JOURNAL OF MATERIALS SCIENCE: MATERIALS IN MEDICINE 1 (1990) 140–145

Effect of palladium addition on the tarnishing of dental gold alloys

M. OHTA, M. NAKAGAWA, S. MATSUYA
Department of Dental Materials Engineering, School of Dentistry, Kyushu University, Fukuoka 812, Japan

Tarnishing tests were carried out on Au–Cu–Ag and Au–Cu–Pd alloys. This study focused on the individual and combined effects of nobility, palladium content and microstructure. Tarnish resistance was almost perfect for the alloys with nobility higher than 50 at %, but it seemed to relate to the palladium : gold atomic ratio for the alloys with low nobility. Palladium inclusion reduced the tarnish susceptibility up to about 10 at %. This decrease in the degree of tarnishing was attributed to the decrease in the diffusion rate of S^{2-} ion which resulted in a decrease in the growth rate of sulphide layer. Tarnishing of the alloy with low nobility was very sensitive to its microstructure. The tarnishing susceptibility of dual-phase Au–Cu–Ag alloy was twice as high as that of the single-phase alloy. However, palladium-bearing alloy showed no increase in the degree of tarnishing by phase separation. This may be attributed to the enrichment of palladium in the copper-rich phase.

1. Introduction

Chemical stability is the first requirement of dental materials, from the standpoint not only of disintegration of materials but also of biocompatibility. For dental alloys, corrosion in the oral environment is the most important problem to be solved. The common conclusions of numerous studies have pointed out that the total amount of precious metals included (nobility) [1–3] and the microstructure [4–6] are important factors which control the degree of corrosion.

Tarnishing of dental alloys is another problem in clinical performance. Results of tarnishing tests on Au–Cu–Ag [7–11], Ag–Pd [12], Ag–Pd–Cu [13, 14] and Ag–Pd–Au–Cu [15, 16] alloys indicate that tarnishing is a complex process and is sensitive to the alloy composition, the microstructure and the tarnishing solution, analogously to the corrosion problem. As regards the alloy composition, Lang *et al.* [15] indicated that palladium had a greater effect on increasing tarnish resistance than gold. Suoninen *et al.* [11] examined the effect of palladium on sulphide tarnishing by means of X-ray photoelectron spectroscopic analysis of the alloy surface. They concluded that palladium enriched just below the silver sulphide layer, and this enrichment was thought to help in reducing the thickness of the sulphide layer.

Most commercial dental alloys have a complex micro structure with multiple phases in both the as-cast and age-hardened states. All experimental results so far indicate qualitatively that a two-phase microstructure tends to promote rapid tarnishing by producing microgalvanic cells.

The authors have already reported the advantages of single phase Au-Cu-Pd ternary alloys in age-hardenability [17] and in corrosion resistivity [18]. In this study we focused on the role of palladium on the tarnishing resistance. The principal interest was centred on the individual and combined effect of nobility, palladium content and microstructure on the tarnish of Au–Cu–Ag and Au–Cu–Ag–Pd alloys.

2. Materials and methods

2.1. Specimen preparation

The chemical composition of alloys used are listed in Table I. Group 1 and group 2 alloys are the Au–Cu–11 at % Pd and Au–Cu–11 at % Ag systems, respectively. To understand the role of palladium on tarnishing resistance, two types of alloys were prepared. In the alloys of group 3, a part of gold in III-Ag was replaced with palladium. The alloy of group 4 was designed so that 5 at % of palladium was added to the III–Ag without any change in the atomic ratio of gold, copper and silver.

Rectangular sheets of 12 mm × 10 mm × 2 mm were made by casting through a lost-wax technique with a gypsum-bonded silica investment. Casting was performed in argon atmosphere to prevent the oxidation of molten metals. Casts were subjected to alternate hammering (or rolling) and annealing at 800° C for 2 to 5 h, and were finally quenched from 800° C into iced brine to obtain a homogeneous single-phase structure. Unless otherwise noted, specimens used hereinafter were homogenized ones.

Age-hardening heat treatment was performed on the homogenized III-Ag and III-Ag + 5Pd specimens at 450° C for 7200 min. As a result, whole grains were fully covered with nodules that consisted of fine lamellae.

Specimens were mounted in epoxy or acrylic resin and polished with a final polish using 0.3 μm alumina slurry. They were cleaned ultrasonically, rinsed and subjected to tarnish testing.

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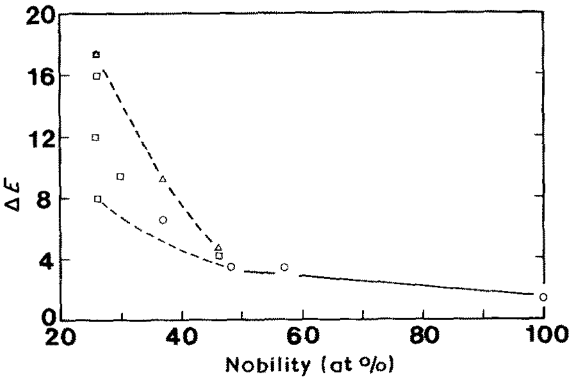

Figure 1 Variation of ΔE with nobility of (○) Au–Cu–Pd, (△) Au–Cu–Ag and (□) Au–Cu–Ag–Pd alloys.

TABLE I Chemical composition of the alloys used (at %)

Group	Alloy	Gold	Copper	Silver	Palladium
1	II	46.0	43.0		11.0
	I	37.0	52.0		11.0
	III	26.0	63.0		11.0
2	II-Ag	46.0	43.0	11.0	
	I-Ag	37.0	52.0	11.0	
	III-Ag	26.0	63.0	11.0	
3	III-Ag-5Pd	21.0	63.0	11.0	5.0
	III-Ag-8Pd	18.0	63.0	11.0	8.0
	III-Ag-10Pd	16.0	63.0	11.0	10.0
	III-Ag-15Pd	11.0	63.0	11.0	15.0
	III-Ag-21Pd	5.0	63.0	11.0	21.0
	III-Ag-26Pd		63.0	11.0	26.0
4	III-Ag + 5Pd	24.7	59.8	10.5	5.0

2.2. Tarnish testing

The solution for tarnish testing was aqueous 0.5% Na_2S solution. The test specimens were placed in jars containing 75 ml test solution maintained at 37° C in a water-bath.

Colour measurements were taken before immersion and every 24 h for the 3 day test period using a computerized spectrophotometer. The amount of tarnish was expressed by the colour vector ΔE which was calculated from

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

where ΔL, Δa and Δb are the changes in the colour co-ordinates on the three-dimensional CIELAB uniform colour scale.

3. Results

3.1. Effect of nobility on ΔE

The effects of nobility on tarnishing are evident in Fig. 1. Alloys with nobility > 50 at % exhibited almost perfect tarnishing resistance. On the other hand, the ΔE of alloys with < 50 at % nobility was not solely determined by nobility, and seemed to depend on the palladium : gold atomic ratio of the alloy.

3.2. Effect of palladium : gold ratio on ΔE

Fig. 2 demonstrates the ΔE of group 3 alloys in which a part (or all) of the gold in the alloy III-Ag was replaced with palladium. The value of ΔE decreased up to about 10 at % replacement, but further replacement increased ΔE monotonically. Comparing the Au–Cu–Ag alloy (left-most composition) with the Pd–Cu–Ag (extreme right) alloy, gold seems to have a greater effect on increasing the tarnishing resistance than palladium.

3.3. Effect of microstructure on ΔE

Microstructures of alloy III-Ag in the as-cast, homogenized and aged states are shown in Figs 3a, b and c, respectively. Ageing heat treatment was performed at 450° C for 7200 min. As a result, the whole surface of the specimen was covered with nodules, which consisted of fine lamellae of copper- and silver-rich phases.

The results of the tarnishing tests on III-Ag and III-Ag + 5Pd alloys are presented in Fig. 4. There is no difference in ΔE between as-cast and homogenized specimens of III-Ag alloy. However, ageing treatment which resulted in the phase separation increased ΔE to about twice its value in the homogenized single-phase state. On the other hand, only 5 at % palladium addition to the alloy decreased ΔE to about half that in the mother alloy. Moreover, ageing heat treatment never decreased the tarnishing resistance of the palladium-bearing alloy. The above results, together with the result in Fig. 2, clearly indicate that a small amount of palladium addition greatly improves the tarnishing resistance of Au–Cu–Ag alloys having both homogeneous and inhomogeneous microstructures.

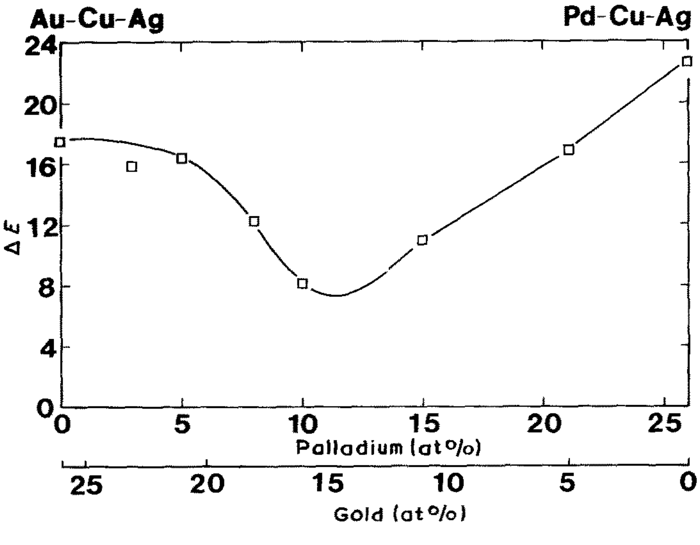

Figure 2 Variation of ΔE with palladium content of group 3 alloys. In the alloys the total amount of gold and palladium was kept constant (26 at %).

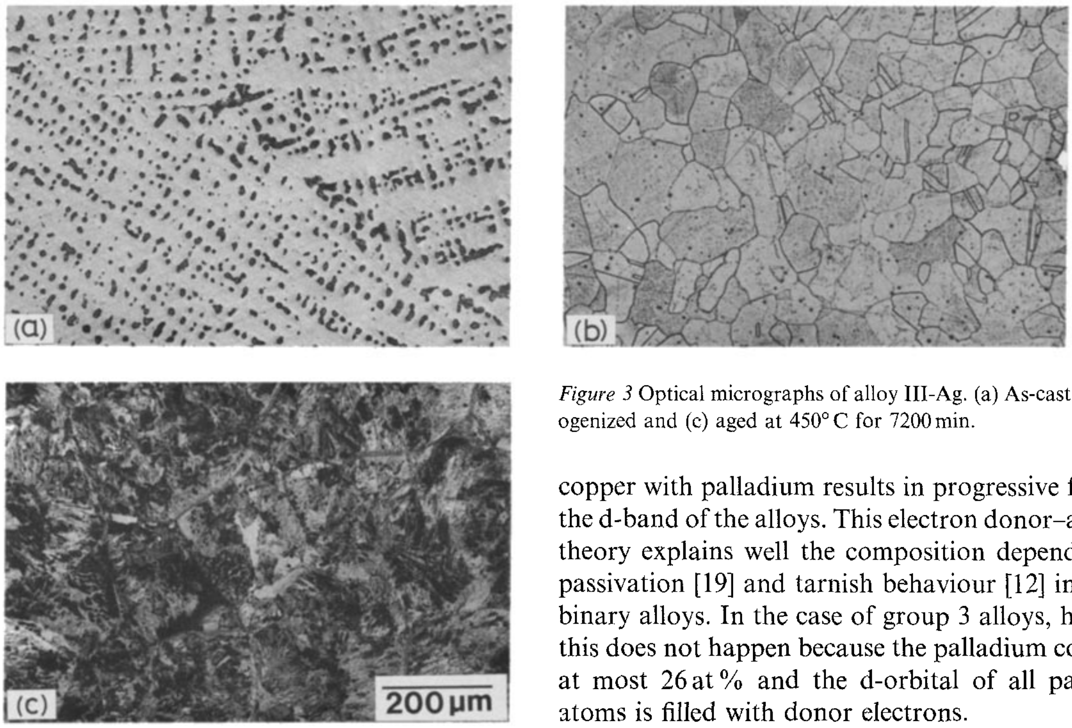

Figure 3 Optical micrographs of alloy III-Ag. (a) As-cast, (b) homogenized and (c) aged at 450° C for 7200 min.

4. Discussion

Comparing the tarnishing resistance of Au–Cu–Ag and Pd–Cu–Ag alloys with the same amount of copper and silver, palladium has a poorer effect than gold on improving the tarnishing resistance, as is evident from Fig. 2. However, a small amount of palladium addition or a small amount of gold replacement with palladium (up to about 10 at %) improves the tarnishing resistance remarkably, in agreement with the results reported in [15, 16].

It seems to be difficult to explain the discontinuous composition dependence of ΔE by a single mechanism, and the peculiar role of palladium must be considered. Palladium has a 0.6 electron vacancy concentration per atom in the 4d-band, and alloying silver, gold or copper with palladium results in progressive filling of the d-band of the alloys. This electron donor–acceptor theory explains well the composition dependence of passivation [19] and tarnish behaviour [12] in Ag–Pd binary alloys. In the case of group 3 alloys, however, this does not happen because the palladium content is at most 26 at % and the d-orbital of all palladium atoms is filled with donor electrons.

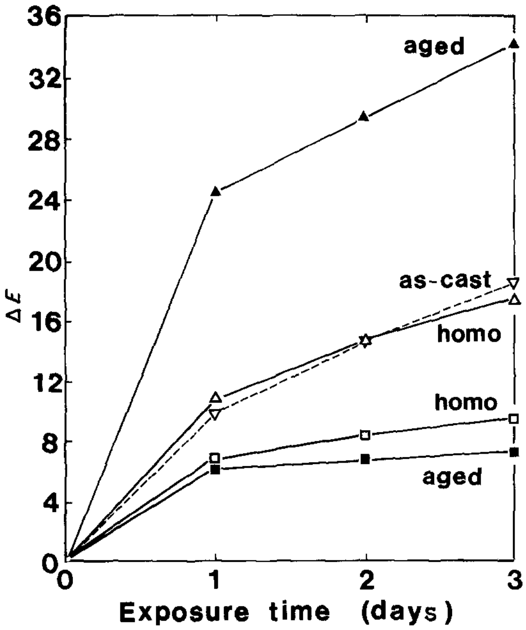

Figure 4 Colour change (ΔE) plotted against the exposure time for (△, ▲, ▽) III-Ag and (□, ■) III-Ag + 5Pd alloys; homo, homogenized.

The decrease in ΔE with increasing palladium content (left-hand side from the bottom of the curve in Fig. 2) is not attributed to the nobility of the alloys, because all alloys in group 3 have the same nobility. Therefore, the result in Fig. 2 simply indicates the effect of palladium on improving the tarnishing susceptibility.

When an alloy specimen is exposed to a test solution, a sulphide film, is expected to form immediately. As the tarnish film grows, it limits further access of the environment to the alloy surface and slows the reaction rate. Therefore, the time-dependent tarnishing curve seems to be expressed by

$$\Delta E = Kt^{1/2} + B$$

where t is the exposure time, K is a constant which is related to the diffusion rate and B is the intercept. The intercept B represents the amount of reaction which immediately occurs at the initial stage of immersion. A diffusion control mechanism of tarnishing was proposed by Treasy and German [20]. They expressed the time-dependence of colour change curves by the first term of the above equation. However, considering the above-mentioned process of tarnishing, B, the second term of the equation, has an important meaning in clarifying the controlling process of tarnishing.

The calculated values of K and B of group 3 alloys are plotted in Fig. 5 together with ΔE. Correlation coefficients of ΔE-time curves ranged between 0.83 and 1.0. The diffusion rate decreased with increasing palladium addition up to about 10 at %. At a palladium content > 5 at %, the intercept B varies in the same way with ΔE. These results suggest that palladium addition reduced diffusion rate up to about 10 at %, but further addition did not affect the diffusion rate, and most of the ΔE of the alloys with palladium content > 5 at % were attained at the initial stage of immersion.

In Fig. 6, ΔE, K and B of group 1 (Au–Cu–11 at % Pd) and group 2 (Au–Cu–11 at % Ag) alloys are

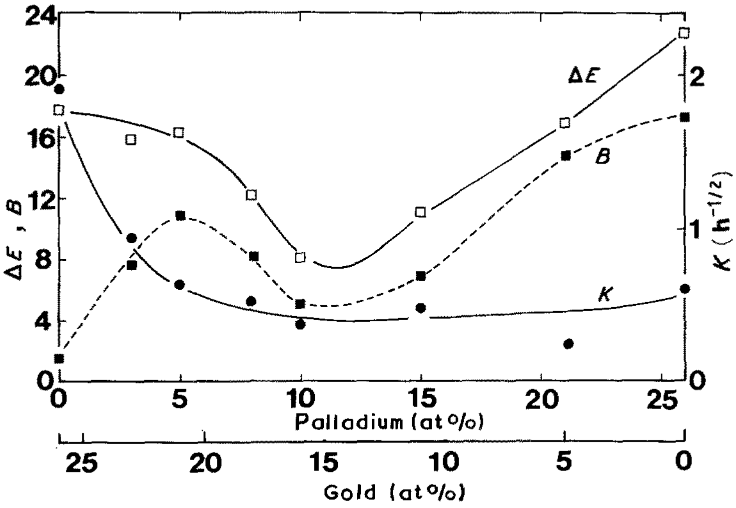

Figure 5 Variation of slope K, intercept B and ΔE with palladium content of group 3 alloys.

plotted. It is clear that palladium-bearing alloys have small K and large B, but the opposite is true in the case of non-palladium alloys.

One of the possible mechanisms of reducing the diffusion rate is the enrichment of palladium just below the sulphide film, which was proposed by Suoninen *et al.* [11]. They showed that small additions of palladium (< 3 wt %) to Au–Cu–Ag alloys reduced essentially the thickness of the sulphide layer formed on the surfaces of samples treated in aqueous Na_2S solutions. They found statistically significant enrichment of palladium immediately below the sulphide layer by electron spectroscopic analysis. The possible role of palladium that they proposed was that the active sites for sulphide formation on the alloy were preferentially blocked by the palladium atom.

It is rather difficult to explain the increase in ΔE with increasing palladium content (right-hand side from the bottom of the curve in Fig. 2). From the result in Fig. 5, it is suggested that most of the ΔE of these alloys originates in the instantaneous surface reaction at the beginning of immersion. It obviously depends on the chemical stability (or reactivity) of the surface, and hence on the chemical composition of the homogenized alloy. To find the corrosion resistance of group 3 alloys, potentiostatic polarization tests were carried out in 1% NaCl aqueous solution at 700 mV for 600 sec, and the parameter Q, which represents the total amount of anodic reaction [18], was obtained. The results are shown in Fig. 7 and indicate clearly that replacement of gold with palladium reduces the corrosion resistance of III-Ag alloy. This fact may support the explanation of an increase in ΔE with palladium content by decreasing chemical stability.

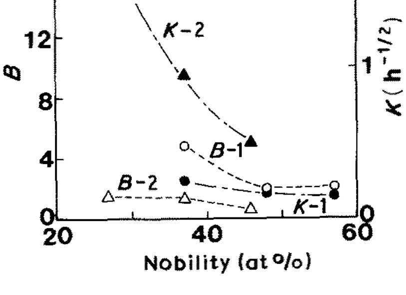

Figure 6 Variation of slope K and intercept B with nobility of group 1 and group 2 alloys. K-1, K of group 1; K-2, K of group 2; B-1, B of group 1 and B-2, B of group 2.

The effectiveness of palladium addition is significantly seen in the dual-phase alloys. Ageing heat treatment on III-Ag at 450° C caused phase separation of α into α_1 (copper-rich) and α_2 (silver-rich), which resulted in an increase in ΔE to about twice that of the single-phase state. In the alloy containing only 5 at % palladium, on the contrary, phase separation did not increase ΔE and seemed rather to improve the tarnishing resistance, as seen in Fig. 4. To understand the above results, it might be helpful to know the chemical compositions of each phase. Accordingly, we attempted to carry out a microanalysis of dual-phase specimens using an energy-dispersive X-ray microanalyser which was attached to a transmission electron microscope. Unfortunately, the results indicated that silver preferentially solved out of the thin foil during the jet polishing of the specimen. Consequently, a quantitative result was not obtained. However, qualitatively it was proved that gold was enriched in the silver-rich α_2-phase and palladium was enriched in the copper-rich α_1-phase by phase separation. These tendencies were also reported by Skjerpe *et al.* [21]. Accordingly, a possible explanation of the tarnishing behaviour of dual-phase Au–Cu–Ag alloys is as follows. After phase seperation, α_2-phase has higher nobility and therefore higher protection to chemical attack than α, but α_1-phase has lower nobility and is preferentially attacked. The addition of palladium causes the enrichment of palladium in the α_1-phase and preferential improvement of the α_1-phase, and then on average, improves the chemical stability of the alloy.

To clarify the above hypothesis and to examine the effect of palladium addition on copper-rich alloy, single-phase alloys which were made as duplicates of α_1-phase of both III-Ag and III-Ag + 5Pd were subjected to tarnishing tests. The composition of α_1-phase of III-Ag alloy was estimated to be the composition at which the tie-line crosses the phase boundary in the isothermal section of the Au–Cu–Ag ternary phase diagram [22]. At room temperature the solubility of silver was negligibly small, and the estimated composition was 27 at % Au–73 at % Cu. Two more alloys

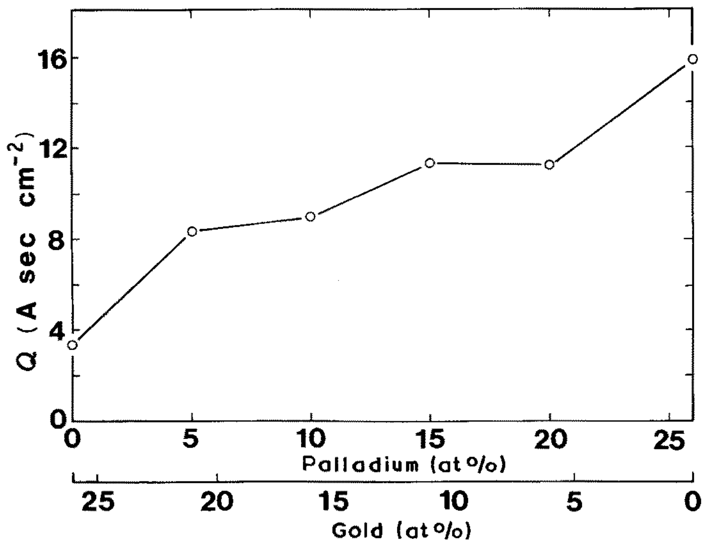

Figure 7 Variation of Q with palladium content of group 3 alloys.

were prepared by adding 5 and 8 at % palladium to the above binary alloy without any change in the gold: copper atomic ratio. The former (α_l + 5Pd) contained a nominal concentration of palladium in the III-Ag alloy and the latter (α_l + 8Pd) was hypothetical α_l-phase in which palladium was enriched. The results of tarnishing tests are shown in Fig. 8, which clearly indicates the efficacy of palladium addition on copper-rich phase. In Fig. 9 the effect of palladium on decreasing the diffusion rate is clear for copper-rich and non-silver alloys. Therefore, it seems that the palladium enrichment model is applicable also to copper-rich alloys.

Evidence of palladium enrichment was obtained by electron spectroscopic analysis [11] which included the sputtering of the sample surface with an ion-gun. In sputtering an alloy, however, it is found that the surface composition is changed due to preferential sputtering of some elements. In the binary alloys of Au–Pd, Ag–Pd and Cu–Pd, surface enrichment of palladium due to preferential sputtering was reported [23]. Therefore, careful attention is required in the microanalysis of the surface composition of alloys.

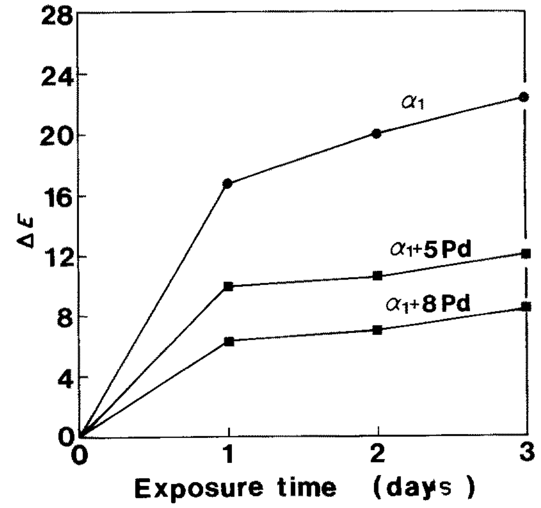

Figure 8 Colour change (ΔE) plotted against the exposure time for α_l (27 at % Au–73 at % Cu), α_l + 5Pd (25.6 at % Au–69.4 at % Cu–5.0 at % Pd) and α_l + 8Pd (24.8 at % Au–67.2 at % Cu–8.0 at % Pd) alloys.

5. Conclusions

The tarnishing susceptibility of Au-Cu-Ag and Au-Cu-Ag-Pd alloys was examined in order to understand the role of palladium in improving the tarnishing resistance. The following results were obtained.

1. Alloys with > 50 at % nobility exhibited almost perfect tarnishing resistance. The ΔE of alloys with < 50 at % nobility seemed to depend on the palladium: gold atomic ratio of the alloy.

2. The ΔE of alloys, in which some gold was replaced with palladium up to about 10 at %, decreased with the palladium content. However, further replacement increased ΔE. This increase in ΔE was attributed to the decrease in the chemical stability by the replacement of gold with palladium. The decrease in ΔE by the addition of a small amount of palladium may be explained by the mechanism of palladium enrichment just below the sulphide layer. This enrichment may suppress the diffusion of S^{2-} ion, which results in the decrease in the growth rate of sulphide layer.

3. The tarnishing susceptibility of low-nobility alloy was very sensitive to the microstructure. Phase separation increased ΔE to about twice that of the homogenized single-phase state. However, a small amount of palladium addition improved the tarnishing sensitivity of dual-phase alloy. This may be attributed to the enrichment of palladium in the copper-rich phase.

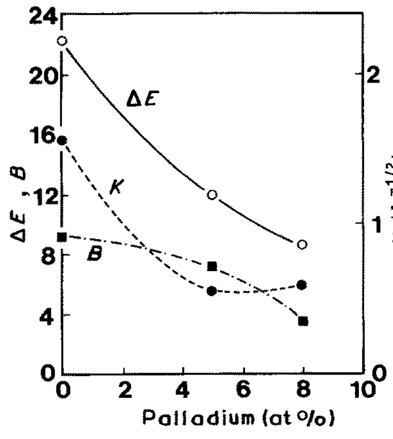

Figure 9 Slope K, intercept B and ΔE of α_l, α_l + 5Pd and α_l + 8Pd alloys.

Acknowledgements

Part of this work was done at Rensselaer Polytechnic Institute, Troy, New York. One of the authors (M. O.) expresses his thanks to Professor R. M. German of RPI for offering facilities and useful suggestions to this work. Julie Gold provided valuable guidance and assistance in the course of the tarnishing tests.

We thank Dr T. Shiraishi of Kyushu University for the sample preparation. This study was partly supported by a Grant-in-Aid from the Ministry of Education, Science and Culture, Japan (No. 63470123).

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Received 10 July
and accepted 21 December 1989