A comparative study of the corrosion resistance of stainless steels obtained by powder metallurgy techniques for application in dental prosthesis

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Abstract - Ferromagnetic stainless steels (SS) produced by powder metallurgy (PM) techniques have been investigated as potential candidates for dental prosthesis applications in replacement of magnetic attachments made of noble and expensive alloys. Two SS were investigated: SS 17-4 PH produced by powder injection (PIM) and SS PM2000 obtained by mechanical alloying. *In vitro* cytotoxicity analysis of the two SS showed no cytotoxic effects. The magnetic retention force of both tested SS was also evaluated and they were comparable to noble commercially available material that is in use at the moment. The corrosion resistance of both SS was evaluated by electrochemical techniques in sodium phosphate buffer solution (PBS) at 37°C. The AISI 316L SS was also tested under the same conditions for comparison reasons. SS samples tested showed passive behaviour in the electrolyte, but they also presented susceptibility to pitting. The best pitting resistance was associated to the PM2000 whereas the 17-4PH PIM showed the highest pitting susceptibility among the tested steels. The results pointed out that the PM2000 SS might be considered a potential candidate for substitution of high cost magnetic alloys used in dental prosthesis.

Introduction

Prosthesis retained by magnets play an important role in dental implants applications [1], such as dental combination prosthesis [2], and orofacial prosthesis [3]. The magnetic force necessary for retaining dental prosthesis can be obtained by the retention between a small magnet and a ferromagnetic attachment. This attachment is mainly made of noble alloys or special soft magnetic SS of high production costs.

The PM2000 (trademark of *Plansee)* is a Fe-based oxide dispersion strengthened (ODS) super alloy processed by mechanical alloying. Recently, it has been reported [4] that this alloy shows excellent corrosion resistance in physiological medium, besides of magnetic properties typical of soft magnetic materials [5]. This alloy has also been related to *in vitro* biocompatibility [5], which is relevant for applications as biomaterials.

The 17-4 PH alloy is a precipitation hardenable martensitic SS. Due to its high strength and good corrosion resistance, 17-4 PH has a wide range of applications, especially in medical, automotive, military and aircraft components. However, due to its high hardness it is difficult to be machined. Consequently, near net-shape techniques as powder injection moulding (PIM) can be very useful in fabrication of devices made of this type of SS. Many components made of 17-4 PH SS can be manufactured by powder injection, a net-shape forming process with the advantage of shape complexity and high final density. One of the possible applications is the production of orthodontics brackets [6].

The aim at evaluating the corrosion resistance and *in vitro* cytotoxicity of stainless steels with ferromagnetic properties was their potential as biomaterial.

Materials and Methods

Materials - Samples of PM2000 SS (*Plansee – Austria*) and powder injection moulded 17-4PH PIM SS (LUPATECH, *Steelinject, Caxias do Sul, Brazil*) were the materials used in this study. The corrosion resistance of these steels was evaluated by electrochemical techniques and the results compared to 316L SS chosen as a reference material, since this is the most SS for orthopaedic prosthesis. Table 1 displays the chemical composition of the PM2000, 17-4PH PIM and 316L steel used.

Table 1 - Chemical composition (mass %).

	Cr	Al	Y_2O_3	Ni	Mo	Ti	Mn	S	Cu	Fe
PM2000	22.0	5.6	0.5			0.51				bal.
17-4PH PIM	17.0			4.0				0.3	3.0	bal
AISI 316L	17.7			13.5	2.1		1.8			bal.

The corrosion resistance of the studied alloys was evaluated in naturally aerated phosphate buffered saline solution (PBS) at 37 °C and pH 7. The chemical composition of the test solution is shown in Table 2. The magnetic retention force and *in vitro* cytotoxicity were also investigated.

Table 2 – Chemical composition of phosphate buffered saline solution (PBS) (mass %)

NaCl	Na_2PO_4	KH_2PO_4
0.9	0.142	0.272

Magnetic retention force - Samples of PM2000 and 17-4PH PIM were drilled in 4 mm diameter cylinder. The magnetic retention force between tested samples and commercial dental magnet (*Dyna Dental)* was measured using an *Instron Tensile Machine* (Fig.1). Five readings were obtained for each SS. A ferromagnetic commercial noble alloy (also supplied by *Dyna Dental)* was used for comparison as a control specimen.

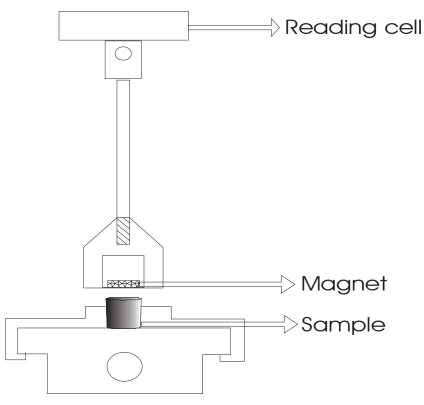

Figure 1- Magnetic traction apparatus

Cytotoxicity assay - The cytotoxicity was performed by neutral red uptake method according to ISO 10993-5 [7] where the described methodology was presented previously [8]. Mouse fibroblastic cell line NCTC L929 from ATCC bank was used.

Corrosion tests - The samples surface was prepared by grinding with silicon carbide paper up to #2000, followed by polishing with diamond paste (3 µm and 1 µm) to get a mirror surface, degreased in acetone, washed with deionised water and drying under hot air stream. All electrochemical tests were carried out in a corrosion cell, with a three-electrode arrangement. The potentiodynamic polarization tests were carried out using a 273A EG&G PAR Potentiostat. The EIS measurements were carried out with a Solartron 1260 frequency response analyzer coupled to a 273A EG&G PAR electrochemical interface. The saturated calomel electrode (SCE) was used as reference and a Pt-plate as counter electrode. The polarization curves were obtained with a scan rate of 1 mV/s. EIS measurements were performed at the open circuit potential using a 10 mV amplitude sinusoidal signal in a frequency range from 100 kHz down to10 mHz.

Results and Discussion

Magnetic retention force - The tensile strength necessary to separate the magnet and the samples is displayed in Fig. 2. The saturation magnetization is closely related to the Fe percentage of the alloy. The increase in iron content increases the saturation magnetization values. The 17-4PH PIM has an iron content of about 74 at. % and PM 2000 about 69%, which is higher than that of the reference noble alloy (64%). Due to this PM2000 (588.2 gf) and 17-4PH PIM (701.4 gf) showed better scores than the reference group (476.4 gf).

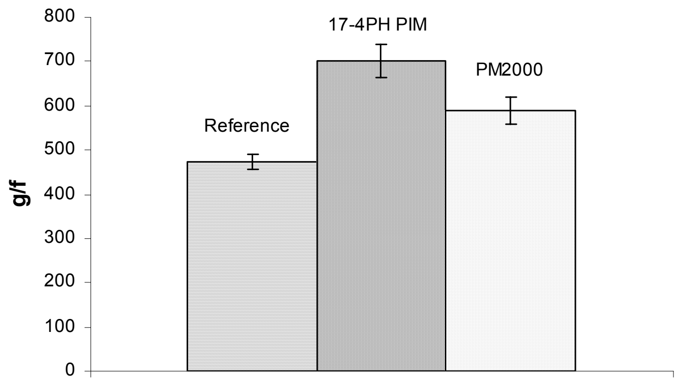

Figure 2. Magnetic retention force of 17-4PH PIM and PM2000.

Cytotoxicity assay - Cytotoxicity results (Fig. 3) showed that the PM2000 and 17-4PH presented similar behaviour to the negative control. The cell viability curves are above cytotoxicity index ($IC_{50\%}$) line which means that none of them presented cytotoxic effect in this assay. These results agree with previous ones reported in literature for 17-4PH PIM [9] and PM2000 [5].

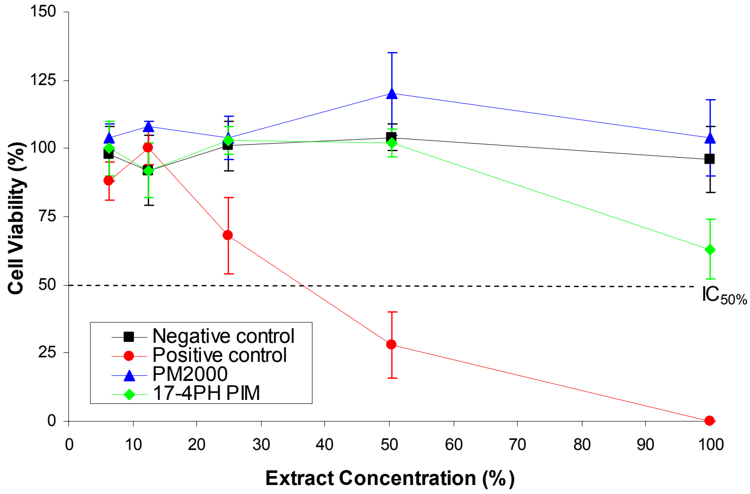

Figure 3. Cytotoxicity assay cell viability curves by neutral red uptake method of 17-4PH PIM and PM2000.

Potentiodynamic polarization - Fig. 4 shows the anodic polarization curves for the tested SS after 2 days of immersion in the PBS solution. The materials presented passive behaviour up to potential values around 500mV. For the 17-4PH PIM sample, there was a significant current increase, indicating pitting onset, around 520 mV (E_{pit}). The same trend was observed for the 316L SS, for which pitting occurred around 680mV; for the PM2000 it was detected at approximately 1150mV. The results indicated a higher pit corrosion resistance for PM2000, followed by 316L and finally by 17-4 PH PIM. Surface observation by optical microscopy after polarization tests confirmed the polarization curves. A unique and shallow pit was found on the PM2000 SS whereas on the 17-4PH PIM SS larger and deeper pits were observed.

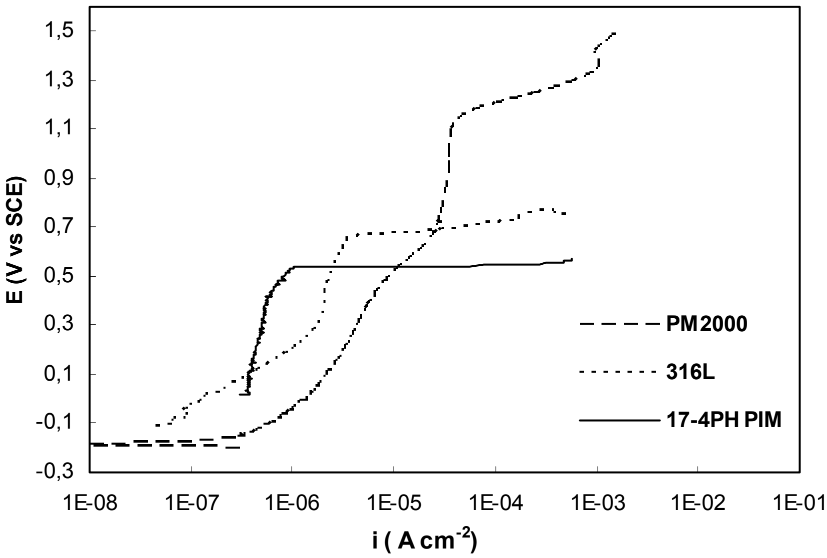

Figure 4 -Potentiodynamic polarization curves for 2 days immersion in PBS solution at 37^{o} C.

EIS - The Bode phase diagrams, depicted in Fig. 5, reveal the presence of a constant angle phase region, from 100 Hz until 0.01 Hz, characteristic of a passive behaviour. The Bode plots show that all the steels presented high corrosion resistance and it was not possible to make a clear distinction among the materials tested. However, it seems that the PM 2000 presented slightly higher impedance values.

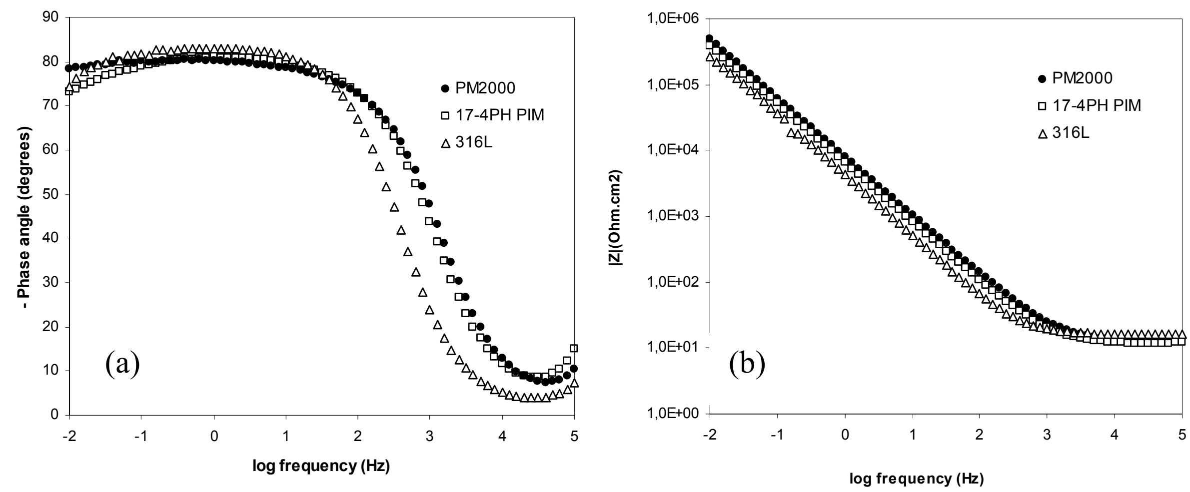

Figure 5. EIS results as (a) Bode phase angle and (b) impedance modulus diagrams, for 2 days immersion in PBS solution at 37^{o} C.

X-ray photoelectron spectroscopy - XPS results were obtained after different immersion times. For short immersion times (first two days of immersion), the surface film was mainly composed of Fe(II) and Fe(III) oxides and hydroxides, together with Cr(III) oxides and traces of Cr(VI) oxide. The XPS also revealed the presence of phosphates and aluminium oxides. Chlorides were not detected. No other elements were detected and the composition is typical of a passive film. The Fe2p, Cr2p and O1s spectra obtained after two hours and 2 days of immersion (Fig. 6) illustrate this behaviour and explain the passive film observed in the EIS diagrams.

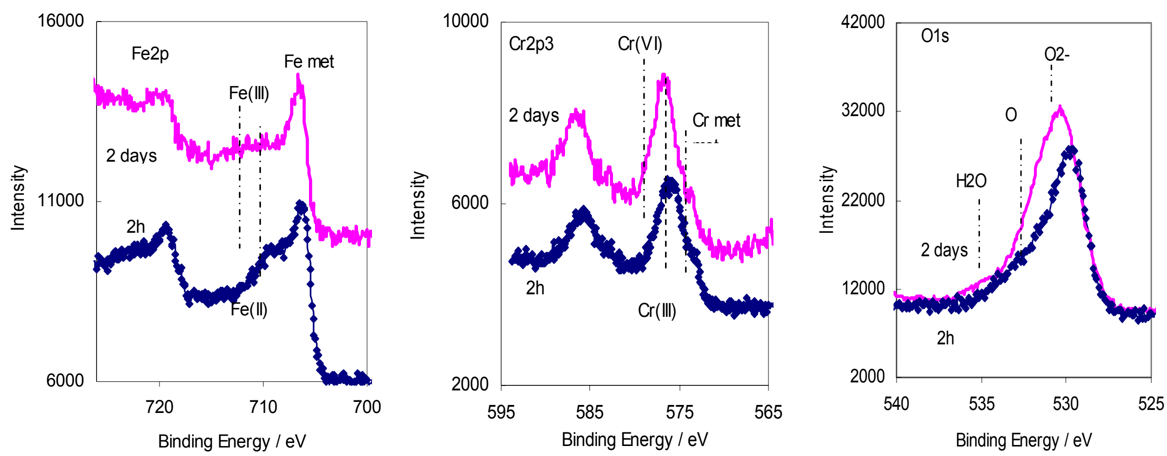

Figure 6 – XPS spectra obtained for Fe2p, Cr2p and O1s after 2h and 2 days of immersion.

Conclusions - The PM2000 and 17-4PH PIM SS showed no cytotoxic effects. Both materials showed higher magnetic retention force than that used as control. The corrosion resistance evaluated by electrochemical techniques in sodium phosphate buffer solution (PBS) at 37°C indicated that the best pitting resistance was associated to the PM2000 SS. The 17-4PH PIM SS showed the lowest pitting resistance among the tested steels. The EIS results showed a passive behaviour under stationary state. The passive film is mainly composed of a mixture of

Cr(III) and Cr(IV) oxides and Fe(II) and Fe(III) oxides/hydroxides. The results pointed out the PM2000 material as a potential candidate to substitute the noble alloys, used in magnetic dental attachments.

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