Corrosion process development of a Ni-Cr-Mo alloy used in dental prosthesis

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Abstract:- The 59.6% Ni, 24.0% Cr and 9.8% Mo alloy, used in dental prosthesis was recast in open fire - oxy-GLP torch and naturally cooled. The electrochemical study has shown that the alloy has behavior similar to chrome, displaying an extensive passivity area due to formation of a chrome oxide layer. The development study of corrosive process was carried out by interrupting the potentiodynamic polarization curve in four different potentials and their surfaces were analyzed by optical microscopy and scanning electronic microscopy. The material micrograph, before being subjected to the electrochemical test, displayed homogeneous surface, showing some pores, probably formed during the recast procedure. The wear and tear process begins after the transpassivity potential, with intergranular corrosion characteristics with preferential dissolution of region with the smallest Mo content, as quantified by EDS. The obtained surface has appearance of a sample electrolitically attacked in HCl, displaying Mo-rich precipitates in the grains boundaries.

Keyword:- Corrosion, Dental, Materials, Wironia, Ni-Cr-Mo alloys.

I.   INTRODUCTION

Noble and alternative alloys have been used in manufacture of fixed and removable dental prostheses. Despite their attractive mechanical properties, susceptibility to corrosion of non-precious materials has limited their application because of corrosion products containing a variety of potentially toxic metal ions [1-2]. More recently, laws and regulations aiming to reduce costs in health revived interest in alloys cheaper and more resistant to corrosion. Among them, it is remarkable the Ni-Cr alloys with chromium content between 18 and 30% which have high mechanical strength, good biocompatibility with the oral environment, high elasticity modulus, melting facility, low density, high hardness, deflection resistance, good adhesion to ceramic, low cost, easy processing, good corrosion resistance due to passivation phenomenon, by forming a chromium oxide film [1,3-5]. This layer, in some alloys, is not sufficiently protective to prevent the selective dissolution of less noble components. Other metals are also added to the alloy to improve some specific properties. Nb, Mo and W harden the alloy forming a solid solution. Mo and W form carbides which increase the hardness; Al, Mo, Ti, W and Ta form intermetallic phases and harden the alloy by forming precipitates [6]; Mo is essential for oxidation reactions, increasing the sample surface affinity for oxygen and increase of pitting corrosion resistance in an electrolyte containing chloride [7].

Most Ni-Cr alloys are formed by Ni (68% to 89%) and Cr (11.9% to 26.3%), and smaller percentages of other elements such as Mo, Be, Si, Al and The Ti. Cr, although it has an important role in passive capacity of alloy tends to increase hardness and melting temperature, the latter being important feature to increase the safety margin during ceramics firing [8]. Now, Mo improves corrosion resistance [1]. Molybdenum (Mo) is a refractory metal that oxidizes is slowly, but the oxide produced (e.g. MoO_3) easily volatilized if the temperature exceeds 700ºC [9].

Chromium and molybdenum content in an alloy is significant to increase its corrosion resistance, because it improves the surface passivation. As an alloying element, chromium has capability to increase the resistance to corrosion, to oxidation and to staining, in other words, increasing surface stability due to chromium oxide formation (Cr_2O_3) [10-13].

Corrosion can be enhanced by chemical composition of alloys or by microstructure displayed on the material surface. Release of metal ions coming from the corrosion process depends on several characteristics such as surface roughness, oxidation degree, alloy potential, inhibitors presence, holes and crevices [14,15].

Electrochemical behavior of metallic alloys used in manufacturing dental implants is of great interest for the corrosive process understanding which can occur in the oral environment. The oral cavity particularly represents an ideal habitat for the biodegradation of metals due to microbiological, thermal, chemical, enzyme properties that can accelerate the corrosion process and expose patients to this corrosion products [16-19]. The

aim of this study is to study the corrosive development of a Ni-Cr-Mo alloy, after remelting in an open flame, in a 0.9% NaCl solution, pH 6.0 at 37 °C, by means of measures of open-circuit potential, potentiodynamic polarization curve, surface analysis by optical microscopy, scanning electron microscopy and energy dispersive spectroscopy (EDS).

II. MATERIALS AND METHODS

A commercial dental alloy of Ni-Cr-Mo mainly used in the manufacture of fixed dental prostheses (Wironia, Bego, Germany) was used in developing this work. Table 1 shows the chemical composition of this alloy and Table 2, its mechanical properties, provided by the manufacturer.

Table 1 - Chemical Composition (% m / m)

Ni-Cr-Mo Alloy	Ni	Cr	Mo
	59.6	24.0	9.8

Table 2 - Mechanical Properties of Ni-Cr-Mo Alloy

Flow Limit (MPa)	390
Elasticity Modulus (GPa)	200
Vickers Hardness (HV 10)	200
Ductile Flexibility (%)	19
Density (g/cm³)	8.2
Thermal Expansion Coefficient	
20-600ºC	14.4×10^{-6} k^{-1}
25-500ºC	14.2×10^{-6} k^{-1}
Casting Range	
Solid	1380ºC
Liquid	1280ºC
Casting Temperature	1430°C
Preheating Temperature	900- 950°C

This alloy was recast from patterns in wax of cylindrical shape included in a silicone ring coated with a phosphate-based. The Ni-Cr alloys have a contraction coefficient for casting relatively high (2.22%) and for that it is needed to use phosphate coating associated with a thermal and hygroscopic expansion [1]. For making samples it was used two wax cylinders of about 0.5 cm^2 cross-sectional area of 3 cm in length, which were set in a silicone base. These rings were heated in an oven at 800º C for 1 hour for removal of wax. Then the mold was filled with the alloy recast in open flame - torch oxy-GLP. The flame was focused on the metal, and after formation of an egg the mold was removed from the oven, placed near the crucible and by centrifuge the molten metal penetrated into the mold. The cooling was done slowly at room temperature without atmospheric control for a period of 24 hours. After casting the samples were removed from the mold, machined in the cylindrical shape and cut with a diamond saw (about 1 cm long) and in this condition used in electrochemical experiments and in metallographic analysis.

To prepare the working electrode, the samples were embedded in acrylic resin of rapid polymerization, with the exposed area of 0.528 cm², subjected to manual grinding with wet-granulation 220 to 1200 mesh, followed by mechanical polishing with felt soaked in diamond paste of grain 3 µm, which allowed good reproducibility of measurements.

The electrochemical study was developed by means of analysis of open circuit potential / time measures, measuring potential against time for a period of 12 hours and obtaining potentiodynamic polarization curves in NaCl 0.9% solution, pH 6.0 at 37ºC, using a conventional glass cell thermostated, a reference saturated calomel electrode (SCE), an auxiliary platinum electrode and a working electrode using the potentiostat EG & G PAR 283, interfaced to a microcomputer GS - Pentium II through a GPIB interface fitted program Softcorr III. Potentiodynamic polarization experiments were interrupted in four distinct stages and the electrode surface analyzed by optical microscopy and scanning electron microscopy.

The metallic material microstructure was revealed by electrolytic attack in a 20% HCl. The analysis was carried out using an optical microscope Nikon EPIPHOT 200 camera with video PIXERA PROFISSIONAL attached to a microcomputer DELL DIMESION L666Tr (PENTIUM III – 66MHz) using the SPOT program to capture images and a scanning electron microscope (SEM) LEO 1450VP.

III.   RESULTS AND DISCUSSION

3.1 Results

Figure 1 illustrates the open circuit potential curve with time obtained for the electrode of Ni-Cr-Mo and the electrodes of the alloy constituents metals, immersed in 0.9% NaCl solution, pH 6.0 at 37 °C.

The open circuit potential curves for alloy Wironia and pure metals Cr, Ni and Mo for a period of 12 hours have a tendency to stabilize at more positive potentials. The shift of potential to values more noble than that observed at the instant of immersion indicates the formation of a protective surface film. The Ni stabilized after 40 minutes, the Mo after 100 minutes, the alloy Wironia after 200 minutes and Cr after 250 minutes, as seen in **Figure 1.**
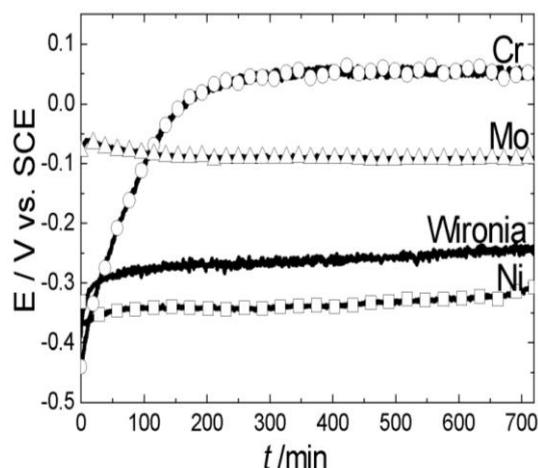

Fig. 01 - Variation of open circuit potential against time

The potentiodynamic polarization curves obtained for Wironia alloy and for metal electrodes constituents of the alloy, immersed in 0.9% NaCl, pH 6.0 at 37 °C, can be seen in Figure 2.

The alloy presented a cathodic region, where there is a reduction of H^+ ions, an oxygen limit current in a narrow range of potential (~ 0.2 V) and then the potential corresponding to zero current, in the anodic region it is observed a small active-passive transition followed by an extensive passivation region (~ 0.8 V) ranging from about -200mV to +500 mV. This passivation is attributed to a chromium oxide layer formation, since the alloy is similar to the Cr behavior [20]. For higher potentials (~ 0.6 V) there is a progressive increase of current density due to transpassivation and oxygen release at more anodic potentials. At Ni and Mo curves it is not observed passivity, the process is cathodically controlled and the corrosion rate is much higher than the one of the alloy.
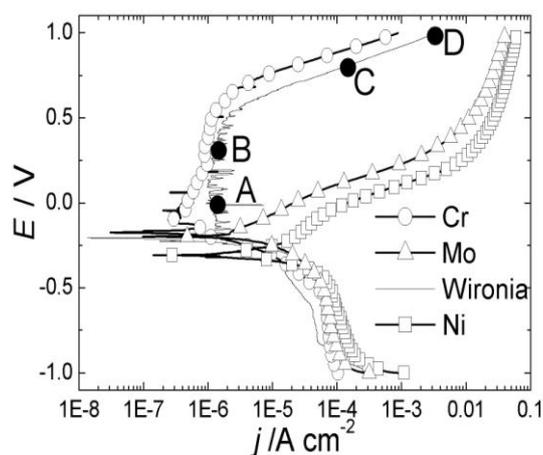

Fig. 02 - Potentiodynamic polarization curves of alloy Wironia interrupted at different potentials

The material micrograph before it is submitted to the electrochemical test displayed a homogeneous surface, with some pores and other defects probably formed during the recasting process, observing microstructural revelation evidence initiated at the surface preparation process, Figure 03.
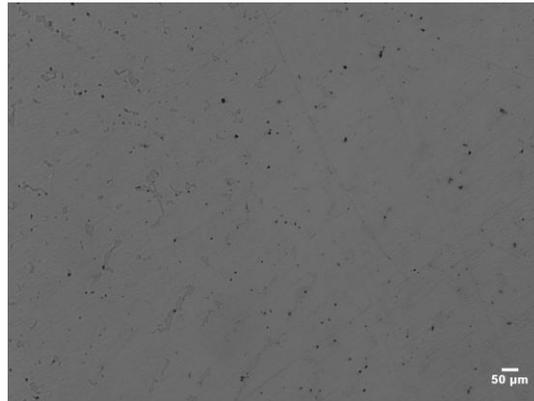
Fig. 03 - Optical micrograph of Wironia alloy before the electrochemical test

To study the corrosion process development, the tests were interrupted at the potentials of anodic region corresponding to points A, B, C and D (Figure 2). After each interruption, the electrode was immediately washed with distilled water and dried with air flow, and its surface examined by optical microscopy with magnification of 500 times, as seen in Figures 04 to 07.
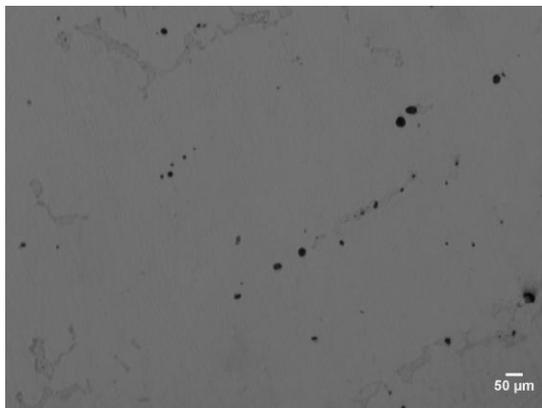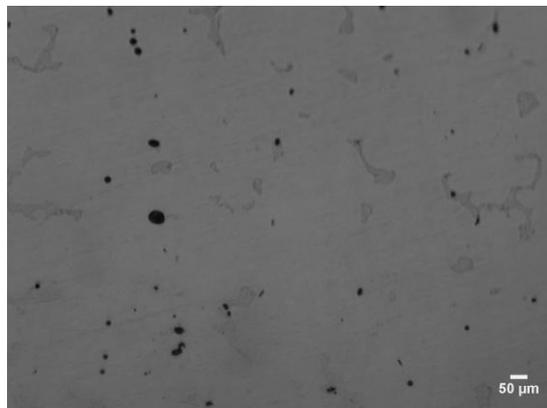

Fig. 04 - Ni-Cr-Mo alloy in point A

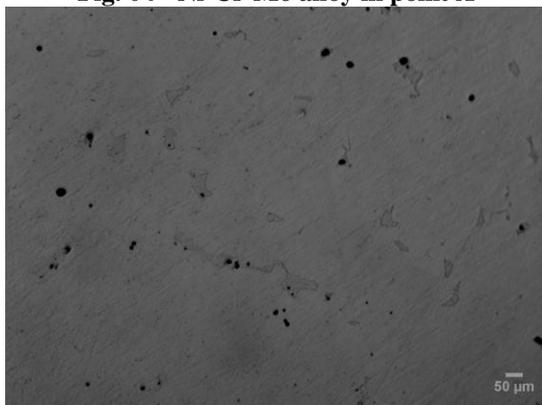
Fig. 05 - Ni-Cr-Mo alloy in point B

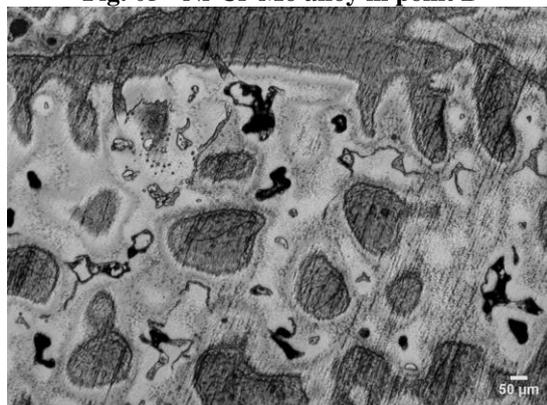**Fig. 06 - Ni-Cr-Mo alloy in point C**

Fig. 07 - Ni-Cr-Mo alloy in point D

In micrograph corresponding to point A (Figure 04) it is observed the appearance of particles with the homogeneous phase. At point B (Figure 05) it is observed a slight increase in particulates in relation to homogeneous area. Point C (Figure 06) is similar to the micrograph before the test indicating that there was no apparent corrosion. The dissolution process after the break potential is clearly revealed at point D, Figure 07, with intergranular corrosion characteristics and preferential dissolution of region with the lowest Mo content, as measured by EDS. This image is similar to that obtained on the alloy surface after electrolytic revelation with HCl 20%, showing Mo-rich phases at the grain boundaries, Figure 8.

Micrograph obtained by Scanning Electron Microscopy (SEM) in this region is displayed in Figure 08, showing formation of two phases: principal and the grain boundary. The principal, also known as homogeneous is constituted by a solid solution of Ni-Cr-Mo which still maintains a dendritic structural character; at the grain

boundary it is observed clusters, probably consisting of Cr and Mo carbides. The Ni-Cr alloys are austenitic from solidification up to room temperature, showing no phase transformations [21].
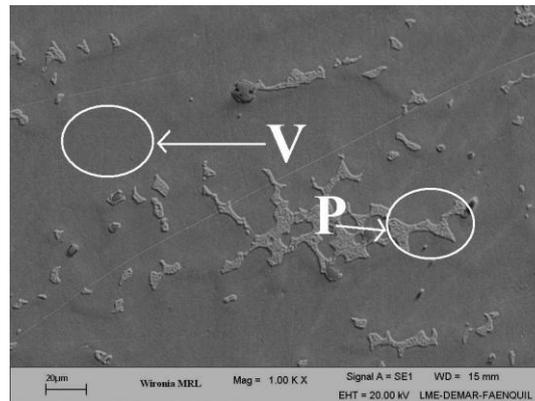

Fig. 08 - Photomicrograph of Wironia alloy with a magnification of 1000x

In Figure 8, it is shown regions analyzed by Energy Dispersive Spectroscopy (EDS). In region P (precipitated region), it is observed an enrichment in Mo content in relation to region V (homogeneous phase). Ni and Cr content is higher in region V in relation to P, as seen in Table 3.

Table 3. EDS alloy Wironia (% mass)

V			P		
Ni	Cr	Mo	Ni	Cr	Mo
65.85	25.07	9.08	57.63	22.26	20.12

3.2 Discussion

The corrosion process appears to initiate in the anodic region onset with selective dissolution, Figure 12 – point A, then passivation occurs which reduces this process by forming a film probably from a oxides and hydroxides mixture [20,22], which is a very thin film without interfering in the micrograph as shown in Figure 13.

The process is accelerated in potential above the point B (Figure 13) where transpassivation occurs, consisting, in this case, in the oxide layer breakdown.

The result of selective dissolution, as shown in point D (Fig. 15) by means of EDS obtained for points V and P (Figure 17), displays that precipitates are mainly Cr and Mo carbides, with the highest level for Mo.

It is during the cast alloy solidification that formation of metal carbides takes place [23]. The facility of carbon reaction with other metal elements results in formation of a variety of carbides type MC, M_6C e $M_{23}C_6$, M being represented by several metallic elements [23-26].

The globular shaped carbides are predominantly of variety M_6C [24], similar to globular phases found within dendrites of recast alloys. These carbides are characterized largely by Mo, although other elements with different densities, such as Cr and Ni, can replace them by improving the mechanical strength of matrix, already determined by alloying elements presence, mainly Cr. The primary matrix (dendrites) is rich in Ni, nevertheless other elements in smaller proportions, such as Cr and Mo, are also present. Silicon, niobium and aluminum can also are part of the primary matrix, when present in the composition [23].

Because they are the final stages of the alloy that solidify [24], the carbides are located predominantly in the interdendritic phase, and this region they seem to be fully responsible for the hardness and mechanical strength [24,27], appearing to be particularly important in abrasion resistance [28]. Carbides which are predominant in interdendritic region are of type $M_{23}C_6$, irregularly shaped, being M represented by Cr, mainly, but with possible contributions of Mo and other elements, if present [23-26]. According to BARAN [23], the interdendritic structure of Ni alloys is rich in Cr, Mo and in a lesser extent, Ni. This being so, the typical carbides phases, with irregular shapes, which are present in the interdendritic region of the alloy are possibly carbides of variety $M_{23}C_6$.

It is known that the latent heat, released by the initial solidification, rises the temperature in the vicinities of solidification areas, and this condition becomes favorable to dendritic growth, resulting in grains called columnar grains. In the grain boundaries region, many impurities can be found; moreover it is easily damaged by chemicals [29].

Presence of high levels of Cr (~ 21%) and Mo (~ 10%) in Wironia alloy promote the formation of a passive surface film that results in immunity to pitting corrosion, which is not the case with other alloys with lower levels of these elements [20].

The corrosive behavior of Ni-Cr-Mo based alloys was studied in acid medium [22], and was hypothesized that a higher amount of molybdenum content in the alloy increases the corrosion resistance, for alloys containing chromium, nickel and molybdenum were resistant to corrosion. The passive layer composition, containing $Ni(OH)_2$, NiO, Cr_2O_3 e MoO_3, is responsible for such behavior of these alloys. Thus, it is pointed out that alloys containing at least 16-22% chromium and 9-14% molybdenum can form a passive oxide layer more stable by forming Cr_2O_3 e $Cr(OH)_3$, which protect ten times more than NiO e $Ni(OH)_2$ [20]. However, the presence of 14% chromium in the alloy has no significant effect in improving its behavior, even if a content of 8% molybdenum, high according to the author, is present. Finally, it is concluded from this study that the corrosion resistance of the alloy is related to the passive layer that is formed on surface and this depends on the chemical composition of the alloy [30].

Pimenta [31] in his study revealed for the base metal the significant presence of Mn and Al, detected by energy dispersion spectroscopy. The possible presence of C was considered due to micrograph aspects obtained. The elements Mn, Al and C are not included in the information provided by the manufacturer about the chemical composition of the used alloy, but it is known that small amounts of carbon are already significant for formation of carbides in nickel alloys.

In 2002, Wataha emphasized the influence of grains and microstructure size on the physical properties and in corrosion of alloys. The alloy cooling rate during casting interferes in the crystallization way and the resulting microstructure of the material. The microstructure affects the corrosion, which is related to biocompatibility. Thus, the casting method can indirectly affect the biological properties of metal alloys, nonetheless there are no reports in the literature that demonstrate this relationship [32].

IV.   CONCLUSIONS

The microstructure of the recast alloys has partly dendritic character with the appearance of clusters, probably consisting of carbides of Cr and Mo. The corrosion process involves preferential dissolution of Ni-rich regions and a lower Mo content. There is no evidence of pitting corrosion in the conditions studied for this alloy.

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