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Tarnish and corrosion behaviour of palladium–silver alloys

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Binary and commercial palladium–silver dental alloys show a greatest resistance to both tarnish and corrosion at compositions of between 50 and 75% Ag, most probably due to saturation of the d-electron shell in this composition range. The commercial Pd–Ag alloys have more corrosion resistance, but a lower tarnish resistance than the binary Pd–Ag alloys, due in part to the minor alloying with indium or zinc. The addition of copper increases the segregtion of silver, which adversely affects both tarnish and corrosion resistance. A solutionization heat treatment degrades tarnish resistance, but does not affect corrosion resistance.

1. Introduction

Restorative dental materials based on the palladium–silver binary system have recently become available. Although these alloys provide competitive mechanical properties and lower costs when compared with the established gold-based alloys, little information is available on their resistance to chemical attack while in service. Chemical degradation of the palladium–silver systems, although not documented, could result in the formation of insoluble tarnish deposits or dissolution of the metal via corrosion.

To date, tarnish, corrosion, and cytotoxicity have been extensively documented in the established gold-based alloy systems [1–11]. The current research performs a similar characterization of Pd–Ag alloys, evaluating the tarnish and corrosion behaviour of both binary and commercial dental compositions based on the Pd–Ag system. The experimental design consists of eight alloys (five Pd–Ag binary and three commercial variants), two heat treatments, two tarnish environments, and four corrosion environments. In addition, optical microscopy, X-ray diffraction, scanning electron microscopy, and microhardness tests are used to supplement the experimental findings. For this study, a minimum, but comprehensive, test battery [9–11] was used to determine the role of nobility, composition, microstructure, and environment on tarnish and corrosion resistance. This is a first step toward establishing a performance standard for palladium-based dental casting alloys.

2. Background

Tarnish is the visible discoloration of an alloy surface due to the formation of an insoluble compound involving chemical species from the surrounding environment. Tarnish of dental alloys has been studied and quantified using spectrophotometer-based colour readings compared with exposure time in various simulated oral environments [4, 9, 11–13]. The degree of tarnish is expressed by the discoloration measured over the duration of the test. Because most alloys approach a saturation tarnish level in a relatively short period of time, the test has the benefits of a short duration and quantitative output. The discoloration associated with tarnish is usually the result of either copper or silver compounds, typically sulphides or chlorides [8]. Increased sensitivity to tarnish is observed either in two-phase alloys, in segregated microstructures, or at casting defects such as pores [3, 4, 12–16]. Consequently, various heat treatments alter the tarnish response of an alloy through changes in the composition, distribution, and amount of phases [11, 17]. For gold-based alloys, the low noble metal content compositions or phases are typically most sensitive to tarnish [9]. Alternatively, corrosion appears to be less dependent on microstructural inhomogeneities [18].

The Pd–Ag system is a solid solution with a possible low-temperature miscibility gap [19–24]. Past studies on these single-phase Pd–Ag binary alloys have reported adequate tarnish resistance for alloys with greater than 40% Pd [25, 26]. However, the commercial palladium–silver dental alloys also contain various levels of copper, indium, and zinc. The two-phase region of the Pd–Ag–Cu system causes concern for its tarnish and corrosion resistance. In the past, two-phase dental alloys have exhibited inferior resistance to chemical attack [4, 13, 14, 16]; thus, Pd–Ag–Cu dental alloys with large copper contents may have inferior properties resulting from the two-phase microstructure.

Although tarnish on dental alloys is both aesthetically and clinically undesirable, corrosion poses a more serious problem because of its potential cytotoxicity. One concern is that living tissue responds to ions released by the corrosion of low-nobility dental alloys [7]. Potentiodynamic polarization provides a measure of corrosion of which quantitatively rates the stability of an alloy [27]. A standardized 1% NaCl

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solution, more aggressive than artificial saliva, has been used for corrosion testing [6, 9–11, 28]. Recently, the integrated forward potentiodynamic scan from -300 to $+300$ mV has been used to provide a corrosion index for an alloy [9, 10, 18]. The integrated current density provides an overall assessment of corrosion in the voltage range experienced in the oral environment [29]. Previous studies using this technique have directly related corrosion susceptibility to nobility [17, 30].

The corrosion behaviour of the Pd–Ag based alloys is not well established. Ishizaki's [31] use of potentiostatic polarization in artificial saliva to characterize the corrosion response of alloys ranging from 0 to 30% Pd showed that corrosion resistance increased with the palladium content. Sarkar *et al.* [28] used an electrochemical hysteresis technique to investigate the chloride corrosion behaviour of five Pd–Ag dental casting alloys. They felt that the corrosion and breakdown potentials could not be used as discriminating parameters in this alloy group. However, the magnitude of the peak current density associated with the silver and copper electrochemical reactions did indicate the relative amount of corrodable species. Other studies have suggested that over 40% Pd is required to attain passivity in Pd–Ag alloys [32, 33]. Bessing *et al.* [34] have recently published corrosion results on two commercial Pd–Ag alloys. They report a strong interaction between environment and heat treatment not noted in prior research.

Despite the past investigations, no attempt has been made simultaneously to examine tarnish and corrosion of the Pd–Ag dental alloys. Further, study is needed of the basic component effects to explain the behaviour of the more complex commercial alloys. The interplay between nobility, composition, microstructure, heat treatment, and environment have not been examined to date. This study, using both binary Pd–Ag alloys and commercial dental casting alloys, provides a fundamental examination of these factors in tarnish and corrosion.

3. Experimental procedure

The experimental design consisted of eight alloys, two heat treatments, two tarnish environments, and four corrosion environments. Three commercial dental casting alloys and five binary Pd–Ag alloys were used, as identified in Table I. The commercial alloys were similar in palladium content, yet differed in copper, indium, and zinc content. Because there is a two-phase field in the Pd–Ag–Cu ternary, a difference in microstructure and chemical stability was expected for alloy 3 in comparison with alloys 1 and 2. The binary alloys ranged from 100% Ag to 100% Pd in equal intervals on an atomic basis. These provided a foundation for examining the commercial alloys. Composition in this paper will be based on atomic per cent, yet the similarity in atomic weights of silver and palladium make these values close to the weight per cent values.

TABLE I Alloy identification: change in microhardness caused by solution treatment

Alloy	Composition (at %)				Hardness (DPH)	
	Pd	Ag	Cu	In/Zn	As-cast	Solution treated
1*	25	70	0	5	174	62
2†	25	69	0	6	151	109
3‡	22	53	21	3	187	211
Ag	0	100	0	0	35	35
75% Ag	25	75	0	0	67	59
50% Ag	50	50	0	0	92	73
25% Ag	75	25	0	0	113	104
Pd	100	0	0	0	69	69

*PMW, Rx Jeneric Gold Co., Wallingford, Connecticut, USA.
†Albacast, J. F. Jelenko Co., Armonk, New York, USA.
‡Neycast III, J. M. Ney Co., Bloomfield, Connecticut, USA.

Prealloyed pieces of commercial alloys were cast into square paddles 10 mm × 10 mm × 2 mm using the lost wax investment casting technique. The binary alloys were melted in alumina crucibles from pure palladium (99.95%) and silver (99.999%). Melting was performed in an argon atmosphere. All samples were slowly cooled after melting. The binary alloys were slightly compressed to form a flat surface, reheated to 67% of the absolute solidus temperature for 15 min, and furnace cooled at 20 K min^{-1}. A minimum of four samples was formed from each alloy. These were mounted in epoxy with a 1 cm^2 exposed surface area, and polished for metallographic, tarnish, and corrosion examinations. X-ray diffraction was used to measure the lattice parameter, and standard metallographic techniques were used to analyse both tarnished and corroded specimens.

After testing in the above condition, termed as-cast, each sample was removed from the epoxy and solution treated at 40 K below the respective solidus temperatures for 16 h in argon, followed by a water quench. After being solution treated, the alloys were remounted in epoxy and the tarnish testing was repeated. Past observations [10, 18] have indicated less variation in an alloy's corrosion response after heat treatment, although its tarnish can undergo a substantial change. For this reason, only a few corrosion tests were repeated on the solution treated alloys. Table I includes diamond pyramid microhardness measurements taken in both heat-treatment conditions showing the relative change brought about by solution treatment. The 50% Ag alloy was further aged using an exposure of 8 h at 400° C to induce possible ordering.

Tarnish and corrosion tests were performed using the standardized test battery described earlier [9–11, 18]. This consisted of tarnish exposures in both artificial saliva and 0.5% sodium sulphide solutions. The composition of the artificial saliva was 0.4 g NaCl, 0.4 g KCl, 0.795 g $CaCl_2 \cdot 2H_2O$, 0.69 g $NaH_2PO_4 \cdot H_2O$, 0.005 g $Na_2S \cdot 9H_2O$, 1.0 g urea and 1000 ml water. The specimens were immersed in 75 ml of solution in sealed containers at 37° C for 3 days. Colour was remeasured every 24 h when the solution was changed. A computerized spectrophotometer was used to measure the surface colour, which gave the degree of tarnish as the distance in colour space between the initial and tarnished conditions. This tarnish is expressed as nondimensional colour space units of ΔE^*. Typically the degree of tarnish approached a saturation value within 3 days [11] and this value proved satisfactory for comparing and ranking tarnish resistance.

TABLE II X-ray analysis of as-cast, solution treated and aged 50% Ag alloy

Condition	Lattice parameter (nm)	Intensities of fundamental lines				
		(1 1 1)	(2 0 0)	(2 2 0)	(3 1 1)	(2 2 2)
As-cast	0.3971	100	29	45	43	8
Solution treated	0.3963	100	94	98	76	5
Aged	0.3968	100	40	15	29	5

The procedure for the corrosion tests evolved from a recognized standard [35]. Both artificial saliva and 1 % NaCl solutions were used in the aerated and deaerated conditions; the corresponding oxygen ion concentrations were approximately 6.7 and 0 p.p.m. (± 0.2 p.p.m.). The test cell contained the alloy, platinum counter electrode, saturated calomel reference electrode (SCE), gas filter, pH meter, and oxygen ion probe. This cell was filled with 800 ml of fresh solution and heated to 37° C. Aeration or deaeration conditions were maintained by bubbling air or nitrogen gas through the test cell at 300 ml min^{-1} for 15 min, and then at 150 ml min^{-1} during the balance of the test. The prepared and cleaned specimen was surface polished to 600 grit and then placed in the test cell for 55 min to establish equilibrium and determine the open circuit potential. The anodic forward scan was initiated at − 1.0 V (against SCE) and continued to + 1.0 V at a rate of 1 mV sec^{-1}. At this point the scan was reversed until − 1.0 V was reached. In this test, the rest potential is determined prior to the potentiodynamic scan, after the alloy has equilibrated with the test solution. The breakdown potential corresponds to the point in the anodic region where the current density abruptly rises, indicating loss of passivation. The critical and passive current densities roughly correspond to the corrosion rates in the active and passive regions. Increased corrosion resistance is expected as the breakdown potential becomes more noble and as the difference in potential between the breakdown and rest potentials becomes larger. This difference in potentials is termed the anodic overpotential, and is indicative of the voltage required for active dissolution of the alloy.

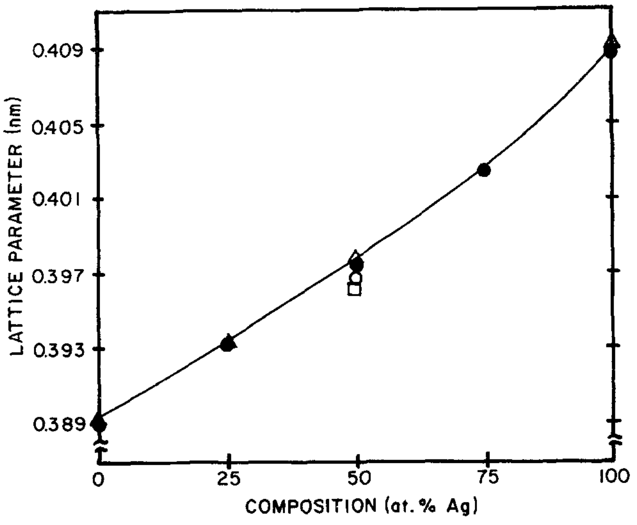

Figure 1 The measured lattice parameter shown as a function of the alloy composition for the Pd–Ag binary, including past measurements by Rao and Rao [24]. (●) As-cast, (△) Rao and Rao, (○) aged, (□) solution treated.

4. Results

Fig. 1 shows lattice parameters for the as-cast binary Pd–Ag alloys as determined by variation of X-ray diffraction with composition. The reproducibility of these values was 0.0004 nm. The results of a prior study [24], also given in this figure, show good agreement with the current values. The lattice constant exhibits a slight upward slope, as previously noted [36]. Past research has lead to the suggestion of ordering at the 50% composition [37]. The diffraction pattern was examined for ordering, but no evidence of a superlattice was observed, even after ageing for 8 h at 400° C. The intensities of the major diffraction peaks did change with heat treatment as noted in Table II, but no significant intensities were noted at the superlattice conditions.

The microhardness measurements in Table I indicate that copper contributes to the hardening of commercial alloy 3 during the solution treatment. For the other alloys, solution treatment softens the alloy, except for pure palladium and silver, which show no effect from heat treatment.

The tarnish testing results are summarized in Table III. Examples of tarnish discoloration with exposure time are given in Fig. 2 for all eight as-cast alloys in the 0.5% sodium sulphide solution. A slight effect of test environment is evident in Table III. Typically, the artificial saliva was more aggressive in the first day of testing, yet showed comparable tarnish results after 3 days.

Heat-treatment effects on tarnish showed a similar rank ordering of the alloys, yet generally a higher discoloration followed solution treatment for the commercial alloys.

The effect of nobility on the tarnish response is best seen with the binary alloys. The 50% Ag and 25% Ag alloys exhibited superior tarnish resistance while pure palladium and the 75% Ag alloy showed intermediate resistance. Pure silver exhibited the lowest tarnish resistance. These groupings were essentially independent of test solution and heat treatment.

TABLE III Mean and deviation colour changes after 3 day tarnish exposure

Alloy	0.5% Sodium sulphide		Artificial saliva	
	As-cast	Solutionized	As-cast	Solutionized
1	12 ± 1	25 ± 4	16 ± 3	26 ± 3
2	11 ± 1	20 ± 3	14 ± 4	25 ± 5
3	14 ± 1	21 ± 7	14 ± 3	24 ± 5
Ag	40 ± 3	41 ± 3	39 ± 2	42 ± 3
75% Ag	9 ± 3	9 ± 1	13 ± 6	10 ± 3
50% Ag	2 ± 1	5 ± 1	4 ± 1	4 ± 1
25% Ag	3 ± 1	2 ± 1	4 ± 1	4 ± 1
Pd	10 ± 1	7 ± 1	7 ± 2	7 ± 2

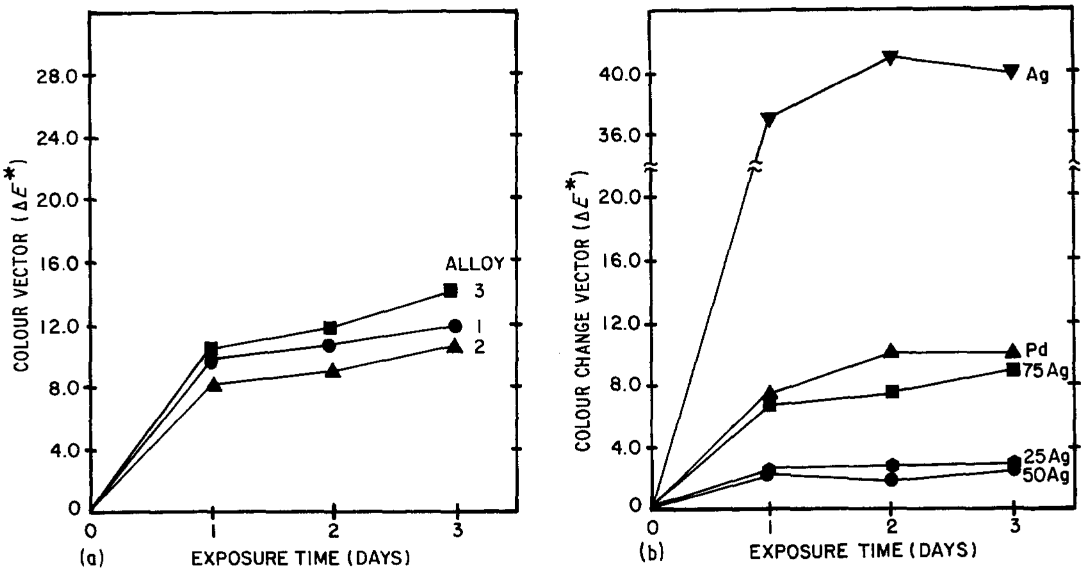

Figure 2 Tarnish discoloration plotted against exposure time for as-cast alloys in the 0.5% sodium sulphide solution; (a) dental alloys and (b) binary alloys.

The corrosion response of the alloys was based on the potentiodynamic polarization curves [6, 10, 11, 28, 32, 33]. The assessment of corrosion resistance depends on the traditional corrosion parameters of rest and breakdown potentials, as well as on current densities during the scan. Additionally, corrosion resistance was assessed by the integrated current density over the potential range encountered in the oral environment. Table 4 tabulates this parameter for the deaerated 1% NaCl and aerated artificial saliva solutions. Example potentiodynamic scans for the binary and commercial alloys are given in Figs 3 and 4 for these same solutions. Fig. 5 plots the corrosion parameters for the as-cast binary alloys against composition, using the 1% NaCl test solution data (aerated and deaerated). The behaviour is not a simple function of silver content.

The deaerated 1% NaCl solution is generally more aggressive than artificial saliva and provides a good basis for comparison with prior observations [9, 11, 33]. A sulphide-containing artificial saliva promotes preferential sulphidation of low nobility alloys at low anodic overpotentials [38].

Because both aerobic and anaerobic conditions exist in the oral environment, the effects of aeration are of concern. More active rest potentials were measured under deaerated conditions. Because of a change in the cathodic reaction with aeration, the rest potential is expected to be higher in the presence of oxygen, in agreement with these observations. The breakdown potential became more and more noble as the palladium content increased. Below the breakdown potentials, the alloys were characterized by relatively low corrosion rates, indicating immunity. Pure silver exhibited a high corrosion current density at low anodic overpotentials. Likewise, the 75% Ag alloy exhibited active corrosion above its breakdown potential.

In contrast, pure palladium, 25% Ag and 50% Ag exhibited passive behaviour similar to that previously noted [32, 33]. The transition from active behaviour for silver-rich alloys to passive behaviour

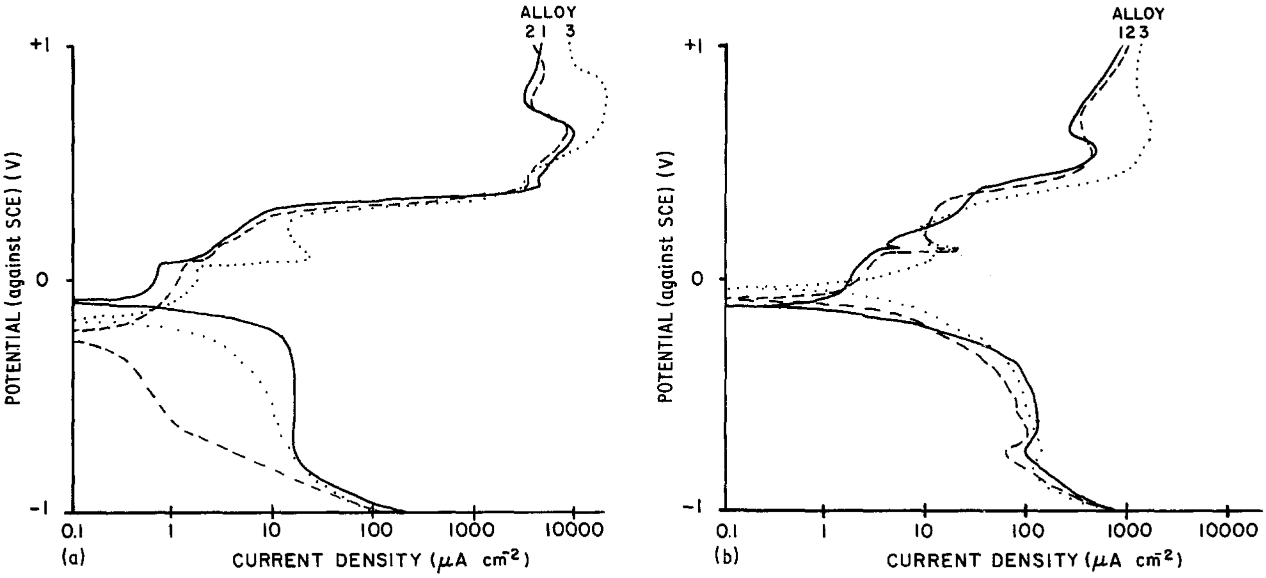

Figure 3 Forward potentiodynamic corrosion scans for the as-cast dental alloys tested in (a) deaerated 1% NaCl solution, and (b) aerated artificial saliva.

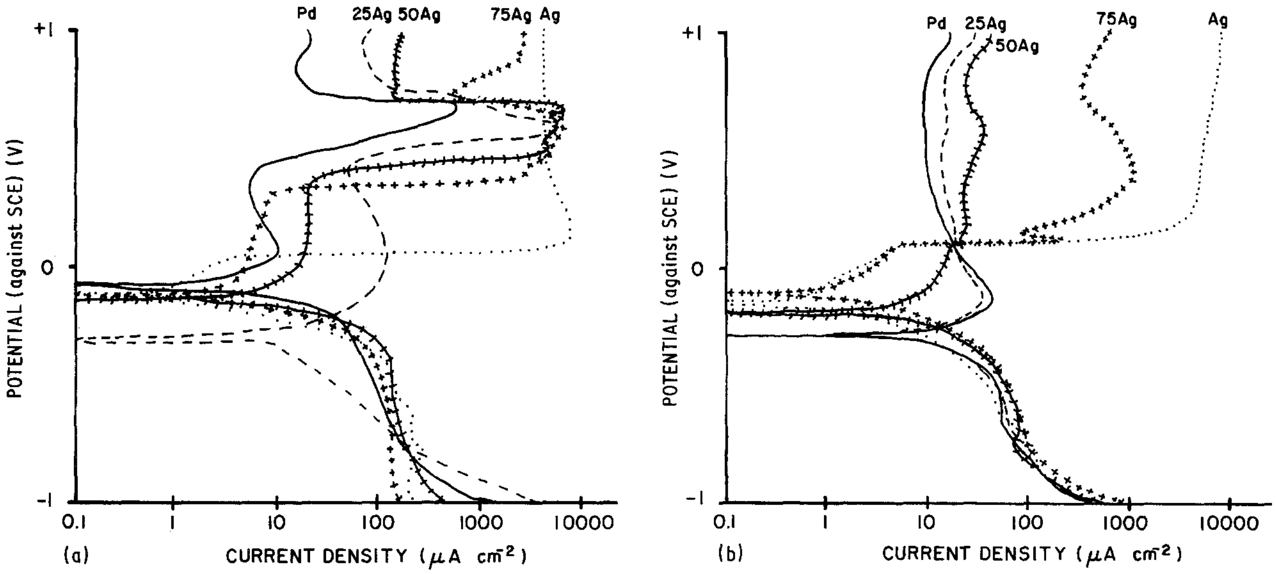

Figure 4 Forward potentiodynamic corrosion scans for the as-cast binary alloys tested in (a) deaerated 1% NaCl solution, and (b) aerated artificial saliva.

for palladium-rich alloys corresponds with the previous observation of a transition point near 60% Ag. The occurrence of a transition in behaviour typically was observed near 50% Ag, as is evident in Table IV and Fig. 5.

The corrosion curves for the commercial alloys resemble those for the 75% Ag alloy, as expected from their similar compositions. The commercial alloy corrosion was characterized by a sharp current density increase at low anodic over-potentials and active corrosion behaviour above their breakdown potentials. The breakdown potentials were more active in the artificial saliva solution. Of the three commercial alloys, number 3 showed the greatest corrosion, as expected from its high copper content. Alternatively, alloy number 2 generally exhibited the best corrosion resistance of the three commercial alloys, although alloy 1 was similar.

The cathodic polarization profiles (reverse scans) exhibit a substantial hysteresis, indicating compound formation on the alloy surface. This is related to growth of the AgCl compound, as shown in the scanning electron micrographs of Fig. 6 taken from the 25% Ag alloy in the as-cast condition. Fig. 6a is a low magnification view taken after the forward scan, showing the preferential deposition of corrosion products on the silver-rich interdendritic areas. The higher magnification view given in Fig. 6b shows more detail of the AgCl crystallite formation on the corroded surface. This compound breaks down during the cathodic scan, giving the current density peak at approximately 0 mV [6, 30].

TABLE IV Integrated current densities (from −300 to +300 mV, units of 10^{-6} A V m^{-2})

Alloy	Deaerated 1% NaCl	Artificial saliva
1	3	7
2	1	5
3	5	9
Ag	1700	470
75% Ag	3	55
50% Ag	11	9
25% Ag	21	12
Pd	34	13

Microstructural observations of the alloys showed evidence of segregation in the as-cast condition. In turn, the location of tarnish and corrosion products correlated with the microstructural inhomogeneities. Fig. 7 provides one example of this correlation. Fig. 7a shows an etched microstructure of alloy 3 in the solutionized condition, while Fig. 7b shows the alloy's appearance after tarnishing in the sodium sulphide solution for 3 days. The scanning electron micrograph shown in Fig. 7c was taken after the forward potentiodynamic scan in 1% NaCl. The corrosion deposits were identified as silver chloride, while the areas free of corrosion were rich in palladium and copper. The localized tarnish and corrosion deposits correspond with the second phase evident in the etched microstructure. Other observations evidenced preferential tarnish along grain boundaries, especially when a second phase was present. Although both the dendrites and interdendritic areas are solid solutions of silver and palladium, the interdendritic areas are enriched in the lower melting temperature silver. Examination of the tarnished binary alloys indicated that microstructure was directly related to tarnish in the high silver content alloys. The solution heat treatment eliminated the casting segregation and contributed to substantial grain growth. The alloy homogeneity was significantly improved by solution treatment. However, tarnish films on the solution-treated binary alloys were uniformly distributed, in contrast with the corresponding as-cast samples.

5. Discussion

The differences in the rate of tarnish of the two test solutions result from the differences in solution chemistry. The artificial saliva is more complex and the resulting tarnish deposits may reflect this difference, although the overall degree and ranking of tarnish was similar between solutions. Based on scanning electron microscopy and energy dispersive X-ray analysis, it was established that the tarnish films are

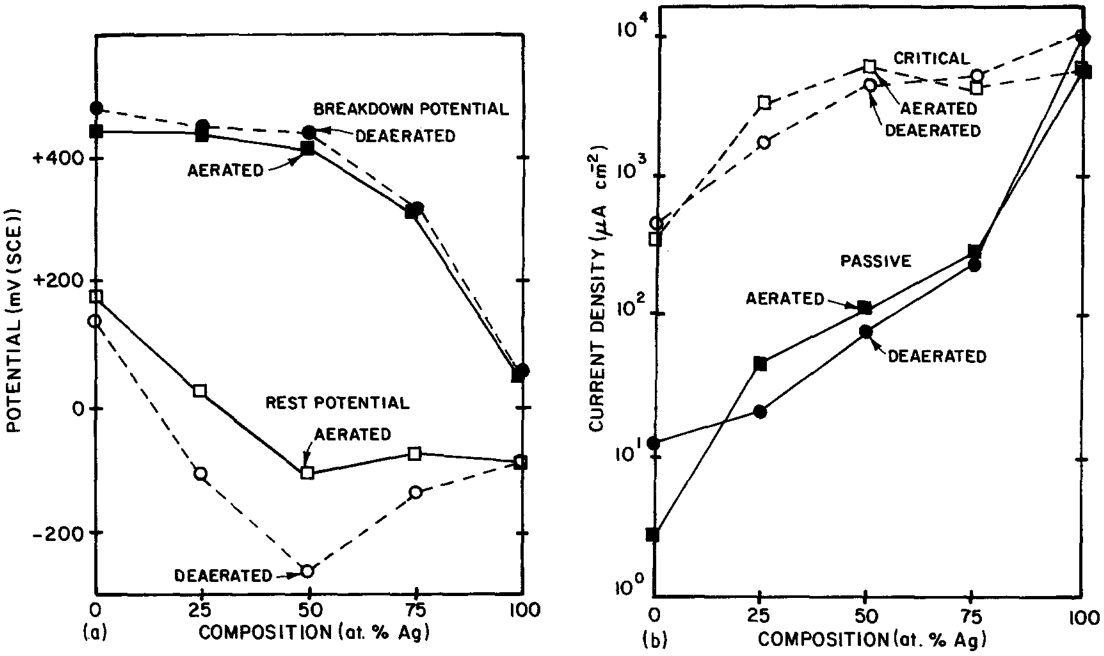

Figure 5 The corrosion behaviour in deaerated 1% NaCl for the as-cast Pd–Ag binary alloys shown plotted against composition; (a) rest and breakdown potentials, and (b) critical and passive current densities.

composed of silver sulphide or silver chloride, which are protective according to the Pilling–Bedworth ratios. In these cases, tarnishing is governed by rate of penetration through the protective film, which should vary with the square root of time [11]. The degree of tarnish approached a plateau during the three day test period and the total level of tarnish in both solutions was similar. These observations support a model of tarnishing where localized regions form protective films [4]. The net tarnish discoloration then represents the availability of low chemical stability sites on the surface. In the past these tarnish deposits have proven to be Ag_2S or AgCl compounds; thus, their formation is expected at microstructural features rich in silver and depleted of noble or passivating elements. The higher concentration of chloride ions in the artificial saliva (compared with sulphur ions in the sodium sulphide) would contribute to faster tarnish film

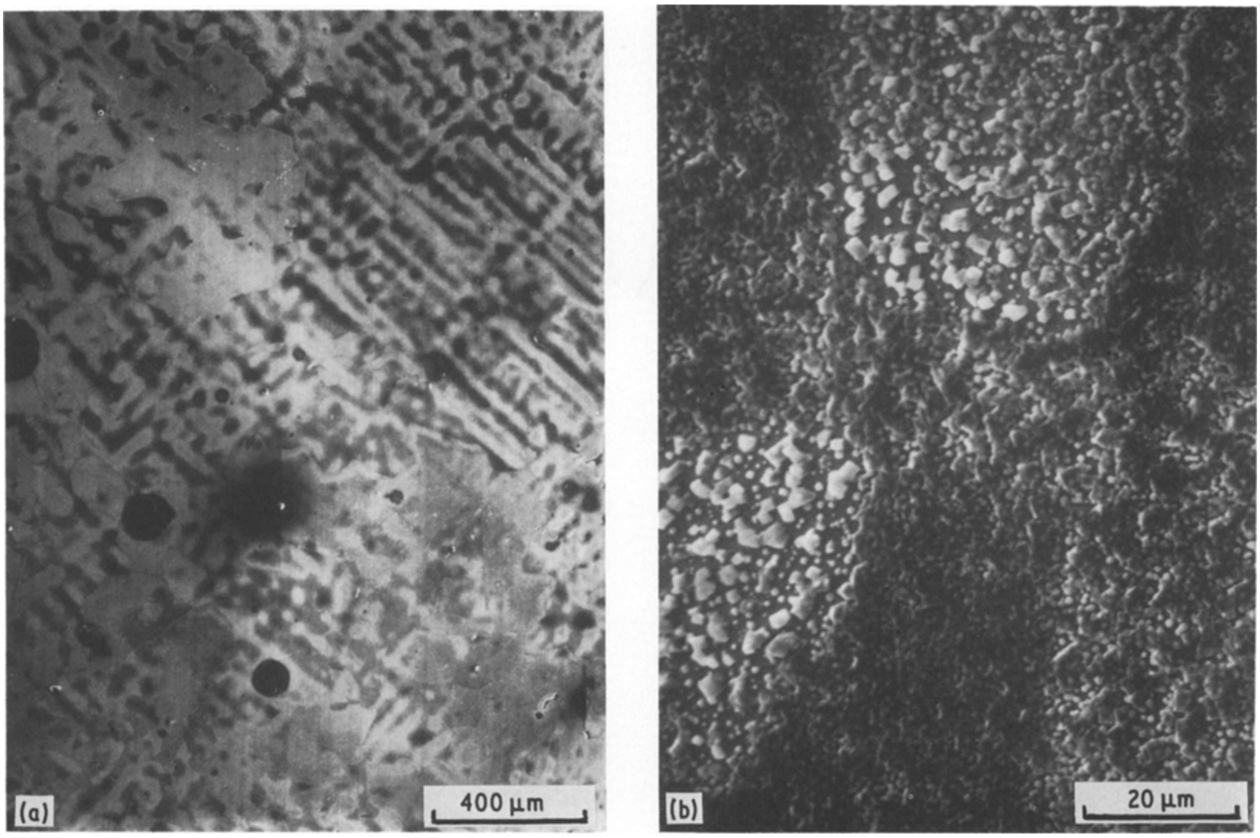

Figure 6 Scanning electron micrographs of the as-cast 25% Ag alloy after forward potentiodynamic scanning in deaerated 1% NaCl; (a) a low-magnification view showing preferential deposition of the corrosion products on silver-rich interdendritic, and (b) a high-magnification view of the silver chloride deposits.

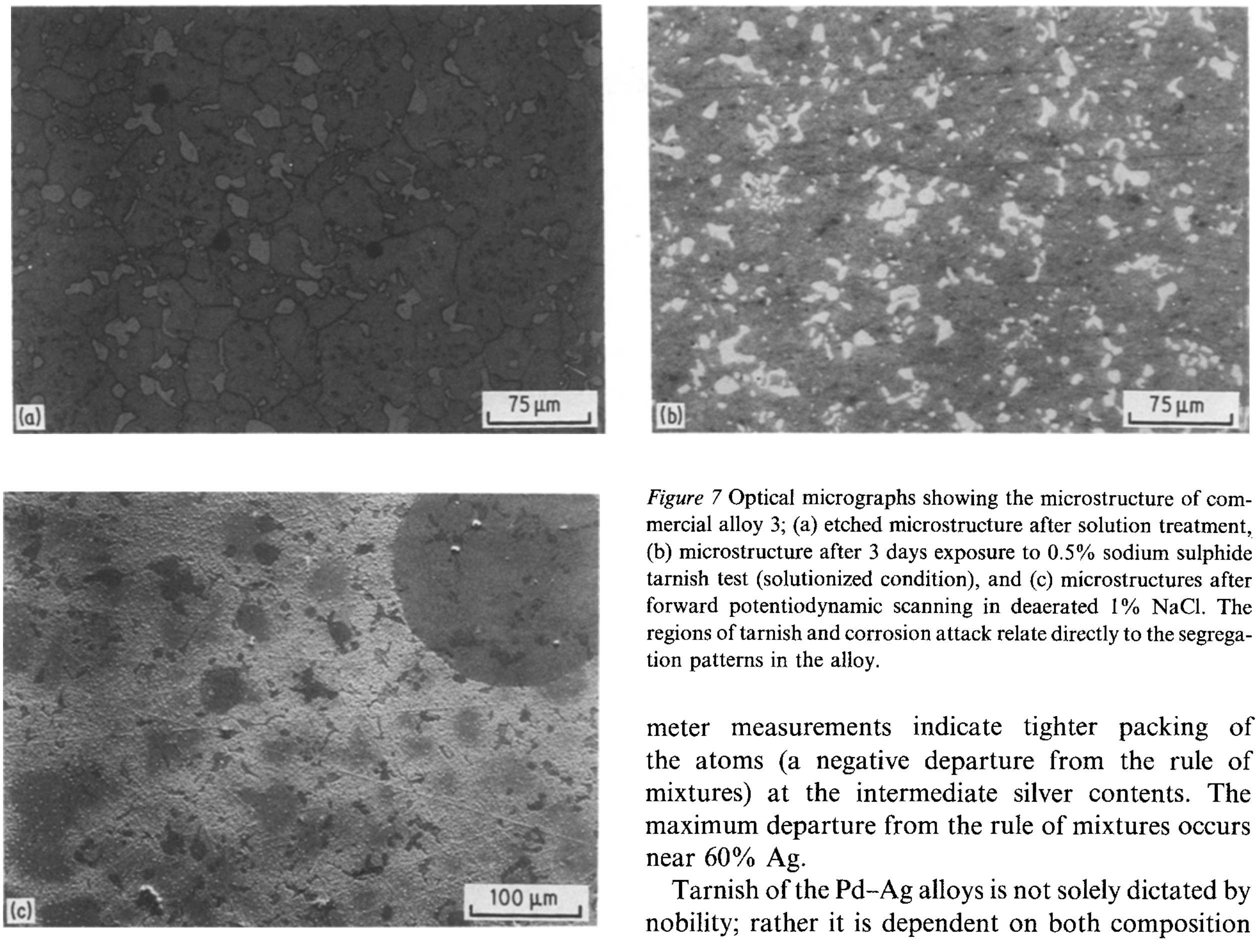

Figure 7 Optical micrographs showing the microstructure of commercial alloy 3; (a) etched microstructure after solution treatment, (b) microstructure after 3 days exposure to 0.5% sodium sulphide tarnish test (solutionized condition), and (c) microstructures after forward potentiodynamic scanning in deaerated 1% NaCl. The regions of tarnish and corrosion attack relate directly to the segregation patterns in the alloy.

production, but the total amount of tarnish would be limited by the available silver segregated in the microstructure. Hence, after sufficient time the final level of tarnish would be similar for both solutions, yet there would be a difference in the rate of tarnish formation dependent on the solution chemistry.

Alloy composition effects on tarnish were not as strong as initially expected, especially with the commercial alloys. In the artificial saliva solution there was no statistically significant difference between commercial alloys. Alternatively, in the sodium sulphide solution alloy 3 showed a greater amount of tarnish in comparison with alloys 1 and 2. This demonstrates that nobility is not the sole determinant of tarnish in commercial dental alloys. The large copper content in alloy 3 induced greater casting segregation, giving microgalvanic cells which accentuated tarnish. Comparing the binary alloys with the commercial alloys shows that the 75% Ag alloy consistently had lower levels of tarnish. The difference was larger in the solution treated condition.

The binary alloys exhibited minimum tarnish at intermediate silver levels. In spite of the greater nobility of palladium, alloying with silver proves beneficial. Prior studies have reported only minor amounts of tarnish in alloys containing intermediate silver contents [32, 39]. This tarnish minimum probably occurs near the composition where the d-electron orbitals become saturated [32, 33, 40–42]. The critical level of silver for d-orbital saturation is estimated to be 60% Ag, which corresponds well with the present determination of a minimum in corrosion and tarnish in the 50 to 75% Ag range. Furthermore, the lattice parameter measurements indicate tighter packing of the atoms (a negative departure from the rule of mixtures) at the intermediate silver contents. The maximum departure from the rule of mixtures occurs near 60% Ag.

Tarnish of the Pd–Ag alloys is not solely dictated by nobility; rather it is dependent on both composition and microstructure. The solution-treatment anneals were intended to reduce the segregation and contribute to improved tarnish resistance. Unfortunately, the commercial alloys increased their segregation and were more prone to tarnish following solution treatment, while the binary alloy showed little effect from solution treatment.

Homogenization heat treatments have shown variable effects with alloy systems in the past. Earlier work has shown both benefit and degradation in chemical stability for dental alloys subjected to homogenization treatments [9–11, 18]. In this examination, the relative tarnish rank order of the alloys did not change substantially in either test solution with solution treatment. However, the commercial dental alloys showed more tarnish when subjected to solution treatment. Microstructural observations indicated tarnish attack was more uniform over the surface of the solution-treated alloys.

Fig. 8 plots the over-potential voltage against the silver content for the binary alloys. The 50% Ag alloy exhibits the highest voltage in all four test environments, while pure silver exhibits the lowest voltage. A similar maximization of corrosion resistance at the 50 at % Ag level has been noted before [32, 33]. Although large over-potentials are not anticipated in oral corrosion, this plot does indicate the relative merits of the various binary alloys for designing dental alloys. As the relative corrosion resistance is not simply a function of the palladium content, factors such as the electron structure must be operating in this system. The correlation between tarnish and corrosion resistance is further illustrated in Fig. 8 through the inclusion of spectrophotometer tarnish data for the as-cast

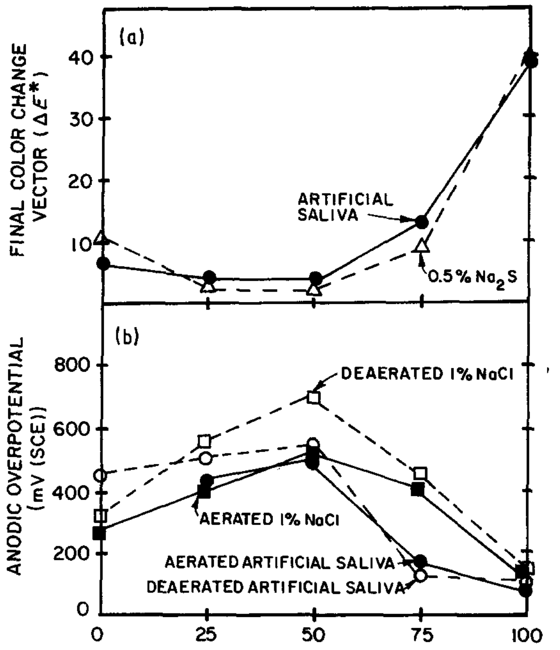

Figure 8 A comparison of compositional effects on (a) tarnish and (b) corrosion behaviour of the as-cast Pd–Ag binary alloys, showing the high immunity to both forms of attack at approximately the 50% composition.

alloys. The maxima in the corrosion resistance (as measured by the over-potential curves) occur at approximately the same composition as the minima in the tarnish discoloration curves. These findings demonstrate the high stability associated with intermediate silver contents. It is theorized that the closure of the nearly complete d-electron shell during the silver alloying of palladium results in a more stable electronic structure for the alloy. Two competing effects are observed in silver additions above this critical level: the alloy's structure may be destabilized, and less stability is observed because of the low nobility.

Commercial alloy 3 consistently exhibited higher corrosion rates above 0 mV than alloys 1 and 2 during the forward corrosion scans. In addition, alloy 3 had a more active breakdown potential. Because the alloys contain approximately the same noble metal content, the differences in corrosion behaviour are attributed to the adverse effects of copper in alloy 3. Previous studies [10, 28] have established that copper degrades corrosion resistance in low nobility dental alloys. The high stability of the PdCu compound enhances the phase separation and rejection of silver from the matrix. The resulting material then contains silver-rich regions low in palladium, which are preferentially attacked in tarnish and corrosion environments. In comparison with the 75% Ag binary composition, the commercial alloys all have lower integrated current densities, indicative of the passivating role of the indium and zinc additions. However, there is no evidence that such alloying additions aid the tarnish resistance of the commercial alloys.

Solution heat treatments were applied to the alloys of this study, but no significant effect was isolated with respect to corrosion behaviour. Alternatively, tarnish was significantly altered by solution treatment, with the best tarnish resistance in the as-cast condition.

One concern is the relative corrosion and tarnish resistance of the Pd–Ag based alloys compared with other dental casting alloys. Table V provides a comparison of the current results with past evaluations of cast dental alloys [9–11, 18]. The selected tests for this comparison are the tarnish discoloration in 0.5% sodium sulphide after 3 days' exposure and the integrated current density from −300 to 300 mV in deaerated 1% NaCl. On the basis of these standardized tests, it is evident the alloys based on roughly a 3 : 1 ratio of Ag : Pd are comparable with the intermediate nobility alloys.

6. Conclusion

A minimum, yet comprehensive test battery was used to evaluate the tarnish and corrosion behaviour of Pd–Ag based alloys. These measures of chemical stability give evidence of similar dependencies on alloy composition. A minimum in tarnish and corrosion attack is evident in the 50 to 75% Ag range. This establishes that nobility is not the sole determinant of chemical stability in this alloy system. The progressive filling of vacant d-electron orbitals is one possible cause for the nonsystematic behaviour of this system. At silver contents between 50 and 75% the transition shell is filled, resulting in saturated bonding and improved resistance to chemical attack. On this basis, the selection of Ag : Pd atomic ratios between 2 : 1 and 3 : 1 for commercial alloys appears acceptable.

TABLE V Relative comparison of as-cast commercial dental alloys for tarnish and corrosion* using the current results and those from [9–11, 18]

Alloy and nominal composition (at %)	Tarnish discoloration	Integrated corrosion
B2 Ney (56% Au, 16% Ag, 22% Cu, 6% Pd)	4	0.5
Densilay Aderer (42% Au, 34% Ag, 19% Cu)	9	1
CB Ney (40% Au, 28% Ag, 28% Cu, 5% Pd)	13	4
Midigold 50 Williams (33% Au, 42% Ag, 21% Cu)	11	1
Duallor R Aderer (24% Au, 44% Ag, 25% Cu)	19	6
Miracast Ney (20% Au, 8% Ag, 58% Cu)	8	17
Sunrise Sterngold (24% Au, 45% Ag, 24% Cu)	13	13
Tiffany Sterngold (31% Au, 28% Ag, 37% Cu)	6	1
Alloy 1 (25% Pd, 70% Ag, 5% In/Zn)	12	3
Alloy 2 (25% Pd, 69% Ag, 6% In/Zn)	11	1
Alloy 3 (22% Pd, 53% Ag, 21% Cu, 3% In/Zn)	14	5

*Tarnish discoloration based on 3 days' exposure to 0.5% sodium sulphide solution and integrated corrosion based on integration from −300 to +300 mV for the forward potentiodynamic scan in deaerated 1% NaCl solution.

Microstructure becomes more important tarnish at silver contents over 50%. The presence of casting segregation and second phases induces lower tarnish resistance because of preferencial deposition attack at silver-rich microstructural inhomogeneities. No significant microstructural (heat treatment) effect was detected in the corrosion response. Copper as an alloying addition to the Pd–Ag binary induced silver segregation. Thus, the commercial alloy with copper showed evidence of higher tarnish and corrosion rates in spite of a similar palladium content. In comparison with other noble metal dental alloys, the Pd–Ag alloys rank fairly high in both tarnish and corrosion resistance. For this reason, their consideration as dental alloys appears acceptable.

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