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INFLUENCE OF pH VALUE AND NaF ADDITION ON THE CORROSION BEHAVIOR OF Ni-Cr AND Co-Cr DENTAL ALLOYS

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The Ni-Cr and Co-Cr alloys used in dental practice were evaluated for in vitro corrosion resistance in different environments: artificial saliva and fluoridated artificial saliva with pH = 5.2, acidified artificial saliva and fluoridated acidified artificial saliva with pH = 2.5. The environments were chosen to mimic the oral environment with content and pH variations mainly due to the food intake and hygiene products used. The results showed that NaF additions or decreasing the pH value led to a marked decrease in corrosion resistance of both alloys.

Keywords: dentistry, corrosion, artificial saliva, fluoride, lactic acid

1. Introduction

The study of electrochemical properties of dental alloys is necessary since inappropriate materials may cause hypersensitivity due to metallic ions and corrosion products release. For this reason, the first dental materials used were Au based alloys. Even if these alloys possess high corrosion resistance, the lack of mechanical properties and the high cost determined their replacement in partial, integral metallic and metal-ceramic restorations with nonprecious alloys. Nowadays, about 90% of all partial restorations are made of Co and Ni based alloys [1]. Dental alloys containing Ni, Cr or Co successfully continue to be used in oral repair techniques. Both dental alloys have extensive application in prosthetic dentistry (crowns, fixed bridges, partial mobile dental prostheses, etc.) and are designed to remain in clinical service for many years.

The electrochemical properties of dental alloys are influenced by many factors such as alloy's microstructure, the possibility of formation oxide films at

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the surface, but mostly by the aggressive environment caused by variation in temperature due to the ingested food and fluids. Also, the pH of an electrolyte has a major influence on the material's corrosion behavior, since a low pH value results in dissolution with soluble products, and a neutral value leads to oxides formation [2]. The pH variation can be also due to the food intake or due to hygiene products used, diet or medication administration.

In order to prevent dental plaque formation, a lot of commercially available products, such as toothpastes and mouthwashes, have a NaF content [3], since fluoride protects against tooth decay, tooth sensitivity and enamel erosion [4,5]. A lot of studies were reported regarding Ni-Cr and Co-Cr alloys, with results in formation of a passive film in artificial saliva [6] or NaCl solution with neutral pH [7], but few evidences exist about the electrochemical behavior of these alloys in NaF containing electrolytes.

For this reason, electrochemical tests must be performed since corrosion behavior is the most important criterion in selecting dental alloys and since the content of the oral cavity has a decisive influence on the corrosion resistance of the materials used [8]. Therefore, the present study investigates the corrosion behavior of Ni-Cr and Co-Cr dental alloys in different solutions to investigate the influence of pH value and also the effect of NaF content on the corrosion behavior of dental alloys.

2. Materials and Methods

Ni-Cr and Co-Cr dental alloys existing on the actual market were used for the present experiments. The composition of the studied Ni-Cr and Co-Cr alloys as mentioned by the manufacturer (Argen USA), are presented in Table 1.

Table 1

The elemental compositions of Ni-Cr and Co-Cr alloys

Alloy	Composition (wt.%)									
	Co	Ni	Cr	Mo	Al	Si	Be	Mn	Fe	C
Ni-Cr	-	76	14	6	2	<1	1.8	-	<1	<1
Co-Cr	59.5	-	31.5	5	-	2	-	1	<1	<1

For electrochemical tests the alloy samples were cut into 0.2 mm thick discs (20 mm in diameter) and polished using colloidal silica slurry (0.02 μm).

The corrosion behavior of the alloys was tested in different environments (Table 2), according to ASTM 59-97 (reapproved in 2003) [9]. Fusayama artificial saliva was chosen as the reference electrolyte because it is often mentioned in literature, having a pH of 5.2 and the following chemical composition: KCl (0.4 g/l), NaCl (0.4 g/l), $CaCl_2$, $2H_2O$ (0.906 g/l), NaH_2PO_4, $2H_2O$ (0.690 g/l), Na_2S, $9H_2O$ (0.005 g/l), urea (1 g/l) [10].

Table 2

The environnements for electrochemical tests

Test solution	Concentration of NaF (%)	pH
Artificial saliva	□	5.2
Acidified artificial saliva	□	2.5
Fluoridated artificial saliva	0.1	5.2
Fluoridated acidified artificial saliva	0.1	2.5

The corrosion resistance measurements must be performed in an environment similar to the real one. Therefore, based on the consideration that in the mouth the environment varies from one individual to another and it is influenced by food intake leading to low pH values of saliva, the pH of test solution was decreased by lactic acid addition (supplied by Sigma Aldrich Co) up to a pH=2.5 (the most unfavorable situation was chosen). The lactic acid was added since it is naturally released by bacteria in the oral cavity [11]. Also, saliva solution with 0.1 % NaF addition (supplied by Carl Roth GmbH) was used in order to simulate the effect of hygiene products on corrosion behavior.

The pH values were measured with a pH-meter (Hanna Instruments - HI 254). Potentiodynamic polarization curves were recorded at room temperature (24 ± 1°C) using a VersaSTAT 3 Potentiostat/Galvanostat, equipped with a conventional three electrode cell, with a Pt counter electrode, a saturated calomel (SCE) reference electrode and the sample as working electrode with an exposed area of 1 cm^2.

The samples were immersed in solution at room temperature for 10 min. The open circuit potential (E_{OC}) was monitored for 24 hours. The polarization curves from −1.5 V to +2 V (vs. E_{OC}) with a scanning rate of 0.4 mV/s were plotted. The main corrosion parameters (the corrosion potential (E_{corr}), the corrosion current density (i_{corr}), the polarization resistance (R_p) and the corrosion rate (CR)) were determined from the polarization curves.

3. Results and Discussion

3.1. Open circuit potential, E_{OC}

The evolution of open circuit potential (E_{oc}) vs. time of the Ni-Cr and Co-Cr alloys in four types of environments, after 24 h immersion, are presented in Figs. 1 and 2. According to the scientific literature, the surface with a high value of open circuit potential is indicative of a high corrosion resistance [12].

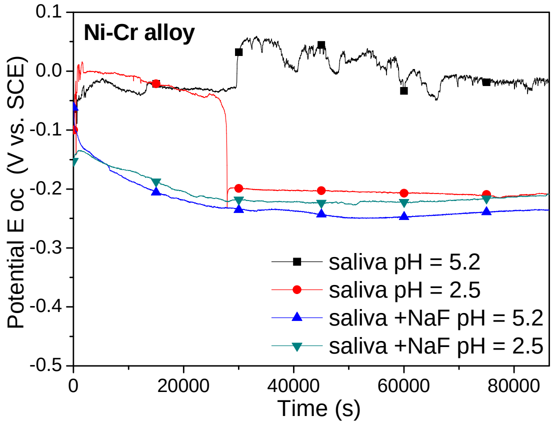

Fig. 1. The evolution of open circuit potential (E_{oc}) for Ni-Cr alloys after 24 h of immersion in different environments

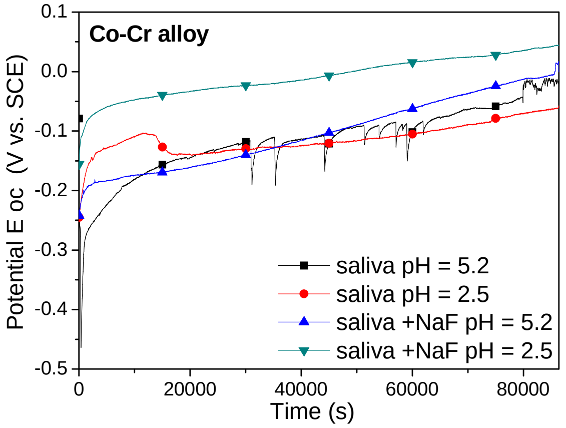

Fig. 2. The evolution of open circuit potential (E_{oc}) for Co-Cr alloys after 24 h of immersion in different environments

The open circuit potential of the Ni-Cr dental alloy (Fig. 1) in all environments reached equilibrium after about 7 h of immersion. The Ni-Cr dental alloy immersed in saliva (pH=5.2) represented an exception, which showed a stable E_{OC} even at the beginning of the test. This finding suggests that the oxide layer formed at the alloy's surface is much stable when immersed in this solution.

Moreover, the shape of the Ni-Cr curve changed very little and the potential was the most electropositive, suggesting that the material retained its protective passive layer [13].

This stability of Ni-Cr alloy showed in artificial saliva with pH=5.2 was greatly reduced at pH 2.5. In this case, the corrosion potential decreased to a value of -209 mV/ SCE, suggesting the complete disappearance of the protective passive layer and a consequent reduction of the material corrosion resistance.

The addition of NaF in the saliva resulted in a large decreased of Eoc and these results confirmed the negative influence of fluoride on the electrochemical behavior of Ni-Cr dental alloys.

In the case of Co-Cr alloy (Fig. 2) the E_{OC} curves in saliva solution were almost the same as those in the saliva with NaF addition. The continuous increase of the open circuit potential in all environments indicated the passivation of the Co-Cr alloy. The fluoridated saliva did not confirm a large decrease as for the Ni-Cr dental alloys. Moreover, after NaF addition into the saliva environment, the E_{OC} potential of Co-Cr alloy increased from -9 mV to 13 mV.

Since the pH of oral environment can be modified due to the food intake [14], the surface of dental restorations may exhibit local acidity or alkalinity. These changes in pH values can generate potential gradients, favoring the occurrence of galvanic corrosion. It was demonstrated that potential gradients with values between 600 mV and 700 mV can initiate and maintain galvanic cells [15].

The E_{OC} values of the studied alloys in different media and the corresponding potential gradients ΔE_{OC} calculated with Eq. (1) [16] are summarized in Table 3.

$$\Delta E_{OC} = E_{OC}^{\,pH=2.5} - E_{OC}^{\,pH=5.2} \tag{1}$$

Table 3

The open circuit potential values (E_{OC}) of the studied alloys in different media and the corresponding potential gradients (ΔE_{OC})

Alloy	Test solution	Time (h)	$E_{OC}^{pH=2.5}$ (mV)	$E_{OC}^{pH=5.2}$ (mV)	ΔE_{oc} (mV)
Ni-Cr	Artificial saliva	1	-201	51	-252
		12	-203	40	-243
		24	-208	-21	-187
	Fluoridated artificial saliva	1	-221	-234	13
		12	-223	-240	17
		24	-209	-235	26
Co-Cr	Artificial saliva	1	-127	-132	5
		12	-121	-109	-12
		24	-60	-16	-44
	Fluoridated artificial saliva	1	-18	-126	108
		12	-9	-107	98
		24	43	16	27

The results regarding the potential gradients showed that for Ni-Cr alloy the highest value was 252 mV in artificial saliva and 26 mV in saliva with NaF addition. In the case of Co-Cr alloy, the potential gradients did not exceed 44 mV in artificial saliva and 108 mV in saliva with NaF addition, respectively. The obtained results demonstrated that Ni-Cr and Co-Cr alloys are not susceptible for initiation of galvanic cells.

3.2. Potentiodynamic polarization curves

The polarization curves of the investigated alloys in all environments are shown in Figs. 3 and 4, and the main corrosion parameters of alloys in corrosive solutions are presented in Table 4. The corrosion behavior was evaluated using the parameters E_{corr}, i_{corr}, R_p and CR.

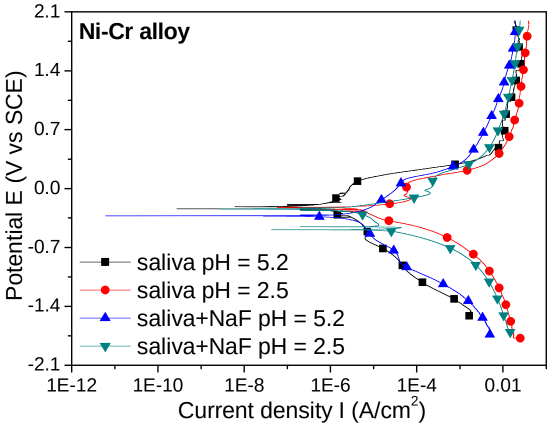

Fig. 3. Potentiodynamic polarization curves for Ni-Cr alloys after 24 h of immersion in different environments

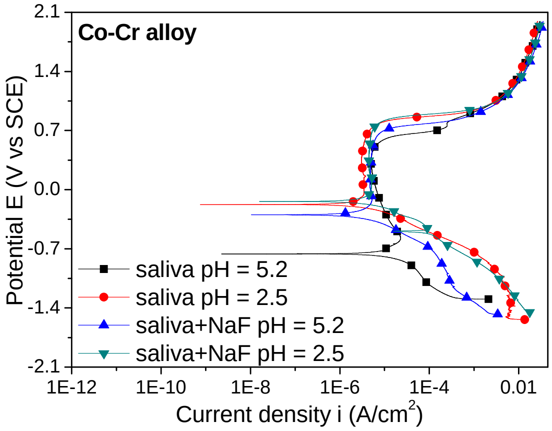

Fig. 4. Potentiodynamic polarization curves for Co-Cr alloys after 24 h of immersion in different environments

As summarized in Table 4, the Ni-Cr alloy presented in artificial saliva the most electropositive E_{corr} value (-212 mV) as compared to the other environments. In fluoridated saliva environment, with a pH value as in saliva environment, corrosion current density (i_{corr}) increased abruptly. This enhanced corrosion process with addition of fluoride and lactic acid was also proved by the decrease of the polarization resistance (R_p) and increased corrosion rate (CR). For Co-Cr alloy, additions of NaF and the decrease of pH value also resulted in higher i_{corr} and lower R_p and CR values, respectively, indicating an accelerated corrosion process.

Table 4

Electrochemical parameters of the samples in different biological environments

Sample	Test solution	pH	E_{corr} (mV)	i_{corr} ($\mu A/cm^2$)	R_p (kΩ)	CR (mm* $year^{-1}$)
Ni-Cr	Artificial saliva	5.2	-212	0.87	84.83	0.012
	Acidified artificial saliva	2.5	-235	1.80	57.645	0.022
	Fluoridated artificial saliva	5.2	-326	10.74	19.439	0.128
	Fluoridated acidified artificial saliva	2.5	-241	57.87	14.184	0.688
Co-Cr	Artificial saliva	5.2	-809	5.94	54.379	0.062
	Acidified artificial saliva	2.5	-175	1.46	14.045	0.015
	Fluoridated artificial saliva	5.2	-297	7.80	18.150	0.081
	Fluoridated acidified artificial saliva	2.5	-139	7.53	12.597	0.078

Considering R_p value as a function of pH (Fig. 5), it can be seen that Ni-Cr alloy exhibited the highest value of R_p in artificial saliva and also overall higher values compared to Co-Cr alloy irrespective of test solution and pH. Also, it can be seen that higher R_p values were measured for the tested alloys in neutral saliva, which is likely due to the presence of a very stable protective layer, particularly based on chromium oxides formed at the surface at this pH value.

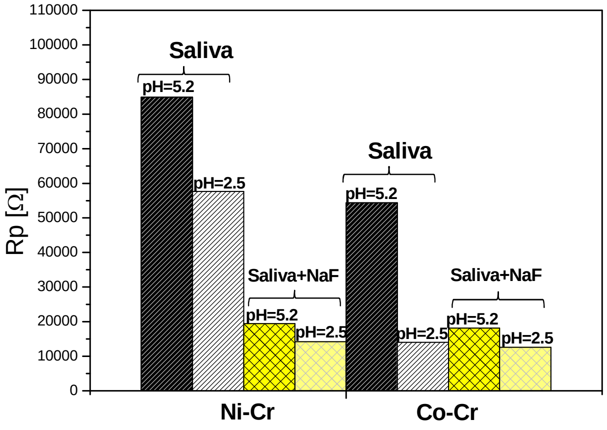

Fig. 5. The influence of pH on the polarization resistance (Rp) of Ni-Cr and Co-Cr alloys

The alloys tested in acidified artificial saliva (pH=2.5) showed a decrease in R_p value, with the most significant drop for Co-Cr alloy, indicating a more pronounced negative influence of low pH on its corrosion behavior. When NaF is added, a relatively large decrease in corrosion resistance is observed, and both dental alloys displayed similar values. It has been reported the formation of fluoride compounds [17] which are responsible for rapid dissolution of the passive oxide film. Moreover, when the pH is reduced, hydrofluoric acid is formed leading to a severe decrease of polarization resistance.

Evaluating the corrosion rates, Co-Cr alloy can be considered stable in the electrolytes tested, according to the Standard resistance classes [18], while the Ni-Cr alloy exhibited a less stable behavior in artificial saliva with addition of NaF, mainly at pH=2.5.

4. Conclusions

The influence of NaF addition and pH value on Ni-Cr and Co-Cr electrochemical behavior in artificial saliva was evaluated. The experimental results showed that open circuit potential of the studied alloys was stable after 24 h of immersion, regardless of the medium used. Also, in fluoridated (pH = 5.2) and acidified saliva (pH = 2.5), the Ni-Cr dental alloy exhibited the lowest corrosion resistance, as compared to saliva without addition. Higher current density and corrosion rate were measured for the Co-Cr dental alloy immersed in fluoridated and fluoridated acidified saliva, indicating that the addition of NaF and lactic acid led to a decrease in corrosion resistance. Moreover, the results indicated a large decrease of polarization resistance with addition of NaF in acidic environment, confirming that Ni-Cr and Co-Cr dental alloys undergo an accelerated corrosion process in oral environment with fluctuations of composition and pH.

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