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Corrosion and Cytotoxicity Evaluation of AISI 316L Stainless Steel Produced by Powder Injection Molding (PIM) Technology

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Abstract: This study investigates the *in vitro* corrosion and cytotoxicity response of AISI 316L stainless steel produced by powder injection molding (PIM) technology in a solution that simulates physiological fluids (MEM) by electrochemical techniques and neutral red uptake cytotoxicity assay. The results were compared with those of AISI 316L produced by conventional metallurgy. Both steels showed high corrosion resistance and no toxic effect in the cytotoxicity test. The corrosion products were analyzed by instrumental neutron activation analysis (INAA). The surfaces of the alloys were evaluated before and after corrosion test by scanning electron microscopy and a passive behaviour was indicated supporting the results from other techniques.

Introduction

Austenitic stainless steels are among the most widely used metallic materials for biomedical applications. For implants, stainless steels of chemical composition based on AISI 316L type are the most largely employed. This kind of stainless steel has high intergranular corrosion resistance due to its low carbon content, that is, lower than 0.03 wt %. This feature increases the *in vivo* corrosion resistance of the steel. The high corrosion resistance of stainless steels is due to a passive oxide film formed on their surface. It is well known, however, that sintered stainless steels have lower corrosion resistance than steels produced by conventional metallurgy, due to the inherent porosity of the first ones [1]. Porosities increase the susceptibility to crevice and/or pitting corrosion [2]. Recent investigations have demonstrated a particular interest in the corrosion behavior of sintered steels with different alloying elements and porosity [2-5]. In the porosities, crevice corrosion may take place [2] with the formation of concentration cells within the pores, reducing the passivity of sintered alloys [2,5,6].

Powder injection molding (PIM) is a fairly recent powder metallurgy technology that uses fine powders (< 25 μm) to produce high-density materials with few and rounded pores. The final density of materials produced with this technology can reach values as high as 98% of the density of non-porous materials, and these microstructure characteristics result in increased corrosion resistance comparatively to other powder metallurgy techniques.

Metallic materials produced by PIM technology have many applications and among these they have been considered for use as biomaterials, such as for orthodontic and surgical devices. Biomedical devices in contact with physiological fluids in the body might undergo corrosion reactions and the corrosion products can adversely affect the human body. The corrosion and dissolution of surface films are two mechanisms that lead to the introduction of strange ions into the organism. The release of large amounts of these ions into the body fluids can lead to cytotoxic effects, allergic reactions and implant mechanical failure.

In this study, the *in vitro* corrosion and cytotoxicity response of AISI 316L steel produced by powder injection molding (PIM) technology, have been investigated in a solution that simulates physiological fluids by electrochemical techniques and neutral red uptake cytotoxicity assay.

Materials and Methods

The chemical composition of the AISI 316L steels used in this study, either produced by conventional metallurgy techniques or by PIM technology, was determined by instrumental neutron activation analysis (INAA), and it is shown in Table 1.

Table 1. Elemental composition of stainless steels tested obtained by INAA.

Element	AISI 316L	AISI 316L PIM
As, μg g^{-1}	46.8 ± 0.4*	17.5 ± 0.6
Co, μg g^{-1}	1229 ± 16	2388 ± 31
Cr, %	17.80 ± 0.03	14.81 ± 0.02
Cu, %	ND**	0.37 ± 0.03
Fe, %	57.8 ± 0.2	60.0 ± 0.2
Mn, %	1.44 ± 0.02	0.179 ± 0.002
Mo, %	1.97 ± 0.12	1.88 ± 0.01
Ni, %	12.9 ± 0.1	11.61 ± 0.09
V, μg g^{-1}	120 ± 23	763 ± 14

* Uncertainties calculated using statistical counting errors of standards and samples.

** ND – Indicates that the element was not detected.

Electrodes of the two types of steel were prepared for electrochemical measurements by cold resin mounting after electrical contact has been provided with a copper wire. The electrodes surface was prepared by grinding with silicon carbide paper up to grade #1000, followed by degreasing with acetone, using an ultrasonic bath, rinsing with deionized water and drying under a hot air stream.

Experimental set-up: A three-electrode cell arrangement was used for the electrochemical measurements, with a platinum wire and a saturated calomel electrode (SCE) as counter and reference electrodes, respectively. Electrochemical impedance spectroscopy (EIS) measurements were accomplished with a 1255 Solartron frequency response analyzer coupled to an EG&G 273A Potentiostat. All EIS measurements were performed in

potentiostatic mode at the open circuit potential, E_{ocp}. The amplitude of the perturbation signal was 10 mV, and the frequency range studied from 10^5 to 10^{-2} Hz, with 6 points per decade. Potentiodynamic anodic polarization measurements were carried out after 10 days of immersion by means of an EG&G 273A potentiostat coupled to a computer, in the potential range from the corrosion potential (E_{corr}) to a current limit of 10^{-3} A.cm^{-2}, with the scan rate of 1 mV/s. EIS measurements were obtained at increasing test times, from 1 until 10 days of immersion. The test medium was a naturally aerated solution known as minimum Eagle's medium (MEM), whose composition is given elsewhere [7]. This solution is made of a mixture of salts enriched with aminoacids, vitamins and other essential components for cell growing. All tests were carried out at (37 ± 1) °C.

Samples of the two types of tested steels were also immersed in MEM solution for 10 days, and after this period, this solution, here called extract, was analyzed by INAA to identify the elements released from the steels due to corrosion. The cytotoxicity of both steels was studied by *in vitro* assay, carried out with the exposures of cell culture of different concentrations to the extract. The cytotoxic effect was evaluated using the neutral red uptake method, according to Ciapetti *et al* [8] and previous report [9]. Phenol solution (0.02%) and high purity titanium were used as the positive and negative control, respectively, according to International Standard Organization (ISO) procedure [10].

Results and Discussion

The open circuit potential, E_{ocp}, variation with time of immersion for both types of AISI 316L steel in MEM solution, during a period of approximately 17 hours, is shown in Fig. 1. The E_{ocp} of the steel fabricated by conventional metallurgy was initially around -5 mV (SCE) and after few oscillations, that lasted until 2 hours of immersion, it steadily increased reaching a fairly stable potential, around 80 mV (SCE), after nearly 16 hours of immersion. For the steel prepared by PIM technology, the initial potential was about -100 mV. It increased to about 30 mV in the first minutes of immersion but soon afterwards showed great oscillations that lasted until approximately 8 hours of immersion From 8 hours onwards it steadily decreased and was fairly stable at -140 mV (SCE) after around 17 hours of test. The variation of the E_{ocp} with time for the steel prepared by conventional metallurgy is typical of passive metals in aerated solutions, the change of potential to nobler values indicating the increase in passive film thickness. On the other hand, the large oscillations observed on the E_{ocp} with time of immersion for the steel fabricated by PIM technique suggests repeated passive film breakdown followed by film repair, as for pit nucleation and repassivation. These events indicate a less stable film on the PIM steel comparatively to that produced by conventional methods. This is expected since the porosities inherent to the PIM steel lead to a less uniform passive film and increase pitting susceptibility. The stable potential at open circuit is called here corrosion potential, E_{corr}.

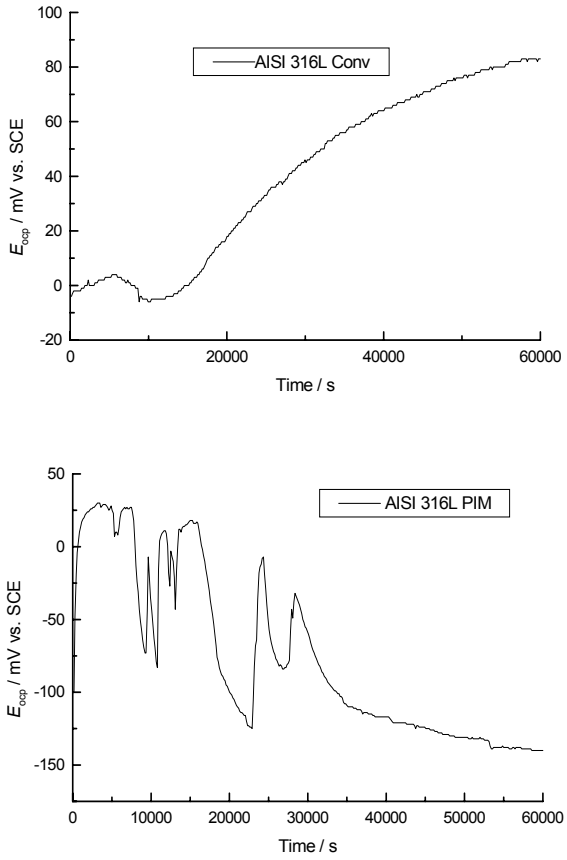


Fig. 1. Open circuit potential (E_{ocp})variation with time for conventional and PIM 316L steels in MEM solution.

Typical potentiodynamic polarization curves of AISI 316L alloy samples, either prepared by conventional metallurgy or by PIM technique, after corrosion potential stabilization in naturally aerated MEM's solution at 37 °C, are shown in Fig. 2.

The E_{corr} values, estimated from the polarization curve for the steels prepared by conventional metallurgy and PIM technique, after 10 days of immersion in MEM's solution, were 30 mV (SCE) and -10 mV (SCE), respectively. This result shows that the potential continued to change slowly between 1 and 10 days of test. Low current densities (order of 10^{-6} Acm^{-2} or lower) were obtained for both steels from E_{corr} until approximately 550 mV (SCE), that is, typical of passive materials. However, the polarization curve for the PIM steel has a typical behavior of activation polarization with an approximately linear variation of the current density with the potential until 550 mV (ECS), suggesting active dissolution. This could be related to a localized attack of the steel substrate, for instance, at the pores in the PIM steel. At about this last potential, the current increased significantly, indicating passive film breakdown. For the steel fabricated by conventional metallurgy film breakdown occurred at approximately 520 mV (SCE).

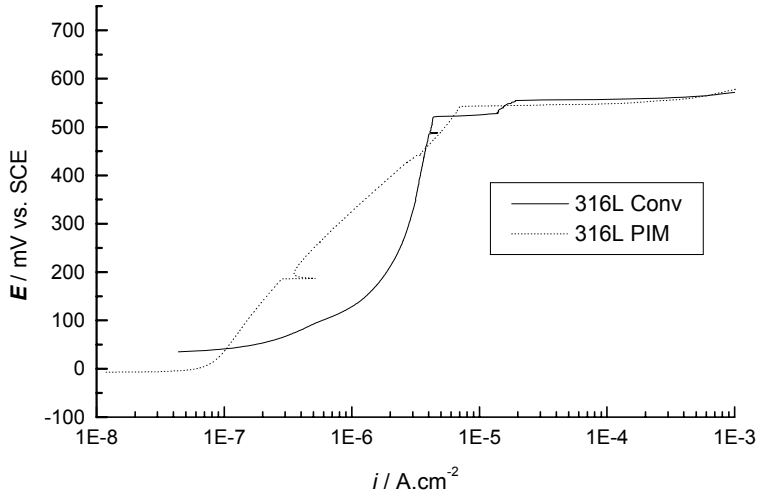
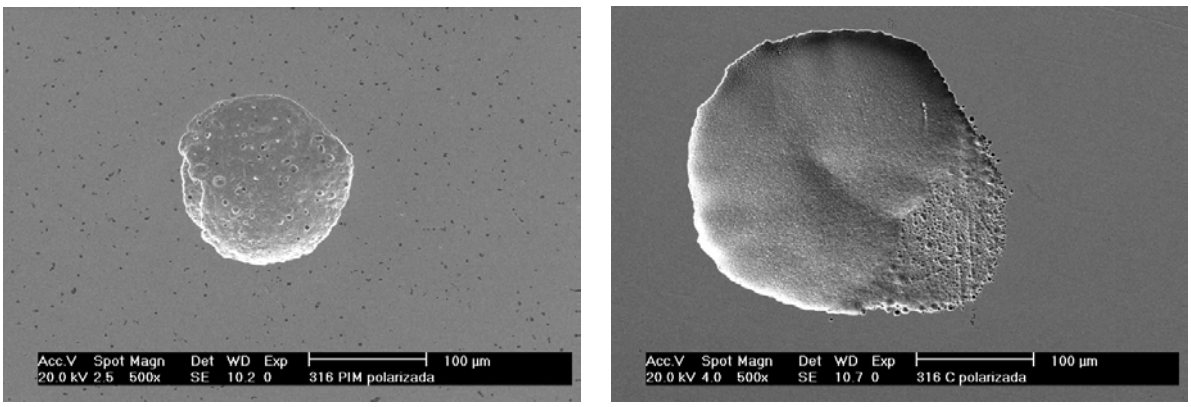


Fig. 2. Potentiodynamic polarization curves of conventional and PIM 316L steels after 10 days immersion in MEM's solution at 37 °C. Scanning rate: 1 mV/s.

From these results it can be said that very similar breakdown potentials were obtained for both types of steel, even though the PIM steel seemingly presented higher susceptibility to active dissolution from the corrosion potential until the pitting potential comparatively to the steel produced by conventional metallurgy. The exposed surface of the polarized specimens was observed by scanning electron microscopy (SEM) after polarization and the micrographies corresponding to the conventional and PIM steels are shown in Fig. 3 (a) and (b), respectively.

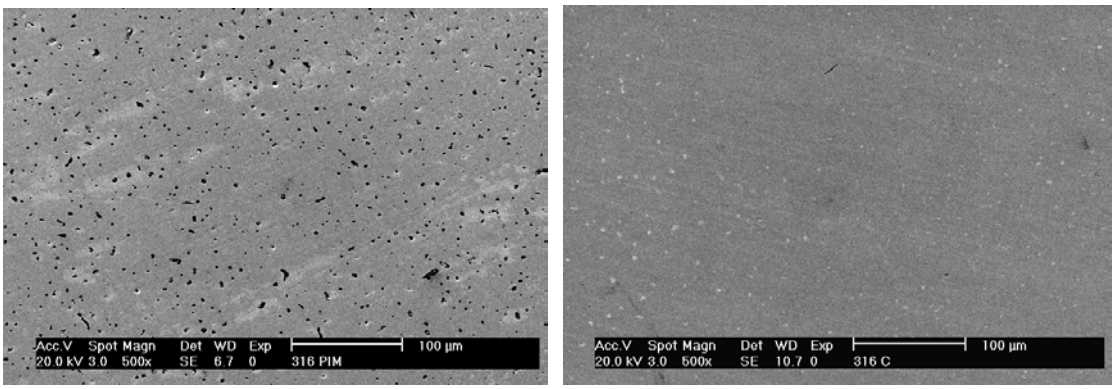
A shallow and round pit of about 250 μm diameter is clearly seen on the steel fabricated by conventional metallurgy, whereas the rest of the surface showed no signs of corrosion. For the PIM steel, a slightly deeper and round pit, of approximately 150 μm diameter, is also found. White particles are observed on the pit bottom in this last type of steel. These particles were previously analyzed and they are silica particles [5].



(a) (b)

Fig.3. SEM of 316L samples prepared by (a) conventional metallurgy and (b) PIM technique, after polarization test in MEM's solution. Specimens were immersed in the test solution for 10 days previous to polarization.

The shallow morphology of the pits formed on both types of 316L steel, indicates that the solution is not much aggressive towards the tested steels, and, consequently, pits do not penetrate deep into these materials. This result was also supported by the observation of not polarized specimens after 10 days of immersion in MEM's solution, as Fig. 4 shows.



(a) (b)

Fig. 4. Surface of the steels fabricated by (a) conventional metallurgy and (b) PIM technology, after 10 days of immersion in naturally aerated MEM's solution at 37 °C.

Surface analysis by SEM of the tested steels after 10 days of immersion in MEM's solution at 37 °C confirmed the high corrosion resistance of the steels. It can be seen that no signs of corrosion were found, suggesting a passive behaviour for the steels in this solution. This observation was also supported by the EIS results for both steels tested and by the results obtained from the analyses of the corrosion products in the extract. The chemical analyses of the steel extract showed that after 10 days of immersion in MEM, only cobalt was found in concentrations higher than that of the blank (MEM). The concentrations of the other alloying elements were in the range of the blank. This result supports the passivity of the steels tested in MEM's solution.

The results obtained from EIS technique are presented in Fig. 5.

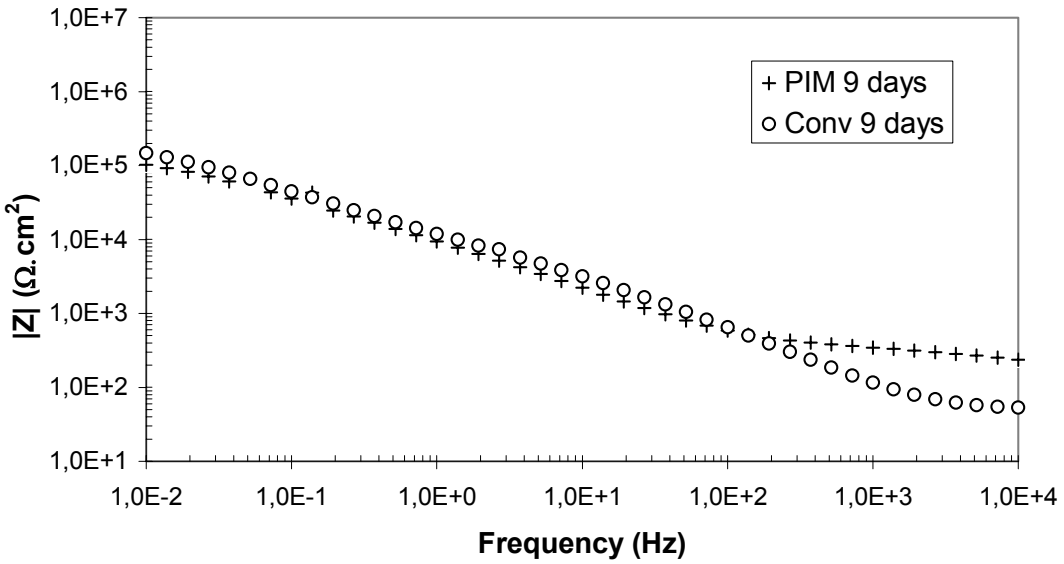


Fig. 5. Bode diagrams for AISI 316L steels, after 9 days of immersion in MEM solution at 37 °C.

The EIS data show that high impedance values (order of 10^5 ohm.cm^2) were obtained at low frequencies, after 9 days of immersion, although slightly lower impedance was associated to the PIM steel, suggesting a decreased corrosion resistance for the porous steel comparatively to that fabricated by conventional metallurgy, as it could be expected.

The results of the cytotoxicity assay were expressed as the cytotoxicity index ($IC_{50\%}$), that is, the extract concentration which injury or kills 50% of cell population in the test, as shown in Fig. 6. The behavior of the 316L PIM steel was similar to that of the negative control, that is, no cytotoxic, and the 316L steel prepared by conventional metallurgy showed $IC_{50\%}$ around 92, that is, practically non toxic, whereas for the positive control, which might show toxic effect, $IC_{50\%} = 24$.

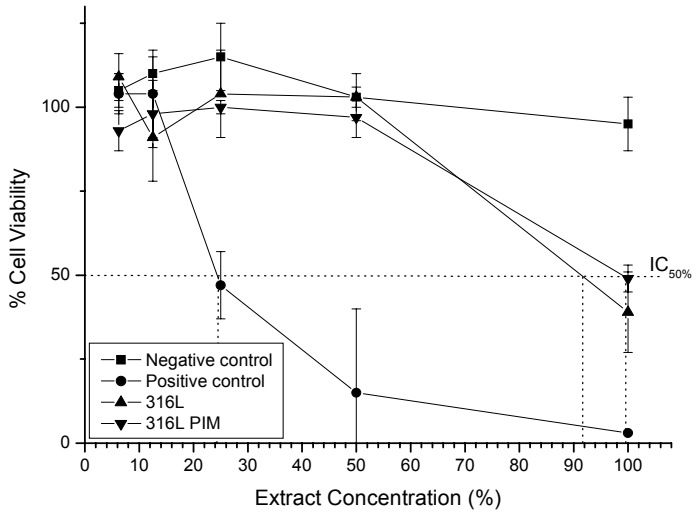


Fig.6. Viability curves of 316L and 316L PIM in the cytotoxicity test by neutral red uptake assay

Conclusions

The results of this study indicated that both tested AISI 316L steels, either prepared by PIM technique or conventional metallurgy, have high corrosion resistance in the test medium (MEM). Corrosion products were not detected in significant amounts in the solution where the steels had been immersed for 10 days at 37 ^{o}C, suggesting a passive behaviour. This indication was supported by EIS results and surface analysis by SEM after the immersion test. Both types of tested steels were not cytotoxic indicating that they can be considered as potential materials for biomedical applications.

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