ELECTROCHEMICAL STUDIES OF COBALT-CHROMIUM-MOLYBDENUM ALLOYS IN ARTIFICIAL SALIVA

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The electrochemical behaviour and corrosion resistance *in vitro* of two CoCrMo alloys (Vitallium, Vera PDI) has been evaluated in AFNOR artificial saliva, at 25 °C. The evaluation was carried out through the analysis of the open circuit potential variation with time, potentiodynamic polarization curves and electrochemical impedance spectroscopy (EIS) tests. The microstructure and surface condition after corrosion measurements was evaluated by Optical Microscopy. Very low current densities were obtained (order of nA/cm^2) from the polarization curves and EIS, indicating a typical passive behavior for both investigated alloys. The EIS results exhibited near capacitive behavior which is indicative of the formation of a stable film on both CoCrMo alloys in artificial saliva.

INTRODUCTION

Metallic biomaterials, including stainless steels, CoCr-based alloys, titanium and its alloys play an essential role in repair or replacement of the diseased or damaged bone tissue. The metals are more suitable for load-bearing applications compared with ceramics or polymeric materials because they combine high mechanical strength with fracture toughness.[1] The performance of biomaterial in direct contact with living tissue is controlled by biofunctionality and biocompatibility. The biocompatibility of metallic biomaterial is closely related to their corrosion behaviour. 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]

Co-based alloys and titanium and its alloys are among the most common biomaterials used in dentistry, due to biocompatibility problems of the Ni-based alloys.[3] Co-based alloys have been used as a dental material owing to their excellent strength, hardness, toughness and adequate corrosion resistance.[4] These materials are currently used for crowns, bridges casting and denture bases. Chromium and molybdenum are added to Co-based alloys to improve the ability of the alloy to form a protective oxide film on the surface. The difference in corrosion behaviour of metals and alloys is due to the spontaneous formation of a thin, compact layer oxides called the passive layer.[5,6]

Corrosion manifestations on dental alloys might exhibit biological, functional and esthetic effects. The oxidation of CoCr-based alloys may produce soluble Co and Cr species, which can be released to the neighboring tissues. Depending on the nature and concentration of such chemical species, several adverse reactions may take place, including allergic, irritant reactions and local symptoms in gingiva when used as dental implants.[7,8]

Though the allergic properties of the metal ions of CoCr-based alloys should be considered carefully, these alloys still remain very popular for dental use. Knowledge of the corrosion behaviour of CoCr alloys is essential to the understanding of their biocompatibility. The modifications of the biomaterials properties could be determined using rapid electrochemical tests as a qualitative criterion to estimate the corrosion resistance.[9-12]

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The present paper made a comparative study of two CoCrMo dental alloys: Vitallium and Vera PDI, regarding the electrochemical behaviour in acidified artificial saliva.

RESULTS AND DISCUSSION

The microstructure of both CoCrMo alloys after chemical attack (time: 3 minutes, temperature: 25°C) is shown in Fig. 1(A-D). Both surfaces of Vitallium and Vera PDI alloys showed dendrite microstructure, a rippled structure between the matrix and particle phases.
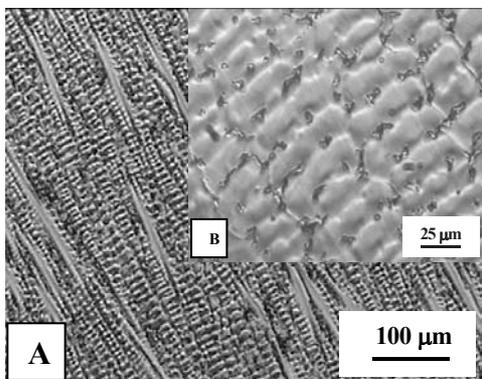
Microstructure characterisation

Fig. 1 – Optical micrographs of the surface of: (A-B) Vitallium alloy used in electrochemical study.
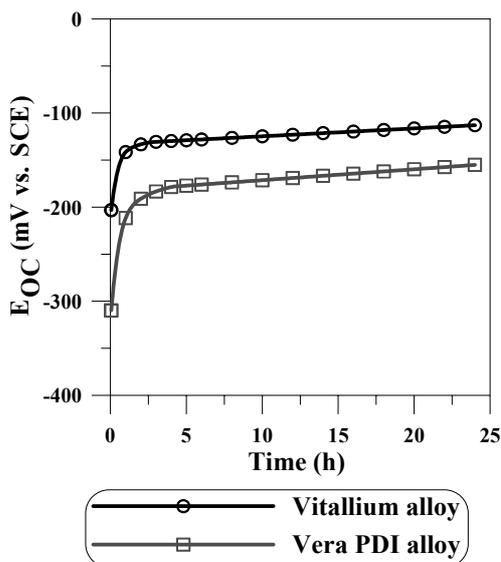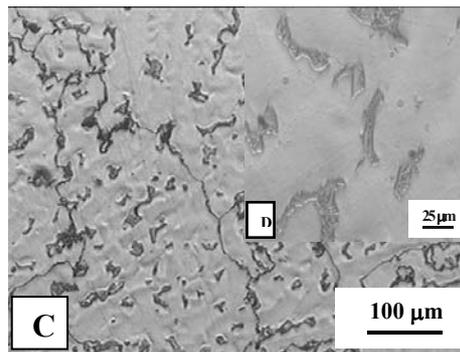

Fig. 1 – Optical micrographs of the surface of: (C-D) Vera PDI alloy used in electrochemical study.

Electrochemical measurements

Electrochemical test methods are sensitive enough to accurately measure the potential and current changes, which occur during the corrosion process.[13] The intra-orally temperature widely fluctuates because of ingestion of hot or cold food and beverage. Furthermore, different areas of oral cavity exhibit different temperature. Nevertheless, it can be reasonably approximated in experimental settings between 35°C and 37°C if we consider the environmental temperature 25°C.[14]

Fig. 2 shows the open circuit potential (E_{OC}) vs. time behaviour of Vitallium and Vera PDI alloys in artificial saliva. These results are based on the CoCrMo samples studied after 24 hours of immersion in artificial saliva.

Fig. 2 – Variation of open circuit potential (E_{OC}) with time for both CoCrMo alloys in artificial saliva.
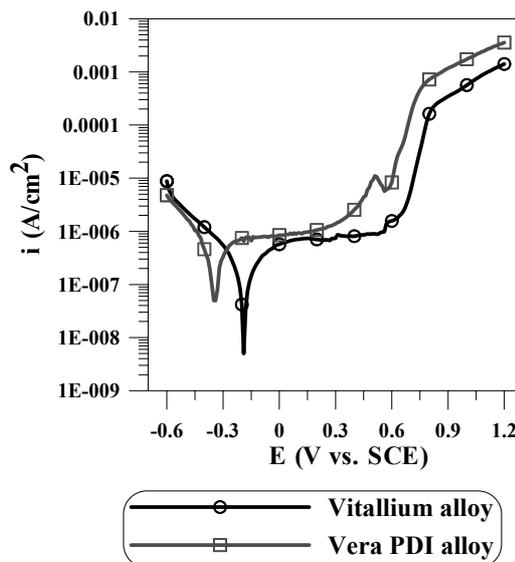

Fig. 3 – Potentiodynamic polarisation curves of CoCrMo alloy tested after 24 hours maintained in artificial saliva, on semi-logarithmic axes.

From Fig. 2 both samples have a tendency to form a passive film by the shift of open circuit potential (E_{OC}) to more positive (noble) direction with respect to time. After 2 hours of immersion E_{OC} displacement towards positive potentials was noticed in Fig. 2. This increase seems to be related to the thickening of the oxide film improving its corrosion protection ability.

Both specimens: Vitallium and Vera PDI did not exhibit potential drops associated with surface activation during 24 hours exposure in test solution. This kind of behaviour suggests that the air-formed native oxide is thermodynamically resistant at chemical dissolution in artificial saliva

Potentiodynamic polarization

Plots in a semi-logarithmic version between -600 mV and +1200 mV SCE of both CoCrMo alloys after 24 hours in artificial saliva are displayed in Fig. 3. Standard techniques were used to extract zero corrosion potential (ZCP) and corrosion current (i_{corr}) values from the potentiodynamic polarization plots. The average values b_a, b_c, ZCP and i_{corr} from polarization curves determined by the VoltaMaster 4 software are presented in Table 1.

An alloy that prone to passivity will have the value of b_a greater than b_c, while an alloy that corrodes will have b_a less than b_c.[15] The high value

of b_a in comparison with the values of b_c for both alloys indicates an anodic control in the corrosion process. The control implies the existence of a passive layer on the material's surface. The two Tafel slopes intercept at the point of the coordinates (ZCP, i_{corr}). In both cases the values determined for the ZCP, are smaller than those corresponding to E_{OC} (Fig. 2). The variation is probably due to depassivation phenomena on the surface during cathodic scanning. The corrosion currents for both CoCrMo alloys were of the same order of magnitude (nA/cm^2).

Both CoCrMo alloys translated directly into a stable passive behaviour from the "Tafel region" without exhibiting a traditional active-passive transition.

Fig. 4 shows in linear representation the part of the polarisation curve for both CoCrMo alloys after 24 hours in artificial saliva, in the scale of anodic currents comprising between 0 and 500 $\mu A/cm^2$. This help to visualise the breakdown potential E_{bd}, another electrochemical parameter, which characterises the corrosion behaviour of the alloys. It marks the point beyond which degradation becomes significant. The potential range situated between the ZCP and E_{br} represents the passivity zone in which corrosion is weak or even insignificant. Table 1 presents the values of the breakdown potential.
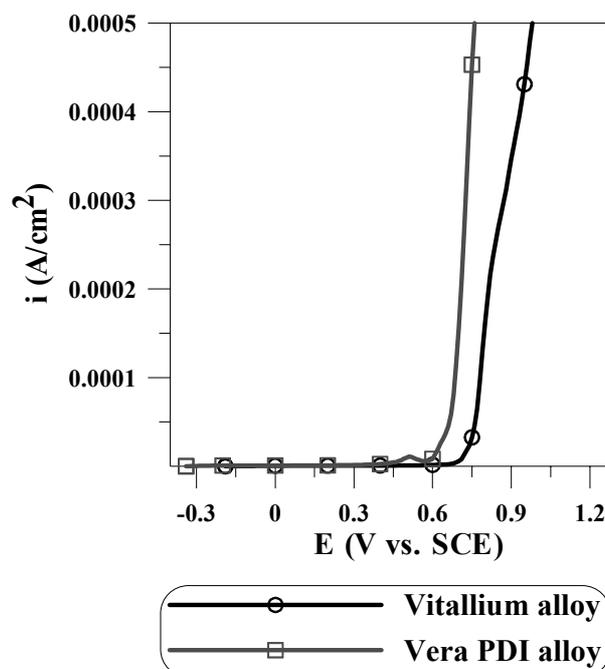

Fig. 4 – Potentiodynamic polarisation curves presented on linear axes in order to reveal the breakdown potential for CoCrMo alloys after 24 hours in artificial saliva.

E_{bd} of Vitallium alloy is around 650 mV. The passive zone is large, around 850 mV (E_{bd} – ZCP), implying the corrosion start from 650 mV. The Vera PDI alloy presents a similar behaviour, with E_{bd} larger, around 570 mV and the passive zone around 900 mV.

In this study, the presence of larger passive range for both CoCrMo alloys was ascribed mainly to a higher amount of Cr-Mo in the chemical composition of specimens.

Passive current density (i_{pass}) was also determined from the potentiodynamic anodic diagram of each specimen in artificial saliva. Passive current densities (i_{pass}) are obtained around the middle of the passive range as listed in Table 1. The passive current densities of both samples investigated were of the same order of magnitude (about 1 $\mu A/cm^2$). 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.

Electrochemical Impedance Spectroscopy

In a complementary study, electrochemical impedance spectroscopy (EIS) was used to investigate the corrosion resistance of CoCrMo alloys.

EIS measurements were performed in aerated artificial saliva at open circuit potential and at +400 mV, because it is known that dental alloys in the oral cavity may be exposed to potentials of up to +400 mV.[16-18]

Impedance spectroscopy results for Vitallium and Vera PDI alloys in artificial saliva at selected potential values are presented as Bode diagrams (Figs. 5 and 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.

Table1

The corrosion parameters of the studied CoCrMo alloys

Alloy	ZCP (mV)	b_a (mV/decade)	b_c (mV/decade)	i_{corr} (nA/cm^2)	i_{pass} ($\mu A/cm^2$)	E_{bd} (mV)
Vitallium	-190	150	115	280	0.8	655
Vera PDI	-340	170	95	360	1.1	575

In this table: ZCP – corrosion potential, b_c and b_a – Tafel slopes, i_{corr} – corrosion current density, E_{bd} – breakdown potential, i_{pass} - passive current density
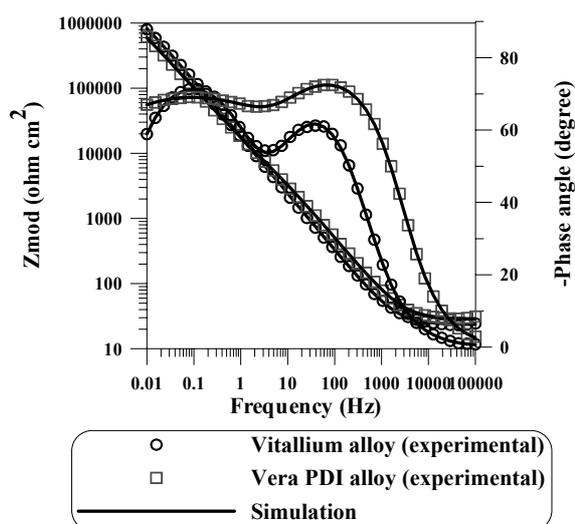

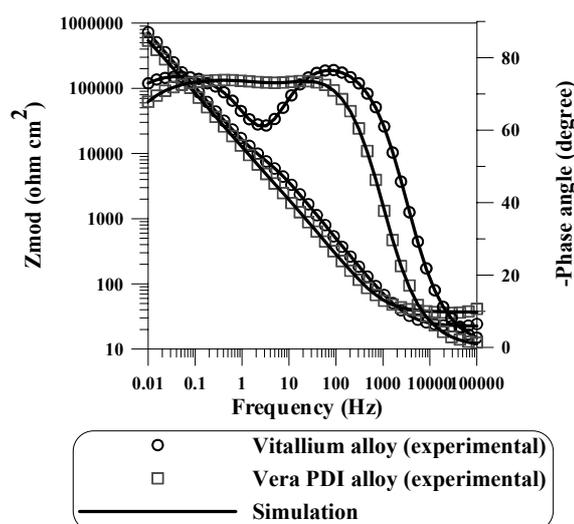Fig. 5 – Impedance spectra of Vitallium and Vera PDI alloys tested at E_{OC} in artificial saliva.

Fig. 6 – Impedance spectra of Vitallium and Vera PDI alloys tested at +400 mV in artificial saliva.

All the spectra show that in a higher frequency region, Log (Zmod) tends to become constant. This is a typical response for the resistive behaviour and corresponds to the solution resistance, R_{sol}. In the medium frequency range, a linear relationship between Log (Zmod) and log frequency is observed for all the samples, but with different slopes (always less than -1) and phase angle maxim (less than $-90°$), indicating that the passive films were not fully capacitive. The phase angle maximum observed for both samples at E_{OC} was found to lie in the range of approximately $-70°$ to $-80°$. High impedance values (order of 10^5 Ω cm^2) were obtained from medium to low frequencies for this samples suggesting, high corrosion resistance in the artificial saliva.

For the interpretation of the electrochemical behaviour of a system from EIS spectra, it is necessary an appropriate physical model of the electrochemical reactions occurred on the electrodes. Because the electrochemical cell presents impedance at a small sinusoidal excitation it can be represented by an equivalent circuit (EC). The 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 are employed; the χ^2 error was suitably low ($\chi^2 < 10^{-4}$), and the error associated with each element was up to 5%.

The EC that satisfied the above criteria and presented in Fig. 7 was used to fit the experimental data. Instead of pure capacitors, constant phase elements (CPE) were introduced in the fitting procedure to obtain good agreement between the simulated and experimental data. The impedance of the CPE is given by:

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

where for n = 1, the Q element reduces to a capacitor with a capacitance C and, for n = 0, to a simple resistor.[19] The n is related to a slope of the Log(Zmod) vs. Log(Frequency) Bode–plots, ω is the angular frequency and j is imaginary number ($j^2 = -1$). The quality of fitting to the EC was judged first by the χ^2 value that was < 5 x 10^{-4}, and second by the error distribution versus frequency comparing experimental with simulated data.

The results of the analysis are shown in Table 2. The EC contain two RQ elements in paralel: $R_{sol}(Q_1(R_1(R_2Q_2)))$. Other combinations of resistance and capacitances were tried, in particular one RQ elements in parallel: $R_{sol}(R_1Q_1)$ or two RQ parallel combinations: $R_{sol}(R_1Q_1)(R_2Q_2)$, to model the corrosion process of samples in artificial saliva, but none of these were found to give a satisfactory fit (values of chi-square (χ^2) test were about 10^{-2}).
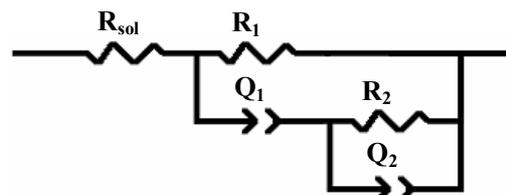

Fig. 7 – Proposed equivalent circuit (EC) for modelling impedance data for both CoCrMo alloys in artificial saliva.

In Figs. 5 and 6, the experimental data are shown as individual points, while the theoretical spectra resulted from the fits with a relevant EC model are shown as lines.

Table 2

Values of fitted parameters of the equivalent circuit as a function of applied potential of CoCrMo alloys in artificial saliva

Alloy	E, mV	R_1, kΩ cm^2	10^6Q_1, S cm^{-2} s^n	n_1	R_2, kΩ cm^2	10^6Q_2, S cm^{-2} s^n	n_2	i_{corr}, nA/cm^2
Vitallium	E_{OC}	8.9	28	0.86	815	13	0.81	340
Vitallium	+400	7.5	22	0.87	710	11	0.83	-
Vera PDI	E_{OC}	6.4	35	0.85	720	15	0.80	370
Vera PDI	+400	5.7	26	0.87	650	12	0.82	-

The physical meaning given to the circuit is the association of the film/electrolyte interface (R_1Q_1) with the passive film itself (R_2Q_2). The time constant at high frequencies is originated from the R_1Q_1 combination while the one at low frequencies initiated from the R_2Q_2 combination. R_1 representing the charge transfer resistance and Q_1 the double layer capacitance are shown by the high value of the n_1 exponent. The double layer capacitances for both samples are typical for the C_{dl} of the passive oxide layers.[20-23] The same value for cell resistance, R_{sol}, equals 35 ± 5 Ω, was observed for all of the specimens indifferent the time of immersion and it wasn't inserted in Table 2.

The overall polarization resistance R_p is represented by the sum of partial resistance ($R_1 + R_2$).[24] R_p allows a quantitative analysis based on the specific magnitudes of the corrosion rate. R_p related to the rate of corrosion reaction(s) and is inversely proportional to the corrosion current; the Stern-Geary equation:[25]

$$i_{corr} = \frac{b_a b_c}{2.3 R_p (b_a + b_c)} = \frac{B}{R_p} \qquad (2)$$

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

$$B = \frac{b_a b_c}{2.3(b_a + b_c)} \qquad (3)$$

The polarisation resistance (R_p) of both alloys are largest, of the same order of magnitude (around 5×10^5 Ω cm^2). For highly corrosion resistance materials the R_p may even reach 10^6 Ω cm^2.[15]

The corrosion currents obtained from the Stern-Geary equation for both CoCrMo alloys maintained for 24 hours in artificial saliva are in agreement with the polarization data.

Similar plots (Fig. 6) obtained for Vitallium and Vera PDI alloys polarized in artificial saliva at 400 mV. The experimental curves were fitted using the EC presented in Fig. 7 and in Table 2 are presented the main parameters of the proposed EC.

As the potential increases from E_{OC} to +400 mV the R_p decreases slowly. But, the R_p, of both samples, in artificial saliva was large at +400 mV (order of 5×10^5 Ω cm^2) as seen in Table 2. This indicates that the samples are still highly resistant to corrosion even at large overpotentials.

Optical microscopy of polarized surfaces

Fig. 8(A-D) shows the surface micrographs of alloys after the polarization measurements from -600 mV to +1200 mV. The analysis of Fig. 8(A-D) indicates the appearance of a generalized corrosion process at the surface of both alloys, the localized corrosion being unremarked. However, the surfaces of both alloys are completely heterogeneous.

Fig. 9 (A-B) shows typical optical images of the resulting surface oxide films after anodic polarization at +400 mV, 30 minutes after the overpotential has been applied, in artificial saliva for Vitallium and Vera PDI alloys. A homogeneous oxide layer is developed at the surface of the both alloys sample. No pitting or cracks appeared on the alloy surfaces after this anodic polarization test.
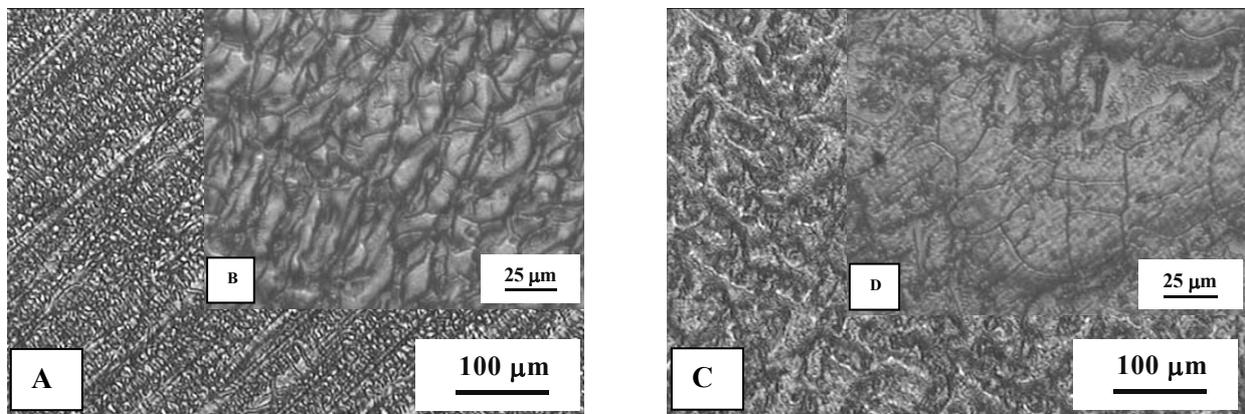

Fig. 8 – Surface attack morphology: (A-B) Vitallium alloy and (C-D) Vera PDI alloy, after potentiodynamic polarization tests from -600 mV to +1200 mV.
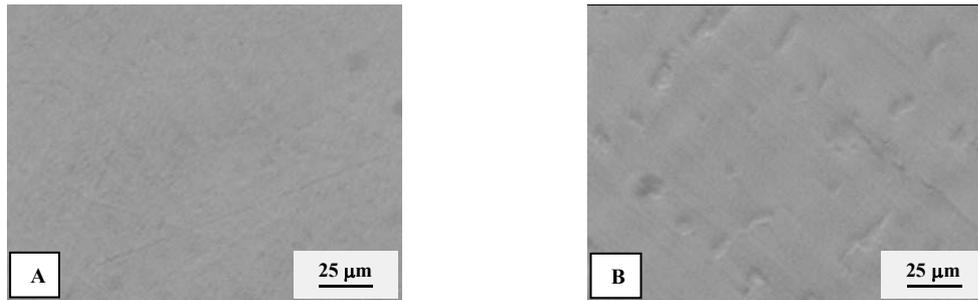
Fig. 9 – Optical observations of: (A) Vitallium alloy and (B) Vera PDI alloy, anodic polarization at +400 mV in artificial saliva, 30 minutes after the overpotential has been applied.

EXPERIMENTAL

Materials

Two CoCrMo alloys used in dental prosthetics construction were investigated, Vitallium and Vera PDI. The nominal chemical compositions of alloys are: 63.8%Co, 28.5%Cr, 6%Mo, 1%Si (Vitallium) and 63.5%Co, 27%Cr, 5.5%Mo, 2%Fe, 1%Ni (Vera PDI).

The tests specimens were in a polytetrafluoroethylene (P.T.F.E.) holder specifically designed to connect to a rotating disc electrode (type EDI 101T; Radiometer Analytical, Villeurbanne, France). Resin was used to ensure a tight seal between the alloy specimen and the P.T.F.E. holder to avoid crevice corrosion. Prior to corrosion tests and surface examination, the electrodes were wet-ground with 400, 600, 1000, 1500 and 2000 grit metallographic abrasive papers, final polishing was done with 1 μm 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.

Microstructure characterisation

For structural analysis the samples were prepared by polishing using emery paper up to 2000 grit and final mirror polishing with 1 μm alumina suspension, which was succeeded by appropiate etching. In this case, the chemical attack was realized with a (10 mL HNO_3 + 20 mL HCl + 30 mL glycerol) solution.[26] The treated surfaces were examined by optical microscopy, with an OLIMPUS PME 3- ADL apparatus.

Test electrochemical media

The Carter-Brugirard AFNOR/NF (French Association of Normalization) artificial aerated saliva used as corrosion medium was prepared immediately before being used and consisted of: 0.7 g NaCl; 1.2 g KCl; 0.26 g $Na_2HPO_4H_2O$; 1.5 $NaHCO_3$; 0.33 g KSCN; 1.35 g NH_2CONH_2 and distilled water up to 1000 mL. The pH of such solution is about 8. Because the short-term pH variances include the intake of acidic beverages (pH 2-3) and secretion of gastric acid (pH 1), we added lactic acid to the AFNOR artificial saliva to decrease the pH to 3.1 in order to accentuate corrosion.

Electrochemical measurements

The electrochemical measurements were made with a potentiostatic assembly of three electrodes: a working electrode (rotating electrode), a platinum counter-electrode and a reference electrode of saturated calomel (SCE). All potentials referred to in this article are with respect to SCE. Given that diffusion phenomena play a very major role with regard to the changes which are produced at the metal/solution interface and consequently on the state and composition of the layers of the metal surfaces, readings were taken in a laminar system (criterion Re < 2300) with a rotational velocity at 500 rpm in order to control the mass transfer phenomena. The measurement system was managed by a VoltaLab 40 potentiostat controlled by a personal computer with dedicate software (VoltaMaster 4).

For both specimens, 24 hours open circuit potential, E_{OC}, measurement was performed initially followed by the linear potentiodynamic polarization measurement. These tests were conducted by stepping the potential using a scanning rate of 0.5 mV/s from -600 mV (SCE) to +1200 mV (SCE). Using an automatic data acquisition system, the potentiodynamic polarization curves were plotted and both corrosion current density (i_{corr}) and zero current potential (ZCP) were estimated by Tafel plots by using both anodic and cathodic branches. In addition, for evaluate the stability of passivation, passivation current density (i_{pass}) and breakdown potential (E_{bd}) were obtained from the potentiodynamic polarization curves.

Electrochemical impedance spectroscopy (EIS) was also used to evaluate the samples. The alternating current (AC) impedance spectra for CoCrMo alloys were obtained, with a scan frequency range of 100 kHz to 10 mHz with amplitude of 10 mV. EIS measurements were performed in aerated artificial saliva at different potentials. The measurement at the open circuit potential was performed after 24 hours immersion in the solution at 25°C. EIS results at +400 mV were obtained in 30 minutes after the overall potential has been applied. In order to supply quantitative support for discussions of these experimental EIS results, an appropriate model (Convertor-Radiometer, France and ZSimpWin-PAR, USA) for equivalent circuit (EC) quantification has also been used.

CONCLUSIONS

In the present study, the electrochemical behaviour of two CoCrMo alloys was evaluated using electrochemical techniques.

The good corrosion resistance of the CoCrMo alloys in artificial saliva is due to the highly protective passive film that is the key factor for its

biocompatibility. Both the alloys translated directly into a stable passive region, without exhibiting the traditional active-passive transition. Very low corrosion current densities, typical of passive materials, were obtained for both samples tested in artificial saliva. Over the surface of both alloys a generalized corrosion appears.

The EIS results show that CoCrMo alloys exhibit passivity at open circuit potential. For both alloys the EIS measurements at +400 mV in artificial saliva indicate that the protectiveness of passive film is present.

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