THE ALLOYING INFLUENCE ON CORROSION BEHAVIOUR
OF CHROMIUM SURGICAL ALLOYS

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The aim of this study was to present the corrosion behavior of two alloys (CrCo and CrNi) in artificial biofluids. The electrochemical behavior of chromium alloys was investigated by electrochemical means in artificial biofluids. Open circuit potentials, potentiodynamic curves, polarization resistance and impedance spectroscopy are the electrochemical procedures selected for this work. Especially the passivity characteristics (active-passive transition, passivity potential, critical current density and passivity current density, pitting potential) were obtained for two alloys in the absence and presence of 3% sodium chloride solution.

INTRODUCTION

Chromium–Cobalt (CrCo) and Chromium-Nickel (CrNi) alloys belong to a class of engineering materials that are utilized in various practical applications because of their excellent combination of mechanical and corrosion properties. Because of their good biocompatibility they are used as surgical implants or dental resistant materials. CrCo and CrNi alloys have advantages over other alloys such as higher strength, satisfactory hardness and ductility, good resistance to general and localized corrosion.

It is accepted that the passive films formed on many transition metals (Fe, Cr, Ni, Co etc.) and alloys are responsible for their excellent corrosion resistance in a variety of aqueous solutions.

Numerous investigations have been carried out to define the structural, chemical and electrochemical properties of passive films.[1-5] Among these, the polymeric hydrated oxide model of passivity implies a significant role of water in the structure and stability of the passive film. Thus the water molecules are incorporated in the metal films where metal atoms are connected via hydroxo and oxo bonds. [6, 7]

The behavior of CrCo and CrNi with respect to the passive (oxide) film formation is more complicated than that of Nickel, Cobalt or Chromium metals because of the effect that the alloying elements exert on the films. [8,9]

The goal of this work is to determine the electrochemical behavior of the CrCo and CrNi alloys, especially the formation and stability of the passive films in lactic acid (racemic α oxipropionic acid, CH_3-CH (OH)-COOH) solutions in the absence and presence of 3% sodium chloride solution.

These corrosive media were chosen because lactic acid is a principal metabolic product in muscular tissues and consequently is the principal corrosion agent towards the metallic surgical implants, and thus it is recommended as a standard synthetic biofluid for implant corrosion tests.[10]

EXPERIMENTAL

Two chromium alloys were used as the materials for this investigation. The chemical composition of these alloys is given in Table 1.

The samples were obtained from a laboratory casting materials. The sample's surface was prepared by mechanical polishing with emery paper and silica powder and finally rinsed with distilled water and ultrasonically cleaned in izprolilic alcohol and finally dried in argon.

The electrochemical experiments were carried out using Gamry computerized equipment, in a conventional three electrode glass cell provided with a saturated Hg/Hg_2Cl_2//KCl, and a platinum electrode as reference and auxiliary electrodes respectively.

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Table 1

Chemical composition of casting chromium alloys (% weight)

No.	Cr, %	Mo, %	Fe, %	Si, %	Mn, %	Ti, %	Ni, %	Co, %
1.	19.17	5.15	2.06	2.09	1.53	0.33	Base	-
2.	27.97	4.23	-	0.92	0.6	0.42	-	Base

Corrosion potential–time measurements were performed during 168 hours (7 days) of exposure according to static immersion method, in lactic acid 0.1 M and sodium chloride 0.1 M solution (artificial biofluid), at pH=2.3 and 37.2°C. Simultaneously, weight loss of the samples was measured and at the end of the exposure time by AAS analytical methods.

Potentiodynamic polarization was performed in the potential range from -1000mV to +1000mV, with a scan rate of 150mVmin[-1] for electrochemical and corrosion parameters measurements, in the potential range from OCP to +1000 mV and scan rate of 15mVmin[-1] for pitting corrosion.

Electrochemical Impedance Spectroscopy measurements were carried out in the frequency range from 100 KHz to 0.01Hz at zero, at the different time of exposure in corroding media.

RESULTS AND DISCUSSION

1. Open Circuit Potential (OCP) measurements

OCP is a mixt potential associated with redox reaction occurring on an alloy surface, and the metals dissolution in the electrolyte solutions.

For a given electrolyte solution chemistry the OCP is dependent on the surface oxide nature, such as oxide thickness, composition, conductivity, structure e.a. Also, a change in the electrocatalytic nature of the surface associated with the chemical composition of the oxide layers can play a significant role in the OCP behavior of alloys.

Fig. 1 shows the OCP behavior of a CrCo alloy exposed for 8000 minutes in 0.1M (pH=2) lactic acid without (a) and with (b) NaCl solution at 37.2° and natural aeration conditions.

The time response of OCP of CrCo alloy in this environment shows for both electrolytic solutions an initial rapid (2000minutes) increase of OCP from −100mV/sce to +100mV/sce followed by a slow and monotonous increase in the next 6000 minutes from 100mV/sce to 150mV/sce.

This OCP response in studied electrolyte solutions indicates that the initial existing (air formed) passive film is slightly growing under aeration condition up to a steady state thickness which could block the aggressiveness of the electrolyte solution.

The presence of chloride ions, Cl⁻, produces not only slight oscillations of OCP. These OCP oscillations may result from slight chemical interactions between Cl⁻ and the structured passive film which are unable to produce anion penetration and consequently no local dissolution of the film.[11]

Fig. 2 shows the OCP response of CrNi alloy exposed in the same conditions as CrCo alloy. The time response of OCP shows an oscillation variation from 20mV/sce to − 150mV/sce. The time evolution of OCP in lactic acid condition indicates that the passive film is thinning and consequently became vulnerable toward anion penetration of Cl⁻ ions. This behavior of both CrCo and CrNi alloys shows that the slight increase in OCP of CrCo alloy and slight decrease in OCP of CrNi alloy depend strongly on chromium content of the alloy.
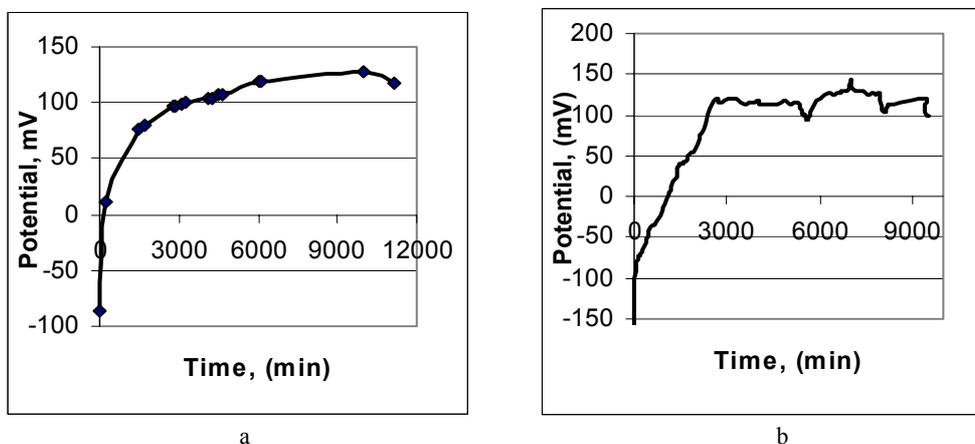

a

b

Fig. 1 – The OCP versus time evolution of a CrCo alloy in 0.1 M lactic acid without (a)
and with (b) NaCl solution at 37.2°C and natural aeration conditions.

Because of this, the CrCo alloy passive film is more stable and more corrosion resistant than CrNi alloy is, in given corrosive biofluids.
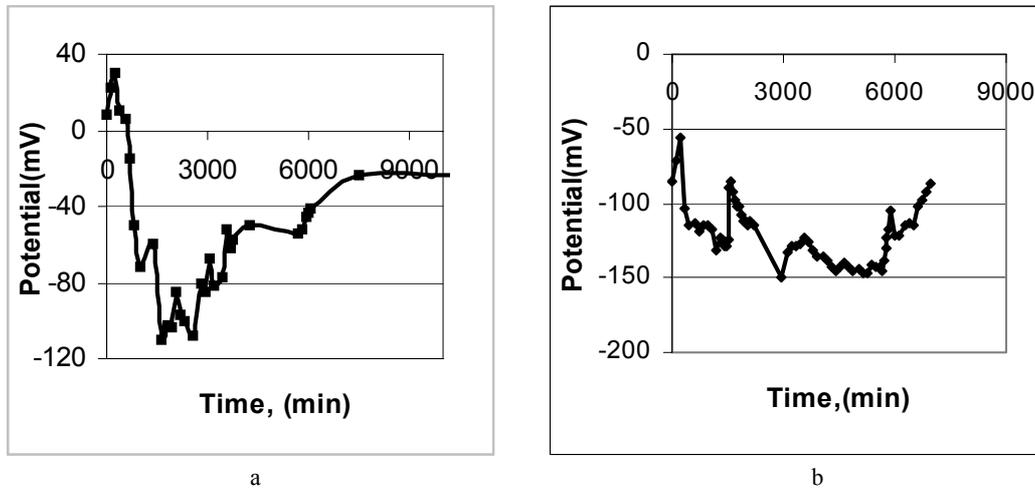

a

b

Fig. 2 – The OCP versus time evolution of a Cr Ni alloy in 0.1M lactic acid without (a)
and with (b) NaCl solution at 37,2°C and natural aeration conditions.

2. Potentiodynamic Polarization

Figs. 3 and 4 present the potentiodynamic polarization curves obtained on CrCo and CrNi in lactic acid with and without the addition of NaCl.

All polarization curves present cathodic and anodic regions. Cathodic curves present cathodic Tafel slope for primary cathodic reaction at pH=2. This reaction is a charge transfer controlled H^+ reduction. All the anodic curves exhibit an apparent active region and a potential independent plateau indicating the existence of an oxide layer on the electrode surface. An abrupt current rise at about +0.7V/sce is correlated with the transpassive behavior.

Table 2 lists corrosion potential ε_{corr} and the electrochemical parameters b_a and b_c, both determined from polarization curves, i_{corr}, and R_p.

The corrosion current density i_{corr} at OCP was obtained from Stern -Geary relation:[12]

$$i_{corr} = \frac{b_a b_c}{2.3(b_a + b_c)R_p} = \frac{B}{R_p} \qquad (1)$$

were b_a and b_c are anode and cathode Tafel coefficients and B is a constant.

a

b
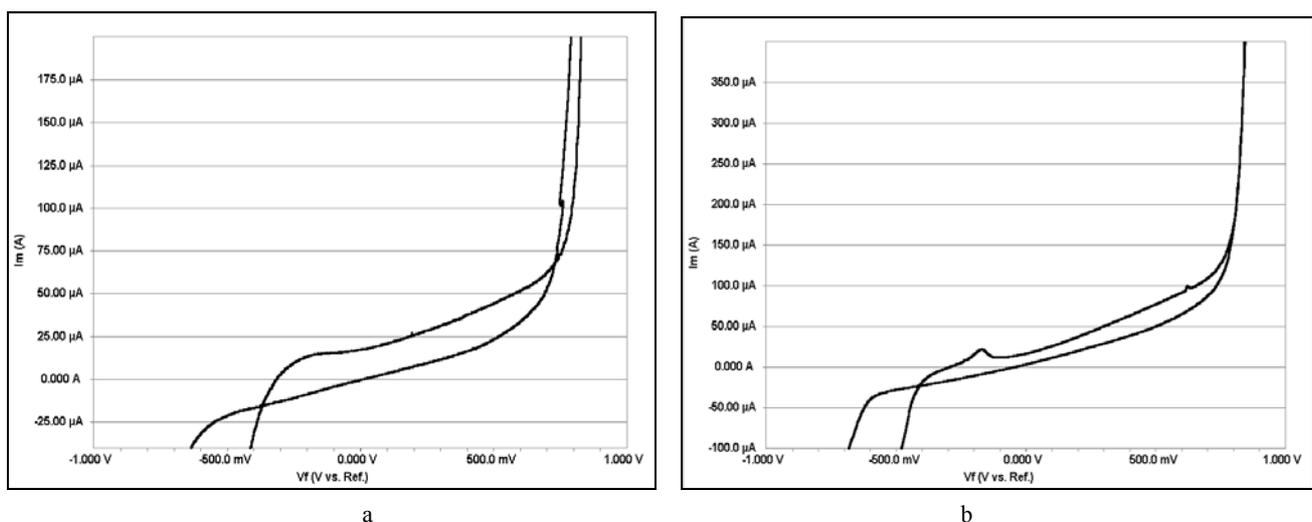
Fig. 3 – The polarization curve of CrCo alloy in 0.1M lactic acid without (a) and with (b) NaCl solution at 37,2°C
and natural aeration conditions.

a   b
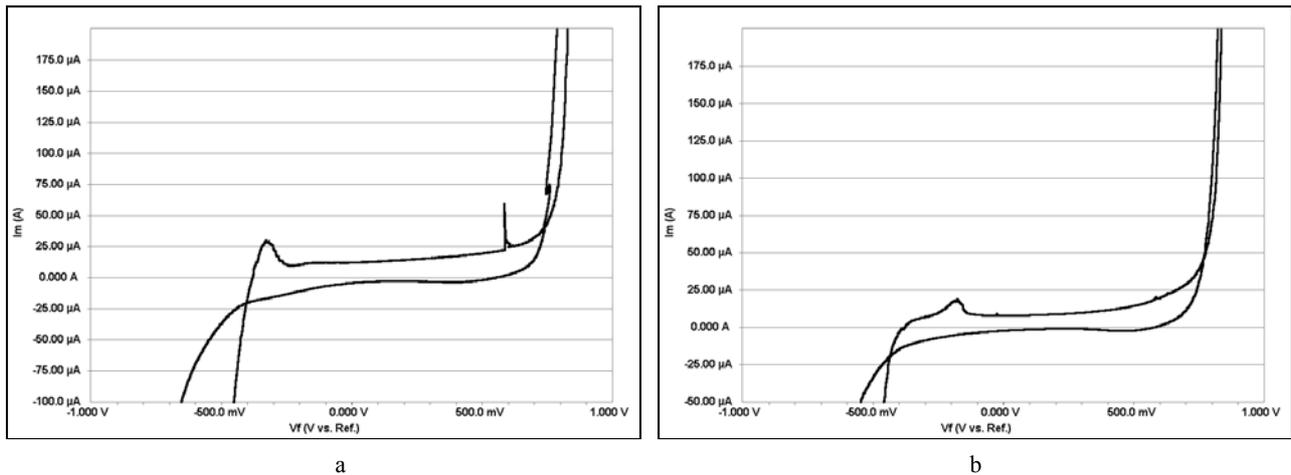
Fig. 4 – The polarization curve of CrNi alloy in 0.1M lactic acid without (a) and with (b) NaCl solution at 37,2°C
and natural aeration conditions.

Owing to the linear behavior of the current - potential curves in the vicinity of ε_{corr} ($\pm$ 10mV), R_p values were determined from DC measurements in a region of $\pm$ 10mV around ε_{corr}.

Table 2

The main electrochemical and corrosion parameters of CrCo and CrNi alloys in 0.1M lactic acid without (a) and with (b) NaCl solution at 37,2° and natural aeration conditions

alloy	solution	ε_{corr}, mV/esc	b_a mV/dec	b_c mV/dec	i_{corr} μAcm^{-2}	R_p KΩcm^{-2}		v_{corr}R μm/y	v_{corr}AA gm^{-2}h
						R_{p1}	R_{p2}		
Cr-Co	LA +NaCl	-473	-	120	3.1	5.3	5.5	55	0.048
	LA	-417	-	160	14.2	4.6	8	81.5	-
Cr-Ni	LA +NaCl	-380	-	118	3.1	4	3	90	0.06
	LA	-383	-	0.05	12.5	1	2	330	-

Where: LA is lactic acid solution and LA +NaCl is lactic acid solution with NaCl;
v_{corr}T is corrosion rate calculated from Tafel slopes;
v_{corr}R is corrosion rate calculated from polarization resistance Mansfeld methode.
v_{corr}AA is corrosion rate calculated from electrolyte analysis by atomic absorption method;
R_{p1} from Rp measurements
R_{p2} from EIS mesaurements

Accordingly, R_p is defined [13-15]as the tangent of a polarization curve at $\varepsilon = \varepsilon_{corr} \pm 15$mV:

$$R_p = \left(\frac{d\varepsilon}{di} \right)_{\varepsilon = \varepsilon_{corr}} \qquad (2)$$

The experimental values of Rp are prezented too in Table 2. The b_c was controlled by reduction of H$^+$ and O$_2$ with an average value of b_a has a very high value consistent with an anodic control of electrochemical process because of formation and increase of the thickness of passive film.

The corrosion rate v_{corr} μm/y or m (mm/y) was obtained for en equation based on Faraday's law:

$$v_{corr} = K \frac{i_{corr}W}{\rho F} \qquad (3)$$

Where: W is equivalent weight, ρ is alloy density; F is Faraday's constant and K is a conversion factor.

In the case of the anodic polarization curve of CrNi alloy in lactic acid with sodium chloride solution, at polarization rate 15mV/min, (fig.5 b, curve1) the abrupt current rise at about –0.2V/sce is correlated with a breakdown of the passive film (starting pitting corrosion). This behavior may by correlated with the metalographic analysis of the surface after polarization, which indicate the pitting corrosion of CrNi alloy (Fig. 6b) and no pitting corrosion on surface of CrCo alloy, (Fig 6a), in similar condition of immersion test.
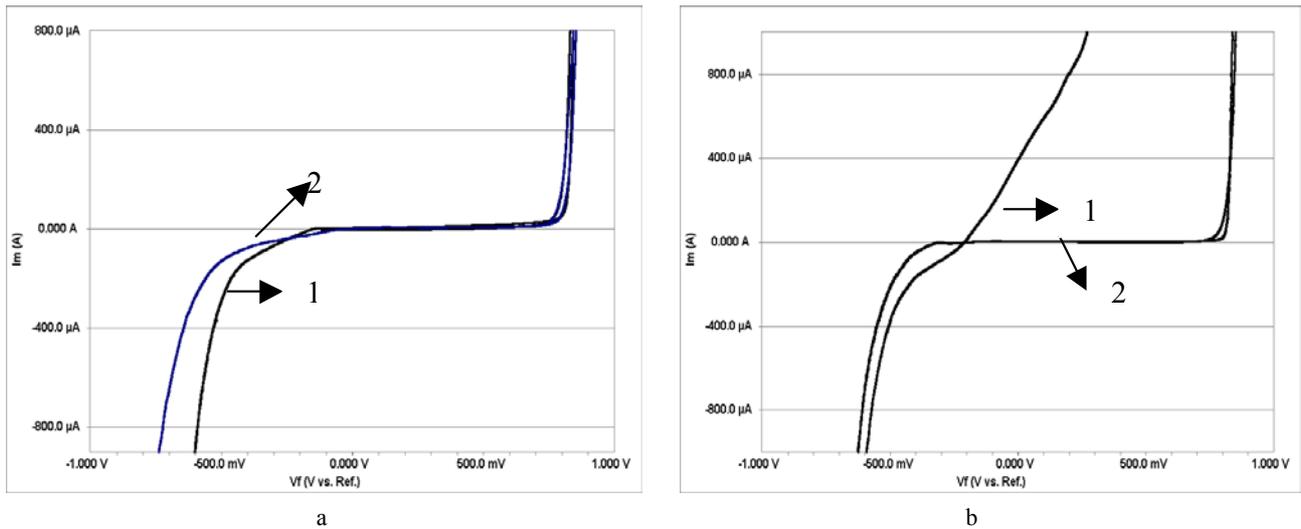
Fig. 5 – The polarization curves at 15 mV/min for both alloys (a-CrCo alloy and b CrNi alloy) in 0.1M lactic acid with NaCl curves 1 and without NaCl curves 2 solution at 37.2°C and natural aeration conditions.
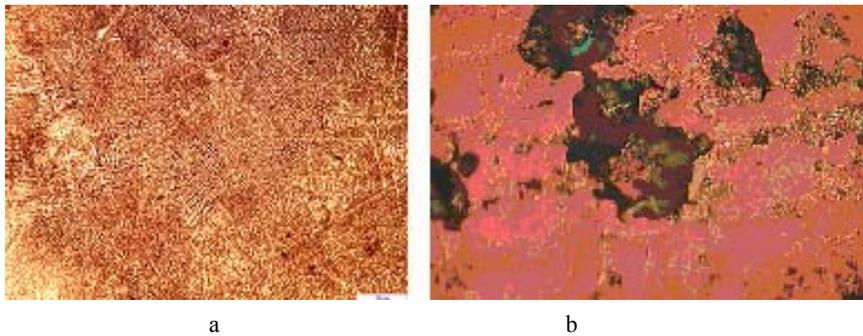

Fig. 6 – The aspects of the sample's surface after 168 hours in lactic acid with sodium chloride
a) CrCo alloy and b) CrNi alloy.

3. EIS measurements

Some of the impedance diagrams, obtained for CrCo and CrNi alloys at different potential and time exposure are shown in the Figs. 7 and 8. Shapes of the impedance diagrams depended strongly on potential. Diagrams were selected at characteristic regions in such a way to depict clearly the changes of the impedance by changing potential.
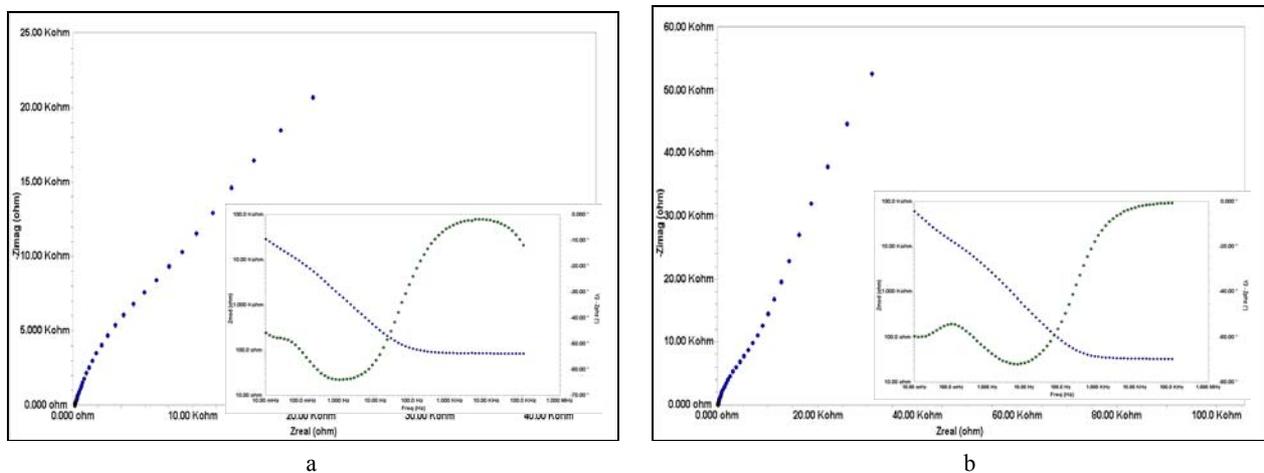

Fig. 7 – The Electrochemical Impedance Spectra of CrCo alloy at different potential values: a) -0.108V/sce in lactic acid without chlorine; b) +0.103V/sce in lactic acid with chlorine.
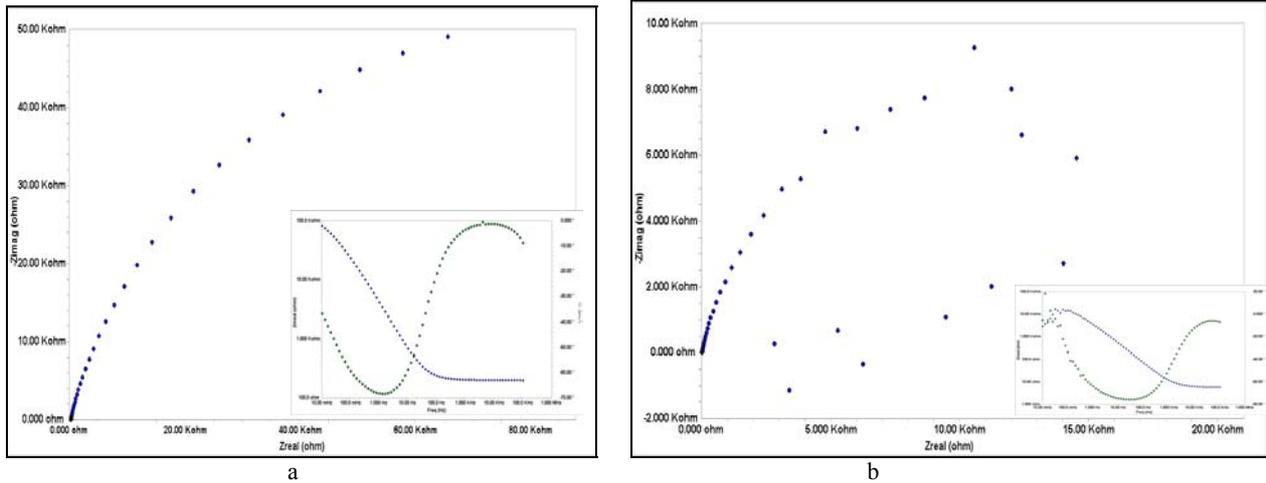
Fig. 8 – The Electrochemical Impedance Spectra of CrNi alloy at different potential values:
a) 0.028V/sce in lactic acid without chlorine b) 0 V/sce in lactic acid with chloride.

In the potential range –0.3V/sce and 0.8V/sce the impedance spectra are described with the circuit equivalent to two resistance–constant phase element (CPE) series combinations, Fig. 9.[16]
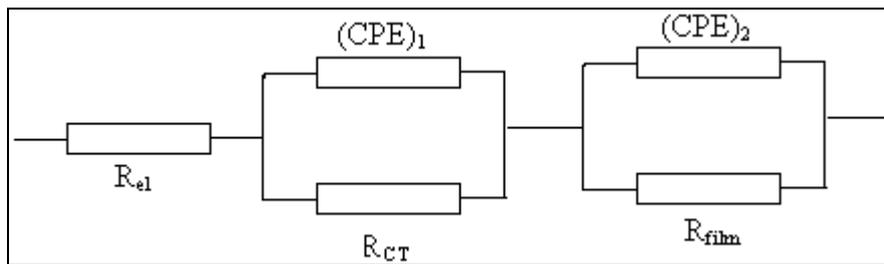

Fig. 9 – Equivalent circuit.

CPE is represented by

$$Z = \frac{1}{\left(C_{CT}[i\omega]\right)^n} \qquad (4)$$

Where: Z is complex impedance Ωcm^{-2}; $i = \sqrt{-1}$; ω is frequency (Hz); n is CPE exponent. Depending on n, CPE can represent resistance (n=0, CPE=R); capacitance (n=1, CPE =C); inductance (n=-1, CPE =L) or Warburg impedance (n=0.5, CPE=W).

The Nyquist and Bode plots shown in Fig. 7 are characteristic for the full passive range of CrCo alloy in lactic acid without (a) and with chloride addition (b).

The Nyquist and Bode plots for CrNi alloy in lactic acid without chloride (Fig. 8a) is characteristic for passive surface. Fig. 8b presents impedance plots, which show that some faradaic processes became more evident as result of interaction of chloride ions with passive film (dissolution of nickel and chromium oxide in the film with pits formation). Similar plots were obtained by different authors for pitting corrosion.[17]

Such behavior either could be the results of two thinner oxides or an oxide with a greater dielectric constant. Also the oxide may grow in thickness but becomes increasingly hydrated and porous.

Impedance measurements are only meaningful when the system satisfies the criteria of linearity, causality and stability. In our media this goal is difficult to be satisfied. However, EIS data compare satisfactory with the Tafel plots, weight loss and polarization resistance measurements as is presented in Table 2.

CONCLUSIONS

The electrochemical characterization of the two samples of CrCo and CrNi alloys agrees with the compositional and structural characterization.

Open circuit results showed an increase of ε_{corr} toward positive values for CrCo alloy, and decrease of ε_{corr} for CrNi alloy. This behavior is

associated with good passivity properties for CrCo (27%Cr) alloy in both corroding media and a difficult passivation for CrNi (17%Cr) alloy.

Potentiodynamic polarization curves reveal the same behavior as OCP, i.e. a large passive range in both corroding media for CrCo alloy and a pitting corrosion for CrNi alloy in chloride solution.

The equivalent circuit that best fits the EIS plots is the same two terms circuit for the CrCo and CrNi alloys. The major difference and difficulties are found in the phenomenological interpretation of the circuit of both alloys. The capacitance and resistance components of CrNi alloy in the presence of chloride ions can be attributed to the presence of the chloride ions in the pores of the passive film and so, the pitting corrosion of the surface of the alloy.

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