Passivity Study of Dental Ni-Cr-Mo Alloys in Fluorides Media

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Abstract

A large number of metal alloys is used in dentistry to manufacture fixed and removable prostheses. In 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 pH, which can vary from 2 to 11, depending on the food ingested. One of the most important factors determining the use of an alloy for making prosthesis is its corrosion resistance. The tests were performed with the Ni-Cr-Mo alloys, commercially called Nichrom, Wiron 99 and Superbond in a buffer HF/NaF, pH between 4.5 and 5.0 at a temperature of about 37° C, simulating an oral environment. The obtained data suggest that the alloy Nichrom has a higher corrosion resistance when compared to the other two under the same conditions.

Keywords: Corrosion, Alloy Ni-Cr-Mo, Mouthwash

1. Introduction

Metal alloys are often used in dentistry for the manufacture of fixed and removable prostheses. In the oral cavity, these structures are exposed to a chemically adverse environment, the saliva being the most corrosive agent, due to the high chloride ions concentration which is causing localized corrosion. Another very important factor is pH, which can vary from 2 to 11, depending on the food ingested. One of the most important factors which determine the use of a metal alloy for making prosthesis is its corrosion resistance [1,2]. Non-precious metal alloys are being used due to low cost and appropriate mechanical properties. In the '60s, basic alloys such as Nickel-Chromium (Ni-Cr) were developed. Basically, these alloys are composed of Ni (68% to 80%) and Cr (12% to 27%) [3], but it is necessary to add other elements to ensure the achievement of high mechanical strength and adequate corrosion resistance, further the ease of shaping and connection with porcelain. Molybdenum, iron, aluminum, silicon, beryllium, cobalt, carbon, niobium, titanium are the most frequently used alloys elements [3,4]. Chromium presence increases the alloys corrosion resistance in salt solutions typical of physiological means by forming an oxide surface layer, particularly chromium oxides [5,6].

This layer thickness is typically a few nanometers, which is sufficient to act as a protective barrier between the metal surface and the aggressive environment. The passive film retards the metals dissolution rate, making the metal ions transfer to the solution more difficult. 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]. Most studies about dental alloys corrosion are carried out in artificial saliva means [8-13]. There are few corrosion studies records which use salt solutions in order to simulate the aggressive conditions of oral cavity. Sun et al. [14] used NaCl solutions (0.9% and 0.09%) as media to study corrosion on noble and precious dental alloys, using the open circuit potential and cyclic potentiodynamic polarization techniques. Lucas [15] used NaCl solution (0.9%) as "in vitro" means to study corrosion resistance of Co-Cr alloys and Ni-Cr using electrochemical techniques. Geis-Geistorfer [16] analyzed several types of corrosion of Ni-Cr-Mo and Co-Cr-Mo by mass loss in NaCl solution (0.1 M) during 5 weeks. Sharma [17] studied the corrosive behavior of alloys for dental implants in NaCl solution (3%) using electrochemical techniques such as Tafel polarization, cyclic polarization and electrochemical impedance spectroscopy.

However, in all cases, corrosion resistance seems to depend, in a greater degree, more on the means than on the alloy thermal processing. NaF and other fluorides are often used as prophylactic agents in dental treatment to prevent dental plaque formation and caries development. Fluoride is present in all toothpastes that are commonly used in the market. Although beneficial, it should be used or consumed in the correct dosage, so that prevention does not result in adverse health effects. Toothpastes, gels and mouthwashes are not the only existing fluoride sources which population has access. The state and federal governments, through dental caries prevention program, use methods to bring fluoride to all population, including the poorest, trying to reduce caries incidence, as for instance:

- fluoride addition to public supply water (fluoridated water);
- fluoride addition to the milk (usually in food programs in public schools) in the form of tablets or drops;
- free distribuition of toothbrush and toothpaste.

However, the prophylactic action can have as collateral effect the metallic materials corrosion caused by that ion. Food friction and saliva infiltration containing fluoride in structure that holds the implant, in the crowns and bridges, are the corrosive attack causes. Due to large advertising campaigns, there has been increased use of mouthwashes containing fluoride to prevent dental caries. Fluoride use to attack reactive metals such as titanium, particularly in acid means, causing corrosion due to their passivity destruction and mechanical properties decrease. To date, just a few researches have been carried out in order to analyze fluoridated mouthwashes influence on dental alloys corrosion resistance. Schiff and others [18] studied the fluoridated mouthwashes influence on corrosion resistance of titanium alloys used in orthodontic wires manufacture, using electrochemical techniques. Such techniques suggest that mouthwashes are more aggressive than the fluoride-free artificial saliva. Nevertheless, corrosion resistance seems to depend on a complex relationship among alloy composition, fluoride concentration and mouthwash pH. Mayont [19], analyzing titanium alloys corrosion behavior, found high corrosion rates in neutral solutions with lower fluoride amount and in acid solutions with low fluoride amounts. According to the author, the fluoride concentration increase leads to a thickness decrease and porosity increase on the oxide layer which reduces its corrosion protection. Rezende [20] evaluated the effect of three commercial mouthwashes on corrosion resistance of a Ti-10Mo alloy developed in the laboratory, comparing it with comercially pure titanium behavior. Through electrochemical techniques, it was concluded that corrosion resistance is predominantly dependent on mouthwash composition. Regarding to Ni-Cr-Mo alloy it was found in literature only non conclusive citation that the prophylactic fluoride solution (pH = 6.5) is a reactive agent and can cause damage to metal restorations [21]. This being so, it is important to deepen knowledge about Ni-Cr-Mo alloys reactivity in acid aqueous media containing fluoride which simulate creams, gels and mouthwashes.

The alloys which were used for this work development were provided by thecompany American Dent-All (USA), Wilcos Commercial Ltd (Brazil) and BEGO (Germany).

The nickel-chromium-molybdenum alloys are sold in billets form in as-cast condition and their chemical compositions are specified in the European standards (CE 0044). The mass percentage composition of the alloys is in the table below:

Table 1: Alloys composition used in the work

ALLOY	MASS COMPOSITION (%)						
	Ni	Cr	Mo	Be	Si	Al	Co
Superbond	61	25	10.5	–	1.5	-	-
Wiron 99	65	22.5	9.5	–	–	-	-
Nichrom	62	32.7	1.0	-	-	-	3.0

2. *Materials and Methods*

The work methodology consisted of making the specimen and working electrodes, metallographic analysis before and after corrosion test, using optical microscopy and image analysis. For corrosion studies, different electrochemical corrosion tests such as potential measurements at open circuit potentiodynamic polarization curves register and cyclic voltammetry were used. The used medium was a buffer HF / NaF, pH between 4.5 and 5.0. For the electrochemical tests a reference electrode Ag / AgCl KClsat was used and as an auxiliary electrode, a graphite rod.

Measurements were carried out using a thermostated conventional electrochemical cell made of borosilicate glass. This cell is composed by two compartments: inside, a glass cup with 250 mL electrolyte size, which has a nylon cover with four holes in order to adapt the working, auxiliary and reference electrodes and also a thermometer; outside, a compartment where water, for electrolyte thermostatting at 37° C, circulates.

For the tests achievement, it was used the following documents: Ordinance No. 71, May 29, 1996, the Health Surveillance Secretariat of the Ministry of Health: it provides the essential information that must appear on toothpaste packages.

ISO 11609, December 1995: Toothpastes - Requirements, Test Methods and Marking: it sets the parameters and test methods to check physical and chemical properties and labeling of toothpastes. Ordinance No. 21, October 25, 1989, the Health Surveillance Secretariat of the Ministry of Health: it sets requirements to ensure quality and efficiency of toothpastes.

3. Results and Discussion

The potentiodynamic polarization curves for the different alloys were carried out in potentials range from - 0.5 V to -0.8 V at a potential scan rate of 20 mV min^{-1}. The potential scan beginning was -0.25 V below the open-circuit potential of the alloy studied in the medium, towards positive potentials. Figure 1 shows the polarization curves for alloys Nicrhom, Superbond and Wiron 99 in 0.08 M NaF solution, pH 4.7.

For Nichrom, it is noted a cathodic current associated with proton reduction, due to the slightly acidic medium. The cathodic curve for Superbond and Wiron 99 has similar appearance with a limit current presence, which may be associated with possible oxides reduction formed on electrodes. The corrosion potentials obtained from polarization curves are, respectively, -0.28 V (Wiron 99), -0.26 V (Superbond) and -0.23 V (nichrom). It is clearly observed a nobility increase in that order, and it can be deduced that this behavior is due to the chromium content increase and nickel decrease in alloy composition.

In the anodic region, all studied alloys display passivity current. The current density values measured at +0.20 V are, respectively, Nichrom (1.1×10^{-6} A cm^{-2}), Superbond (3.1×10^{-6} A cm^{-2}) and Wiron 99 (1.2×10^{-5} A cm^{-2}). Therefore, it can be verified that current density in passivity region is very higher for Wiron 99, about 10 times the one observed for Nichrom. The alloy Wiron 99 shows, at passivity region, a behavior different from the other two alloys. The constant current value observed for Nichrom and Superbond is oxide growth characteristic in this potential region. It is noted that the highest current density for Superbond indicates that the formed oxide is probably more susceptible to the electrolyte attack, when compared to Nichrom. This behavior can be attributed to the film properties, as for instance, its porosity and composition. The alloy Wiron 99 discloses a current increase at -0.05 V forming two current shoulders located at -0.35 V and +0.14 V. This current increase indicates that, different from other studied alloys, Wiron 99 displays passive layer breakdown and its subsequent restoration after about 0.20 V, nevertheless with a current density about four times higher.

For a better interpretation of the alloys behavior in the studied medium, it has been carried out tests with pure metal, alloys components, in the same experimental conditions. Figure 2 shows polarization curves for commercially pure metals chromium, nickel, molybdenum and cobalt in 0.08 M NaF solution, pH 4.7. As expected, Cr presents a passive behavior with a current density at passive region of about 7.7×10^{-7} A cm^{-2}. The passive behavior, observed for the studied alloys, is due mainly to the chromium presence, which oxidizes firstly, forming an extremely thin Cr_2O_3 film, which is adherent and little permeable to ions passage. This oxide gives stability to the alloys because it is very resistant to corrosion. Ni presence in oxide film is also important in metal protection, however, as it can be seen, it presents a current density at passive region of about 5.6×10^{-6}, with oxide film rupture occurring around +0.16 V.

Polarization curves superposition of Cr and Nichrom alloy, Figure 3, clearly shows that their behaviors are similar, except for passivity current density values, which for Cr case is about 1.4 times smaller. This current increase for alloy, certainly results from the high Ni content (62%) and also from 3% Co addition to it. When Wiron 99 behavior is compared with Ni, Figure 4, it is verified that the current shoulder, observed in the passive alloy region, practically coincides with Ni disruption potential for that medium. Therefore, it can be deduced that anomalous Wiron 99 behavior is due to two factors combination: higher Ni percentage and lower Cr content, which makes this material more susceptible to fluoride ions attack.

Molybdenum which is present in the alloy should also reduce these materials corrosion resistance, however, this element seems not to interfere directly in this behavior because, as can be seen in Table 1, both alloys Superbond and Wiron 99 have molybdenum content very similar, but do not exhibit the same behavior at passive region.

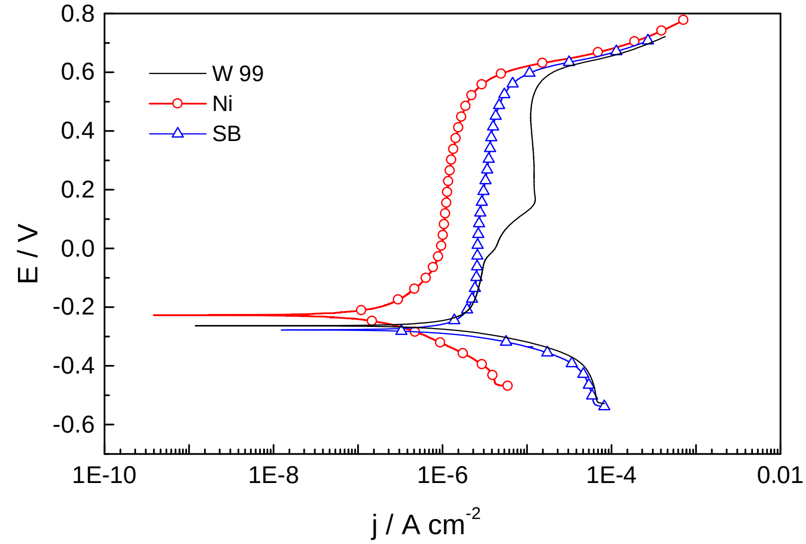

Fig. 1 - Polarization curves of alloys Wiron 99, Nichrom and Superbond in NaF 0.08 M, pH 4.7.

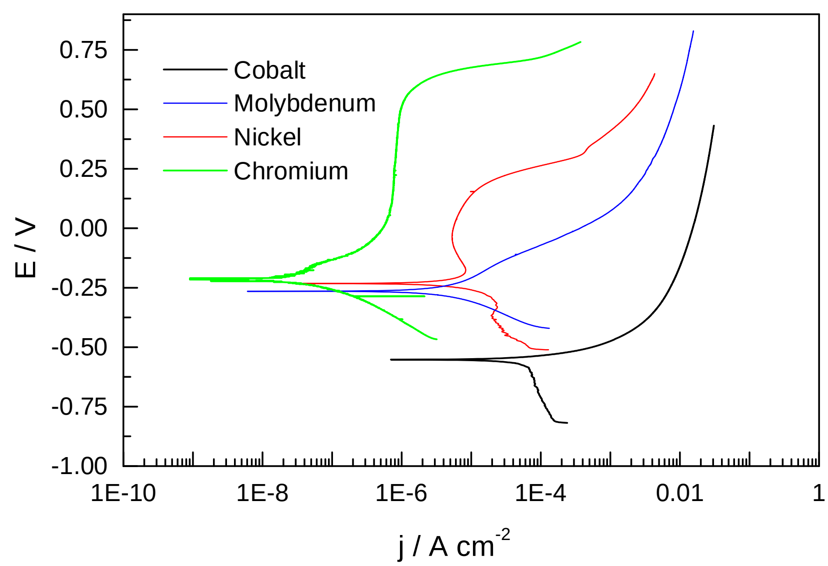

Fig. 2 - Polarization curves of pure metals Cobalt, Molybdenum, Nickel and Chromium in 0.08 M NaF, pH 4.7.

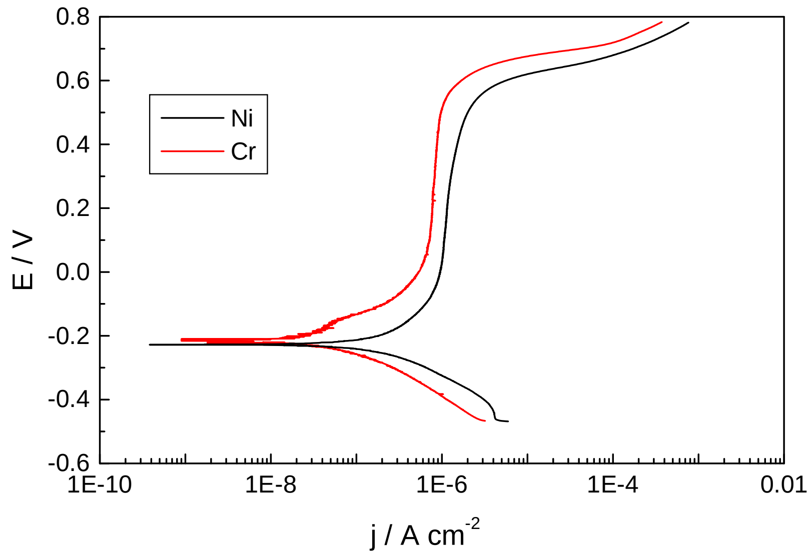

Fig. 3 - Polarization curves of alloy Nichrom and pure metal Chromium in 0.08 M NaF, pH 4.7.

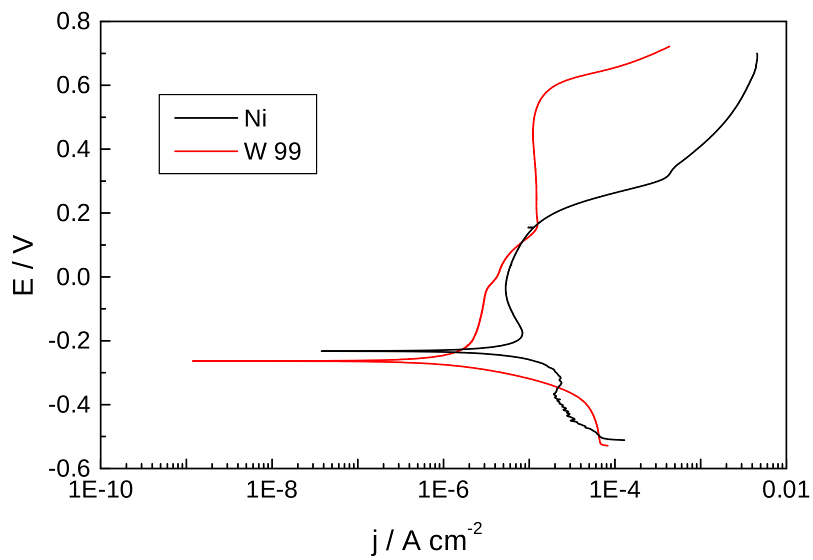

Fig. 4 - Polarization curves of Alloy Wiron 99 and pure metal nickel in 0.08 M NaF, pH 4.7.

Conclusion

Nichrom presents a higher corrosion resistance in relation to the other studied alloys, even with high nickel percentage. This behavior results mainly from the high chromium content (32.7%) whose oxide protects metal from fluoride ions attack.

The anomalous behavior of alloy Wiron 99, at passivity region, can be explained due to a higher Ni percentage and chromium reduction in its composition, as has been observed in comparative study with pure metals.

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