A COMPARATIVE STUDY OF THE CORROSION RESISTANCE OF INCOLOY MA 956 AND PM 2000 SUPERALLOYS

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Abstract

Austenitic stainless steels, titanium or cobalt alloys are widely used as biomaterials. However, new medical devices require innovative materials with specific properties, depending on their application. The magnetic properties are among the properties of interest for some biomedical applications. However, due to the interaction of magnetic materials with Magnetic Resonance Image (MRI) equipments they might used only as not fixed implants or for medical devices. The ferromagnetic superalloys, Incoloy MA 956 and PM 2000, produced by mechanical alloying, have similar chemical composition, high corrosion resistance and are used in high temperature applications. In this study, the corrosion resistance of these two ferritic superalloys was compared in a phosphate buffer solution (PBS). The electrochemical results showed that both superalloys are passive in this solution and the PM 2000 present a more protective passive film on it associated to higher impedances than the MA 956.

Keywords: biomaterials, corrosion, Incoloy MA 956, PM 2000.

INTRODUCTION

Metallic materials are widely used in dental implants, orthodontic appliances as bands, arch wires, ligature wires, hooks, tubes, brackets and springs, and orthopedic devices as implants and prosthesis for fractured bones healing.[1] However, the use of ferromagnetic alloys in orthopedic area is undesirable due to the size of the implant,[2,3] that can move or heat during MRI tests.[4] Most of these equipments generate magnetic fields of 1,5 T, but some achieves 3 T, or 50.000 times the magnetic field of the Earth.[3] It was proven that small devices, as dental implants and dental prosthesis attachments, are not affected by MRI tests.[5,6]

Both superalloys, Incoloy MA 956 and PM 2000, are produced by mechanical alloying followed by hot extrusion. They have similar chemical compositions, but the literature shows differences in their kinetic oxidation and the oxide particles morphology, comparing samples heat treated at 1100 °C for 100 h. The authors attributed these differences to the aluminum amount in these alloys, as the PM 2000 has a larger Al concentration (1 % wt) than the Incoloy MA 956.[7]

Previous researches concluded that the Incoloy MA 956 has outstanding properties for applications as biomaterial.[8-10] The aluminum oxide layer formed at the outer porous layer, favours osseointegration. Besides, the yttrium oxide improves the superalloy corrosion resistance.[11]

Recently, the PM 2000 has also been investigated for biomaterials applications, and its biocompatibility has already been reported.[12,13] Its mechanical[14] and magnetic properties have also been investigated.[15]

MATERIALS AND METHODS

The superalloys investigated in the present study were produced by mechanical alloying and their chemical composition is shown in Table 1.

Table 1. Chemical composition (wt %) of Incoloy MA 956 and PM 2000.

	C	Cr	Ni	Mo	Si	Mn	Al	Y	Ti	Fe
PM 2000	-	22.01	0.08	0.31	-	0.12	5.59	0.50	0.56	Bal.
Incoloy MA 956	0.02	21.26	0.09	0.16	0,07	0.14	4.61	0.42	0.39	Bal.

Samples with 0.90 cm² were cut from a transversal section of extruded cylindrical bars (d = 30 mm) of the Incoloy MA 956. The PM 2000 samples were taken from a transversal section of extruded cylindrical bars (d = 5 mm). The area of the samples was 0.196 cm².

All the samples were ground with silicon carbide paper up to #4000, then rinsed with deionised water and immersed in PBS solution at 25 °C, whose composition is shown in Table 2. The electrochemical tests were performed using a three-electrode cell set-up, with a platinum wire and a saturated calomel electrode (SCE) as counter and reference electrodes, respectively. Electrochemical impedance spectroscopy (EIS) measurements were accomplished using a 1255 Solartron frequency response analyzer coupled to an EG&G 273A potentiostat. All EIS measurements were obtained in the potentiostatic mode at the stabilized open circuit potential after 48 hours of immersion. The amplitude of the sinusoidal signal was 10 mV (rms) and the investigated frequency was from 100 kHz to 10 mHz, with an acquisition rate of 6 points per decade. After the EIS tests, potentiodynamic polarization measurements were obtained in the range from the open circuit potential (OCP) up to 1200 mV at a scan rate of 1 mVs^{-1}. After polarization tests, the tested surface was analyzed by scanning electron microscopy (SEM) using a Philips XL30 microscope.

Table 2 - Chemical composition (g L^{-1}) of the phosphate buffer solution (PBS).

NaCl	Na_2PO_4	KH_2PO_4
8.77	1.42	2.72

RESULTS AND DISCUSSION

The EIS results of both tested alloys after 48h immersion in PBS are shown in Figure 1. Impedance values around 10^5 Ω.cm² were obtained at 0.01 Hz. for both alloys with slightly higher impedances associated to the PM 2000 alloy. The phase angle diagrams indicate two time constants, one at high frequencies (order of 10^2 Hz) and another at medium frequencies (around 1 Hz) likely associated to the duplex nature of the oxide passive film.

The EIS diagrams were fitted using two equivalent electric circuits shown in Figure 2 a and b. According to literature, the proposed model in Figure 2a represents the Incoloy MA 956 immersed in Hanks solution and characterizes a passive system.[16,17] These results indicate one time constant due to the alumina layer.[9] However, X-ray photoelectron spectroscopy (XPS) results of as received Incoloy MA 956 show a duplex oxide layer, rich in chromium (inner layer) and iron (outer layer), with little amounts of alumina and without titanium or yttrium oxides . [18]

Figure 2b shows the another electric equivalent circuit that presented better fitting to the experimental results of both tested alloys than the previous circuit (Figure 2a). This circuit indicates represents the duplex nature of the oxide layer on the alloys surface.[19,20] The literature[21,22] reports this circuit as consequence of a duplex oxide layer, being the inner one rich in chromium and the outer one, in iron and nickel.

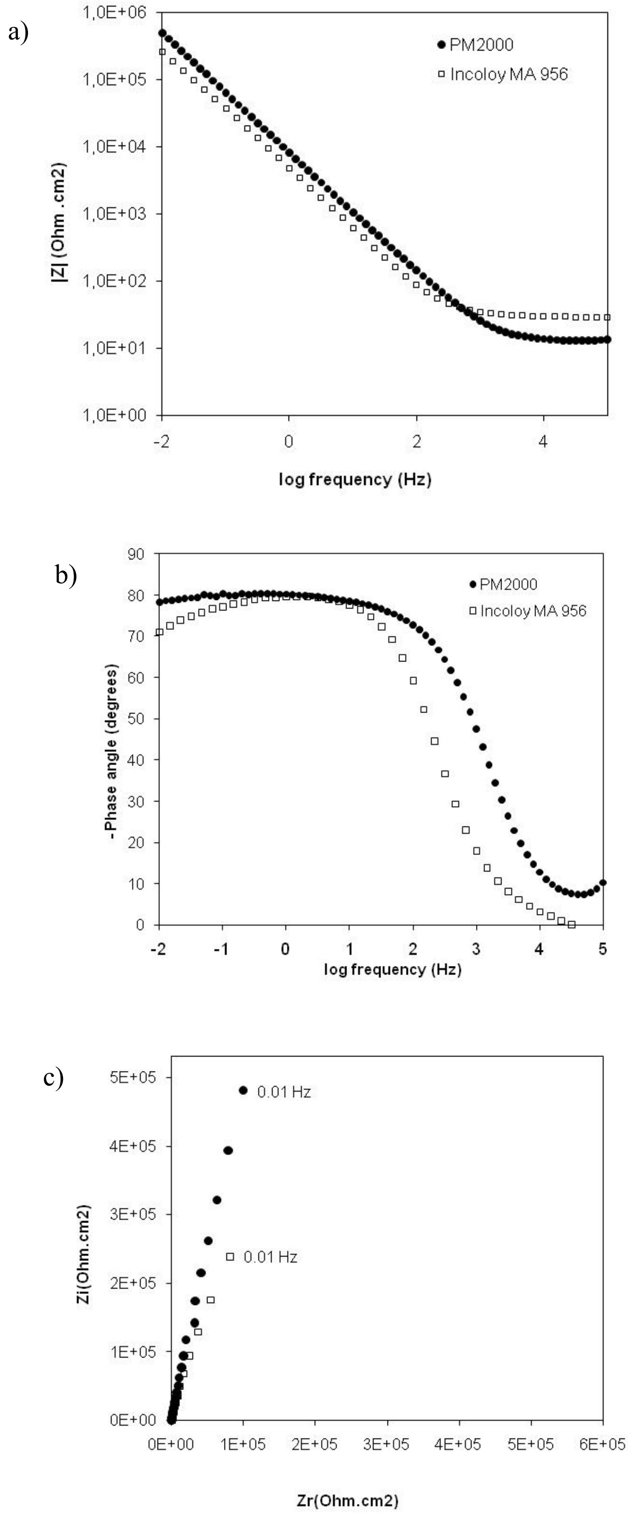

Figure 1: EIS diagrams obtained for the Incoloy MA 956 and the PM 2000 after 48 h of immersion in PBS at 25 °C. a) Z modulus; b) phase angle and c) Nyquist diagrams.

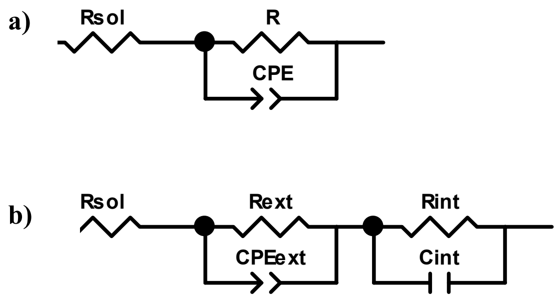

Figure 2: Equivalent electric circuits used to fit the EIS results of MA 956 and PM 2000 alloys. [22-26]

The circuit components values are presented in Table 3. It shows that the external oxide layer resistance on PM 2000 is four times higher than that of the Incoloy MA 956. It also shows that the inner layer is mainly accountable for corrosion resistance in both materials, and the resistance of the inner layer on the PM 2000 is eight times higher than that on the Incoloy MA 956.

Table 3. Comparison of the values of the components of the equivalent electric circuit associated to Figure 2b, for Incoloy MA 956 and the PM 2000 alloys in PBS solution.

	PM 2000	Incoloy MA 956
R_{sol} ($\Omega.cm^2$)	12.53	16.75
CPE_{ext} (F $cm^{-2}s^{-n}$)	$6.52x10^{-5}$	$1.74x10^{-4}$
R_{ext} ($\Omega.cm^2$)	$7.08x10^{4}$	$1.90x10^{4}$
n	0.79	0.82
C_{int} (F $cm^{-2}s^{-1}$)	$3.44x10^{-5}$	$1.10x10^{-4}$
R_{int}($\Omega.cm^2$)	$4.54x10^{6}$	$5.52x10^{5}$

The potentiodynamic polarization curves obtained for both studied alloys are shown in Figure 3. These curves reveal that lower current densities, higher corrosion potentials and higher oxide film breakdown potentials were associated to the PM 2000 comparatively to the Incoloy MA 956. Both tested alloys, however, presented breakdown potentials around 1.1 V_{SCE}, and the current density increase at this potential could indicate oxygen evolution instead of pitting. The samples were analyzed by scanning electron microscopy (SEM) after anodic polarization tests to investigate the presence of pits. Figure 4 shows the surfaces of both polarized alloys were found.

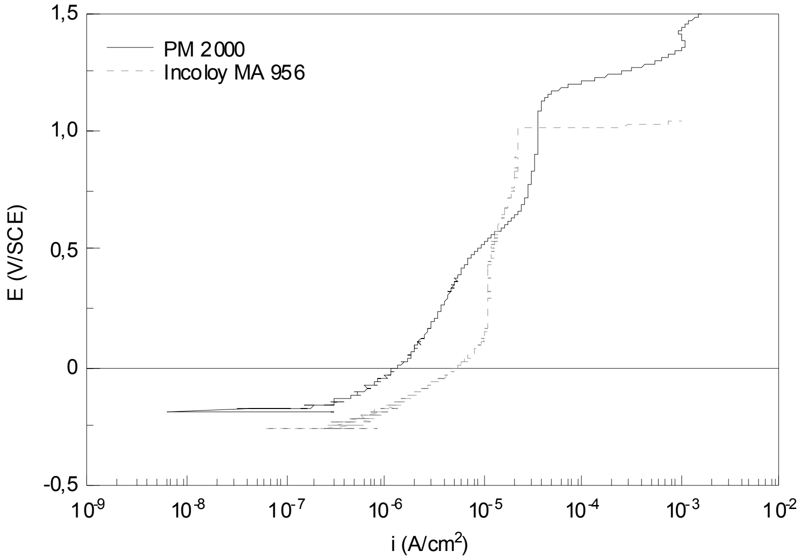

Figure 3: Potentiodynamic polarization curves for Incoloy MA 956 and PM 2000 obtained after 48 h of immersion in PBS solution.

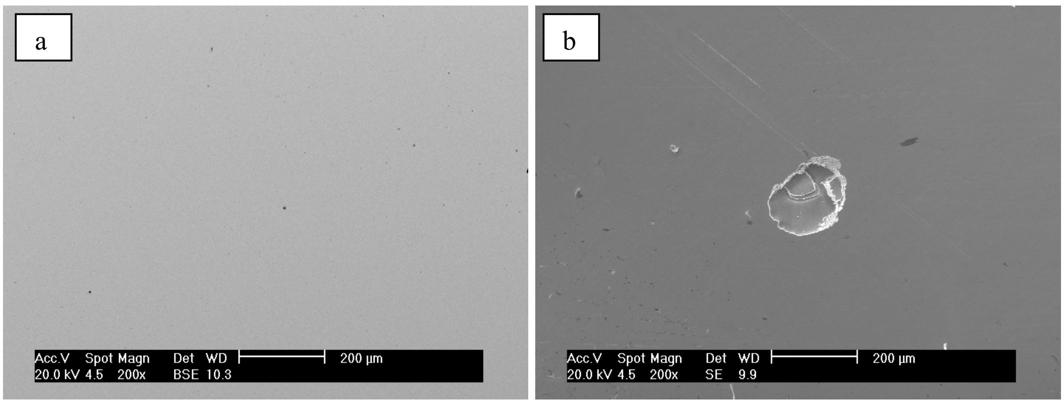

Figure 4: SEM micrographs of surface of the superalloys investigated after polarization tests. (a) PM 2000 and (b) MA956, showing pits on the surface of the tested samples.

The PM 2000 revealed a large number of very small pits (d < 2 µm) whereas the on the Incoloy MA 956 surface only one pit was seen, but it was about one hundred times larger than the pits on the PM 2000. The singularity of only one pit on the Incoloy MA 956 cannot be associated to physical characteristics as porosity or microdefects, as the same situation was found in a lot of samples. Further analyzes will be necessary to understand this process.

CONCLUSIONS

The electrochemical tests and surface observation after polarization tests showed that the passive film on the PM 2000 alloy is more resistant to corrosion than the Incoloy MA 956, despite of their compositional similarities. Further investigation is necessary to evaluate whether the small difference in Al content between the two alloys (The Al content in PM 2000 is 1% (wt) higher than in the Incoloy MA 956) is the reason for this result. The electric equivalent circuit proposed suggests that both superalloys have a passive oxide film with a duplex nature, composed of an inner and more resistant layer, and an outer layer.

The potentiodynamic polarization curves show higher corrosion rates associated to the Incoloy MA 956 comparatively to the PM 2000, supporting the EIS results. Both materials presented pitting corrosion, but the pits formed on the PM 2000 were of smaller sizes (d < 2 μm) but found in larger amounts than on the Incoloy MA 956 that only showed one larger pit associated to it.

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