

Electrochemical Behavior of Corroding Ni-Cr Dental Alloy in Artificial Saliva

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Abstract

The influence of chemical composition (pH, concentration of chemical species) of some biofluids, on electrochemical behavior of nickel base dental alloy was determined using Potential -time and Potentiodynamic Polarization Curves measurements. The experimental results show an important influence of pH on the main electrochemical and corrosion parameters.

Keywords: Nickel chromium dental alloy, electrochemical properties, artificial saliva, pH,

Introduction

The nickel base alloys are usually employed for removable partial dentures and as support structures implanted in the lower and upper jaws. Because of their high mechanical properties and for their excellent corrosion resistance they remain of prime importance in this field.

Also because dental materials generally present a very good corrosion resistance, the biocompatibility can be maintained during the entire periode of service, and consequently the normal biting function and aesthetics of the danture.

It is known that there is an important differences in the oral environmental conditions from person to person, from location to location and from time to time and thus the agressive saliva properties depend on various factors as, nature and concentration of agressive species, pH, temperature, bacterial flora e.a.[1,2].

In conclusion, the chemical composition of the saliva, directly influence the biocompatibility, biting function and aesthetics of dental alloys.

The main objective of this work is to study the effect of pH, of chloride and phosphate ions concentration on the anodic behavior of nickel chromium dental alloy.

Materials and Methods

Samples

The chemical composition of the used alloy is shown in the (**Table 1**).

The sample's surface was prepared by mechanical polishing with emery paper and diamond powder and finally rinsed with distilled water.

Table 1. Chemical composition of dental alloy (% wight)

Cr, %	Mo, %	Fe, %	Si, %	Mn, %	Ti, %	Ni, %
19.17	5.15	2.06	2.09	1.53	0.33	base

Before each experiment all sample were degreased by immersion in alkali solution (NaOH 40%, Na₂CO₃ 40%, Na₂SiO₃ 20% NaH₂PO₄ 10%) at 60°C, followed by ultrasonic cleaning for 4 minutes in acetone and izopropanol, and rinsed finally in demineralized water and dried in argon.

Electrochemical Experiments

Electrochemical measurements were carried out in a conventional three electrode glass cell with a computerized Gamry electrochemical instrumentation. A saturated KCl/silver electrode Ag/AgCl//KCl, and a platinum electrode were used as reference and auxiliary electrodes respectively.

The experiments were performed utilizing the following techniques.

*Potential -time measurements at pH -5.5, and 2.5.

*Potentiodynamic polarization curves in the following conditions:

- potential range from ϵ_{oc} -1000mV to 1000mV;
- potential scan rate: 150mVmin⁻¹;

*Experimental environment was artificial saliva with different ions content:

- base composition (-mg mL⁻¹): NaCl-40; KCl-40; CaCl₂.2H₂O -79.5; NaNH₂PO₄ H₂O-69; Na₂S.9H₂O-0.5; UREA-100; pH-5.4 [3]
- base composition without chloride ions;
- base composition without phosphate ions;
- base composition at different pH value: 1.5; 2.5; 4.5; 7; 8.2;
- All solutions were made of p.a. grade substances and demineralized water. The correction of the pH values was obtained using hydrochloric acid and Sodium Hydroxide, p.a. grade.

Results and Discussions

I. The influence of pH.

Open circuit rest potential (OCP) and potentiodynamic measurements were utilized to investigate the influence of pH of saliva.

Time evolution of Open Circuit rest Potential (OCP)

OCP were determined using the criterion that corrosion of Ni-Cr naturally passivated alloys will depend of pH of saliva. Time variation of OCP for the two values of pH, selected for this study, are presented in (Figure 1).

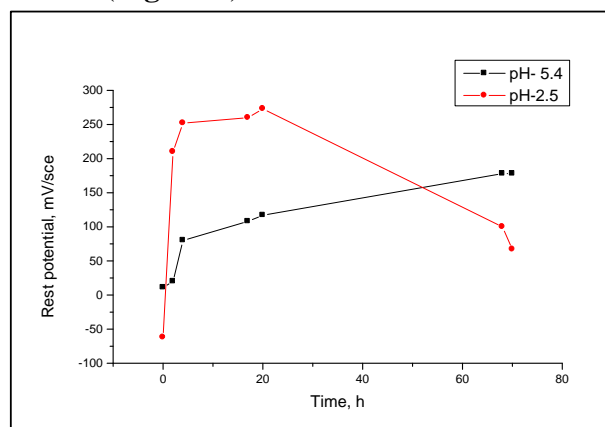


Figure1. The dependence of (OCP) on immersion time for 2 pH values in artificial saliva.

Significant change in the OCP was observed at pH = 2.5 and pH = 5.4. The main effect of both pH values is the increase toward positive values of OCP starting from zero time. At low pH values a sudden increase of OCP from -50mV toward +250mV in the first four hours, followed by an insignificant changes of ($\varepsilon \cong +250\text{mV}$) from 4 to 20 hours and afterwards a monotonous decrease from 20 to 60 hours. A monotonous increasing of OCP was observed at high pH values (5.4) starting from about + 25mV at zero time, to about +250 mV at 70 hours.

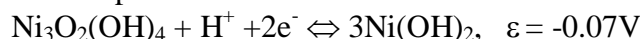
It is commonly accepted that the pH values may control the corrosion process as follows: At low pH values (2.0), OCP is controlled by the reduction of H^+ ions, whereas at near neutral pH (5.4-6), the reduction of oxygen was the most significant cathodic reduction reaction.

However the corrosion process is generally anodically controlled because the hydrated Ni^{+2} and Cr^{+3} ions formed are oxidized to hydrated oxide, which are adsorbed as a passive film on the alloy surface.

So, the increase toward positive values of OCP attests a reinforcement of the natural passive film. At pH 2.5 after about 20 hours the native film start to dissolve slowly.

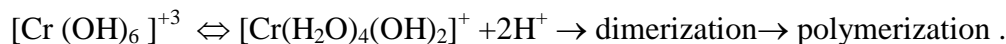
The mechanism of dissolution of the passive film is as follows:

Hydrated nickel oxide formed on the alloy surface, $\text{Ni}_3\text{O}_2(\text{OH})_4$, as a result of anodic process start to dissolve in the presence of H^+ ions.

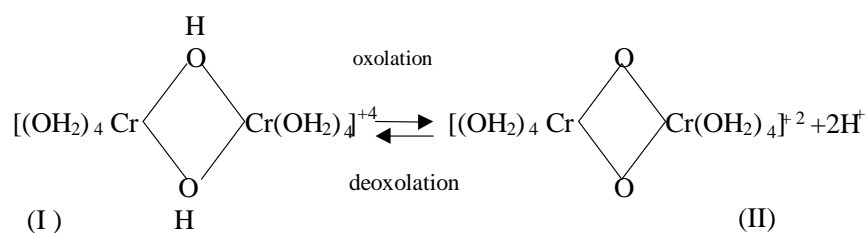


$\text{Ni}(\text{OH})_2$ readily soluble in acid media as is shown by Ni-pH Pourbaix diagrams [4].

Chromium hydroxide does not dissolve so easily because of the process of dimerization and polymerization which transform the anodic chromium oxide film in a polymeric nanostructure linked by "ol", -OH-, or "oxo" -O- bridges which present more stability toward dissolution in acids and in the presence of Cl^- ions [5].



The process of oxolation is favored by increase of concentration of Cr^{+++} hydrated ions and especially by the increase of alkalinity. So, at pH=5.4 the stability of chromium passive film is high enough because of deoxolation is a very slow process [5].



The influence of pH on the solubility of hydrated chromium oxide according to potential- pH Pourbaix diagrams [4] shows that the solubility product in acids solutions without chloride ions is $[\text{Cr}] = 10^{-14.3}$ ie. $0.38 \times 10^{-10} \text{ mgCr}_2\text{O}_3 / \text{L}$ and in solution with chloride ions is $[\text{Cr}] = 10^{-6.1}$ ie. $0.06 \text{ mgCr}_2\text{O}_3 / \text{L}$.

The increase of (OCP) toward positive values for both pH values, can be easily explained by the formation and aging of chromium polymeric inorganic film via "olation" and "oxolation" processes as follows: The process of aging which means the transformation of "ol" bridges,

increases the degree of oxidation state which is expressed by the increase of OCP toward positive values.

Potentiodynamic tests

To study the anodic behavior of the alloy surface in artificial saliva at different pH values, the potentiodynamic curves were recorded in a wide potential region, from hydrogen evolution -0.8 V to oxygen evolution +1.0 V. **Figure 2** shows representative potentiodynamic curves recorded for different pH values.

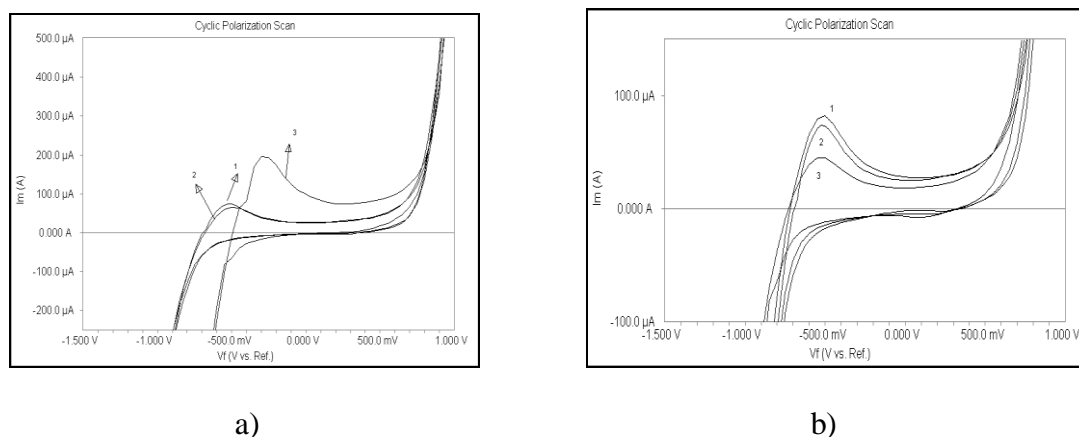
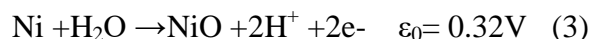
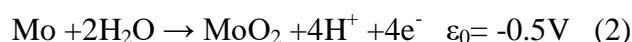
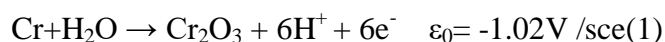


Figure 2. Anodic polarization curves for different pH values.
a) 1- pH=5.4; 2- pH=4.5; 3- pH=2.5; b) 1- pH= 8,2; 2- pH= 5,4; 3- pH=7

It was observed a poorly defined shoulder and a well defined current peak before the passive region is reached in the anodic scan. In the reverse cathodic scan both polarization curves (a, b) show a negligible reduction peak. Comparison of the polarization curves from fig. 2 with those of individual components (chromium, nickel and molybdenum) and with thermodynamic [4] and XPS [6] analysis, suggest that the potential region of the shoulder and the peak, agree with the potential region where the successive oxidation of Mo and respectively Ni to higher oxidation state occur.

These processes proceed on the previously formed Cr(III) oxide following equilibrium reaction:



Studies [7,8] of passive films formed on NiCr alloys have indicated that Cr- rich film is responsible for maintaining passivity. It was suggested that Cr-rich film consist of a hydrated form of CrOOH. The Cr rich phase suggested that the direct reaction of Cr with water to form Cr₂O₃ is preceded by formation of Cr(OH)₃. These reaction constitute the initial passivation process. Some studies have shown that nickel oxide film on the surface is very thin. Molybdenum was detected in the form of Mo, MoO₂, MoO₄⁻ and MoNi₄ compound in Cr-Ni-Mo alloy. Thus, the XPS studies of passive film help reveal the role played by the three metal hydrated oxides in the stability of the passive film of Cr-Ni-Mo alloys.

The value of the critical current density i_{crit} and of the passive current density i_{pass} as a function of pH is presented in (**Figure 3**).

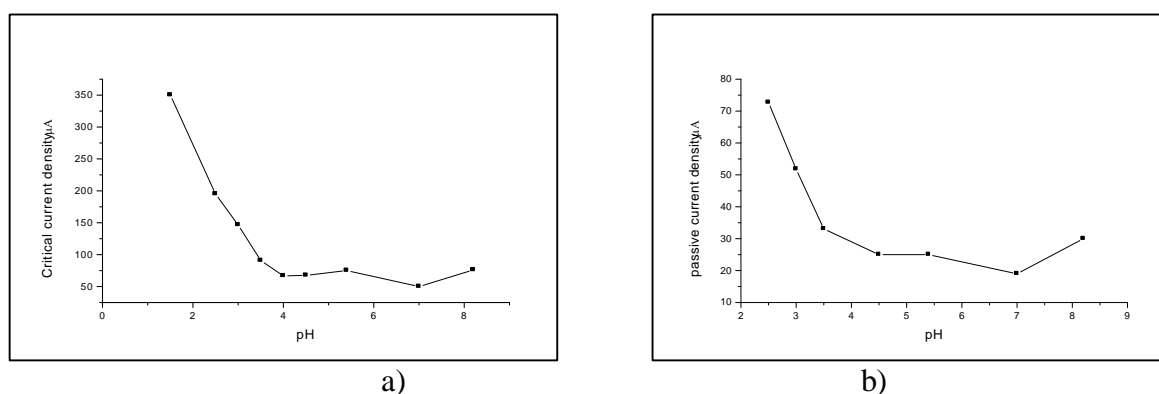


Figure 3. The influence of pH on: a) critical current density; b) passive current density

The shape of the pH- current dependence shows an increase of both i_{crt} and i_{pass} with the increase of hydrogen ion concentration.

At pH higher than 4.5 the shape of anodic curve is similarly but the passive current density are smaller and does not change significantly which the increase of pH.

The small increase of critical and passive current density at pH=8 in the figure 4b can be explained taking in account the solubility product of nickel and chromium compounds as is presented in Pourbaix Atlas [4] in which can be seen that the solubility product start to increase at pH=8 for chromium compounds and from pH=10 for nickel compounds.

II. The influence of chloride and phosphate ions

The polarization curves of alloy in solution without chloride and phosphate ions are presented in (Figure 4).

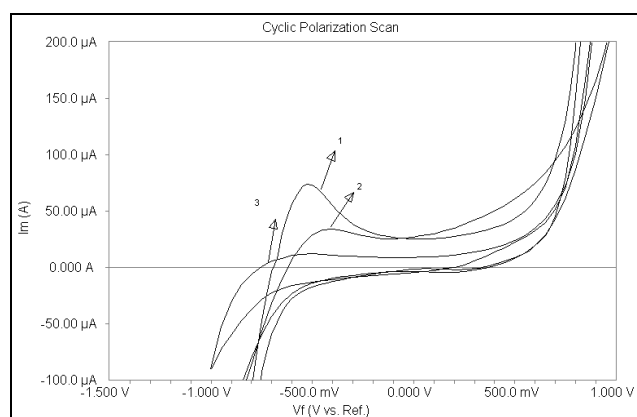


Figure 4. The anodic polarization curves for: 1) saliva; 2) saliva without chloride; 3) saliva without phosphate

From these curves an important influence, of chloride and phosphate ions on the anodic behavior of the alloy is observed.

At pH = 4-6 in the presence of H_2PO_4^- ions, Nickel corrodes forming Ni^{+2} ions, so the current density decrease in saliva without phosphate, curve 3 figure4 and increase in saliva without chloride ions curve 2.

This behavior can be explained by the theory of anion penetration which shows that because Cl^- ions are in low concentration, and especially because has a very low coordinating tendencies toward hydroxo- chromium complex their penetration in the film is negligible and the curve 3 shows a passive behavior. From the figure 4 result a synergetic negative influence

of phosphate and chloride on nickel passivity in a good correlation with Pourbaix diagrams [4] which emphasize that nickel does not passivate in phosphate medium and that the chloride ions increase this instability, despite the very good resistance of chromium.

We may conclude that the corrosion resistance of Nickel Chromium dental alloys is due to the fact that chromium forms an insoluble nanostructured oxidized network which prevents the dissolution of the alloy. This means that chromium atoms in the alloy are close enough to bridges by “ol” or “oxo” groups as they are exposed to corroding solution. In NiCr alloy [9,10] chromium enrichment in the passive layer is limited by nickel. This means that Cr^{+3} and Ni^{+2} species are present in the structure of passive layer of the alloy, but Ni^{+2} must be regarded as much less effective than chromium in forming complex stable structured films as was shown by R.W. Staehle [11] and A. Desestret [12].

In this way Cl^- and H^+ ions can diffuse through the passive film and replacing H_2O and $-\text{OH}$ groups and so, accumulate in the structure of the film and cause local or general breakdown of the passive film to occur.

Finally, it must be mentioned the influence of the third major component of the alloy, molybdenum. It plays a negligible role in the anodic process of film formation, but will present a significant role in the cathodic reaction of corrosion process of the alloy in low pH media due to its high hydrogen overvoltage.

Conclusions

1. The present investigation shows that the electrochemical behavior of Ni-Cr-Mo alloy depends especially on the pH of saliva.
2. Potentiodynamic measurements showed that the electrochemical behavior of Ni-Cr-Mo electrode under anodic potentiodynamic conditions in different artificial saliva solutions is very complex. Several oxidation-reduction processes occurred on its surface the mechanism and kinetics of which depend on the surface state and experimental conditions (pH, solution composition, electrode potential E).

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