A COMPARATIVE STUDY ON THE CORROSION BEHAVIOUR OF CoCr AND NiCr DENTAL ALLOYS IN SALINE MEDIUM

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Two non-precious CoCr and NiCr based dental alloys were analyzed with respect to their corrosion behaviour. Electrochemical impedance spectroscopy (EIS) measurements were used to characterize the electrochemical corrosion behaviour of the CoCr and NiCr based dental alloys during aging in 3 wt.% NaCl solution. The EIS results exhibited large impedance values (order 10^5 Ω cm^2) obtained from medium to low frequency which is indicative of the formation of a stable passive film on both CoCr and NiCr based dental alloys. Equivalent circuit (EC) was used to model the EIS data in order to characterize samples' surface. Polarization resistance values, obtained from EIS spectra, increase with the maintenance time due to their passivation in solution. The surface morphology of both CoCr and NiCr based dental alloys after 10 hours immersion time in 3 wt.% NaCl solution was studied using scanning electron microscopy (SEM) technique. The microscopic analysis of both alloys surfaces shows that passivation in 3 wt.% NaCl solution.
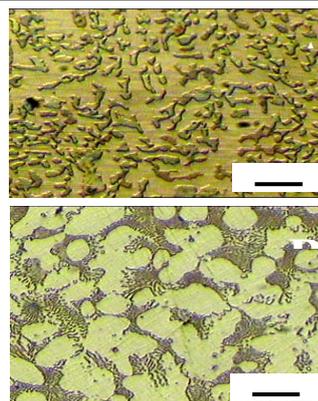
INTRODUCTION

Metallic materials have many uses in dentistry. The wide variety of dental alloy products found on the market varied in both their composition and their applications or performance.[1-6]

Non precious cobalt-chromium (CoCr) and nickel-chromium (NiCr) alloys are commonly used for crow, bridge and denture bases, used substitutes for much expensive precious metallic materials (Au, Pt, and Pd).[6]

In addition to their lower price the advantages of these alloys possess machining thermal expansion coefficient with ceramics of metal-ceramic restoration, and acceptable mechanical and tribological properties in vivo.[7]

The most important factors that affect the choice of dental metallic materials are the mouth/intra-orally cavity acceptability for metallic materials.[1-3] The CoCr and NiCr commercial dental materials react easy with the complex medium from intra-orally cavity due to their complex composition, being especially degraded by electrochemical corrosion.[8, 9] Cr is added to Co-based and Ni-based alloy to form a protective oxide layer on the surface.[2, 10]

Corrosion of dental alloys in intra-orally cavity not only results in the deterioration of restoration, but also involves a release of ions that is related directly to their biocompatibility.[11]

Knowledge of the corrosion behaviour of dental alloy is essential to the understanding of their

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biocompatibility. The corrosion resistance of metals and alloys is due to the spontaneous formation of a thin compact layer of oxides named the passive layer. However, degradation occurs on metallic biomaterials surfaces due to the chemical reactions between passive oxide layer and chloride ions present in the environment. The 0.09 wt.% NaCl solution has similar Cl⁻ ion concentration that in human saliva.[12]

However, the dental materials are exposed to aggressive conditions in intra-orally cavity. The intra-oral chemical environment widely fluctuates because of the ingestion of hot or cold food and beverage. Furthermore, different areas of intra-orally cavity are in contact with food and beverage.[13]

Electrochemical impedance spectroscopy (EIS) techniques have been used in a number of studies on the corrosion of dental materials and EIS spectra differ in shape and in the numerical values. However, different electrochemical processes may occur on the dental alloys surfaces function on the nature of the electrolytes, composition and microstructures of dental alloys or immersion time.[14-22]

The aim of this work is to study the corrosion performance of two CoCr and NiCr commercial dental alloys in 3 wt.% NaCl solution by EIS technique.

MATERIALS AND METHODS

Two dental alloys employed in dental prosthetics construction for crowns and bridges were selected for this study. The names and chemical composition of the alloys are shown in Table 1.

The samples were cut to obtain a 0.95 cm² flat surface. Prior to testing, the samples were mechanically abraded using emery paper up to 4000 grit, next polished with 0.3 µm alumina suspension, ultrasonically cleaned in acetone and deionized water, and finally dried in open air.

Surface analysis

Both CoCr and NiCr dental alloys were electrolytic etched in an aqueous solution containing 20% HCl, and application of a constant potential of 2 V for 5 s through a PAR (Model PARSTAT 4000, Princeton Applied Research, NJ, USA) potentiostat.[23]

The microstructure of both CoCr and NiCr dental alloys were examined using a LEICA DMI5000 M metallographic microscope equipped with a dedicated digital camera connected to a personal computer and analyzed with the Leica Application Suite software program.

Electrochemical impedance spectroscopy (EIS) measurements

The tests were conducted into saline solution with 3 wt.% NaCl. The pH of saline solutions was 6.9. Electrochemical measurements were performed at $37 \pm 1\ ^{\circ}C$.

Electrochemical impedance spectroscopy (EIS) measurements were performed using a potentiostat manufactured by PAR (Model PARSTAT 4000, Princeton Applied Research, NJ, USA). The instrument was controlled by a personal computer and specific software (VersaStudio, PAR, USA). The alternating current (AC) impedance spectra for NiCr and CoCr alloys were obtained with a scan frequency ranging from 100 kHz to 10 mHz with an amplitude of 10 mV. The electrochemical impedance spectra were obtained at open circuit potential at different exposure times (1 hour, 4 hours, and 10 hours) after the electrode was immersed in the saline solution. The EIS experimental data were analyzed in terms of equivalent circuit (EC) using ZSimpWin 3.22 software. The program used a variety of electrical circuits to numerically fit the measured impedance data.

Table 1

Chemical composition of the investigated CoCr and NiCr dental alloys

Name of dental alloys	Co	Ni	Cr	Mo	W	Mn	Al	Fe	Si
Heraenium CE	55.2	-	24.1	9.3	15.0	0.8	-	-	1.1
Heraenium NA	-	59.3	24.1	10.1	-	-	2.7	2.1	2.0

According to the data provided by manufacturer: Heraeus Kulzer GmbH, Hanau, Germany

The surface morphology of both CoCr and NiCr samples after 10 hours exposure times in 3 wt.% NaCl solution was assessed using scanning electron microscopy (SEM; Quanta 3D, FEI, Hillsboro, OR, USA).

RESULTS AND DISCUSSION

Microstructure characterization

The microstructure of both CoCr and NiCr dental alloys is shown in Fig. 1. Both surfaces of CoCr and NiCr dental alloys are characterized by a solid phase solution array in dendritic disposition and an interdendritic phase regularly distributed. The dendritic and interdendritic phase appears to have different colours because each phase is at different orientation to observer and therefore reflects light differently.

Electrochemical impedance spectroscopy (EIS)

For a given environment, corrosion depends on the structure and composition of the alloy.[24] The alloys of the present study have different chemical compositions, and the same dendritic structure.

The electrochemical characteristics of the dental alloys were quantified using electrochemical impedance spectroscopy (EIS). The EIS results are presented in the form of Nyquist plots in which the imaginary impedance (Z_{im}) is plotted against the real impedance (Z_{re}). Figure 2(A-D) shows the Nyquist plots obtained for both CoCr and NiCr dental alloys, at open circuit potential, after 1 hour, 4 hours, and 10 hours of immersion in 3 wt.% NaCl. Notice that there is a similar impedance feature for both dental alloys. EIS data for both CoCr and NiCr alloys alloy in the Nyquist format shows the presence of two depressed, pseudo-capacitive semicircles: one at high frequency

values which related the charge transfer process and a second semicircle present at intermediate and lower frequencies witch related the passive oxide layer.

Bode spectra recorded at open circuit potential, with the CoCr and NiCr alloys for a different period of time immersion (1 hour, 4 hours, and 10 hours) in 3 wt.% NaCl solution at 37 ^{o}C, are shown in Fig. 3(A-B). The advantages of this procedure are that the data for all measured frequencies are shown and a wide range of impedance values can be displayed simultaneously. The frequency dependence of the impedance modulus and the phase shift (Φ) indicate whether one or more time constants are present in the system.

In both cases, the Bode-phase plots show two relaxation constants, i.e., two peaks are observed in the Bode-phase plots. They can be satisfactorily fitted with the equivalent circuit shown in Fig. 4. The equivalent circuit consists of the combination of two parallel RQ elements in series with the resistance of the solution (R_{sol}) occurring between the sample and the reference electrode. The physical meaning of the given circuit is the association of the passive layer /electrolyte interface (R_1Q_1) with the passive layer itself (R_2Q_2). Table 2 shows the values of the fitted parameters according to proposed EC.

Constant phase elements (CPE) were used instead of pure capacitances because of the non-ideal capacitive response due to the distributed relaxation feature of the passive oxide layer thermal generated. The impedance representation of CPE is given by:

$$Z_{(CPE)} = \frac{1}{Y_0(j\omega)^n} \tag{1}$$

where ω is the angular frequency and Y_0 is a constant, and the value of the exponent n indicates the deviation from ideal capacitive behaviour (e.g., when n = 1).
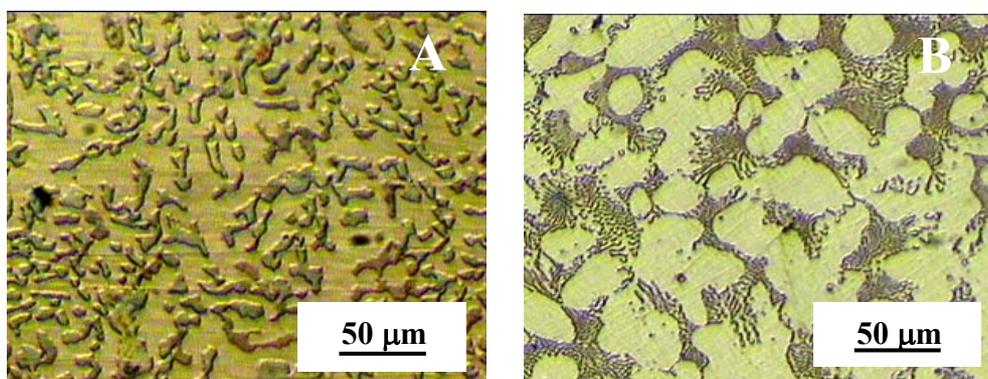

Fig. 1 – Optical micrographs of the surface of: (A) CoCr, and (B) NiCr dental materials.
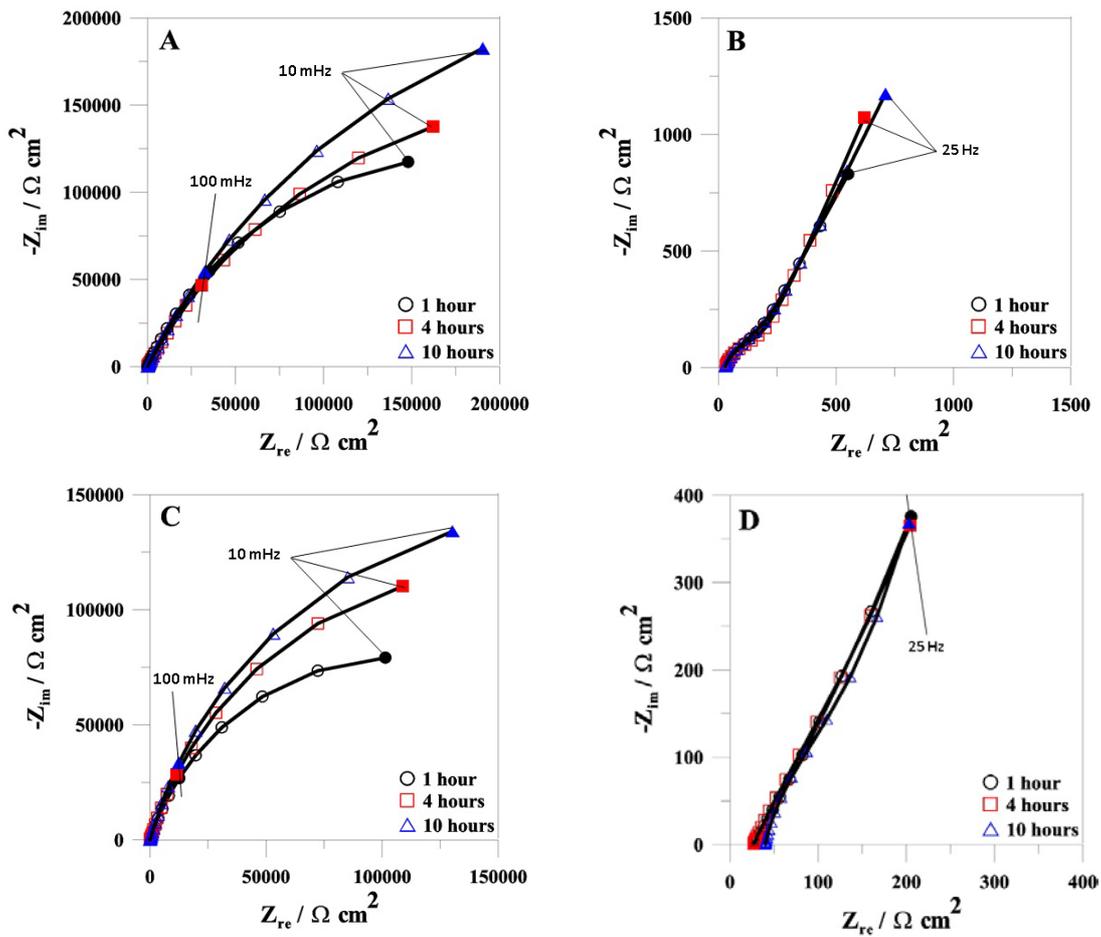
Fig. 2 – Nyquist plots in aerated 3 wt.% NaCl solution, at different immersion exposure times for:
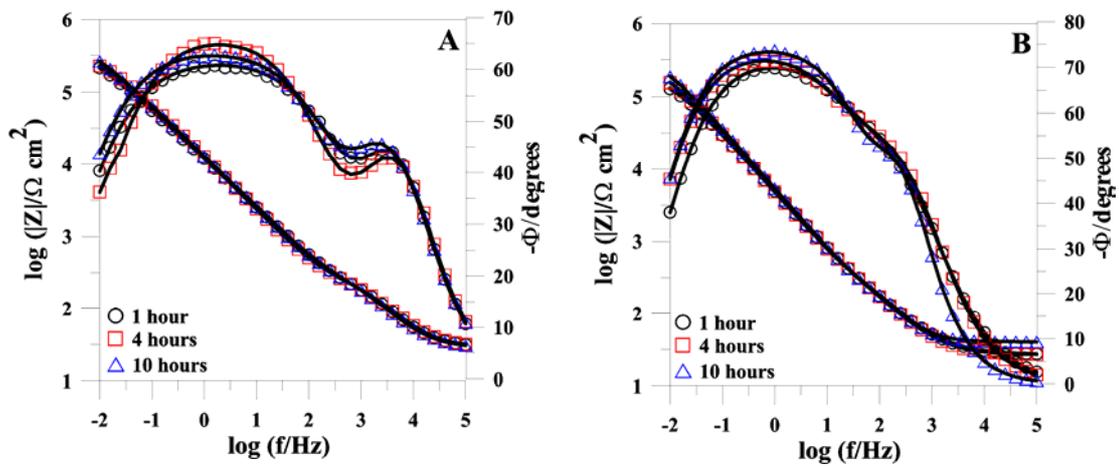(A-B) CoCr dental alloy, and (C-D) NiCr dental alloy.

Fig. 3 – Measured (discrete points) and fitted (solid lines) Bode impedance spectra for:
(A) CoCr and, (B) NiCr dental alloys maintained different immersion times in aerated 3 wt.% NaCl solution
at open circuit potential at 37 °C.

Table 2

Values of fitted parameters of the EC as function of immersion time for CoCr and NiCr dental alloys in 3 wt.% NaCl solution

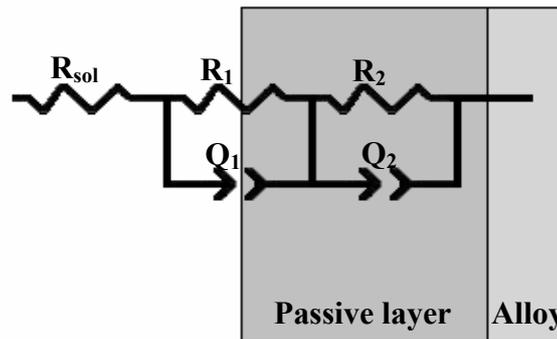| Dental alloys	Immersion time	$10^4 Q_1$ (S cm^{-2} s^n)	n_1	$10^{-3} R_1$ (Ω cm^2)	$10^5 Q_2$ (S cm^{-2} s^n)	n_2	$10^{-5} R_2$ (Ω cm^2)
Heraenium CE (CoCr alloy)	1 hour	3.4	0.81	1.1	2.9	0.80	1.7
	4 hours	3.4	0.81	1.2	2.6	0.81	2.4
	10 hours	3.3	0.82	1.4	2.2	0.81	3.7
Heraenium NA (NiCr alloy)	1 hour	3.5	0.79	0.9	2.9	0.80	1.6
	4 hours	3.4	0.80	1.1	2.9	0.80	1.7
	10 hours	3.3	0.81	1.4	2.7	0.81	2.0

Fig. 4 – Equivalent circuit (EC) used for the interpretation of the measured impedance spectra.

The high frequency R_1 and Q_1, parameters describe charge transfer resistance and double layer constant phase element (n_1 = 0.79-0.82) and R_2 and Q_2 parameters describe the resistance and the constant phase elements of the passive oxide layers (n_2 = 0.80-0.81).

For both dental alloys, the impedance modulus was observed to increase during the exposure of the samples to saline solutions. Large values of R_2 (order of 10^5 Ω cm^2) are observed for both CoCr and NiCr dental materials, confirming good corrosion protection ability in 3 wt.% NaCl solution of passive oxide layer. Charge transfer resistance values, R_1, in the range of 10^3 Ω cm^2 were determined for both samples, and are significantly smaller than R_2. The resistance, R_2, of the passive oxide layer increases with the immersion time. These results seem to correspond to a thickening of both CoCr and NiCr dental samples passive oxide layer.

Passive oxide layer can block the access of electrochemically active species to the electrode surface, restricting ion diffusion to the surface, and thus reducing the overall corrosion rate[25] which can explain the increase in R_2 with increasing immersion time. The passive oxide layer offered approximately the same protection for both dental samples at the short-term immersion (1 hour) in 3 wt.% NaCl solution. The R_2 value observed for CoCr dental alloy after 10 hours immersion time in 3 wt.% NaCl solution is higher than R_2 value for NiCr dental alloy in the same electrolyte.

In the present studies the value of R_2 is much larger than R_1; the values R_2 can be considered corresponding to polarization resistance (R_p). R_p allow a quantitative analysis based on the specific magnitudes of the corrosion rate. The R_p is inversely proportional to the current corrosion (i_{corr}) from Stern-Geary equation:[26]

$$i_{corr} = \frac{B}{R_p} \qquad (2)$$

with B constant determined by Tafel slope tests.

The surface topography of CoCr and NiCr dental alloys samples after 10 hours immersion times 3 wt.% NaCl solution were examined by scanning electron microscopy (SEM) and are displayed in Fig. 5(A-B). They revealed that uniform oxidation occurred on both dental alloys during the corrosion test in the chloride-containing solution, and did not show visible signs of deterioration. No pitting appeared on the both dental alloys surfaces except the presence of polishing scratches.
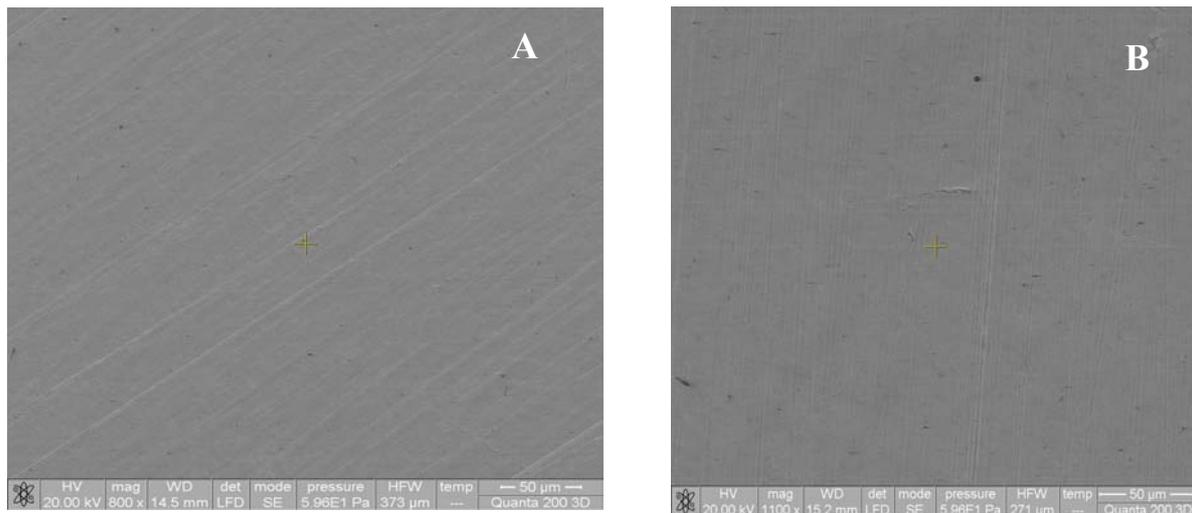
Fig. 5 – SEM micrographs for: (A) CoCr, and (B) NiCr dental alloys after 10 hours exposure times in 3 wt.% NaCl solution at 37 ^{o}C.

CONCLUSIONS

Two NiCr and CoCr alloys used in dental prosthetics construction for crowns and bridge were evaluated for in vitro corrosion resistance in aerated 3 wt.% NaCl solution.

The EIS results show that both dental alloys exhibit passivity at open circuit potential. The EIS Bode phase spectra plots show two relaxation constants. Equivalent circuit (EC) was proposed for the electrochemical behaviour of NiCr and CoCr alloys in 3 wt.% NaCl solution. The EC consists of the combination of two parallel RQ elements in series with the resistance of the solution (R_{sol}) occurring between the sample and the reference electrode. The polarization resistances obtained from EIS spectra increases with immersion time for both alloys and are large (10^5 Ω cm^2). These results seem to correspond to a thickening of both CoCr and NiCr dental samples passive oxide layer. The values of polarization resistance indicates that both dental samples at the short-term exposure (1 hour) in 3 wt.% NaCl solution have the same corrosion resistance. After 10 hours immersion times in 3 wt.% NaCl solution the polarization resistance of the CoCr dental alloy sample was about 2 times higher compared to the NiCr dental alloy samples.

Both CoCr and NiCr dental alloys are pitting corrosion resistant.

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