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ELECTROCHEMICAL BEHAVIOR OF NiCr BASED ALLOYS IN HUMAN AND ARTIFICIAL SALIVA

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Electrochemical Impedance Spectroscopy and potentiodynamic polarization techniques have been used to characterize the behavior of some NiCr alloys in artificial and natural saliva. Experimental data revealed that, the corrosion rate in natural human saliva is higher than in Ericsson artificial saliva. The kinetic parameters have been calculated using two methods: Tafel slope extrapolation and polarization resistance. The determinations of corrosion rate at several temperatures allow activation energy evaluation using Arrhenius law and leads to conclusion about a reduced influence of temperature on corrosion process of alloy.

Keywords: NiCr alloy, human saliva, Ericsson artificial saliva, EIS

1. Introduction

Lately, nickel based alloys have become a widely used substitute for the much more expensive precious metal alloys and their use is on an increasing trend [1-4]. In order to increase the performance of non-noble alloys, chromium is used as the main alloying element in Ni-based alloys. This can provide the formation of a stable passive oxide layer giving it highly resistance to corrosion [5-7]. A direct correlation between the bulk alloy structures and polarization resistance behavior has been established [8]. In recent years, many other metallic substrates with different surface modification are tested for biomaterials application [9-10].

The use of NiCr based alloys in dental practice is increasing, especially in the manufacturing of fixed dental prosthesis [11-13]. Because Ni-Cr alloys can corrode in saliva, they have been investigated in order to establish their safety. A wide variety of studies have tried to investigate the corrosion of Ni-Cr based alloys in the oral cavity. In order to mimic the natural microenvironment, many authors have tested Ni-Cr in artificial saliva [14-16].

The main objective of this work was to study the electrochemical behavior of two NiCr commercial alloys in artificial saliva (Ericsson type) as well as in natural saliva. It is a novelty of this paper such a comparison due to the difficulty in collection and preservation of natural saliva.

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2. Experimental

For this study two types of NiCr alloys were used: Niadur (ND) marketed by the DFS Company from Germany and I Bond (IB) marketed by the „Interdent" company from Slovenia. Both alloys are commercial alloys used in dental medicine with a composition presented in Table 1.

Table 1

Chemical composition of the NiCr alloys

Composition (% atomic)	Ni	Cr	Mo	Si	Fe	Co	Ce	Nb
Niadur (ND)	62	24,5	10,3	1,7	1,5	-	-	-
I-Bond (IB)	64,3	24,2	10	1	< 1	< 1	< 1	< 1

The electrochemical measurements were made using a conventional electrochemical cell composed of three electrodes: one of NiCr alloys as working electrode, a platinum electrode with a large area as counter-electrode and Ag/AgCl, KCl as reference electrode.

First of all, the metallic samples have been reprocessed in wax disc forms being cast using a Castomat equipment at 1350^{0}C, then the alloys have been subsequently ground with abrasive papers until a bright, clear surface was achieved. After that, all substrates were washed with water and ultrasonicated for 10 min in acetone in order to remove grease and impurities present on surface after polishing and drying.

The used electrolytes were artificial (Ericsson type artificial saliva having the composition: 0.584 g L^{-1} NaCl, 0.34 g L^{-1} Na_2HPO_4, 1.5 g L^{-1} $KHCO_3$, 0.34 g L^{-1} KH_2PO_4, 0.014 g L^{-1} $MgCl_2$, 0.166 g L^{-1} $CaCl_2$ and 0.029 g L^{-1} citric acid) and human saliva.

Natural human saliva was collected from six male (SM) and six female (SF) volunteers (approx. 40-45 years old) clinically healthy, all nonsmokers, early in the morning. Biological sampling of saliva was obtained from informed patients. The collection of unstimulated saliva was made continuously in a disposable centrifuge tube for 15 min according to other studies [17].

All electrochemical measurements were performed on AutoLab PGSTAT 12 EcoChemie potentiostat/galvanostat, at different temperatures. Potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) were used as electrochemical methods. In order to allow the corrosion process potentiodynamic polarization tests have been performed starting from cathodic region with very low scan rate of 2 mV / s [18]. EIS characterization was carried out within 10^5 Hz and 10^{-1} Hz frequency range, with an *ac* voltage amplitude of 10 mV at open circuit potential. The impedances were represented as Nyquist and Bode spectra.

3. Results and Discussion

3.1. Potentiodynamic test

First, the NiCr alloys behavior in natural saliva using the potentiodynamic polarization method was studied. The results were compared to the results obtained in an Ericsson type artificial saliva. Figure 1 shows the polarization curves obtained for one of the studied NiCr alloys, Niadur.

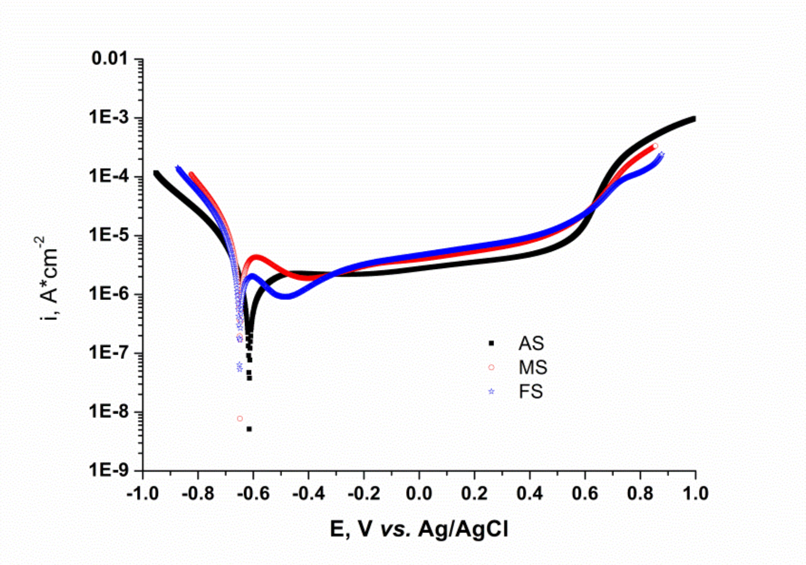

Fig. 1. Polarization curves for ND in natural saliva (MS, FS) and artificial saliva (AS)

From Fig. 1, we can see that Niadur alloy has an active-passive behavior in both natural and artificial saliva. For easier interpretation, the curves can be divided into 3 major domains: potential range between -1000 mV and -400 mV characterized by the transition from cathodic to anodic current; passive domain (-400 mV to 400 mV) and transpassive area (potential higher than 400 mV), characterized by rapid increase of the current due to the dissolution of chromium or nickel oxides and water oxidation. Analyzing Fig. 1, one can say that in natural saliva, a slight shift of the corrosion potential toward cathodic (electronegative) values, as well as an increase of the current density compared to artificial saliva, can be observed. This leads to an increase in the corrosion rate of the biomaterial.

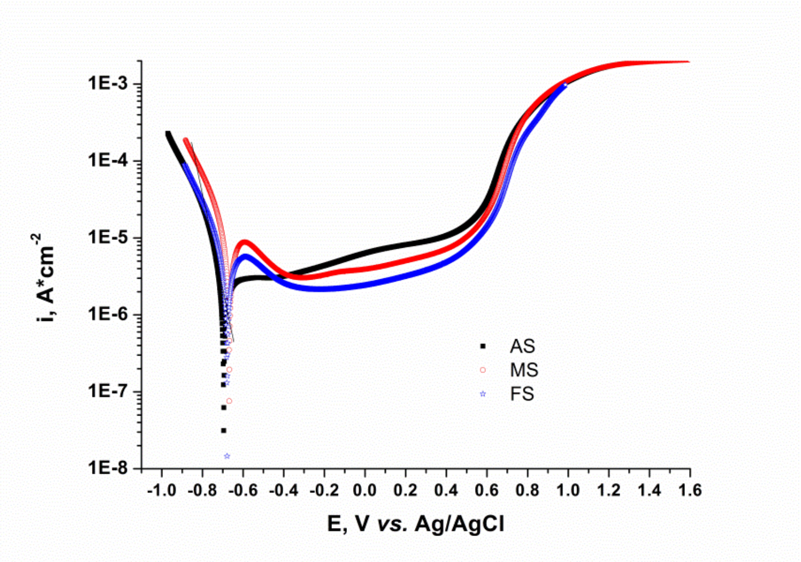

Fig.2. Polarization curves for IB in natural saliva (MS, FS) and artificial saliva (AS)

As in the first studied NiCr alloy, for IB it can be seen an increase of the corrosion current density in the natural compared to artificial saliva. It can also be seen that the passive field is much wider in the case of natural saliva, and the passivation current has a lower value.

Natural saliva collected from male patients is a more corrosive environment than the other natural saliva. Compared to the artificial one taken as a reference, both male and female natural salivas are more corrosive for the two NiCr alloys.

From polarization curves of the two alloys (Figs. 1 and 2), electrochemical corrosion parameters have been computed using two methods as following: Tafel slope extrapolation and polarization resistance; the corresponding values are listed in table 1.

As can be seen, using the two methods close values for the corrosion current density were obtained. The kinetic parameters calculated using the two methods reconfirm those previously found.

Table 1

Corrosion kinetic parameters for NiCr alloys in natural and artificial saliva

Alloy	Saliva	Tafel slope method					Polarization resistance method	
		E_{corr}, mV	i_{corr}, μA/cm^2	R_{mpy}	$K_{g,}$ g/m^{2}h	P, mm/year	R_P, Ω	i_{corr}, μA/cm^2
ND	AS	-612	0.636	0.3046	0.0072	0.0077	33973	0.625

	MS	-637	2.512	1.2023	0.0286	0.0305	9880	2.357
	FS	-632	1.325	0.6347	0.0151	0.0161	17340	1.249
IB	AS	-678	1.322	0.6315	0.0141	0.0160	18320	0.947
	MS	-665	3.718	1.7761	0.0396	0.0451	6450	3.301
	FS	-672	2.013	0.9616	0.0215	0.0244	10520	2.031

Electrochemical behavior of two NiCr alloy in Ericsson artificial saliva at different temperatures, was the next step of our study. In Figure 3, the polarization curves for Niadur (Fig. 3a) and I Bond (3b) in artificial saliva at different temperatures are presented.

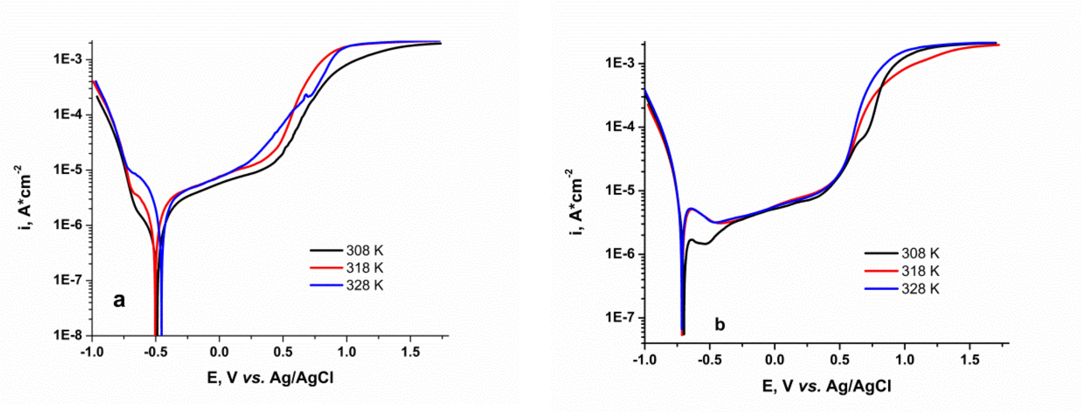

Fig. 3. Polarization curves for NB (a) and IB (b) in artificial saliva (AS) at different temperatures

Kinetic parameters calculated from the polarisation curves presented in Figure 3 are shown in Table 2. It can be noted that the polarization resistance decreases for both alloys with the increase of temperature of artificial saliva, indicating an increase of corrosion rate. The two methods used for corrosion parameters calculation lead to similar values for corrosion current density.

Calculation of kinetic parameters from activation energies was the next step. For electrochemical reactions, the increase of temperature favors the kinetics of the corrosion reactions, more precisely the rate of the anodic dissolution reaction of the metal increase. The value of activation energy for the corrosion processes can be obtained from the Arrhenius graphs, which follow the following equation:

$$i_{corr} = Ae^{-E_a/_{RT}} \qquad (1)$$

Ea is the activation energy of the process expressed in J / mol

R is the universal gas constant (8.314 J / (mol K))
T is the temperature in K
A is a constant called preexponential factor.

Table 2

Corrosion kinetic parameters for NiCr alloys in Ericsson type artificial saliva at different temperatures

Alloy	Temp, K	Tafel slope method					Polarization resistance method	
		E_{corr}, mV	i_{corr}, $\mu A/cm^2$	R_{mpy}	K_{g}, g/m^2h	P, mm/year	R_p, Ω	i_{corr}, $\mu A/cm^2$
ND	308	-499	0.642	0.3075	0.0073	0.0078	32417	0.632
	318	-505	0.686	0.3285	0.0078	0.0083	31923	0.705
	328	-444	0.824	0.3947	0.0093	0.0100	27216	0.801
I-B	308	-676	1.455	0.6950	0.0155	0.0176	16788	1.128
	318	-700	2.256	1.0776	0.0241	0.0273	12756	1.617
	328	-705	2.275	1.0867	0.0242	0.0276	9887	1.737

The activation energy of an electrochemical process refers to the energy level that an electron has to reach to pass through the electrode / electrolyte interface. Thus, a low amount of activation energy indicates a high corrosion rate. Arrhenius equation shows that the higher the activation energy value, the higher is the temperature dependence of the corrosion rate.

In Figure 4, the two Arrhenius plots for NiCr alloys in artificial saliva are presented. The parameters presented in Table 3 were obtained from the equation (1).

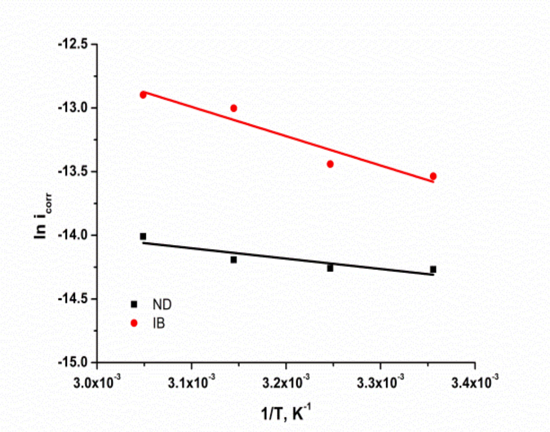

Fig. 4. Arrhenius plot for the two NiCr alloys in artificial saliva Ericsson

Table 3

The kinetic parameters obtained from the Arrhenius equation and the transition state equation for NiCr in artificial saliva

Alloy	Ea, J mol^{-1}	A
Niadur	6760	9.331×10^{-6}
I-Bond	19145	0.00287

3.2. Electrochemical impedance spectroscopy studies

In order to have complete information about the behavior of NiCr alloys in natural (male) and (female) saliva, as well as in artificial saliva, EIS measurements at open circuit potential after 30 min of immersion were made.

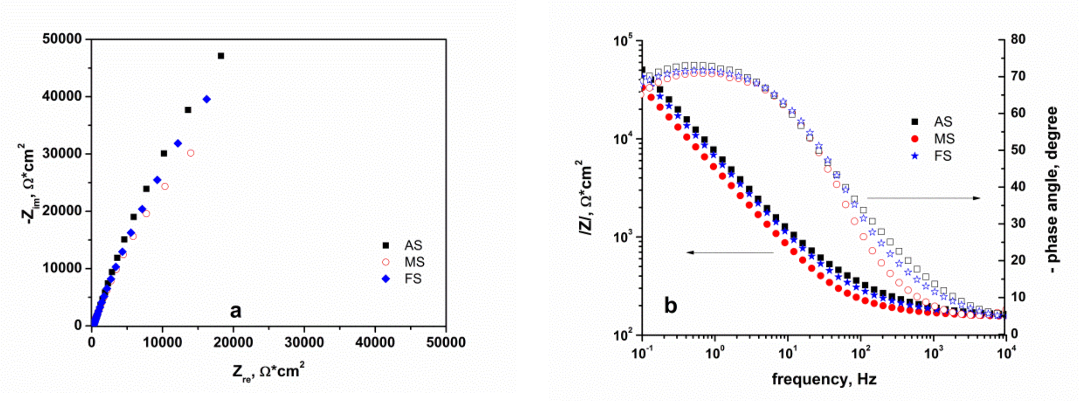

Fig 5. Nyquist (a) and Bode (b) diagrams for Niadur after 30 min of immersion at OCP in natural saliva (MS, FS) and artificial saliva (AS)

From Fig. 5 we can observe the presence of an open capacitive half-circle whose diameter is smaller for male natural saliva than for female or artificial saliva.

This indicates low values of the polarization resistance for Niadur alloy in the natural saliva compared to artificial saliva, which leads to the achievement of high values of corrosion rate. These results confirm the data obtained from the polarization curves. The Bode diagram (Fig. 5b) reveals the presence of a single time constant corresponding to one semicircle from the Nyquist diagram. The maximum phase angle remains at around 70 ° indicating a capacitive behavior of the alloy/electrolyte interface.

The same behavior is also noted for the second studied alloy, I Bond (Fig. 6).

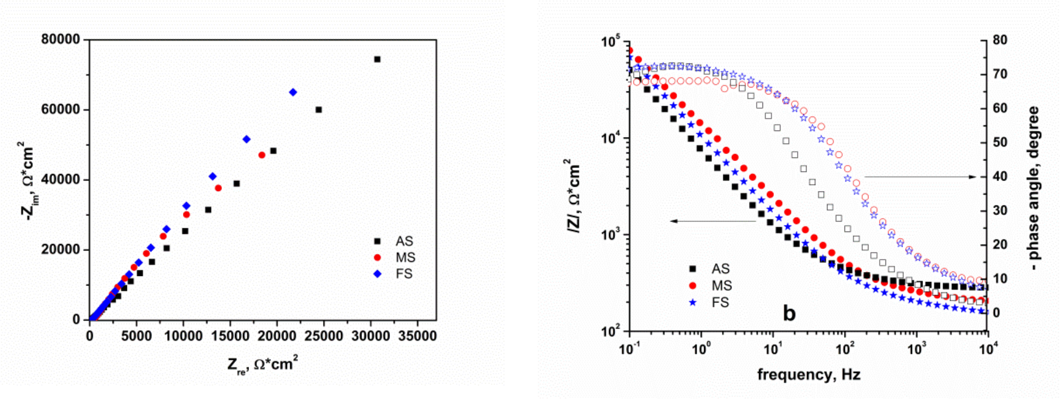

Fig 6. Nyquist (a) and Bode (b) diagrams for IBond after 30 min of immersion at OCP in natural saliva (MS, FS) and artificial saliva (AS)

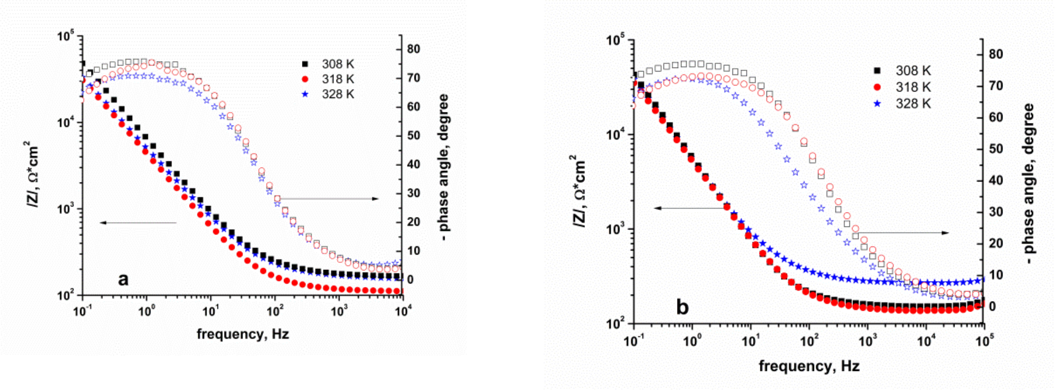

Fig 7. Bode diagrams for Niadur (a) and I Bond (b) after 30 min of immersion at OCP in artificial saliva (AS) at different temperatures

Fig. 7 shows the Bode diagrams recorded for Niadur (a) and I Bond (b) at different temperatures in artificial saliva. It can be seen that an increase of the saliva temperature leads to a decrease of the maximum phase angle value for the two alloys, indicating an increase of the corrosion rate and confirming the data obtained from potentiodynamic polarization tests.

As expected, comparing our data with the data obtained in artificial saliva for Ti and Ti alloys [19], which are in the perfect stable domain, the corrosion rate of NiCr alloy has a lower resistance, but the alloy is placed in very stable class.

4. Conclusions

For the first time the behavior of Niadur and I-Bond, two NiCr commercial dental alloys in natural saliva were investigated by potentiodynamic polarization and electrochemical impedance spectroscopy test.

Based on experimental data it has been established that the corrosion rate in natural human saliva is higher than in Ericsson artificial saliva. The kinetic parameters calculated using two methods: Tafel slope extrapolation and polarization resistance, reconfirm that natural saliva collected from male patients is a more corrosive environment than the other natural saliva.

An increase of artificial saliva temperature leads to a decrease of the polarization resistance for both NiCr alloys, indicating an increase of corrosion rate. EIS test have confirmed the data obtained from potentiodynamic polarization tests.

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