

Influence of Ni and Cr Content on Corrosion Resistance of Ni-Cr-Mo Alloys for Fixed Dental Prostheses in 0.05% NaF Aqueous Solution

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Received August 13th, 2010; revised October 28th, 2010; accepted November 26th, 2010.

ABSTRACT

The Ni-Cr-Mo alloys have been used as dental prostheses because they own a good mechanical strength, high corrosion resistance and even to be economically viable. These alloys corrosion protection against in salt solutions typical of physiological media is due to passivation phenomenon with an oxide surface layer formation, mainly chromium oxides. This protective film, subjected to a mechanical stress in a corrosive environment, can partially dissolve by releasing ions, which have deleterious effects in a human body. Fluoride ions, existing in hygiene products, change the buccal environment and their presence may enable a localized corrosion process initiation. The aim of this work has been to investigate the chemical composition influence of three alloys in corrosion resistance to: A (Ni-73% Cr-14% Mo-8.5% Be-1.8% Al-1.8%), B (Ni-61% Cr-25% Mo-10.5% Si-1.5%) and C (Ni-65% Cr-22.5% Mo-9.5%) in media containing fluorides that simulate mouthwashes solution. The study has been done in a 0.05% NaF solution, pH 6, at 37°C using electrochemical techniques. The alloy with the highest nickel and the lowest chromium content is not passive in the middle studied, showing a continuous increase in current density with the potential increasing, while the other alloys show passivation range of 600 mV and passive current density of about 10^{-6} A/cm².

Keywords: Ni-Cr-Mo Alloys, Dental Prostheses, Corrosion

1. Introduction

A large number of metal alloys are used in dentistry for manufacturing of fixed and removable prostheses. In the oral cavity, these structures are exposed to a chemically adverse environment, with saliva being the most corrosive agent, due to the high concentration of chloride ions that are causing localized corrosion. Another important factor is the pH, which can range from 2 to 11, depending on the ingested food. One of the most important factors determining the use of a metal alloy for making prosthesis is its resistance to corrosion [1,2]. Non-precious metal alloys are being used due to their low cost and adequate mechanical properties. In the '60s, basic alloys such as nickel-chromium were developed. These alloys are basically composed of Ni (68% to 80%) and Cr (12% to 27%) [3], but it is necessary to add other elements to ensure high mechanical strength achievement and adequate corrosion resistance, besides the shaping facility and bonding with porcelains, molybdenum, iron, aluminum, silicon, beryllium, cobalt, niobium, titanium which are the most frequently used alloys elements [3,4]. Chromium presence improves the alloys corrosion resistance in typical salt solutions of physiological media with an oxide surface layer formation, mainly chromium oxides [5,6]. This layer thickness is typical of a few nanometers, which is sufficient to act as a protective barrier between the metal surface and the aggressive medium. The passive film slows the metals dissolution rate, making difficult the ions transfer from metal to solution. The human tissue reaction for dissolved ionic species can vary from a simple allergy to a severe disruption in the region adjacent to the prosthesis [7]. Since the chemical alloys composition can influence the corrosion behavior, studies about corrosion resistance in aggressive media, which simulate the oral environment, may provide information about metals or alloys to be used in dental applications. Sodium Fluoride (NaF) and other fluorides are often used as prophylactic agents

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in dental treatments to prevent dental plaque formation and caries development, however, the prophylactic action may have a side effect of metal materials corrosion caused by this ion. Saliva infiltration containing fluoride in the structure that holds implant and the contact with crowns and bridges can be the corrosive attack cause. Fluorides usually attack reactive metals such as titanium, especially in acidic medium, causing corrosion due to their passivity destruction and mechanical properties decrease. To date, a few researches have been done to analyze the fluorine-containing composites influence in dental alloys corrosion resistance. N. Chiff et al. 2004 [8] studied the fluoridated mouthwashes influence on titanium alloys corrosion resistance used in orthodontic wires manufacture, using electrochemical techniques that indicated correlation between corrosion and mouthwashes composition. Mayont, A. M. et al. 2004 [9] analyzing the titanium alloys corrosion behavior found high corrosion rates in neutral solutions with lesser fluoride contents and in acid solutions with low fluoride levels. According to the authors, the fluoride concentration increase leads to a decrease in thickness and increase in porosity on oxide layer, which reduces its corrosion protection. Rezende, A, B, C. and other [10] evaluated effect of three commercial mouthwashes on corrosion resistance of a Ti-10 Mo alloy developed in their lab, comparing it with the commercially pure titanium behavior. Through electrochemical techniques, they concluded that corrosion resistance depends predominantly on the mouthwash composition. With respect to Ni-Cr, it has only been found in literature one non-conclusive quote that prophylactic fluoride solution (pH = 6.5) is a reactive agent and can cause damage to metal restorations [11]. Therefore, it is important to probe knowledge about the Ni-Cr-Mo reactivity in media containing fluoride, which is this work aim.

2. Materials and Methods

The three Ni-Cr-Mo alloys corrosion resistance has been determined in naturally aerated 0.05% NaF solution, pH 6.0 at 37°C using electrochemical techniques. The alloys have been acquired in the national market, being commercialized in a billet form in the as-cast condition. **Table 1** shows the chemical compositions provided by the manufacturers, being named in this work by the letters A, B and C.

For electrochemical measurements, the alloys, as received, have been embedded in polyester resin, leaving an exposed area in the flat disk form of about 1 cm². Before each experiment, the electrode surfaces have been mechanically polished, degreased with acetone, washed with distilled water and air-dried. Measures have been

Table 1. Alloys mass percentage composition.

Alloy	Ni	Cr	Mo	Be	Si	Al
A	73	14	8.5	1.8		1.8
В	61	25	10.5		1.5	
C	65	22.5	9.5			

taken at 37°C using a conventional thermostated electrochemical cell containing 0.05% NaF solution used as electrolyte and prepared using NaF and distilled water.

The electrochemical measurements have been carried out using a potentiostat/galvanostat EG & PAR 283 and a Frequency Response Analyzer, EG & PAR 1025 (Perkin Elmer Instruments Inc., USA), both interfaced to a computer for collecting and analyzing data. The working electrodes potentials have been determined using a saturated calomel electrode as reference, and used a platinum ring as counter electrode. Open circuit potential (OCP) values have been recorded during 400 minutes of immersion. Potentiodynamic polarization curves have been obtained immediately after obtaining the OCP curves, with a scan rate of 20 mV min⁻¹ towards electropositive. The experiments have been performed in triplicate to observe repeatability. The cyclic voltammetry tests have been carried out with a 10 mV/s speed starting at -600 mV, advancing towards the cathode up to the potential value where the metals dissolution process starts and returning to the initial potential.

3. Results and Discussion

3.1. OCP Measurements

At **Figure 1**, OCP curves for alloys A, B and C in 0.05% NaF are illustrated. An upward trend at the very initial immersion stage has been common for the three studied alloys, but a significant decrease in the OCP values has been observed, specifically for curve A and potential values obtained have been around 200 to 250 mV more negative than those observed for B and C. Fluoride ions presence in solution can alter the oxide layer structure making it more porous, thus leading to a decrease in corrosion resistance in the considered medium. These observations seem to be consistent with the differences in the alloys compositions, since alloy A, by having a smaller chromium amount in its composition, becomes more susceptible to corrosion in medium containing fluoride. Chromium is responsible for corrosion resistance and for an oxide film formation commonly called passive film [11]. It takes at least 12% by weight for this film formation.

In laboratory studies, concentrations of 16%-27% tend to form a more uniform oxide layer of Cr_2O_3 and $Cr(OH)_3$ with higher corrosion resistance [3]. The chromium oxide layer is associated with the aluminum from

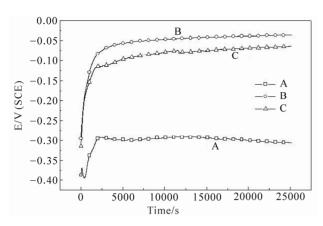


Figure 1. Open circuit potential for alloys A, B and C immersed in 0.05% NaF solution.

the liaison agent between the metal substrate and porcelain [14]. In order to obtain more information that can characterize the corrosion behavior type and allow a comparative analysis of corrosion resistance for the three alloys, potentiodynamic polarization curves have been obtained, as illustrated in **Figure 2**.

3.2. Potentiodynamic Polarization Curves

The different behavior observed for the alloy A in open circuit potential appears again when comparing the potentiodynamic profiles (**Figure 2**) indicating that a smaller chromium content in the chemical alloy composition may lead to corrosion potentials of about 250 mV more negative. Moreover, the passivity limit becomes so narrow that it appears almost imperceptible in potentio-dynamic profile analyze of curve A. While B and C present virtually the same passivation interval, approximately 500 mV and the same passive current density of about 10⁻⁶ A cm⁻², the alloy A has current density 10,000

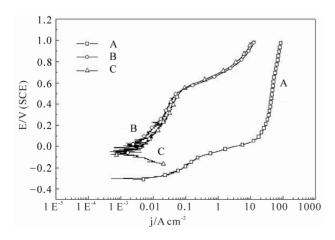


Figure 2. Polarization curves for alloys A, B and C immersed in 0.05% NaF solution.

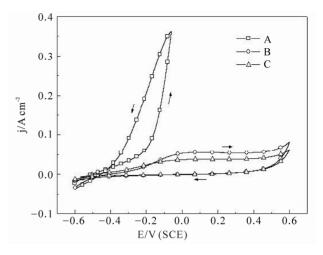


Figure 3. Cyclic voltammograms of alloys A, B and C in 0.05% NaF solution.

times greater, thus showing a low corrosion resistance.

3.3. Cyclic Voltammetry

Figure 3 shows the cyclic voltammograms of alloys A, B and C in 0.05% NaF, pH 6 and 37°C in the interval between –600 mV and 600 mV where it can be observed the alloy A corrosion and alloys B and C passivation. The alloy C shows the largest passivity range (approximately 800 mV). Alloys B and C have showed the greatest disruption potential in terms of passive films to be more resistant. Another interesting parameter is the current density, which indicates alloy reactivity in direct order, namely, the higher the current density, the higher the alloy reactivity, where alloy A owns the highest current density. The potential interval registered for the alloy A has been lesser due to its generalized dissolution in potential values higher than –200 mV. When the scan has been reversed, a hysteresis loop appeared, denoting an active state.

4. Conclusion

A distinct behavior has been verified when the potentiodynamic profiles of three different compositions used in the dental market in NaF 0.05% medium are compared, showing that the highest Ni content to the alloy, coupled with the lowest Cr content, results in the greatest corrosion susceptibility.

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