

Comparative corrosion study of Ag–Pd and Co–Cr alloys used in dental applications

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Abstract. The electrochemical behaviour of two Ag–Pd alloys (Unique White and Paliag) used in dental prosthetics construction for crowns and bridges and one Co–Cr alloy (Vitallium 2000) was studied in artificial saliva using the polarization curves and electrochemical impedance spectroscopy (EIS). The corrosion resistance was evaluated by means of the corrosion currents value and by coulometric analysis. The open circuit potential of Ag–Pd are attributed to dealloying followed by surface enrichment with Ag and the possible formation of an insoluble AgCl surface film on the respective alloy surfaces. Our results have shown that these alloys have a somewhat good corrosion resistance in artificial saliva. The corrosion current densities of Unique White and Vitallium 2000 alloys were very low ($\sim 100 \text{ nA/cm}^2$). For Ag–Pd alloys, when increasing the content of Cu, corrosion resistance decreases. The passivation of all samples occurred spontaneously at the open circuit potential. The electrochemical properties of the spontaneously passivated electrodes at the open circuit potential were studied by EIS. The polarization resistance (R_p) and the electrode capacitance (C_d) were determined. The polarization resistance of all the samples increases with the immersion time. The polarization resistances are largest for Unique White (Ag–Pd) and Vitallium 2000 (Co–Cr) alloys. Because the electrochemical behaviour of the Co–Cr alloy was compared with that of Ag–Pd alloy, this type of alloy may be a suitable alternative for use in the manufacture of fixed dental prostheses. The present study, though limited, has shown that electrochemical characteristics can be used to identify such alloys. Knowledge of the *in vitro* corrosion behaviour of these alloys may lead to better understanding of any biologically adverse effects *in vitro*.

Keywords. Dental alloys; artificial saliva; corrosion; EIS; equivalent circuit.

1. Introduction

Metallic materials play an essential role in assisting with the repair or replacement of bone tissue that has become diseased or damaged. Metals are more suitable for load-bearing applications compared with ceramics or polymeric materials because they combine high mechanical strength and fracture toughness (Staiger and Pietak 2006). However, the main limitation of these metallic materials is the release of the toxic metallic ions that can lead to various adverse tissue reactions and/or hypersensitivity reactions (Wapner 1991).

The wide variety of dental alloy products to be found on the market—varied in both their composition and their applications or performance—has encouraged numerous workers to study their corrosion behaviour and their degree of tolerance towards tissues. ‘Das Dental Vademekum’, which cites 954 noble, highlights the diversity of this type of product clearly and non-noble alloys used in dental prostheses (1991). In the future development of

alloys, an effort should be made to gain a better understanding of the interactions between the surface of the metal and its environment; a particular interest should be taken in the interdependence between the physical and chemical state of the alloy’s surface and its corrosion behaviour. Corrosion resistance is a very important property for dental alloys, in addition to other properties such as strength, ductility and casting accuracy. Corrosion of dental alloys in the oral environment not only results in the deterioration of restoration, but also involves release of ions that is related directly to their biocompatibility (Wataha *et al* 1991a).

The difference in corrosion behaviour of metals and alloys is due to the spontaneous formation of a thin, compact layer of oxides called the passive layer, about 3 nm thick (Mathieu *et al* 1988; Landolt *et al* 1990; Mischler *et al* 1991). Similar studies have been conducted on dental alloys (Mueller 1987; Mueller *et al* 1988). The chemical composition of the passive layers, their thickness and the degree of protection they can provide is related to a number of factors connected with the chemical environment, the composition and microstructure of the alloys, mechanical stresses, etc.

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Ag–Pd alloys have been used in prosthetic dentistry in recent years because of their low price compared with gold and because of the many attractive properties from dental point of view. According to the American Dental Association classification system (Council on Dental Materials, Instruments and Equipment 1984), the Ag–Pd alloys are classified as noble metal, whereas the Au-based alloys are classified as high noble metal. The biological safety of Pd in dental alloys has been a matter of concern in recent years. This concern stems from reports of frequent incidence of ‘Pd-allergy’ (BGA 1993). The element Pd is a known sensitizer with its sensitization rate in the range of 2–18% (Aberer *et al* 1993; Cai *et al* 1995; Wataha and Haks 1996). Thus, it is not surprising that its presence in a dental alloy can trigger adverse biological reactions. These alloys released Pd and Cu ions (Pfeiffer and Schwickerath 1994), which have the potential of being toxic in cell culture studies (Leirskar 1974; Wataha *et al* 1991b, 1994). Because of these problems, some practitioners now prefer to use non-precious alloys such as cobalt chromium (Co–Cr), which, thanks to their excellent properties, have long been used to manufacture removable partial denture frameworks. Cobalt-based alloys are known for their strength, hardness, and resistance to corrosion. Chromium in these alloys provides hardness and resilience and increases corrosion resistance when its concentration is between 16 and 20 wt %.

Knowledge of the corrosion behaviour of alloys is essential to understanding their biocompatibility.

The potentiostatic/potentiodynamic polarization test (Brugirard *et al* 1973; Sarkar *et al* 1979; Holland *et al* 1986) is the method commonly used to study the *in vitro* corrosion of dental alloys. However, this method is not generally accepted as being applicable and clinically relevant for every dental alloy (Holland 1991). Some research on polarization of gold and silver-based dental alloys has been published (Vaidyanathan and Prasad 1981; Johnson *et al* 1983; Mayer and Reclaru 1995; Reclaru and Mayer 1995).

Recently, Al-Hity *et al* (2007) studied the resistance to corrosion of eight commercial alloys by two quantitative methods, electrochemical and immersion tests. The results showed that the correlation between the two measurements, polarization resistance (R_p) and mass loss, was proved statistically significant.

The objective of this study was to obtain information on selected electrochemical characteristics of a Co–Cr alloy and two commercial Ag–Pd alloys for crowns and bridges and characterize their *in vitro* corrosion behaviour with potentiodynamic polarization and electrochemical impedance spectroscopy methods.

2. Experimental

Two Ag–Pd alloys, Unique White (Generic Pentron Inc., USA) and Paliag (J.F. Jelenko & Co., Armonk, NY,

USA), used in dental prosthetics construction for crowns and bridges and one Co–Cr alloy, Vitallium 2000 (Austenal, USA), were selected for the present study. Compositions of these alloys are listed in table 1. Pure metals were purchased from The British Drug Houses LTD, B.D.H. Laboratory Chemicals Group, England.

The samples were cut into 1 cm² size and brass nut attached to each experiments using conductive paint to ensure electrical conductivity. The assembly was then embedded into an epoxy resin disk. Then the samples were ground with SiC abrasive paper up to 1000 grit, final polishing was done with 1 µm alumina suspension. The samples were degreased with ethyl alcohol followed by ultrasonic cleaning with deionized water and dried under a hot air stream, a recommended dental laboratory practice.

The corrosion medium used was Carter–Brugirard AFNOR/NF (French Association of Normalization) artificial aerated saliva. The composition of this artificial saliva is: NaCl (0.7 g/L), KCl (1.2 g/L), Na₂HPO₄H₂O (0.26 g/L), NaHCO₃ (1.5 g/L), KSCN (0.33 g/L), urea (1.35 g/L). The pH was measured with a multiparameter analyser CONSORT 831C. The pH of this reference saliva corresponding to our first medium was 8.1.

Electrochemical measurements were carried out at 25°C under static conditions. The assembled specimen was placed in a glass corrosion cell, which was filled with freshly prepared electrolyte (within 24 h). A saturated calomel electrode (SCE) was used as the reference electrode and a platinum coil as the counter electrode. All potentials were measured with respect to SCE.

The potentiodynamic polarization measurements were performed with a Princeton Applied Research potentiostat (Model 263 A) controlled by a personal computer with dedicated software (PowerCorr, Princeton Applied Research).

For each specimen, 24 h open circuit potential (E_{oc}) measurement was performed initially followed by the general polarization tests from –600 to 1200 mV at a scanning rate of 0.5 mV/s. The b_a (Tafel slopes for the partial anodic processes), b_c (Tafel slopes for the partial cathodic processes), I_{corr} (corrosion current density) and ZCP (zero current potential) were determined using the curve-fitting routine of the corrosion software.

A coulometric zonal analysis was effectuated. The method proposed here consists of dividing the polarization curves into two separate zones: zone (I), from ZCP

Table 1. Composition of Ag–Pd alloys selected for corrosion study (the manufacturer provided compositions).

Alloys	Main components (wt %)
Unique White	66Ag 22Pd 10Cu 1In
Paliag	50Ag 30Pd 15.9Cu 3Au 1Zn
Vitallium 2000	63.8Co 28.5Cr 6Mo

up to +300 mV and zone (II), +300 to +600 mV. The separation is somewhat arbitrary, but the potential span of zone (I) is close to clinical conditions. The intensity of the degradation phenomenon may vary from one patient to another; Reclaru *et al* (2006) consider zone (I) as the high-risk zone and zone (II) a lower-risk zone barring exceptional situations. The limit of zone (I) (ZCP to +300 mV) was chosen because they cover potential ranges most frequently observed in the oral cavity (Corso *et al* 1985).

The electrochemical impedance spectroscopy (EIS) was performed after 1 min, 1 h and 24 h immersion in aerated artificial saliva at the open circuit potential, using a Princeton Applied Research potentiostat (Model 263 A) connected with a Princeton Applied Research 5210 lock-in amplifier.

The spectra were recorded in the 10^{-2} Hz– 10^5 Hz frequency range. The applied alternating potential signal had an amplitude of 10 mV.

Data acquisition and analysis were performed with a personal computer. The spectra were interpreted using the ZSimpWin program. Impedance data were represented in Bode amplitude and phase angle plots. The Bode representation shows the logarithm of the impedance modulus ($\log Z_{\text{mod}}$) and phase angle as a function of the frequency logarithm (\log frequency). The advantage of the Bode plot is that the data for all measured frequencies are shown and that a wide range of impedance values can be displayed. The frequency dependence of the phase angle indicates whether one or more time constants occur and can be used to determine the values of the parameters in the equivalent circuit (EC).

All experiments were performed three times. These replications were not sufficient for carrying out statistical analysis but served to verify the reproducibility of the results obtained.

The analysis of the two (Paliag and Vitallium 2000) alloys surface was performed on an optical microscope, Olympus PME 3-ADL. To perform the surface analyses, the specimens were etched after polishing. The Ag–Pd alloy (Paliag) was etched for 30 s at ambient temperature (22°C) with a prepared solution of 5% (w/v) potassium cyanide and 5% (w/v) ammonium persulfate. The Co–Cr alloy (Vitallium 2000) was etched for 1 min at ambient temperature with a mixture of 80% by volume of hydrochloric acid, and 20% hydrogen peroxide. For each specimen, the first surface examination was carried out before performing the chronoamperometric test (+600 mV vs SCE for 4 h) and the second surface examination was undertaken after this test.

3. Results and discussion

Aerated corrosion media were used in the present study because human saliva is essentially an aerated electrolyte;

a deaerated environment exists in the human oral cavity for regions such as gingival crevices and under the biofilm.

When an alloy is placed in the oral environment, an electrochemical interaction (corrosion) between alloy and environment takes place. The effect of this interaction may be manifested as: (i) release of soluble metallic ions; (ii) retaining of corrosion products on the alloy surface; or (iii) a combination of both. These effects, depending on the altered alloy surface and/or the nature of released metallic ions, may trigger adverse biological reactions such as allergy (Merrit and Brown 1981).

For a specific environment, corrosion depends on the structure and composition of the alloy. The alloys of the present study have different compositions.

3.1 Open circuit potential, E_{OC}

The open circuit potential, E_{OC} , of a metal varies as a function of time but stabilizes at a stationary value after a long period of immersion. This is why our measurements of open circuit potentials are made after 24 h immersion. The nature of the metal–solution interface varies with time and consequently the open circuit potential is no longer a characteristic of the metal. It also depends on the experimental conditions, particularly on the electrolyte composition, the temperature and oxygen content of the electrolyte, and on the surface stage of the metal (Wagner and Traud 1938). All elements, Co, Cr, Mo, Cu, Ag, and Pd, can passivate at different potentials in aqueous environment (Hisatsune *et al* 1995). These elements are electroactive and have the ability to form an anodic film on the surface. As this film grows, it can spread over the surface. Au is immune to corrosion and does not form any reaction film.

The open circuit potential values of materials in artificial saliva after 24 h are shown in tables 2 and 3.

The pure Pd was passive, showing a high open circuit potential after 24 h of immersion in artificial saliva (around 125 mV). The results indicate that of the pure metals, Co is the most electronegative followed by Cu, Cr, Mo, Ag and Pd.

The open circuit potential values of the Ag–Pd alloys are near from that of pure Ag. The alloys are more active than Pd and Ag but more noble than Cu.

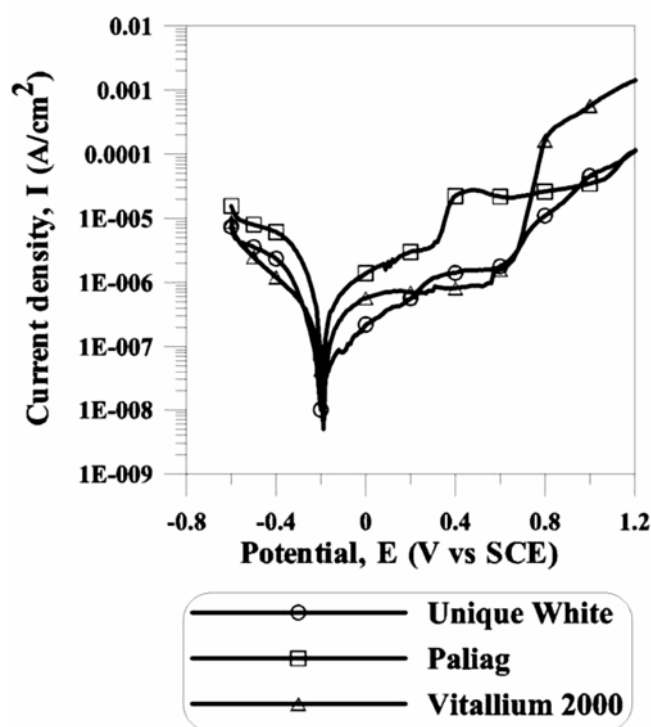
The Ag–Pd alloys studied are composed of both noble and base metals. The fate of the individual components, in particular, the corrosion of the base metals under these conditions, is dependent on the mixed potential. In this alloy, a selective dissolution of Cu takes place, the nobler Au, Pd and Ag remain on the surface. Between Ag and Au, Pd, the former is more corrosion prone and thus diffuses to the surface subsequently. Surface enrichment with Ag due to dealloying in dental alloys has been reported (Hultquist and Hero 1984; Niemi *et al* 1985;

Table 2. Open circuit potential (E_{OC}) values after 24 h of pure metals in artificial saliva.

Pure metals	Pd	Ag	Cu	Co	Cr	Mo
24 h E_{OC} (mV vs SCE)	125 ± 4	-20 ± 5	-175 ± 11	-345 ± 21	-145 ± 17	-95 ± 17

Table 3. Open circuit potential (E_{OC}) values after 24 h of dental alloys in artificial saliva.

Alloys	Unique White	Paliag	Vitallium 2000
24 h E_{OC} (mV vs SCE)	-25 ± 7	-75 ± 8	-155 ± 16

**Figure 1.** Potentiodynamic polarization curves of the alloys studied after 24 h maintained in artificial saliva, on semi-logarithmic axes.

Berzins *et al* 2000; Sarkar *et al* 2000). Unlike other base metals that actively dissolve into electrolyte, Ag in contact with Cl^- ion in artificial saliva forms an AgCl reaction film on the respective alloy surface. The electroformation of AgCl is a multistep process involving a number of chloro-silver complexes (De Mele *et al* 1986). The equilibrium potentials for various AgCl complexes are in the vicinity of 0 mV (Sarkar and Greener 1975). The formation of this AgCl complex, we believe, is responsible for lowering the open circuit potential values of Ag-Pd alloys.

The open circuit potential values of the Vitallium 2000 alloy are near from that of pure Cr. The alloys are more active than Mo and Cr but more noble than Co.

3.2 Potentiodynamic polarization curves

The $E-I$ plots of the dental alloys provide further insight into the corrosion mechanism. Plots in a semi-logarithmic version between -600 mV and $+1200$ mV vs SCE of the three dental alloys after 24 h in artificial saliva are displayed in figure 1.

Applying a potential to the alloy in a systematic manner and measuring the resulting current generate $E-I$ curves.

Standard techniques were used to extract zero current potential (ZCP) and corrosion current (I_{corr}) values from the potentiodynamic polarization plots. The Tafel slopes (b_a and b_c) were determined by fitting the theoretical polarization curve to the experimental polarization curve plotted in a range of ± 150 mV vs ZCP. The two Tafel slopes intercept at the point of the coordinates (ZCP, I_{corr}). An alloy with a tendency toward passivation will have a value of $b_a > b_c$, while an alloy that corrodes will have a $b_a < b_c$ (Mansfeld 1973). Defining the ZCP as the voltage at which the current reaches a minimum during the forward potentiodynamic polarization scan. The corrosion current is representative for the degradation degree of the alloy. The average values of b_a , b_c , ZCP and I_{corr} from three different polarization curves determined by the PowerCorr program are presented in table 4.

The high value of b_a in comparison with the values of b_c for all three alloys in artificial saliva indicates an anodic control in the corrosion process. The control implies the existence of a passive layer on the material surface. An analysis of the corrosion rate data shows little discrimination between alloys. The corrosion current densities of Unique White and Vitallium 2000 alloys were very low (~ 100 nA/cm²) (table 4).

The corrosion for Paliag alloy are approximately five times higher than in the case of Unique White alloy obtained in the same experimental conditions.

In all cases the values determined for the ZCP are smaller than those corresponding to E_{OC} (table 3). The variation is probably due to depassivation phenomena on the surface during cathodic scanning.

In the case of Ag-Pd alloys the formation of AgCl is a complex process. It involves double-layer charging, nucleation and growth of AgCl monolayer, and dissolution of the substrate Ag yielding some soluble Ag-Cl complexes (De Mele *et al* 1986). Since the open circuit values of these alloys are above the Ag/AgCl equilibrium potentials, it is likely that at these potentials, the respective alloy surfaces are covered with adsorbed AgCl species at the submonolayer level. With polarization, these

Table 4. Analysis of polarization curves for dental alloys studied after 24 h immersion in artificial saliva.

Alloys	ZCP (mV)	b_a (mV/div)	b_c (mV/div)	I_{corr} (nA/cm ²)	Coulometric analysis	
					ZCP–300 mV (mC/cm ²)	300–600 mV (mC/cm ²)
Unique White	−195 ± 4	185 ± 5	145 ± 5	95 ± 5	0.35 ± 0.03	0.95 ± 0.06
Paliag	−205 ± 5	180 ± 4	135 ± 5	520 ± 5	1.35 ± 0.09	11.95 ± 0.1
Vitallium 2000	−196 ± 12	190 ± 5	150 ± 6	120 ± 6	0.50 ± 0.02	0.55 ± 0.03

layers grow into three-dimensional AgCl and cover the entire surface, limiting further corrosion. However, AgCl film is not considered to be an efficient barrier to dissolution (Sarkar and Greener 1975). As a result, the anodic current shows a monotonical increase near the corrosion potential.

Vitallium 2000 alloy translated directly into a stable passive behaviour from the “Tafel region” without exhibiting a traditional active–passive transition. Above +0.6 V, the passive film breakdown takes place. The potential range situated between the zero current potential (ZCP) and the breakdown potential represents the passive zone in which corrosion is weak. Passive current density (I_{pass}) was also determined from the potentiodynamic anodic diagram and is obtained around the middle of the passive range. The passive current density of the Vitallium 2000 alloy in artificial saliva is ~800 nA/cm² typically for passivable materials. It is well known that if the metal shows lower I_{pass} with longer potential range, the metal is considered to possess a better and more stable passivity.

3.3 Coulometric analysis

Coulometric analysis provides a simple way for a rough clinical risk analysis. It consists of dividing the anodic polarization curves into two distinct zones: a first zone (I) extending from ZCP to +300 mV and a second zone (II) from +300 to +600 mV. The quantities of electrical charge consumed by the corrosion phenomenon by this zone are shown in table 4. The quantities of electrical charge consumed for all the samples in artificial saliva in zones (I) and (II) show significant differences. The quantities of electrical charge consumed in zone (I) for Unique White and Vitallium 2000 alloys was low: 400–500 $\mu\text{C}/\text{cm}^2$.

The charges for high-risk zone for Paliag alloy immersed in artificial saliva are about four times higher than in the case for Unique White alloy in the same conditions. On the other hand, for Paliag alloy in artificial saliva, the quantities of current, in zone (II), are substantial: ~12 mC/cm². The Paliag alloy has much less corrosion resistance than Unique White and Vitallium 2000 alloys in both zones. For Ag–Pd alloys, the electrochemi-

cal results show that with the increasing content of Cu, corrosion resistance decreases.

In the case of Paliag alloy an examination of the microstructure shows that it is a two-phase alloy (figure 2a). After the corrosion test, one notices that one of two phases corrodes with the formation of silver chloride (figure 2b). Figure 2c shows the microstructure of Paliag alloy after elimination of silver chloride by dissolving in a 20% ammonia solution. The surfaces of Vitallium 2000 alloy showed dendrite microstructure, a rippled structure between the matrix and particle phases (figure 3a). Figure 3b shows the surface micrographs of Vitallium 2000 alloy after electrochemical measurements.

During the electrochemical test in acidified saliva (chronoamperometric test at +600 mV vs SCE for 4 h), the surface of Paliag alloy has undergone a significant selective degradation and the surface of Vitallium 2000 alloy has undergone a uniform corrosion process as evidenced in figures 2b and 3b. The Paliag alloy has inferior corrosion behaviour. This is due, probable, to the fact that these alloys are two-phase and therefore, there may be microgalvanism phenomena between the phases.

3.4 Electrochemical impedance spectroscopy (EIS)

In a complementary study, electrochemical impedance spectroscopy was used to investigate the corrosion resistance of these dental alloys. A set of impedance spectra recorded at E_{OC} , with the Ag–Pd and Co–Cr alloys immersed in artificial saliva for a different period of time, presented as Bode plots is shown in figures 4–6.

From the Bode spectra it is possible to indicate the presence of a compact passive film if: (a) the phase angle is close to -90° over a wide frequency range and (b) if the spectrum shows linear portions at intermediate frequency.

All the spectra show that in a higher frequency region, $\log Z_{\text{mod}}$ tends to become constant with a phase angle value of 0° . This is a typical response for the resistive behaviour and corresponds to the solution resistance, R_Ω . In the medium frequency range, a linear relationship between $\log Z_{\text{mod}}$ and \log frequency is observed, with slopes always < -1 and phase angle maxima $< -90^\circ$, indicating that the passive films were not fully capacitive.

Inside the low frequency range, with Paliag alloy immersed in artificial saliva for 1 min, the slope of the $\log Z_{\text{mod}}$ and \log frequency and the phase angle against \log frequency indicate Warburg (W)-like behaviour. In other cases, inside the low frequency range a resistive behaviour was observed.

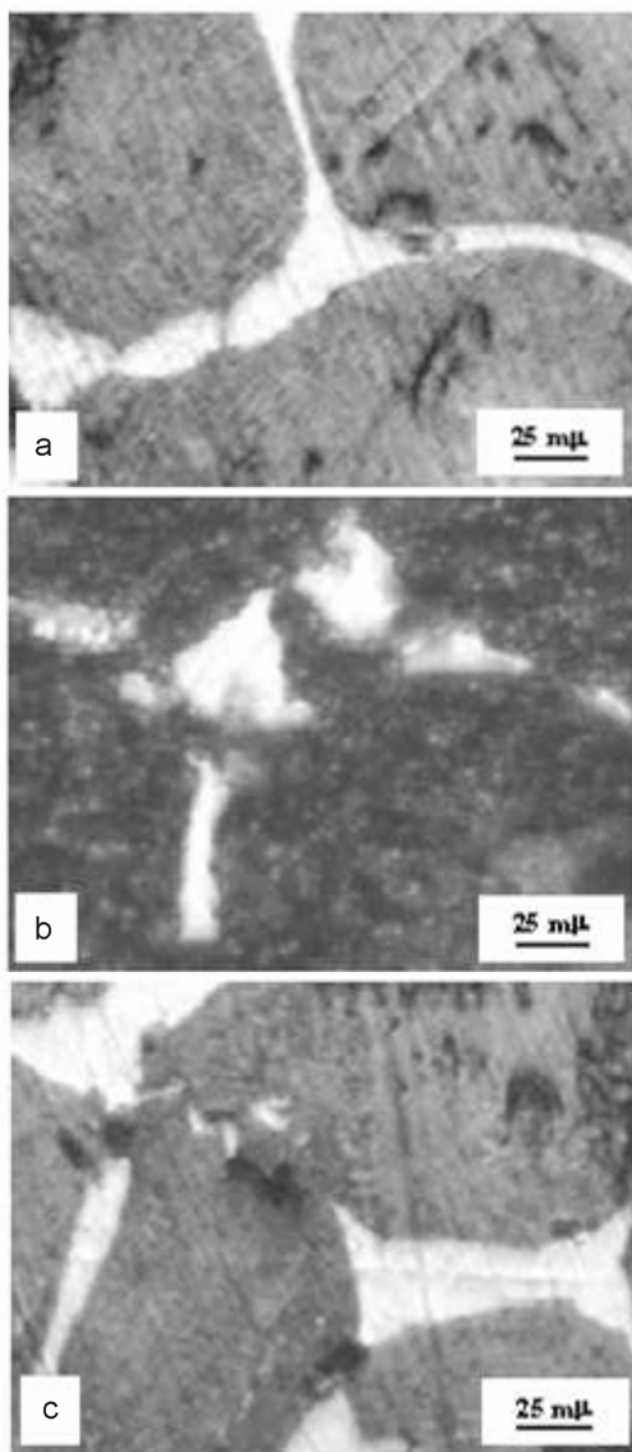


Figure 2. Paliag alloy: **a.** prior to corrosion test, **b.** after corrosion test and **c.** after dissolution of silver chloride.

Since any interface undergoing an electrochemical reaction is typically analogous to an electronic circuit consisting of a specific combination of resistors and capacitors, the electrochemical systems under study can be described in terms of their equivalent circuits (ECs).

An EC consists of various arrangements of resistances, capacitors and other circuit elements, and provides the most relevant corrosion parameters applicable to the substrate/electrolyte system. The usual guidelines for the selection of the best-fit EC were followed:

- a minimum number of circuit elements were to be employed
- the χ^2 error was suitably low ($\chi^2 < 10^{-4}$), and the error associated with each element was up to 5%

The ECs that satisfied the above criteria were used to fit the experimental data and are presented in figure 7. Since the measured capacitive response is not generally ideal due to certain heterogeneity of the electrode surface (MacDonald 1987; Martini and Muller 2000), a constant phase element (CPE) was introduced for fitting the spectra, instead of an ideal capacitance element. Its impedance may be defined by

$$Z_{\text{CPE}} = \frac{1}{Q(j\omega)^n},$$

where Q is the combination of properties related to both the surfaces and electroactive species independent of frequency; n is related to a slope of the $\log Z_{\text{mod}}$ vs \log frequency (Bode plots); ω the angular frequency and j the imaginary number ($j^2 = -1$). n is an adjustable parameter that usually lies between 0.5 and 1. When the value of n is equal to 1, the CPE describes an ideal capacitor with Q equal to the capacitance (C). For $0.5 < n < 1$, the CPE describes a distribution of dielectric relaxation times in frequency space, and when n is equal to 0.5 the CPE represents a Warburg impedance with diffusional character.

The impedance data of Unique White alloy, immersed for 1 min, 1 h and 1 day in artificial saliva were fitted with the EC presented in figure 7a and the resultant EIS parameters are given in table 5. The solution resistance, R_{Ω} , equals $30 \pm 5 \Omega$. The same value was observed for all of the specimens and was not inserted in table 5.

The physical meaning of the given circuit is the association of the passive layer/electrolyte interface ($R_1\text{CPE}_1$) with the passive layer itself ($R_2\text{CPE}_2$). The time constant at high frequencies originated from the $R_1\text{CPE}_1$ combination while the one at low frequencies initiated from the $R_2\text{CPE}_2$ combination. R_1 representing the charge transfer resistance and CPE_1 the double layer capacitance, as shown by the high value of the n_1 exponent. The double layer capacitances are typical for the C_{dl} of the passive layers (Haupt and Strehblow 1989; Moffat and Latanision

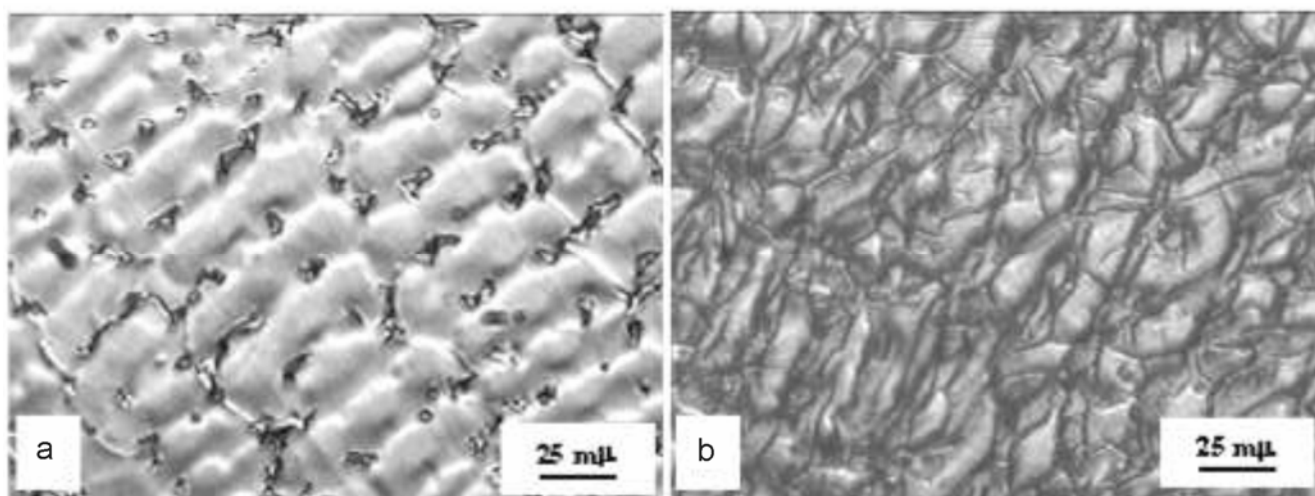


Figure 3. Vitallium 2000 alloy: a. prior to corrosion test and b. after corrosion test.

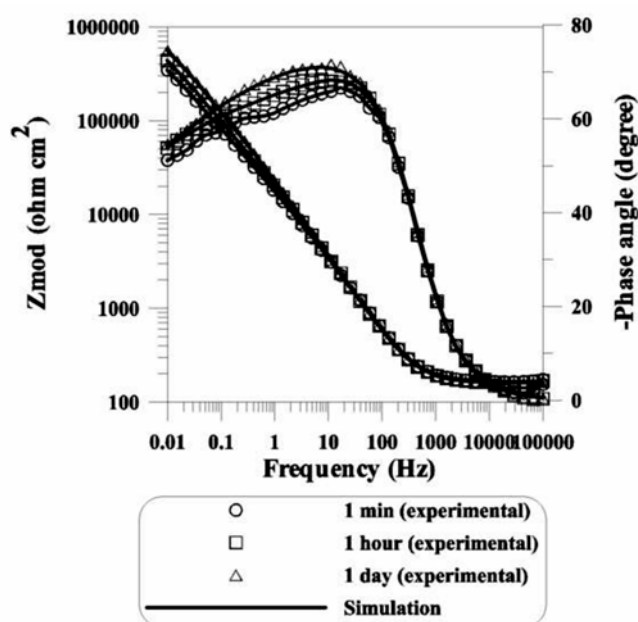


Figure 4. Bode plots of the Unique White alloy for various exposure times to the artificial saliva measured at E_{OC} .

1992; Castro and Vilche 1993). The characteristics of the passive layer are reflected in the values of R_2 .

For the Unique White alloy in artificial saliva the values of n_2 are small, in the range of 0.68–0.76, indicating the presence of a diffusion process within the interfacial layer of the solution. Such a diffusion process indicates a reversible dissolution process; i.e. the passive layer formation under open circuit condition proceeds through a dissolution–precipitation mechanism (Ismail *et al* 2001).

The polarization resistance (R_p) of the Unique White alloy equals the sum of the R_1 (R_{ct}) and the passive layer resistance, R_2 .

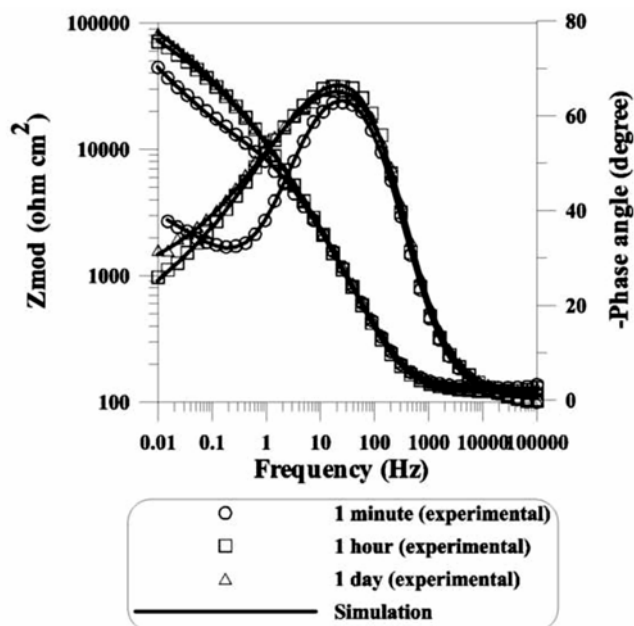


Figure 5. Bode plots of the Paliag alloy for various exposure times to the artificial saliva measured at E_{OC} .

A high R_p value is an indication of the working electrode strongly resisting change from its equilibrium state and is representative of the degree of protection of the passivation layer of the dental alloy surface. The polarization resistance, R_p , of the Unique White alloy immersed for 1 min in an artificial saliva, is larger (around $270 \text{ k}\Omega \text{ cm}^2$) and increases with immersion time (around $470 \text{ k}\Omega \text{ cm}^2$, for alloy maintained for 1 day in an artificial saliva) indicating a continuous growth of the passive film in time until a steady state is attained.

The more the value of R_p increase, the more the dental alloy will resist corrosion. From the Stern–Geary (1957) equation

$$I_{\text{corr}} = \frac{b_a b_c}{2.3 R_p (b_a + b_c)} = \frac{B}{R_p}, \quad (1)$$

where b_a and b_c are the Tafel slopes for the partial anodic and cathodic processes, respectively and B is a constant:

$$B = \frac{b_a b_c}{2.3(b_a + b_c)}. \quad (2)$$

The corrosion current for the Unique White alloy immersed in artificial saliva for 1 day is small, $\sim 75 \text{ nA/cm}^2$ and is in agreement with the polarization data.

The impedance data of Paliag alloy immersed for 1 min in artificial saliva was fitted with the EC presented in

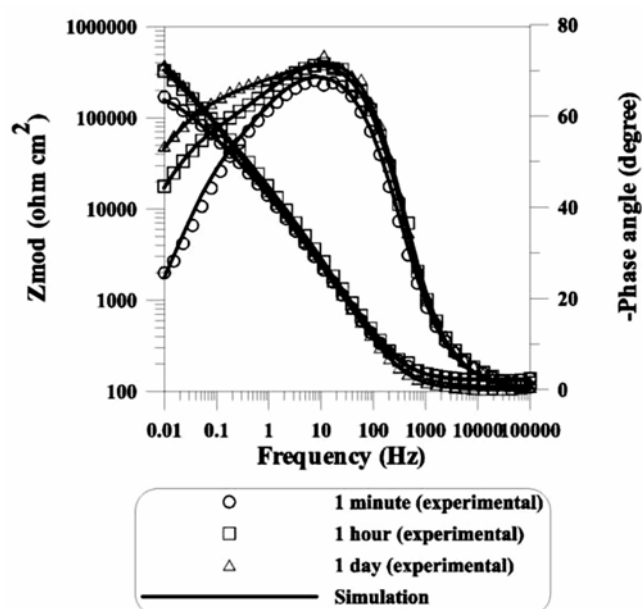


Figure 6. Bode plots of the Vitallium 2000 alloy for various exposure times to the artificial saliva measured at E_{OC} .

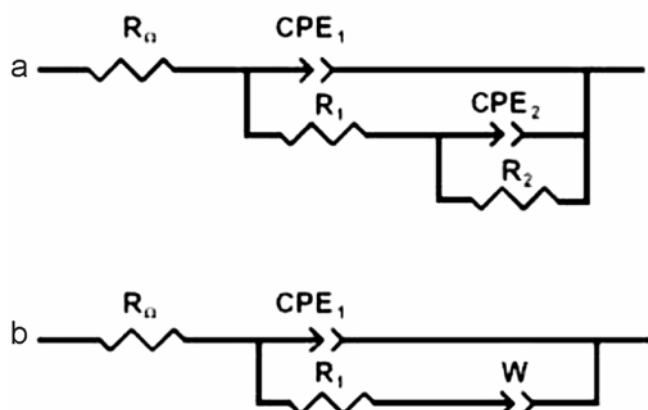


Figure 7. Equivalent circuits (ECs) used to fit the impedance spectra.

figure 7b, and immersed for 1 h and 1 day in artificial saliva which was fitted with the EC presented in figure 7a. The resultant EIS parameters are given in table 5. In the case of Paliag alloy immersed for 1 min in artificial saliva, the polarization resistance, R_p , equals the sum of R_{ct} (R_1) and the diffusion resistance, R_D (Scully 2000). The Paliag alloy maintained for 1 min in artificial saliva shows smaller polarization resistance (around $45 \text{ k}\Omega \text{ cm}^2$) than that of Unique White alloy and increases with the immersion time indicating that after 1 day, good stability of this dental alloy is achieved in artificial saliva (around $95 \text{ k}\Omega \text{ cm}^2$). Since the n_1 exponent is high (0.80–0.83), the constant phase element CPE_1 is essentially the C_{dl} .

The impedance data of Vitallium 2000 alloy immersed for 1 min, 1 h and 1 day in artificial saliva were fitted with the EC presented in figure 7a. After 1 min in artificial saliva the polarization resistance of the alloy (around $200 \text{ k}\Omega \text{ cm}^2$) is largest and increases after 1 day (around $385 \text{ k}\Omega \text{ cm}^2$) indicating high stability of Vitallium 2000 alloy in artificial saliva. CPE_1 is essentially the ideal capacitance, as shown by the high value of n_1 and represents C_{dl} .

Using the Stern-Geary equation the corrosion current for the Vitallium 2000 alloy immersed in artificial saliva for 1 day is small, $\sim 95 \text{ nA/cm}^2$ and is in agreement with the polarization data.

In figures 4–6, the experimental data are shown as individual points, while the theoretical spectra resulting from the fits to relevant ECs are shown as lines.

The polarization resistance of all the specimens increases with immersion time.

Despite the non-precious nature of the Co–Cr alloy (Vitallium 2000), no significant differences in corrosion resistance were found between this alloy and the Ag–Pd alloy (Unique White). On the other hand, electrochemical analysis reveals that Cu reduces the corrosion resistance of Ag–Pd alloy (Paliag).

4. Conclusions

Two Ag–Pd alloys used in dental prosthetics construction for crowns and bridges and one Co–Cr alloy were evaluated for *in vitro* corrosion resistance in aerated artificial saliva. Saliva in the human oral cavity is generally considered to be in an aerated environment. However, a deaerated environment will only affect the reduction reaction, not the oxidation reaction. In addition, certain areas in the oral cavity, such as the subgingival region, and areas under the plaque, are in a deaerated condition. Using various techniques, it was constantly shown that the alloys had somewhat good corrosion resistance. The open circuit potential of Ag–Pd are attributed to dealloying followed by surface enrichment with Ag and the possible formation of an insoluble AgCl surface film on the respective alloy surfaces. The corrosion currents have

Table 5. Impedance parameters of alloys studied in artificial saliva at open circuit potential.

Alloy	R_1 (k Ω cm ²)	10^5 CPE ₁ (S cm ⁻² s ⁿ)	n_1	R_2 (k Ω cm ²)	10^6 CPE ₁ (S cm ⁻² s ⁿ)	n_2	W_R (k Ω cm ²)
Alloys maintained for 1 min in artificial saliva							
Unique White	13 \pm 1	1.1 \pm 0.1	0.84	255 \pm 2	9.8 \pm 0.2	0.68	–
Paliag	10 \pm 1	1.3 \pm 0.1	0.8	–	–	–	36 \pm 1
Vitallium 2000	13 \pm 1	2.4 \pm 0.1	0.82	190 \pm 2	15.0 \pm 0.2	0.67	–
Alloys maintained for 1 h in artificial saliva							
Unique White	12 \pm 1	1.3 \pm 0.1	0.86	321 \pm 3	8.9 \pm 0.2	0.73	–
Paliag	11 \pm 1	1.2 \pm 0.1	0.81	71 \pm 1	26.0 \pm 0.4	0.68	–
Vitallium 2000	18 \pm 2	2.3 \pm 0.1	0.85	275 \pm 2	9.7 \pm 0.2	0.72	–
Alloys maintained for 1 day in artificial saliva							
Unique White	12 \pm 1	1.0 \pm 0.1	0.86	458 \pm 8	8.1 \pm 0.2	0.76	–
Paliag	11 \pm 1	1.3 \pm 0.1	0.83	84 \pm 4	16.0 \pm 0.3	0.72	–
Vitallium 2000	19 \pm 2	1.9 \pm 0.2	0.87	364 \pm 9	8.5 \pm 0.2	0.78	–

values of nA order for all the samples. Coulometric analysis reveals that Cu reduces the corrosion resistance of Ag–Pd alloy. The EIS results show that all alloys exhibit passivity at open circuit potential. The polarization resistance obtained from EIS spectra increases with immersion time. Equivalent circuits were proposed for the electrochemical behaviour of dental alloys in artificial saliva. It can be concluded that the Co–Cr alloy (Vitallium 2000) exhibited excellent corrosion resistance and can be used as an alternative to Ag–Pd alloys to make fixed prosthetic elements.

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