not solely dependent on nobility. If nobility were dominating tarnish response, Argenco Y⁺ alloy would have fared best in solution.

Furthermore, 40Pd-29In-26Ag-2Zn-Au-2Cu(wt.%) and 40Pd-29In-23Ag-2Zn-3Au-3Cu(wt.%) alloys have approximately the equal nobility and yet responded differently to the tarnish test. At the rest of 40Pd-29In-26Ag-2Zn-Au-2Cu(wt.%), 40Pd-29In-25Ag-2Zn-2Au-2Cu(wt.%), 40Pd-29In-23Ag-2Zn-3Au-3Cu(wt.%) and

TABLE II Summary of experimental results from Tafel plots in Pd-In system alloys

Specimen code	E_{corr} (mV)	Breakdown Potential (mV)	I_{corr} ($\mu\text{A}/\text{cm}^2$)	Corrosion rate (MPY)
A	-111.4	116	1.961	1.562
B	-109.9	148	2.317	1.975
C	-112.5	26	5.753	3.822
Argenco Y ⁺	-227.9	50	3.57	2.49

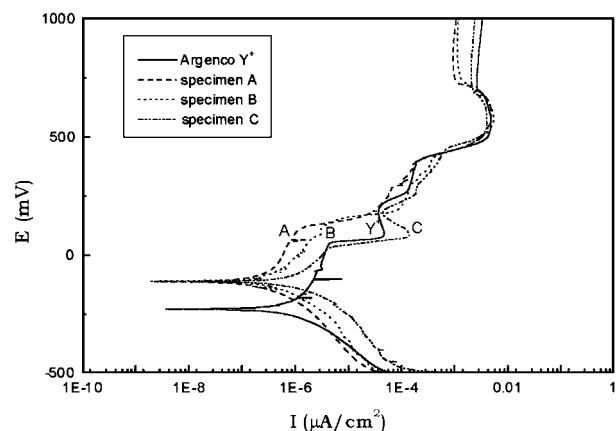


Figure 3 Potentiodynamic plots of new Pd-In system alloys and commercial alloy.

TABLE III Tarnish test result of Pd-In system alloy and commercial alloy in 0.5%Na₂S solution at 36.5°C

	24 Hour	48 Hour	72 Hour
Specimen A	2.06	3.92	5.49
SD	0.26	0.17	0.44
Specimen B	3.77	4.49	6.25
SD	0.88	1.26	1.02
Specimen C	4.99	6.06	7.27
SD	0.41	0.21	0.14
Argenco Y ⁺	4.07	5.8	7.26
SD	0.56	0.74	0.25

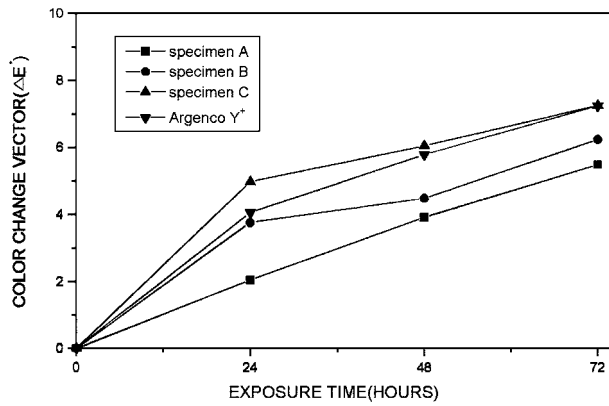


Figure 4 The tarnish color change in 0.5% Na₂S solution vs. exposure time for the as-cast Pd-In system and Argenco Y⁺ alloys at 36.5°C.

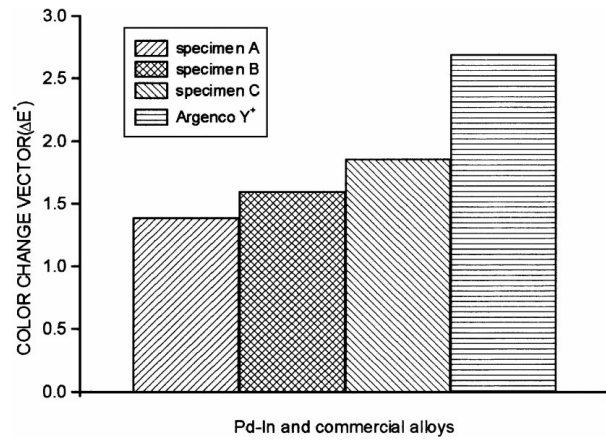
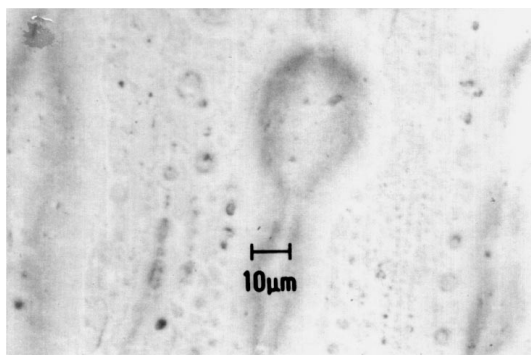
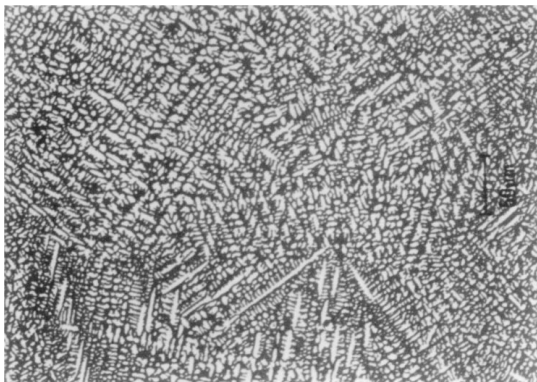


Figure 5 The tarnish color change following 10 minutes exposure to 22% (NH₄)₂S solution at 60°C.



(a)



(b)

Figure 6 Optical microscopic view of phase observed at breakdown potential of selected alloys (a) 40Pd-29In-26Ag-2Zn-Au-2Cu (wt.%) (b) Argenco Y⁺.

Argenco Y⁺ alloy, we find that tarnish which occurs in such alloys seems to be related to the Cu and Pd content. As indicated by the result in Table IV, the degree of tarnish varies with alloy composition at short

TABLE IV Tarnish test result of Pd-In system alloys and commercial alloy in 5.6% (NH₄)₂S solution at 60°C

	10 min
Specimen A	1.39
SD	0.11
Specimen B	1.6
SD	0.46
Specimen C	1.86
SD	1.02
Argenco Y ⁺	2.695
SD	1.25

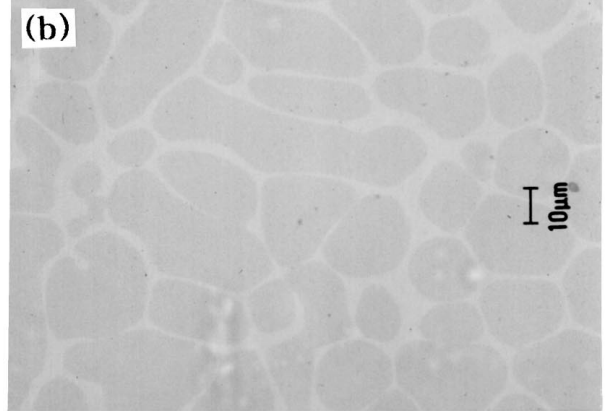
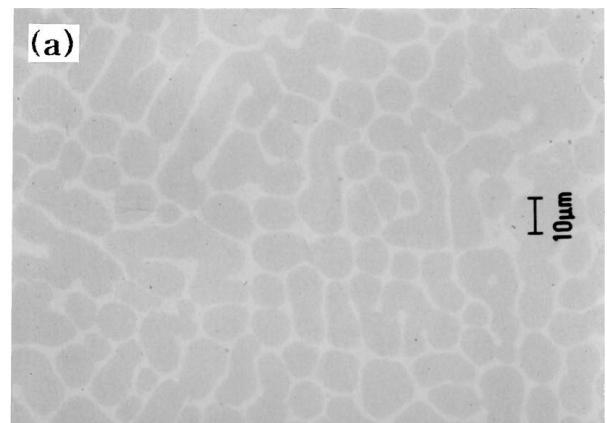


Figure 7 Optical micrographs show the as-cast microstructure of Pd-In system alloy (before the tarnish test) (a) 40Pd-29In-26Ag-2Zn-Au-2Cu (wt.%) (b) 40Pd-29In-25Ag-2Zn-2Au-2Cu (wt.%) (c) 40Pd-29In-23Ag-3Zn-3Au-3Cu (wt.%).

time. Such difference suggest that the tarnish products are highly variable; hence, it is important to generalize the tarnish reaction. One concern is with the rate of tarnish reaction. Argenco Y⁺ would be not preferable for the tarnish reaction to rapidly reach a high value for 10 minutes. Fig. 4 indicates the nobility is not sufficient to explain the results of tarnish tests. It appears that proper alloy design is more important to tarnish resistance than nobility. Below approximately 55 (at.%) noble metal content, microstructure play a dominant role in determining tarnish resistance [4].

Chemical segregation and two-phase microstructures promote tarnish and casting-induced segregation increased the degree of tarnish. Both segregation and two-phase microstructures contribute to galvanic coupling, which promotes tarnish. By the alloy design and heat treatment, low nobility alloy can be designed with acceptable tarnish resistance.

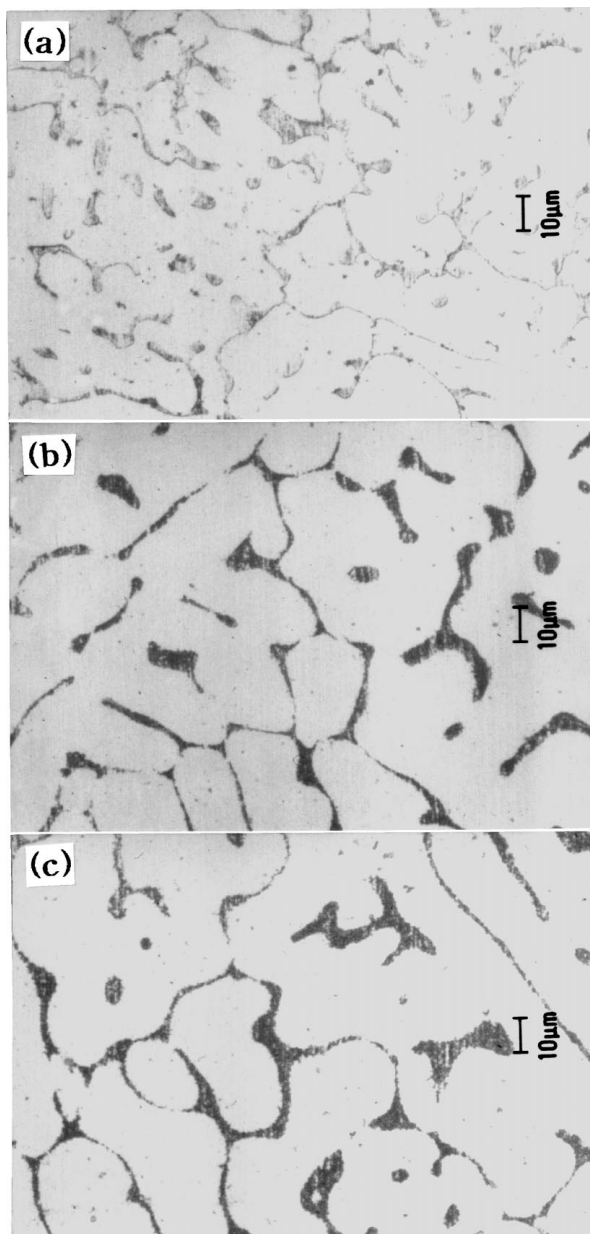


Figure 8 Alloy microstructure following 48 hour exposure to 0.5% Na₂S solution at 36.5°C (a) 40Pd-29In-26Ag-2Zn-Au-2Cu(wt.%) (b) 40Pd-29In-25Ag-2Zn-2Au-2Cu(wt.%) (c) 40Pd-29In-23Ag-3Zn-3Au-3Cu(wt.%).

3.3. Metallurgical microstructure test

The optical micrographic pictures for cast state and at the breakdown potential are such as Fig. 6. The surface of alloy at the breakdown potential of passivity which is predetermined by the curves obtained from potentiodynamic tests were observed by the optical microscope. The matrix of Pd-In system alloys was corroding acting as anode and secondary phases that were segregate at the grain boundary showed the preferential corrosion. Interdendrite region was found to corrode black in Pd-In system alloys. Normally there is an increased in tarnish with a decrease in nobility. However, it is clear that nobility alone is not a predictor of tarnish resistance. Sometimes it is important in the microstructure and composition of alloys.

Microscopic examinations are used to determine the degree to which microstructure factors affect tarnish behavior. Before tarnish test is done, the surface of specimens was checked by the optical microscope (Fig. 7).

40Pd-29In-25Ag-2Zn-2Au-2Cu(wt.%) and 40Pd-29In-23Ag-2Zn-3Au-3Cu(wt.%) is more sensitive than 40Pd-29In-26Ag-2Zn-Au-2Cu(wt.%) (Fig. 8) in tarnish. Tarnish compound formation is increased by a two phase's microstructure via micro-galvanic coupling.

4. Conclusion

40Pd-29In-26Ag-2Zn-Au-2Cu(wt.%) and 40Pd-29In-25Ag-2Zn-2Au-2Cu(wt.%) alloys designed by the multi regression analysis show higher corrosion and tarnish resistance than commercial Argenco Y⁺ alloy. The nobility and corrosion current density have the important correlation. but the amount of copper alter the correlation. The negative effect of copper on corrosion is evident in this test. The results show the combination of nobility, microstructure, composition and environment most likely to avoid corrosion and tarnish difficulties.

References

1. L. A. O'BRIEN and R. M. GERMAN, *J. Mater. Sci.* **23** (1988) 3563.
2. P. P. CORSO, JR., R. M. GERMAN and H. D. SIMMONS, *J. Dent. Res.* **64** (1985) 854.
3. H. S. KIM, K. H. LEE, M. C. SHIN, S. Y. KIM and M. H. DZO, *Scripta Materialia* (1998) in press.
4. P. P. CORSO, JR., R. M. GERMAN and H. D. SIMMONS, JR., *J. Dent. Res.* **64**(5) (1985) 848.
5. S. SASTRI, T. K. VAIDYANATHAN and K. MUKHERJEE, *Metallurgical Transactions A* **13A** (1982) 313.
6. C. BESSING, M. BERGMAN and A. THORE'N, *Dent Mater.* **3** (1987) 153.
7. PR. MERGER, M. M. A. VRIJHOEF and E. H. GREENER, *ibid.* **1** (1985) 177.
8. H. HERØ and R. B. JORGENSEN, *J. Dent. Res.* **63**(6) (1984) 926.
9. I. R. HARRIS, M. NORMAN and A. W. BRYANT, *J. the Less - Common Metals.* **16** (1968) 427.
10. ASTM, 1980 annual book of ASTM Standards, part 10, G5 (ASTM, Philadelphia, PA, 1980). p. 592.
11. J. R. KNIGHT and D. W. RHYS, *J. Less-Common Metals.* **1** (1959) 292.
12. D. OTT and CH. J. RAUB, *Gold Bull.* **14** (1981) 69.

13. T. SHEEHAN, "Corrosion testing techniques using potentiostats and galvanostats," Vol. 10, (1980) p. 18.
14. H. S. KIM and K. H. LEE, *Biomaterials Research* **1** (1997) 15.
15. R. M. GERMAN, D. C. WRIGHT and R. F. GALLANT, *J. Prosthetic Dentistry* **47** (1982) 399.
16. H. J. MUELLER, J. W. LENKE and M. S. BAPNA, *Scanning Microscopy* **2** (1988) 777.
17. D. FORT, R. E. SMALLMAN and I. R. HARRIS, *J. the Less-common Metals* **31** (1973) 263.
18. M. M. KARNOWSKY, *J. Mater. Sci.* **13** (1978) 2339.
19. H. HERØ, R. JØRGENSEN, E. SØRBRØDEN and E. SUONINEN, *J. Dent. Res.* **61**(5) (1982) 673.
20. M. SYVERUD and H. HERØ, *Acta Odontol Scand* **42** (1984) 47.

*Received 6 April 1998
and accepted 3 February 2000*