JOURNAL OF MATERIALS SCIENCE: MATERIALS IN MEDICINE 4 (1993) 142–149

# Low-noble metal alloys: *in vitro* corrosion evaluation

E. ANGELINI
*Department of Materials Science and Chemical Engineering, Polytechnic of Torino, Torino, Italy*
P. BIANCO
*Chemical Laboratory of the Chamber of Commerce, Torino, Italy*
S. MASCELLANI, F. ZUCCHI
*Corrosion Study Center A. Dacco', University of Ferrara, Ferrara, Italy*

The electrochemical behaviour and the resistance to corrosion and tarnishing of seven commercial low-noble metal alloys were investigated, in artificial saliva at two different pH values (3 and 6.7) and in 2% $Na_2S$ solution. The alloys were tested as-received and after a hardening treatment suggested by the manufacturers: ageing 15 min in a temperature range between 360 and 450 °C. Scanning electron microscopy (SEM) examination of the alloys evidenced some slight microstructural modifications. The electrochemical characterization was performed by means of anodic polarization curves. Alloys with noble metal content $> 30\%$ show a good electrochemical behaviour and a satisfactory corrosion resistance against tarnishing, and the hardening treatment had no influence on the corrosion resistance.

## 1. Introduction

The problem of substituting gold alloys with semiprecious ones is still actual, as shown by the constant presence of this item in the literature. The soaring price of noble metals gives the reason for these efforts, which have to be accompanied by the continuous check of the tarnishing and corrosion resistance of semiprecious alloys of new adoption, in order to assure a high biocompatibility, a long-term durability and a good aesthetic result.

The International Organization for Standardization Standard 1562 for "dental casting gold alloys" indicates a content of the elements of the platinum group of $> 75\%$ in order to obtain a satisfactory resistance to tarnishing and corrosion [1].

Hero [2] examined the relationship between the structure, tarnishing and anodic behaviour in some Au–Ag–Cu–Pd commercial gold alloys with decreasing gold content (from 73 to 29%) in a heat-treated state, having previously [3] established that an alloy with 54% Au can be easily solid-solution annealed to a single-phase structure, thus improving noticeably its tarnishing resistance. He found that the possibility of annealing alloys to a single-phase structure decreases with the reduction in the Au content and the increase in Pd and Zn, and that in multiphase systems only the Ag-rich phase is attacked.

Also, Corso *et al.* [4, 5], who studied the behaviour of three commercial gold alloys and three constant-nobility ternary alloys (Au–Ag–Cu), found that the alloy nobility is, of course, an important parameter in determining their behaviour, but the microstructure has to be taken into account; moreover, they affirmed that the electrochemical techniques in addition to tarnish evaluations may provide an excellent quantitative method for alloy evaluation.

Recently introduced copper-free type III alternative alloys, containing approximately 20% Au, were examined by Mezger *et al.* [6]. The low-gold alloys (Ag–Au–In–Pd–Zn) turned out to be two-phase mixtures of an f c c matrix and b c c phase; their corrosion behaviour, based on cyclic polarization, can be considered acceptable in artificial saliva and in 0.9% saline solution.

The aims of this study were to investigate and compare the electrochemical behaviour and the resistance to corrosion and tarnishing of seven commercial gold alloys with increasing noble metal contents, and to evaluate the influence of the hardening treatment suggested by the manufacturers.

## 2. Materials and experimental

The alloys studied were WG (A), alloy 55 (B), alloy 88 (C) and alloy 89 (D), recommended as casting alloys for porcelain, from Rigatti and Lucchini, Italy; Castor (E) and Platinor (F), recommended as crown and bridge alloys, and Alpha (G), recommended as ceramic gold, from Franco Swiss, Italy. Their chemical composition, shown in Fig. 1, was determined by means of a plasma-source mass spectrometer (VG Elemental Plasmaquad ICP-MS).

The alloys were tested as-received and after a hardening treatment suggested by the manufacturers: ageing for 15 min in the temperature range 360–450 °C. The heat treatments were performed in an

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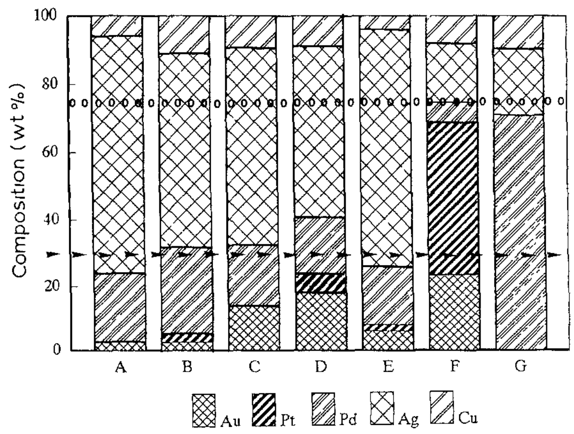

*Figure 1* Dental alloys composition (wt %) as determined by plasma-source mass spectrometry. The dotted line indicates the noble metal content recommended by ISO Standards; the arrows show the 30% noble metal content

electrical resistance tube furnace, the specimens were cooled slowly in air and the consequent surface discoloration was removed with emery paper. An electrical contact was established and the specimens were embedded in epoxy resin, leaving an exposed are of 1 cm$^2$. The samples were polished with no. 600 metallographic emery paper and finally with alumina. The electrodes were ultrasonically degreased with acetone and rinsed in distilled water.

The electrochemical tests were performed in artificial saliva (KCl 1.47 g, $NaHCO_3$ 1.25 g, KSCN 0.52 g, $NaH_2PO_4 \cdot H_2O$ 0.19 g and distilled water up to 1 dm$^3$) buffered at pH 6.7 and 3 with lactic acid, at 37 ± 1 °C. The electrode potentials were determined against a saturated calomel electrode (SCE). The free corrosion potentials were followed for 1 week. The anodic polarization curves were recorded utilizing a commercial computer-controlled potentiostat (PAR model 351). The specimen was immersed 15 min before initiating polarization, then the potential scan was started from the corrosion potential ($E_{corr}$) at a scan rate of 0.5 mV s$^{-1}$. The electrochemical cell was constituted by a Pyrex beaker with an airtight cover, containing in addition to the sample a Pt counter-electrode and a reference electrode.

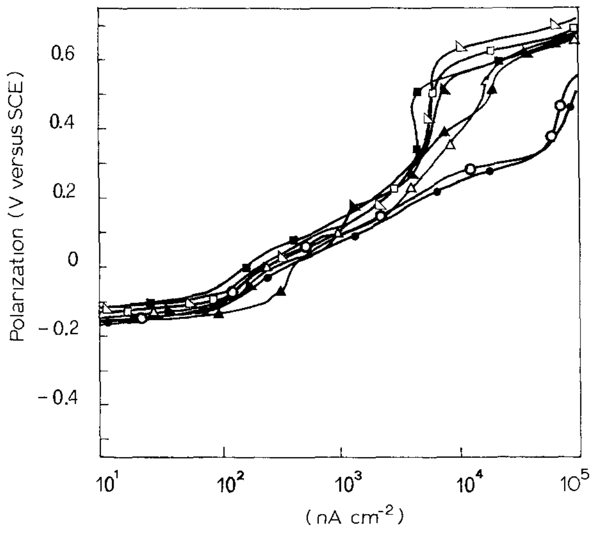

*Figure 2* Anodic polarization curves on dental alloys with noble metal content of about 30%, in artificial saliva, pH 6.7, $T = 37 \pm 1$ °C Alloy A· (●) as-received and (○) after hardening treatment; alloy E· (▲) as-received and (△) after hardening treatment; alloy B. (■) as-received and (□) after hardening treatment; and alloy C: (◣) as-received and (◺) after hardening treatment.

Tarnishing tests were carried out in 2% $Na_2S$ solutions at room temperature and at 80 °C for a period of 1 week. Morphological studies were performed on the alloys by means of optical microscopy (Reichert Jung MeF3) and SEM (Jeol model 6400). The characterization of the various phases was carried out with an energy dispersion microprobe (Tracor Z Max).

## 3. Results

### 3.1. Polarization curves in artificial saliva

The anodic polarization curves obtained on the dental alloys, in the as-received and aged conditions, are reported in Figs 2–5. They were divided as a function

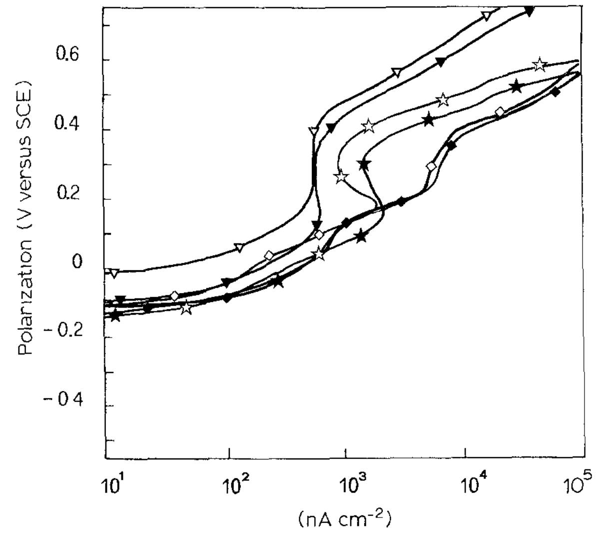

*Figure 3* Anodic polarization curves on dental alloys with noble metal content > 30% in artificial saliva, pH 6.7, $T = 37 \pm 1$ °C Alloy D. (◆) as-received and (◇) after hardening treatment, alloy F. (★) as-received and (☆) after hardening treatment; and alloy G: (▼) as-received and (▽) after hardening treatment

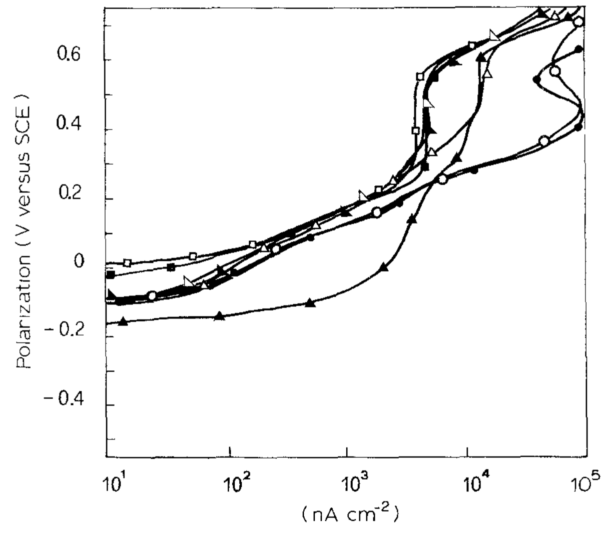

*Figure 4* Anodic polarization curves on dental alloys with noble metal of about 30%, in artificial saliva, pH 3, $T = 37 \pm 1$ °C See Fig 2 for key.

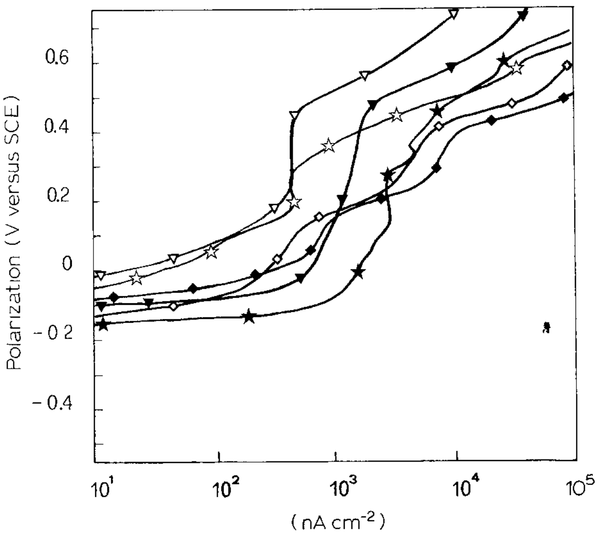

*Figure 5* Anodic polarization curves on dental alloys with noble metal content higher than 30%, in artificial saliva, pH 3, $T = 37 \pm 1$ °C. See Fig. 3 for key.

of the noble metal content (expressed as wt %), which increased, as shown in Fig. 1, in the order $A < E < B < C < D < F < G$. Examination of the anodic curves obtained in nearly neutral artificial saliva (Figs 2 and 3) revealed some interesting common features in the electrochemical behaviour of these alloys. The behaviour of the alloys with a noble metal content of about 30% can be seen in Fig. 2.

The free corrosion potentials had values near − 0.18 V [versus saturated calomel electrode (SCE)]; the shape of the polarization curves was similar, also if at high potentials, above + 0.2 V(SCE), on alloy A the anodic current densities are one order of magnitude higher than on alloys B, C and E. Furthermore, on all curves the presence of two inflexions at potentials − 0.1 and + 0.2 V(SCE) may be observed; after the second flex, for alloys B and C a region of current density independent of the potential value is visible, followed by a noteworthy increase in the anodic current.

No influence of the hardening treatment was detectable on the shape of the curve or on the current densities; the slight variations were in the limits of the reproducibility of the measurements.

In Fig. 3 the polarization curves recorded for the alloys with noble metal content > 30% are shown. Alloy D behaved similarly to the alloys previously described, whereas alloys F and G showed more-positive free corrosion potentials, − 0.1 V(SCE). Their polarization curves showed only one inflexion at + 0.1 V(SCE), the anodic current density did not exceed 0.5 $\mu A\,cm^{-2}$, until + 0.4 V(SCE), then upon shifting the potential in the positive direction the anodic current density increased.

For these alloys too the differences between the polarization curves of as-manufactured or heat-treated samples were negligible. Metallographic analysis of the surfaces after the test revealed only slight superficial attacks on the interdendritic zones of alloy A.

The increase in aggressivity of the electrolyte, decreasing pH from 6.7 to 3, allowed a better differentiation of the alloys (Figs 4 and 5). The shapes were similar to those illustrated before, but the free corrosion potentials became increasingly positive with increasing noble metal content. Furthermore, the hardening treatment seemed to exert a beneficial effect: all anodic curves of aged samples showed anodic current densities lower than the as-received samples.

## 3.2. Free corrosion potentials

In order to obtain more information on the evolution of the corrosion attack, the free corrosion potentials were followed for 1 week, as shown in Fig. 6.

For the alloys with noble metal content of about 30%, except for alloy A, they ranged between 0 and − 0.2 V(SCE) and stabilized within 24 h; the potential of alloy A between the second and third day of immersion decreased abruptly from − 0.1 to near − 0.50 V(SCE), then increased again and stabilized near − 0.38 V(SCE) at the end of the text.

The free corrosion potentials of the three nobler alloys, (Fig. 6b) ranged between − 0.1 and + 0.1 V(SCE); in particular alloy D showed values near 0 V(SCE) and stabilized after the first day of immersion to − 0.050 V(SCE). For alloys F and G the potentials always assumed positive values, and stabilized, respectively, near + 0.020 and + 0.050 V(SCE).

Slight differences were noted among as-received and heat treated samples. It must be emphasized that the similarity of the electrochemical behaviour between the alloys as-manufactured and after hardening treatment was confirmed by microstructural examination of the surfaces: SEM back-scattered observations do not allow a differentiation of the structures of the seven alloys in the two conditions to be observed.

## 3.3. Tarnishing tests

In Fig. 7 two macrographs of the alloys after 1 week immersion in 2% $Na_2S$ solution at 25 and 80 °C are

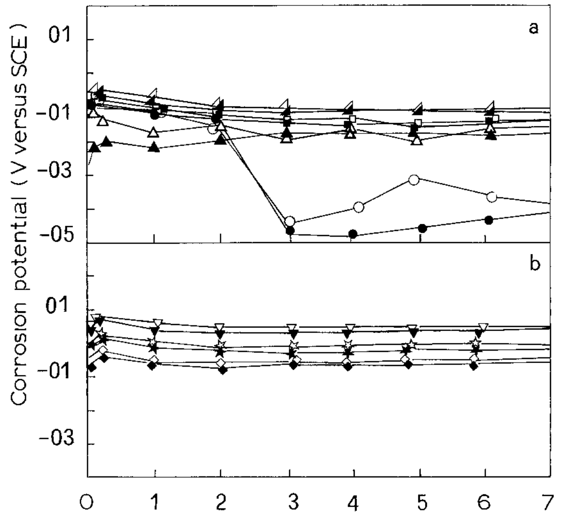

*Figure 6* Free corrosion potentials versus immersion time in artificial saliva, pH 6.7, $T = 37 + 1$ °C, for dental alloys with noble metal content of (a) about 30% and (b) > 30% See Figs 2 and 3 for key

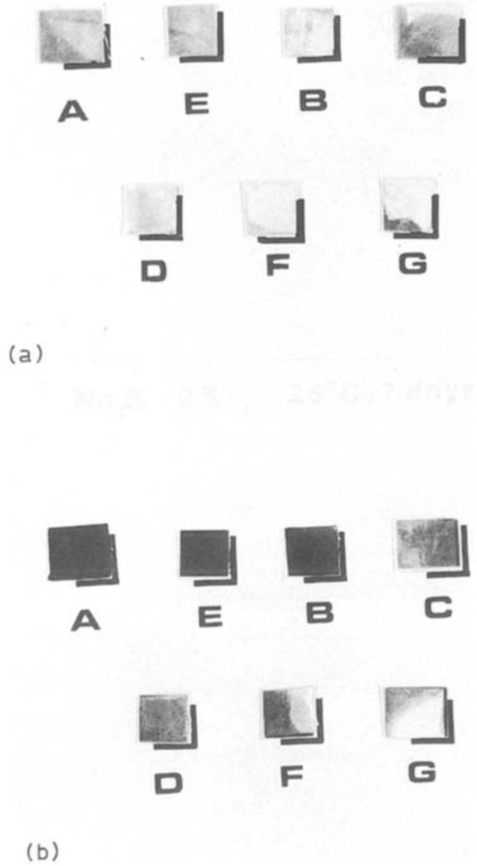

*Figure 7* The alloys after 1 week immersion in 2% $Na_2S$ solution at (a) 25 and (b) 80 °C

shown. As expected, the degree of tarnishing increased with increasing temperature of the aggressive medium and decreasing nobility of the alloy: for alloy A, after 1 day of immersion a certain degree of tarnishing of the surface was already visible, alloys E and B are discoloured to a smaller extent. After a further 6 days immersion the attack increased for the three alloys mentioned above, whereas for the other alloys it was not possible to identify any attack, by eye or by optical microscopy.

As an example, optical micrographs of the surfaces of alloys A and B, after 1 and 7 days immersion, are shown in Fig. 8. Exposure for 1 day is sufficient to discriminate between the two alloys, the discoloration of A, with the lower noble metal content, was noticeably greater.

The darkened surface of alloy A revealed upon SEM observation the presence of voluminous corrosion products and differential corrosion attacks on the surface after 1 week immersion, see Fig. 9, where the SEM micrograph of the surface together with the X-ray concentration maps for S, Ag, Pd and Cu are shown. The matrix, light grey (L), was found to be Ag-rich, whereas the dark phase (D) was observed to be enriched in Cu and Pd. Quantitative microprobe analysis (Fig. 10) revealed that the silver content in the light grey phase was about 78%, the copper and palladium contents in the other phase being, respectively, about 23% and about 27%. The corrosion products were mainly constituted of silver sulphide with small amounts of copper sulphide; see the data obtained by microprobe analysis (68.0% Ag, 4.85% Cu and 12.6% S).

In Fig. 11 an SEM micrograph (back-scattered electrons) of alloy E, after 1 week immersion in 2% $Na_2S$ solution at 25 °C, is shown, together with the energy-dispersive X-ray spectroscopy (EDS) analysis of the various phases. The compositions, shown in Fig. 10, were similar to those found for alloy A: the light grey phase (L) was enriched in silver (about 73%), whereas the dark areas (D) were richer in copper (about 22%) and palladium (about 38%); the intermediate phase (I) showed an enrichment in the sulphur content (about 9%), which may be attributed to the precipitation of silver sulphide and, to a lesser extent, cupric sulphide.

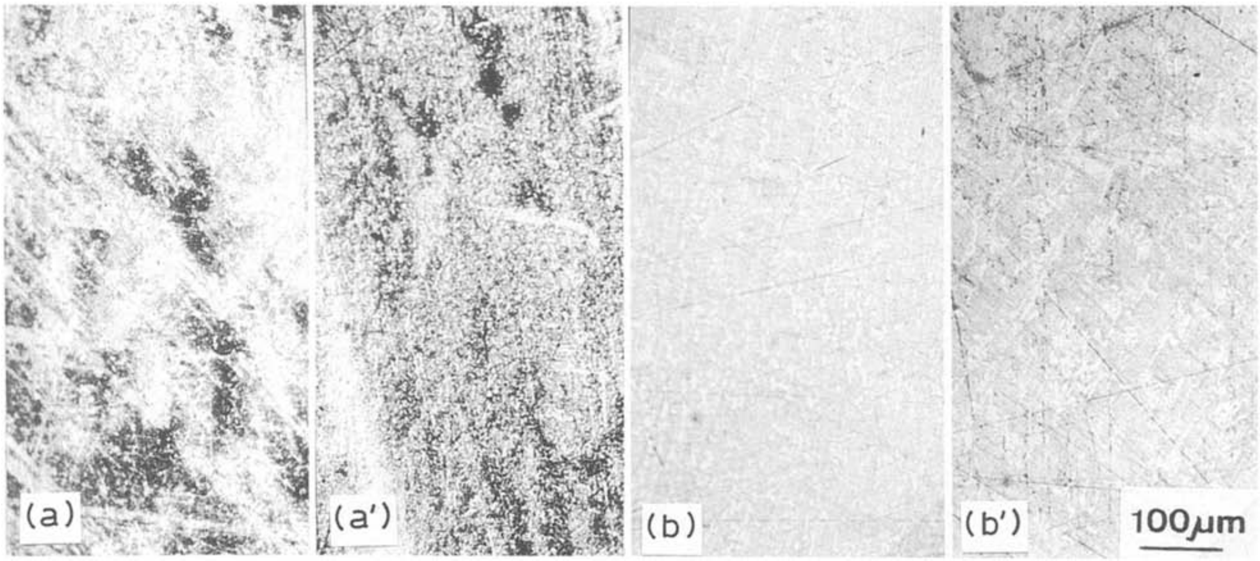

*Figure 8* Optical micrographs of the surfaces of alloys A and B, after immersion in 2% $Na_2S$ solution at 25 °C: alloy A after (a) 1 day and (a') 7 days immersion; and alloy B after (b) 1 day and (b') 7 days immersion.

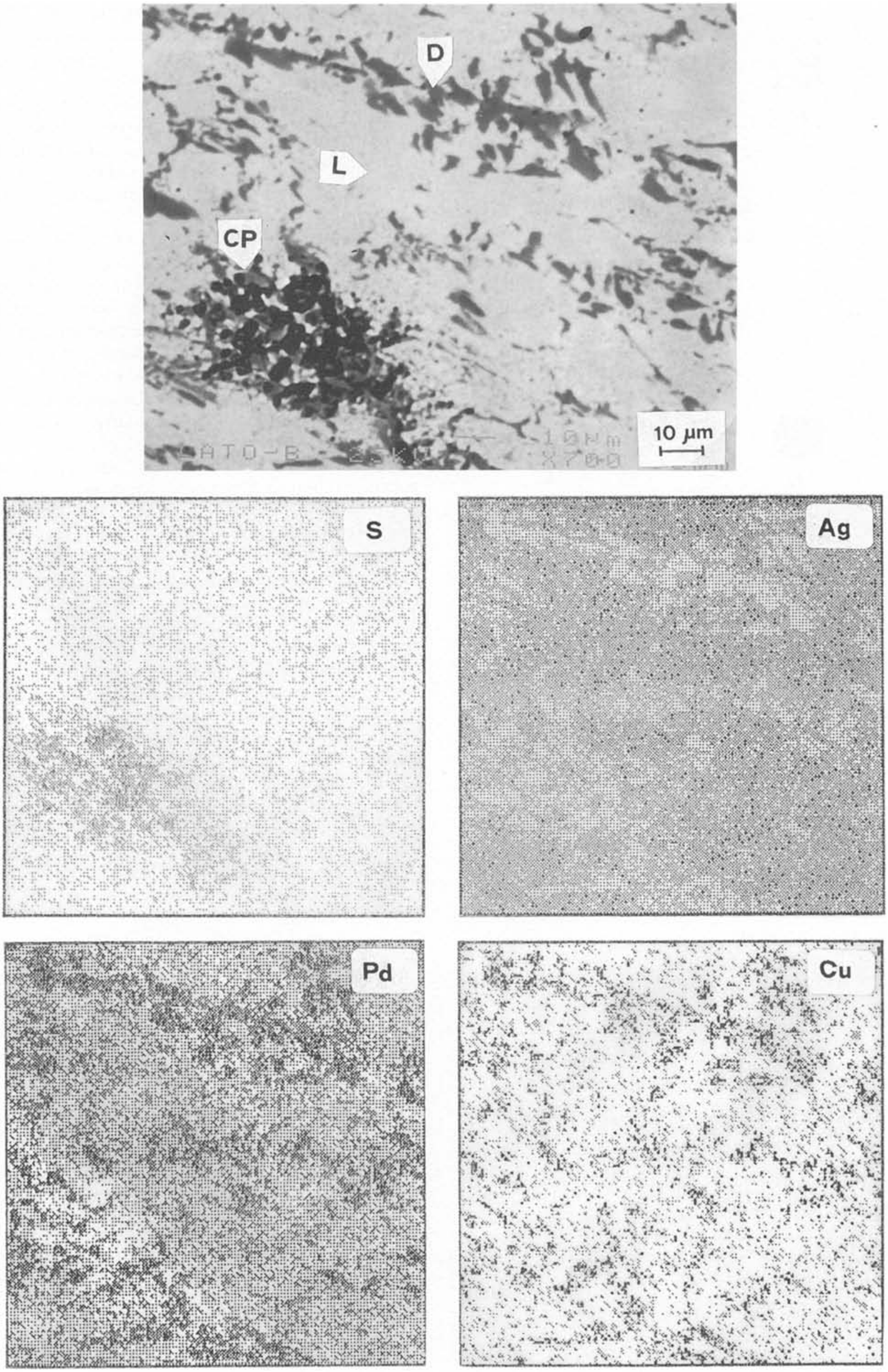

*Figure 9* SEM micrograph (back-scattered electrons) of alloy A, after 1 week immersion in 2% $Na_2S$ solution at 25 °C, together with X-ray maps for S, Ag, Pd and Cu. L, light grey phase; D, dark phase; and CP, corrosion products

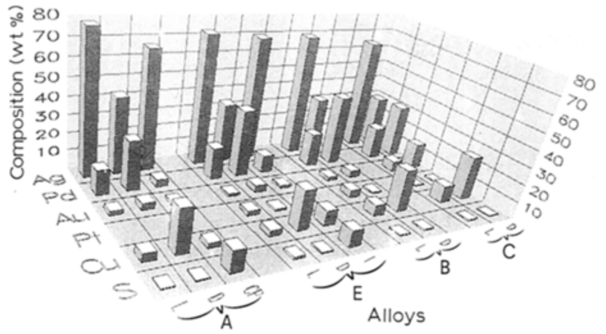

*Figure 10* Microprobe quantitative analysis of the phases evidenced on the surface of the dental alloys A, E, B and C after 1 week immersion in 2% $Na_2S$ solution at 25 °C. L, Light grey phase; D, dark phase; CP, corrosion products; and I, intermediate phase

Alloy B was discoloured to a lesser extent, but the back-scattered image (Fig. 12) evidences the presence of two phases, whose composition was similar to those previously described (see Fig. 10 for quantitative data).

Alloy C, the SEM image of which is not shown for brevity, was characterized by a finer distribution of the phases, which were slightly tarnished. Quantitative analysis (Fig. 10) revealed common features in the elemental distribution, in fact the light grey phase was enriched in Ag (about 65%) and the dark areas enriched in Au (15%), Pd (about 31%) and Cu (about 25%). Slight attacks and a similar elemental distribution were observed for alloy D (Fig. 13).

As noted above, in order to observe attacks on the two nobler alloys that are less susceptible to tarnishing, the temperature was raised to 80 °C. Immersion for 1 week allowed some discolouration of the surface of alloys F and G to be observed. Alloy F, discoloured to a small extent, revealed a degree of homogeneity superior to the other alloys studied (see the quantitative analysis data of Fig. 13). On alloy G, mainly constituted of palladium, some traces of tarnishing were observed on areas richer in copper, as shown by the X-ray maps of the constituent elements of the alloy (Fig. 14).

As a general observation, which can be extended to all of the alloys examined, no appreciable difference with respect to tarnishing susceptibility was observed between as-received and heat-treated samples.

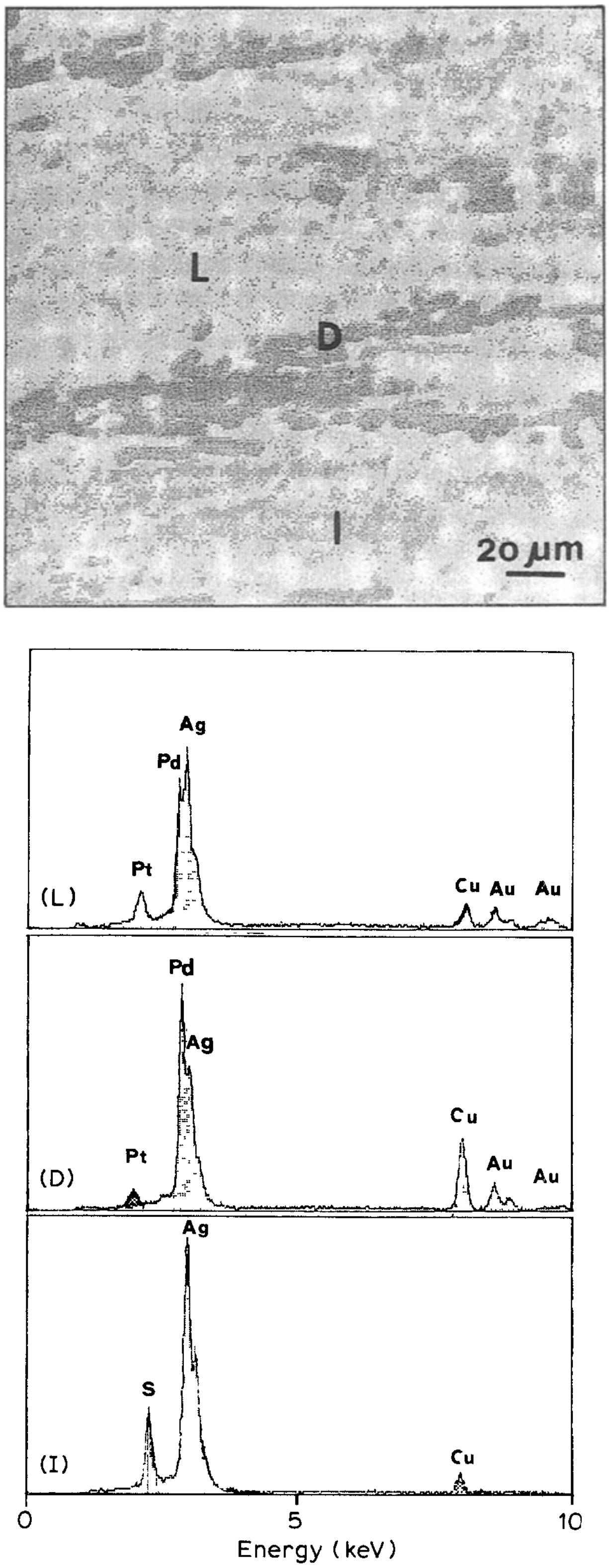

*Figure 11* SEM micrograph (back-scattered electrons) of alloy E, after 1 week immersion in 2% $Na_2S$ solution at 25 °C and EDS analysis of the indicated zones: L, light grey phase, D, dark phase; and I, intermediate phase.

## 4. Discussion

*In vivo* evaluations revealed large variations in results depending on the oral environments differences, so extensive testing was undertaken in the effort of establishing performance criteria for new alloys proposed for odontoiatric use.

In this study seven alloys with low noble metal contents were tested from an electrochemical point of view and with respect to tarnishing corrosion.

The electrochemical characterization, carried out in artificial saliva at two different pH values, supported the observation that these alloys show substantially satisfactory corrosion resistance in the oral environment: in the polarization curves the current density never exceeded the value of 1 µA $cm^{-2}$ in the range of interest in the oral cavity, − 0.2 to + 0.2 V(SCE) [7]. However, the high sensitivity of these tests allows low differences in the corrosion rates to be observed, and to relate them to the presence of phases that are more or less prone to corrosive attacks.

The polarization curves were characterized by a region of immunity, from the free corrosion potential up to a potential value ranging from + 0.2 to + 0.6

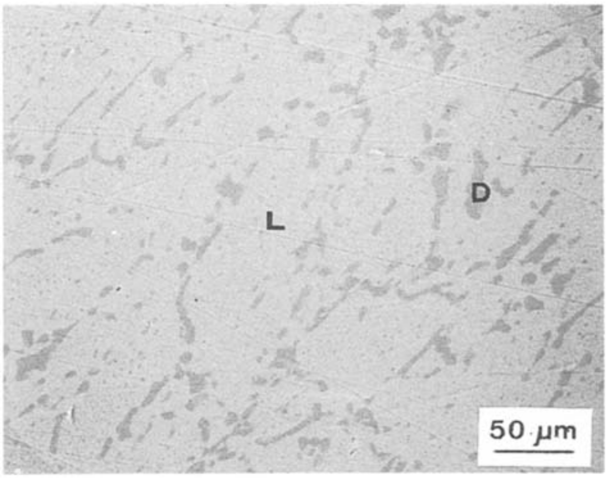

*Figure 12* SEM micrograph (back-scattered electrons) of alloy B, after 1 week immersion in 2% $Na_2S$ solution at 25 °C. L, Light grey phase; and D, dark phase.

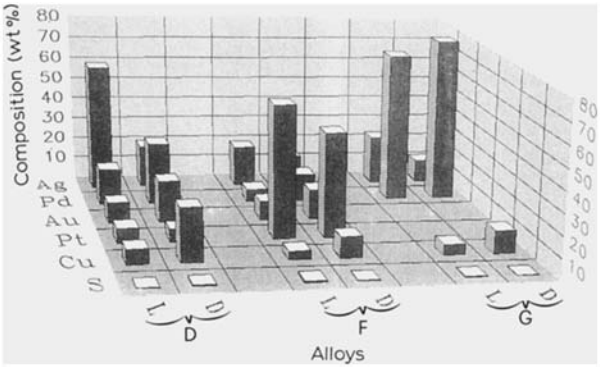

*Figure 13* Microprobe quantitative analysis of the phases evidenced on the surface of the dental alloys D, F and G after 1 week immersion in 2% $Na_2S$ solution at 25 °C for alloy D, and at 80 °C for alloys F and G. L, Light grey phase; and D, dark phase.

V(SCE) in dependence on the noble metal content of the alloy; it must be observed that in this region the current density due to the dissolution of the less-noble components of the alloy is low, and disregarding some minor peaks, has a character of limiting current. Furthermore, the anodic current in this region increased with the decrease in noble metals content. When the potential exceeded the critical breakdown potential, becoming more positive with the noble metal concentration, from + 0.5 to + 0.7 V(SCE), the current increased markedly and the dealloying process accelerated.

Alloy A showed the highest anodic current densities and, contemporarily, the lowest free corrosion potential values during the immersion tests: the passive film poor in noble elements was unstable with respect to the aggressive action of chloride ions. For alloys E and B the anodic current densities decreased and, as observed previously for the remaining four alloys, this decrease was related to the increase in the noble metal content, except for alloy D. That alloy, with a noble metal content of about 41%, showed a polarization curve with two inflexions and a current density higher than that of alloy C, with a noble metal content of about 34%. This behaviour may be explained with the presence in alloy D of a phase rich in copper and poor in silver with a great tendency to anodic dissolution.

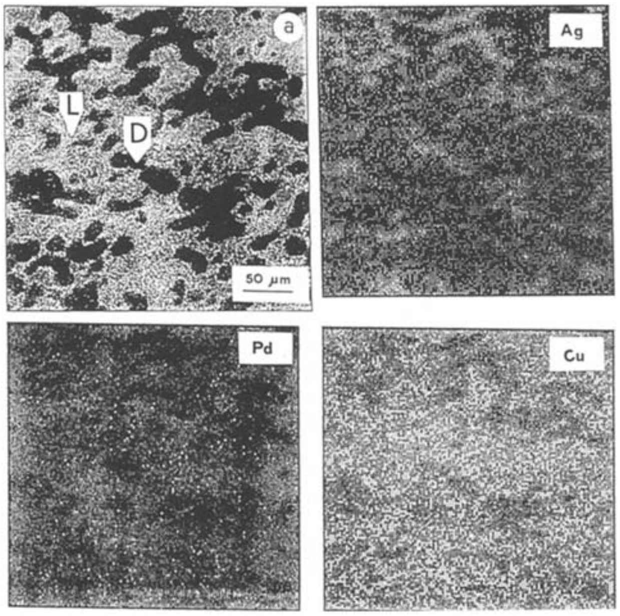

*Figure 14* SEM micrograph (back-scattered electrons) of alloy G, after 1 week immersion in 2% $Na_2S$ solution at 80 °C (a), together with the X-ray maps for Ag, Pd and Cu. L, Light grey phase; and D, dark phase.

The corrosion resistance in artificial saliva revealed resistance to corrosion in chloride media, because the corrosive agents are the chloride ions. However, another important corrosive agent present in saliva is hydrogen sulphide, deriving from protein degradation. This chemical compound has a great affinity for copper and silver, with which it reacts rapidly, forming insoluble black corrosion products. The presence of these films, essentially CuS and $Ag_2S$, affected first the metal colour and in the most dramatic cases the alloy turned black.

In order to evidence the tarnishing resistance, a 2% $Na_2S$ solution was employed as aggressive medium at two different temperatures, 25 and 80 °C. These tests revealed preferential attacks on the alloys with lower noble metal content (A, B and E) already after 1 day immersion at 25 °C. Alloy A, with a noble metal of about 23% mainly given by Pd, was highly heterogeneous; a phase is essentially constituted by Pd and Cu, while regions enriched in silver are easily attacked by sulphides, with the consequent formation of corrosion products as $Ag_2S$. Alloy E, with a noble metal content of about 27% (mainly given by Au, Pt and Pd) showed a slightly lower susceptibility to tarnishing corrosion, because of the presence of Au and Pt in the Ag-rich phase. Still lesser attacks were evidenced on alloy B, with a noble metal content of about 31%. The increase in the immersion time, to 1 week, did not cause the corrosion of the other four alloys with higher noble metal contents; whereas the increase in the temperature, to 80 °C, allowed attacks of different severity to be obtained for the seven alloys, in dependence on the noble metal content.

Furthermore, from the results of the two kinds of tests it is possible to affirm that heat treatment does not affect the electrochemical properties and the tarnishing resistance of the seven alloys. This may be explained with the observation that the hardening treatment (15 min ageing in the temperature range 360–450 °C) is not sufficient to induce modifications in the structure of the alloys. The nucleation of ordered phases or segregations, able to hinder the movement of dislocations in the crystalline lattice, did not influence the chemical reactivity of the alloys.

From a mechanical point of view, the alloys with low noble metal content may substitute for the conventional gold alloys, but the noble metal content must not be reduced below 30% if the corrosion and tarnishing resistance is to remain acceptable.

## 5. Conclusions

From our findings we can conclude that alloys with noble metal content >30% show a good electrochemical behaviour and a satisfactory corrosion resistance against tarnish. Also, the hardening treatment had no influence on the corrosion resistance.

## References

1. INTERNATIONAL ORGANIZATION FOR STANDARDIZATION, ISO Standard 1562. "Dental Casting Gold Alloys", 1st Edn (ISO, Geneva, 1976) p 12.
2. H HERO, *J. Dent. Res.* **63** (1984) 926
3. H HERO, R JORGENSEN and E SORBRODEN, *ibid* **61** (1982) 1292.
4. P P CORSO, R M GERMAN and H D SIMMONS, *ibid.* **64** (1985) 848.
5. *Idem, ibid.* **64** (1985) 853.
6. P. R. MEZGER, A L STOLS M M A VRIJHOEF and E H GREENER, *Dent. Mater.* **5** (1989) 350.
7. G J EWERS and E H GREENER, *J. Oral. Rehab* **12** (1985) 469.

*Received 16 December 1991*
*and accepted 30 July 1992*