Electrochemical Determination of the Corrosion Resistance of Ag-Pd Dental Alloys

DANIEL MARECI[1], IGOR CRETESCU[1], NECULAI AELENEI[1], JULIA CLAUDIA MIRZA ROSCA[2]
[1]Gh. Asachi Technical University of Iasi, Faculty of Chemical Engineering, 71 Mangeron Blvd., 700050, Iasi, Romania
[2]Las Palmas de Gran Canaria University, Chemical Engineering Departament, 35017, Las Palmas de Gran Canaria, Spain

The electrochemical behavior of a three Ag-Pd alloys used in dental prosthetics construction for crowns and bridges 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. 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_{dl}) were determined. The polarisation resistance of all the samples increases with the immersion time. The polarization resistances are largest and decrease when increasing the content of Cu. Cu reduces the Ag-Pd alloy corrosion resistance. The present study, thought limited, has shown that electrochemical characteristics can be use 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, corrosion, polarization curves, electrochemical impedance spectroscopy

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 [1]. 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 [2].

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 authors to study their corrosion behavior 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 [3]. 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 a release of ions that is related directly to their biocompatibility [4].

The difference in corrosion behaviour of metals and alloys is due to the spontaneous formation of a thin, mpact layer of oxides called the passive layer, about 3 n thick [5-7]. Similar studies have been conducted on ntal alloys [8, 9]. The chemical composition of the ive layers, their thickness and the degree of protection y can provide is related to a number of factors nected with the chemical environment, the composition and microstructure of the alloys, mechanical stresses, etc.

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 [10], 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" [11]. The element Pd is a known sensitizer with its sensitization rate in the range of 2-18% [12-14]. Thus, it is not surprising that its presence in a dental alloy can trigger adverse biological reactions. These alloys released Pd and Cu ions [15], which have the potential of being toxic in cell culture studies [16-18].

Knowledge of the corrosion behavior of Ag-Pd alloys is essential to the understanding of their biocompatibility.

The potentiostatic/potentiodynamic polarization test [19-21] 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 [22]. Some research on polarization of gold and silver-based dental alloys has been published [23-26].

Recently R.R Al-Hity et al [27] 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 three commercial Ag-Pd alloys for crowns and bridges and characterize their in vitro corrosion behaviour with

---

: 0741914342

potentiodynamic polarization and electrochemical impedance spectroscopy methods.

Experimental part

Materials and methods

Three Ag-Pd alloys used in dental prosthetics construction for crowns and bridges were selected for the present study. Compositions of these alloys are listed in table 1.

Table 1

COMPOSITION OF Ag-Pd ALLOYS SELECTED FOR CORROSION STUDY (THE MANUFACTURER PROVIDED COMPOSITIONS: J.F. JELENKO & CO., ARMONK, NY. USA)

Alloy	Main Components (wt.%)
Sample 1	2Au 58.5Ag 27.4Pd 10.5Cu 1.5Zn
Sample 2	3Au 50Ag 30Pd 15.9Cu 1Zn
Sample 3	55.1Ag 22.9Pd 18.1Cu 3Zn

The samples were cut into 1 cm^2 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 1μm alumina suspension. The samples were degreased with ethyl alcohol followed by ultrasonic cleaning with deionised water and dried under a hot air stream, 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), $Na_2HPO_4H_2O$ (0.26 g/L), $NaHCO_3$ (1.5 g/L), KSCN (0.33 g/L), Urea (1.35 g/L). The *p*H was measured with a multiparameter analyser CONSORT 831C. The pH of this reference saliva corresponding to our first medium was 8.

Electrochemical measurements were carried out at 25^{0}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 potentidynamic polarization measurements were performed with a Princeton Applied Research potentiostate (Model 263 A) controlled by a personal computer with dedicate 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 mV 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, $E_{(I=0)}$) was determined using the curve-fitting routine of the corrosion software

A coulometric zone analysis was effectuated. The method proposed here consists of dividing the polarization curves into two separate zones: zone I, from ZCP up to + 300 mV and zone II, +300 mV 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, zone I being considered as the high-risk zone and zone II a lower-risk zone barring exceptional situations [28]. The limits of zone I (ZCP to +300mV) were chosen because they cover potential ranges most frequently observed in the oral cavity [29].

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

The spectra were recorded in the 10^{-2} Hz to 10^5 Hz frequency range. The applied alternating potential signal had 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. In the Bode representation shows the logarithm of the impedance modulus (Zmod) and phase angle as a function of the frequency logarithm. 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.

Results and discussions

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 the two takes place. The effect of this interaction may be manifested as: (1) release of soluble metallic ions into the oral environment; (2) formation of corrosion products on the alloy surface; or (3) 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 [30].

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

Open Circuit Potential, E_{OC}

The open circuit potential is the potential at which the alloy is in equilibrium with the specific environment. The open circuit potential of a metal varies as a function of the 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 hours 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

Materials	Pd	Ag	Cu	Sample 1	Sample 2	Sample 3
Open circuit potential E_{OC} (mV vs. SCE)	125	-19	-174	-31	-42	-61

Table 2

OPEN CIRCUIT POTENTIAL VALUES AFTER 24 h OF MATERIALS IMMERSION IN ARTIFICIAL SALI electrolyte, and on the surface stage of the metal [31]. All elements Cu, Ag, Pd can passivate at different potential in aqueous environment [32]. 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 is used as a criterion for the corrosion behaviour. This approach is qualitative and remains insufficient for a complete analysis.

The open circuit potential values of all materials in artificial saliva after 24 hours are shown in table 2.

The pure Pd (99.99 wt%) was passive, showing a high corrosion potential after 24 h of immersion in artificial saliva (125 mV).

The results indicate that of the pure metals, Cu (99.90 wt%) is the most electronegative followed by Ag (99.91 wt%) 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 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 this conditions, is dependent on the mixed potential. In this alloys 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 [33-36]. Unlike other base metals that actively dissolve into electrolyte, Ag in contact with Cl^- ion in artificial saliva forms a AgCl reaction film on the respective alloy surface. The electroformation of AgCl is a multistep process involving a number of chloro-silver complexes [37]. The equilibrium potentials for various AgCl complexes are in the vicinity of 0 mV [38]. The formation of this AgCl complex, we believe, is responsible for lowering the open circuit potential values of Ag-Pd alloys.

Potentiodynamic polarization curves

The E-I plots of the Ag-Pd 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 Ag-Pd 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. The polarization curves of all the alloys appeared to be similar in nature but the anodic currents are bigger for Sample 2 and Sample 3 than in the case of Sample 1.

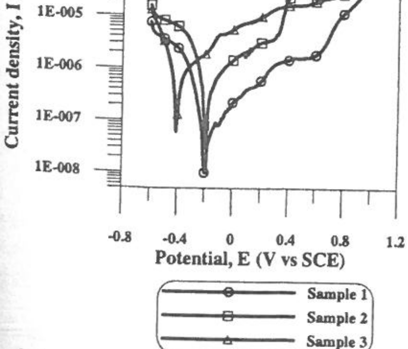

Fig.1. Potentiodynamic polarisation curves of Ag-Pd alloys tested after 24 h maintained in artificial saliva, on semi-logarithmic axes

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 greater than b_c, while an alloy that corrodes will have a b_a less than b_c [39]. Defining the ZCP as the voltage at which the current reaches a minimum during the forward potentidynamic polarization scan. The corrosion current is representative for the degradation degree of the alloy. The average values b_a, b_c, ZCP and I_{corr} from three different polarization curves determined by the PowerCorr program are presented in table 3.

The high value of b_a in comparison with the values of b_c for the 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 average corrosion rate of the Sample 1 was extremely low: 92 nA/cm^2. The corrosion currents for Sample 2 and Sample 3 are 5-8 times higher than in the case of Sample 1 obtained in the same experimental conditions.

In all cases the values determined for the ZCP, are smaller than those corresponding to E_{OC} (table 2). The variation is probably due to depassivation phenomena on the surface during cathodic scanning.

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 [37]. Science 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 layers grow into tridimensional AgCl and cover the entire surface, limiting further corrosion. However, AgCl film is not considered to be an efficient barrier to dissolution [38]. As a result the anodic current show a monotonically increase near the corrosion potential, diffusion controlled process.

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 mV to +600 mV. The quantities of electrical charge consumed by the corrosion phenomenon by zone are shown in tables 3. The quantities of electrical charge consumed for all the samples in artificial saliva in zone I and zone II show significant differences. The quantities of electrical charge consumed in zone I for Sample 1 were low: 380 μC/cm^2.

The charges for high-risk zone for Sample 3 immersed in artificial saliva are about 20 times higher than in the case for Sample 1 in the same conditions. On the other hand, for Sample 2 and Sample 3 in artificial saliva, the quantities of current, in zone II, are substantial: approximately 12 mC/cm^2 for Sample 2, and approximately 9 mC/cm^2 for Sample 3. The Sample 2 and Sample 3 have much less corrosion resistance than Sample 1 in both zones. In all the results it can be observed that the increasing the content of Cu, corrosion resistance decreases.

The results are consistent with the conclusions derived from the electrochemical quantities presented above.

Ag-Pd alloy	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)
Sample 1	-195	185	145	92	0.38	0.98
Sample 2	-205	183	134	521	1.37	11.93
Sample 3	-395	181	132	785	7.1	9.2

Table 3
THE ANALYSIS OF POLARIZATION CURVES
FOR Ag-Pd DENTAL AFTER 24 h
IMMERSION IN ARTIFICIAL SALIVA

Electrochemical impedance spectroscopy (EIS)

In a complementary study, electrochemical impedance spectroscopy was used to investigate the corrosion resistance of these Ag-Pd alloys.

A set of impedance spectra recorded at E_{OC}, with the Ag-Pd alloys immersed in artificial saliva for a different period of time, presented as Bode plots is shown in figures 2-4.

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 Zmod tends to become constant with a phase angle values 0°. This is a typical response for the resistive behaviour and corresponds to the solution resistance, R_W. In the medium frequency range, linear relationships between log Zmod and log Frequency is observed, with slopes always less than -1 and phase angle maxim less than -90°, indicating that the oxide passive films were not fully capacitive. Inside the low frequency range, with

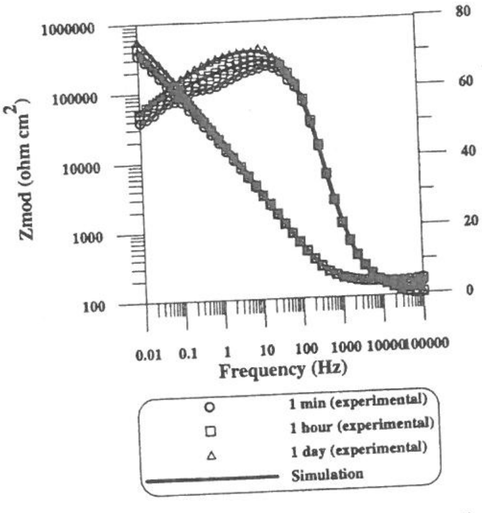

Fig. 2. Bode plots of the Sample 1 for various exposure times to the artificial saliva measured at E_{OC}.

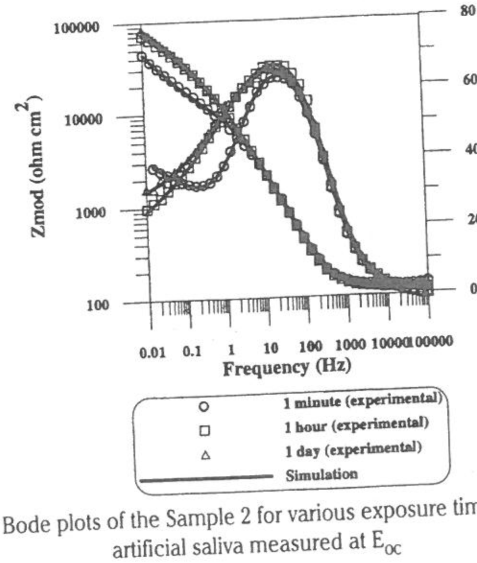

Fig 3. Bode plots of the Sample 2 for various exposure times to the artificial saliva measured at E_{OC}

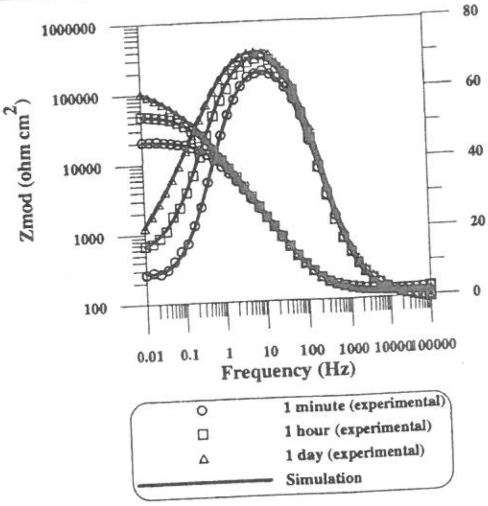

Fig. 4. Bode plots of the Sample 3 for various exposure times to artificial saliva measured at E_{OC}

Sample 2 immersed in artificial saliva for 1 min and Sample 3 immersed in artificial saliva for 1 min and the slope of the log Zmod and log Frequency and the pl angle against log Frequency indicate Warburg behaviour. In other cases, inside the low frequency r a resistive behaviour was observed.

Since any interface undergoing an electrochem reaction is typically analogous to an electronic ci consisting of a specific combination of resistors capacitors, the electrochemical systems under the can be described in terms of their equivalent circuits (An EC consists of various arrangements of resista capacitors and other circuit elements, and provide most relevant corrosion parameters applicable t substrate/electrolyte system. The usual guidelines f selection of the best-fit EC were followed:

-a minimum number of circuit elements has employed,

-the χ^2 error was suitably low ($\chi^2 < 10^{-4}$), and the associated with each element was up to 5%.

The ECs that satisfied the above criteria were use the experimental data and are presented in figure 5. the measured capacitive response is not generally due to the certain heterogeneity of the electrode s [40,41], a constant phase element (CPE) was intro for fitting the spectra, instead of an ideal capac element. Its impedance may be defined by:

$$Z_{CPE} = 1/Q(j\omega)^n$$

where Q is the combination of properties relat

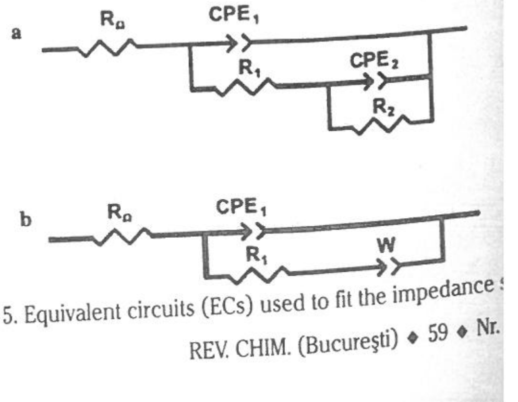

Fig. 5. Equivalent circuits (ECs) used to fit the impedance

Table 4
IMPEDANCE PARAMETERS OF Ag-Pd ALLOYS IN ARTIFICIAL SALIVA AT OPEN CIRCUIT POTENTIAL

Ag-Pd alloys	R_1 (kΩ cm^2)	CPE_1 (S cm^{-2} s^n)	n_1	R_2 (kΩ cm^2)	CPE_1 (S cm^{-2} s^n)	n_2	W_R (kΩ cm^2)
	The alloys maintained for 1 minute in artificial saliva						
Sample 1	13	1.1 10^{-5}	0.84	254	9.8 10^{-6}	0.67	-
Sample 2	10	1.3 10^{-5}	0.8	-	-	-	36
Sample 3	8	2.1 10^{-5}	0.81	-	-	-	11
	The alloys maintained for 1 hour in artificial saliva						
Sample 1	12	1.3 10^{-5}	0.86	321	8.9 10^{-6}	0.73	-
Sample 2	11	1.2 10^{-5}	0.81	71	2.6 10^{-5}	0.68	-
Sample 3	9	2 10^{-5}	0.84	-	-	-	42
	The alloys maintained for 1 day in artificial saliva						
Sample 1	12	9.9 10^{-6}	0.86	458	8.1 10^{-6}	0.76	-
Sample 2	11	1.3 10^{-5}	0.83	84	1.6 10^{-5}	0.72	-
Sample 3	9	1.9 10^{-5}	0.85	82	1.7 10^{-5}	0.75	-

both the surfaces and electroactive species independent of frequency; n is related to a slope of the lgZ vs lgf Bode–plots; ω is the angular frequency and j is 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 Sample 1, immersed 1 minute, 1 hour and 1 day in artificial saliva were fitted with the EC presented in figure 5a and the resultant EIS parameters are given in table 4. The solution resistance, $R_Ω$, equals 30 ± 5Ω. The same value was observed for all of the specimens and was not inserted in table 4.

The physical meaning of the given circuit is the association of the passive layer/electrolyte interface (R_1CPE_1) with the passive layer itself (R_2CPE_2). The time constant at high frequencies is originated from the R_1CPE_1 combination while that one at low frequencies initiated from the R_2CPE_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 [42-44]. The characteristics of the passive layer are reflected in the values of R_2.

For the Sample 1 in artificial saliva the values of n_2 are small, in the range of 0.67-0.76 indicates the presence of a diffusion process within the interfacial layer of the solution. Such a diffusion process indicates a reversible dissolution process; that is, the passive layer formation under open circuit condition proceeds through a dissolution-precipitation mechanism [45]. As mentioned before, Ag-Pd alloys corrosion is a dissolution-precipitation reaction.

The polarization resistance (R_p) of the Sample 1 dental alloy equals the sum of the R_1 (R_{ct}) and the passive layer resistance, R_2.

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 Sample 1 dental alloy immersed 1 min in artificial saliva is larger (267 kΩ cm^2) and increases with the immersion time (470 kΩ cm^2, for alloy maintained 1 day in 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 increases, the more the dental alloy will resist corrosion. From the Stern-Geary equation [46]:

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

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 Sample 1 immersed in artificial saliva for 1 day is small: 75 nA/cm^2 and is in agreement with the polarization data.

The impedance data of Sample 2 immersed 1 minute in artificial saliva was fitted with the EC presented in Figure 5b, and immersed 1 hour and 1 day in artificial saliva was fitted with the EC presented in figure 5a. The resultant EIS parameters are given in table 4. In the case of Sample 2 immersed 1 minute in artificial saliva the polarization resistance, R_p, equals the sum of R_{ct} (R_1) and the diffusion resistance, R_D [47]. The Sample 2 maintained 1 min in artificial saliva show smaller polarization resistance (R_p = 46 kΩ cm^2) than that of Sample 1 and increases with the immersion time indicating after 1 day the good stability of this dental alloy in artificial saliva (R_p = 95 kΩ cm^2). Since the n_1 exponent is high (0.81-0.83), the constant phase element CPE_1 is essentially the C_{dl}.

The impedance data of Sample 3 immersed 1 minute and 1 hour in artificial saliva were fitted with the EC presented in figure 5b, and immersed 1 day in artificial saliva were fitted with the EC presented in figure 5a.

In the figures 2-4 the experimental data are shown as individual points, while the theoretical spectra resulting from the fits to a relevant ECs are shown as lines.

The polarisation resistance of all the samples increase with the immersion time.

The polarization resistances of the Sample 1 are the largest in comparison with the Sample 2 and Sample 3 indicating high stability of this alloy in artificial saliva.

Conclusions

Three Ag-Pd alloys used in dental prosthetics construction for crowns and bridges were evaluated for in vitro corrosion resistance in aerated artificial saliva. Saliva in the human oral cavity is generally considered to be 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 have somewhat good corrosion resistance. The open circuit potential of Ag-Pd is 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 values of nA order for all the samples and increase when increasing the content of Cu in alloys. Coulometric analysis reveals that Cu reduces the corrosion resistance of Ag-Pd alloy. The EIS results show that all Ag-Pd alloys exhibit passivity at open circuit potential The high impedance was mainly ascribed to the presence of a protective passive layer formed on dental alloys. The polarization resistance obtained from EIS spectra increases with immersion time. Equivalent circuits were proposed for the electrochemical behavior of Ag-Pd dental alloys in artificial saliva.

References

1.STAIGER M.P., PIETAK A.M., Magnesium and its Alloys as Orthopedic Biomaterials: A Review, Biomaterials, 27, 2006, p. 1728

2.WAPNER K.L., Implications of Metallic Corrosion in Total Knee Arthroplasty, Clin Orthop Relat Res., 271, 1991, p.12

3. DAS DENTAL VADEMEKUM, Redaktion: Institut der Deutschen Zahntirzte, Deutscher Arzte-Verlag, Koln, 1991

4. WATAHA J.C., CRAIG R.G., HAKS C.T., The Release of Elements of Dental Casting Alloys into Cell-Culture Medium, J. Dent. Res., 70, 1991, p. 1014

5.MISCHLER S., VOGEL A., MATHIEU H.J., LANDOLT P., The Chemical Composition of the Passive Film on Fe-24Cr and Fe-24Cr- 11Mo Studies by AES, XPS and SIMS., Corr. Sci., 32, 1991, p. 942.

6.LANDOLT P., MISCHLER S., VOGEL A., MATHIEU H.J., Chloride Effects on Passive Films on FeCr and FeCrMo Studied by AES, XPS and SIMS, Corr. Sci., 31, 1990, p. 431

7.MATHIEU H.J., MISCHLER S., VOGEL A., SEILER A., REIDL G., Investigation of a Passive Film on an Iron-Chromium Alloy by AES and XPS, Surf. Interf. Analy., 11, 1988, p. 182-188.

8.MUELLER H.J., LENKE J.W., BAPNA M.S., Surface Analysis of Tarnished Dental Alloys, Scan. Microsc., 2, 1988, p. 777

9.MUELLER H.J., Tarnish and Corrosion of Dental Alloys, in: ASM International Handbook Committee, Metals Handbook, 9th Edn., vol. 13. Corrosion, 1987, p.1336

10. CLASSIFICATION SYSTEM FOR CAST ALLOYS, Council on Dental Materials, Instruments and Equipment, J. Am. Dent. Assoc., 109, 1984, p. 766

11.ALLOYS IN DETAL THERAPY, BGA (German Federal Ministry of Health), August 1, 1993 (English translation)

12.ABERER W., HOLUMB H., STROHAL R., SLAVICEK R., Palladium in Dental Alloys-The Dermatologists' Responsibility to Warn?, Contact Dermatitis, 28, 1993, p. 163

13.WATAHA J.C., HAKS C.T., Biological Effects of Palladium and Risk of Using Palladium in Dental Casting Alloys, J. Oral Rehabil., 23, 1996, p. 309

14.CAI Z., CHU X., BRADWAY S.D., PAPAZOGLU E., BRANTLEY W.A., On the Biocompatibility of High-Palladium Dental Alloys, Cell Mater., 5, 1995, p. 357

15.PFEIFFER P., SCHWICKERATH H., Palladiumionnenabgabe von Palladium-legierungen in Milchsaure-/Kochsalz-losung. Dtsch Zahnarz Z, 49, 1994, p. 616

16.LEIRSKAR J., On the Mechanism of Cytotoxicity of Silver and Cooper Amalgams in a Cell Culture System, Scand. J. Dent. Res., 82, 1974, p.74

17.WATAHA J.C., HAKS C.T., CRAIG, R.G., The in vitro Effect of Metal Cations on Eukaryotic Cell Metabolism, J. Biomed. Mater. Res., 25, 1991, p. 1133

18.WATAHA J.C., NAKAJIMA H., HAKS C.T., OKABE T., Correlation of Cytotoxicity with Elemental Release from Mercury- and Gallium-Based Dental Alloys in Vitro, Dent. Mater, 10, 1994, p. 298

19.BRUGIRARD J., BARGAIN R., DUPUY J.C., MAZILLE H., MONNIER G., Study of the Electrochemical Behavior of Gold Dental Alloys, J. Dent. Res., 52, 1973, p.828

20.SARKAR N.K., FUYS R.A., STANFORD J.W., The Chloride Corrosion Behavior of Silver-Base Casting Alloys, J. Dent. Res., 58, 1979, p. 1572

21.HOLLAND R.I., JORGENSTEN R.B., HERO H., Corrosion and Structure of Low-Gold Dental Alloys, Dent. Mater, 2, 1986, p. 143

22.HOLLAND R.I., Use of Potentiodynamic Polarization Technique for Corrosion Testing of Dental Alloys, Scand. J. Dent. Res., 99, 1991, p. 75

23.VAIDYANATHAN T.K., PRASAD A., In Vitro Corrosion and Tarnish Analysis of the Ag-Pd binary system, J. Dent. Res., 60, 1981, p. 707

24.JOHNSON D.L., RINE V.W., BLEICH L.L., Polarization-Corrosion Behavior of Commercial Gold and Silver-Base Casting Alloy in Fusayama Solution, J. Dent. Res., 62, 1983, p. 1221

25.MAYER J.M., RECLARU L., Electrochemical Determination of the Corrosion Resistance of Noble Casting Alloys, J. Mater. Sci.: Mater. In Med, 6, 1995, p. 534

26.RECLARU L., MAYER J.M., Zonal Coulometric Analyses of the Corrosion Resistance of Dental Alloys, J. Dent., 23, 1995, p. 301-311.

27.AL-HITY R.R., KAPPERT H.F., VIENNOT S., DALARD F., GROSGOGEAT B., Corrosion Resistance Measurements of Dental Alloys; Are They Correlated?, Dent. Mater., 23, 2007, p.679

28.RECLARU L., ZIGENHAGEN R., ESCHLER P.-Y., BLATTER A., LEMAÎTRE J., Comparative corrosion study of "Ni-free" austenitic stainless steels in view of medical applications, Acta Biomaterialia, 2 ,2006, p.433

29.CORSO P.P. JR., GERMAN R.M., SIMMONS H.D. JR., Corrosion Evaluation of Gold-Based Dental Alloys, J. Dent. Res., 64, 1985, p. 854

30.MERRIT K., BROWN S.A., Hypersensitivity to Metallic Biomaterials, in: D.F. Williams, Editor. Systemic Aspects of Biocompatibility, vol. 2, Boca Raton, FL: CRC Press, 1981, p. 33

31.WAGNER C.W., TRAUD W., Uber die Deutung von Korrosionsvorgangen durch uberlagerung von elektrochemischen Teilvorgtingen und uber die Potentialbildung an Misch- elektroden, Z. Electrochem., 44, 1938, p. 391

32.HISATSUNE K., BABA K., HASAKA M., MORIMURA T., TANAKA Y., UDOH K., YASUDA K., Phase Transformation in a Dental Pd-Cu-Ga Alloy, Journal of Alloys and Compounds, 230,1995, p. 94

33.HULTQUIST G., HERO H., Surface Ennoblement by Dissolution of Cu, Ag and Zn From Single Phase Gold Alloys, Corr. Sci., 24,1984, p.789

34.NIEMI L., MINNI E., IVASKA A., An Electrochemical and Multispectroscopic Study of Corrosion of Ag-Pd-Cu-Au Alloys, J. Dent. Res., 65, 1985, p. 888

35.BERZINS D.W., KAWASHIMA I., GRAVES R., SARKAR N.K., Electrochemical Characteristics of High-Pd Alloys in Relation to Pd-Allergy, Dent. Mater., 16, 2000, p. 266

36.SARKAR N.K., BERZINS D.W., PRASAD A., Dealloying and Electroformation in high-Pd dental alloys, Dent. Mater, 16, 2000, p. 374

37.DE MELE M.F.L., SALVAREZZA R.C., MOLL VASQUEZ V.D., VIDELA H.A., ARVIA A.J., Kinetics and Mechanism of Silver Chloride Electroformation During the Localized Electrodissolution of Silver in Solutions Containing Sodium Chloride, J. Electrochem. Soc., 133, 1986, p. 746

38.SARKAR N.K., GREENER E.H., Electrochemistry of the Saline Corrosion of Conventional Dental Amalgams, J. Oral. Rehab, 2, 1975, p. 49

39.MANSFELD F., J. Electrochem. Soc., 120, 1973, p.515

40.MACDONALD J.R., Impedance Spectroscopy, Emphasizing Solid Materials and Systems, New York, NY: Wiley, 1987, p. 39

41.Martini E.M.A., Muller I.L., Characterization of The Layer Formed on Iron in Borate Solution by Electrochemical Impedance Spectroscopy, Corros. Sci., 42, 2000, p. 443

42.MOFFAT T.P., LATANISION R.M., An Electrochemical and X-Ray Photoelectron Spectroscopy Study of the Passive State of Chromium, J. Electrochem. Soc., 139, 1992, p. 1869

43.HAUPT S., STREHBLOW H.H., Combined Electrochemical and Surface Analytical Investigations of the Formation of Passive Layers, Corros. Sci., 29, 1989, p. 163

44.CASTRO E.B., VILCHE J.R., Investigation of Passive Layer on Iron and Iron-Chromium Alloys by Electrochemical Impedance Spectroscopy, Electrochim. Acta, 38, 1993, p. 1567.

45.ISMAIL K.M., EL-EGAMY S.S., ABDELFATAH M., J. Appl. Electrochem., 31, 2001, p. 663

46.STERN M., GEARY A., Electrochemical polarization I. A theoretical analysis of the shape of polarization curves, J. Electroch. Soc., 104, 1957, p. 56

47.SCULLY J.R., Polarization Resistance Method for Determination of Instantaneous Corrosion Rates, Corrosion, 56, 2000, p.199

Manuscript received: 4.12.2007