

Corrosion Resistance and Cytotoxicity Study of 17-4PH Steels Produced by Conventional Metallurgy and Powder Injection Molding

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Abstract. The corrosion resistance of 17-4PH stainless steel obtained by powder injection molding (PIM) was investigated in a phosphate buffer solution (PBS) that simulates physiological solution and compared with that of 17-4PH steel obtained by conventional metallurgy. The corrosion resistance was investigated by electrochemical techniques for different immersion times. The cytotoxicity of both types of 17-4PH steel was also investigated using a minimum Eagle's medium (MEM). The MEM solution is a type of cell culture medium, which simulates physiological fluids. The cytotoxicity assay was carried out by neutral red uptake methodology utilizing NCTC L929 cell line from ATCC bank and none of the steels showed cytotoxic effects. The resulting extracts obtained by immersion of the steel samples in MEM were analyzed by neutron activation analysis and the results indicated liberation of chromium and cobalt as corrosion products but in very low amounts. The electrochemical evaluation of both steels indicated that they are passive in PBS but presented susceptibility to pitting. The 17-4PH PIM steel was slightly more susceptible to pitting than that fabricated by conventional metallurgy due to its inherent porosity.

Introduction

The 17-4PH steel is one of the most widely employed precipitation hardened stainless steels being commonly used in nuclear power plants, aircraft and gas turbines, oil and gas wells and chemical process components owing to a combination of good mechanical properties and corrosion resistance at temperatures up to approximately 700 °C. It also has a moderate corrosion resistance to salt spray atmosphere. Some of its properties, such as electrical resistivity, thermal expansion and thermal conductivity are similar to those of austenitic and duplex steels, while its mechanical strength, after the aging heat treatment, is significantly superior to that of austenitic steels such as AISI 304 or AISI 316.

Some publications [1-3] have dealt with corrosion aspects of these alloys produced by conventional metallurgy, such as general corrosion, pitting and hydrogen embrittlement in an alkaline solution [1], stress-corrosion cracking [2] and crevice corrosion [3]. Lately, this steel

has been produced by powder metallurgy (P/M) techniques. The porosity present in P/M steels affects their corrosion resistance and this has been a matter of particular interest from several recent investigations [4-15]. The porosity increases the area of metallic material exposed to the corrosive environment and might, eventually, induce localized corrosion, with concentration cells within the pores. This reduces the passivity of the sintered alloy [6-9].

Powder injection molding (PIM) technique has been applied to powdered materials as an alternative route to manufacture corrosion-resistant sintered components. This last technology has been commercially used for manufacturing small components with high complexity [16]. Fine powders (median particle size below 25 μm) are commonly used, resulting in sintered densities of about 98% of the theoretical density of the alloy. Injection molded alloys generally present few and round pores. This microstructural feature improves the corrosion resistance of the material compared with conventionally sintered types.

Injection-molded materials may be especially important for the manufacture of orthodontic components where 17-4PH steel has been used, due to its high mechanical strength. However, the high hardness of the 17-4PH steel hinders complex shapes conformability, resulting in clear advantages in the use of 17-4PH PIM steel with near final shape orthodontic devices. The corrosion resistance of this steel type has to be investigated in physiological environments in order to evaluate its usefulness for these applications.

In this study, the corrosion resistance of 17-4PH PIM steel was investigated in a phosphate buffer solution (PBS) that simulates a physiological medium and compared to that of the same steel produced by conventional metallurgy. The cytotoxicity of both types of steel was also evaluated using a Minimum Eagle Medium (MEM) that also simulates physiological fluids.

Materials and Methods

Materials.

Samples of powder injection molded 17-4PH steel, supplied by LUPATECH, Steelinject, Caxias do Sul, Brazil, were used in this study. Pre-sintering and debinding was performed at 980 °C for 1 hour under H_2 atmosphere. Sintering was carried out at 1300 °C for 4 hours in a reducing atmosphere of hydrogen (pressure of 50 mmHg), followed by cooling in the furnace. The final density of the sintered material was 7.6 $\text{g}\cdot\text{cm}^{-3}$. The density of the sintered material was approximately 98% of the theoretical density (7.8 $\text{g}\cdot\text{cm}^{-3}$), resulting in about 3% porosity, which means absence of interconnected porosity.

Specimens preparation:

The working electrodes were prepared by cold resin mounting, and the surface, by grinding with silicon carbide paper up to #2000, followed by polishing with diamond paste (6 μm and 1 μm) to a mirror finish, then rinsing in deionised water and drying under a hot air stream prior to immersion in the test medium.

Test medium:

The experiments were performed in un-stirred and naturally aerated PBS solution (NaCl 8,77g/L, Na_2HPO_4 1,42g/L, KH_2PO_4 2,72g/L), at (25 ± 2) °C.

Electrochemical Methods:

The electrochemical methods used in this investigation were open circuit potential (OCP) measurements with time, potentiodynamic polarization tests and electrochemical impedance spectroscopy (EIS). A three-electrode cell arrangement was used for the electrochemical tests, with a platinum wire and a saturated calomel electrode (SCE) as counter and reference electrodes, respectively. The polarization tests were carried out using a 273A EG&G PAR

Potentiostat. The samples were scanned from E_{ocp} in the anodic (positive) direction with a scan rate of 0.1 mV/s. The scan was reversed when the current density reached 10^{-3} A/cm², and it was stopped when the loop was completed. EIS measurements were accomplished using a Solartron 1260 frequency response analyzer coupled to a 273A EG&G PAR Potentiostat. EIS measurements were carried out in potentiostatic mode at the open circuit potential, E_{ocp} with a sinusoid ac voltage signal of 10 mV amplitude. The samples were analyzed in the frequency range from 100 kHz to 10 mHz and 6 points per decade were obtained. All electrochemical and immersion tests were carried out in triplicate. The results obtained in this work showed good reproducibility.

Cytotoxicity assay:

The cytotoxicity assay was performed by neutral red uptake method according to ISO [17] and the described methodology in a previous paper [18]. It was used mouse fibroblastic cell line NCTC L929 from ATCC bank.

Chemical analysis of corrosion products:

The corrosion products in the extracts were analyzed by instrumental neutron activation analysis (INAA), according to the procedure already described in a previous paper [19]. Aliquots of 500 microliters of each solution were pipetted and dried in polyethylene capsules from Faculty of Biology, Vrije Universiteit, Amsterdam, for irradiation at the IEA-R1 nuclear reactor together with synthetic elemental standards. Samples and standards were irradiated for 16h with thermal neutron flux of 5×10^{12} n cm⁻²s⁻¹. After adequate decay times, gamma ray measurements were carried out using a hyperpure Ge detector connected to a gamma ray spectrometer. Analysis of blank of culture media was also carried out using the same experimental conditions adopted in the analysis of corrosion product extracts. Detection limit value for Ni was also evaluated according to Currie criteria [20]

Results and Discussion

The chemical analyses of metallic elements in the corrosion product extracts of steels are presented in Table 1. The results indicated the release of Co and Cr from both steels tested. These steels contain Ni however it was not detected in the extract within detection limit.

Table 1. Elements detected in the corrosion product extracts of steels investigated.

Elements	17-4PH conventional	17-4PH PIM
Co (ng.mL ⁻¹)	19.1 ± 0.7	6.3 ± 0.2
Cr (ng.mL ⁻¹)	50 ± 9	143 ± 4
Ni (ng.mL ⁻¹)	< 0.61	< 0.61

Fig. 1 shows the cytotoxicity results obtained for the steels investigated. Both 17-4PH steels showed similar behavior. The cell viability curves are above cytotoxicity index (IC_{50%}) line which means that none of them presented cytotoxic effect in this assay. The positive control cell viability curve crossed the IC_{50%} line and it was possible to determine the IC_{50%} of 24.

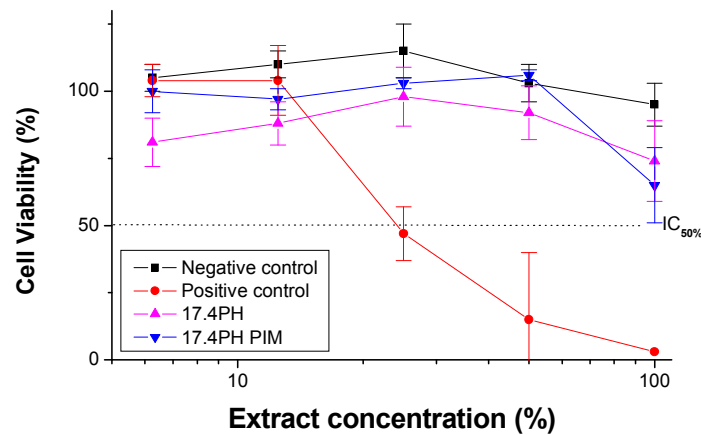


Fig. 1. Cytotoxicity assay cell viability curves by neutral red uptake method of 17-4PH conventional and PIM stainless steel.

The electrochemical behavior of the two types of steel was compared at different times of immersion by polarization curves and EIS tests and the results are presented in Figs. 2 and 3.

The polarization curves show that the PIM type of steel presents only slightly lower pitting resistance than the conventional type, for all the immersion periods tested showing lower E_b (breakdown potential). This is expected considering the presence of surface porosities that favor more aggressive conditions towards the oxide film formed. However, the small differences found in E_b for the two steels must be due to the improved properties of the steel produced by PIM technology comparatively to other powder metallurgy techniques.

Despite of the slightly lower corrosion resistance of the PIM steel, both types of steel tested are highly passive in the phosphate buffer solution used, as the EIS results shows, Fig. 3. The capacitive results with phase angles around -90° , and the high impedance results at low frequencies, for both steels tested, are typical of highly passive materials. The results of this Fig. also indicate oxide film thickening on both types of steel with time of immersion in the phosphate solution causing the increase in impedance with time. This is an advantageous property that results in corrosion resistance improvement with time.

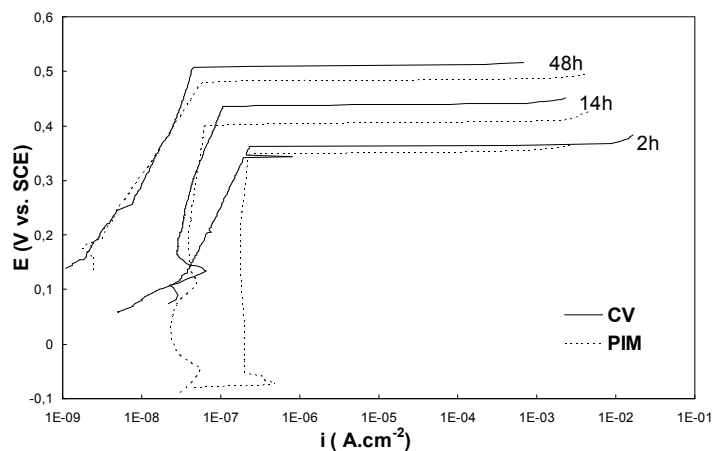


Fig. 2. Polarization curves of 17-4PH PIM and conventional at various times of immersion.

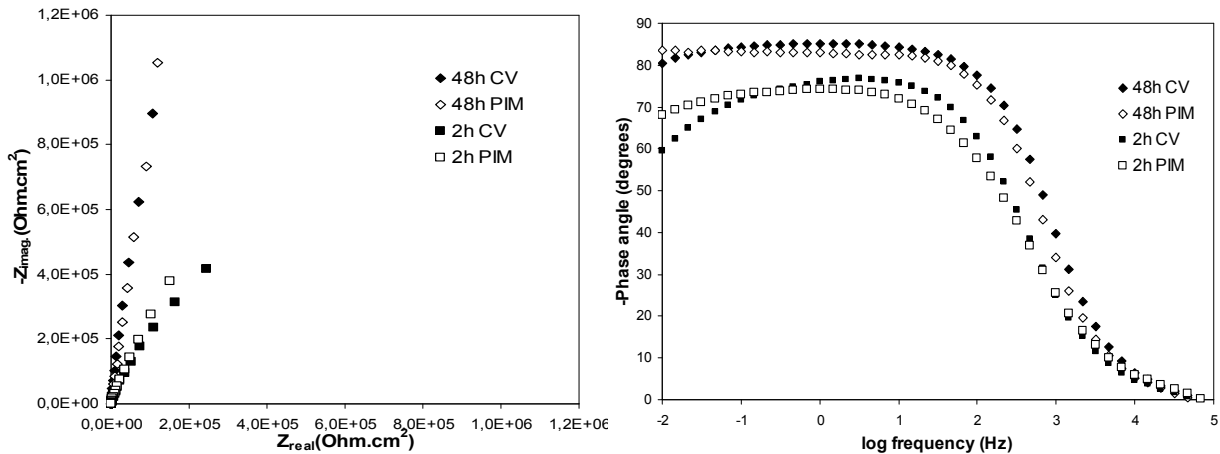


Fig. 3. Nyquist and Bode phase angle diagrams for 17-4PH PIM and conventional at various times of immersion.

The electrochemical results obtained in this work indicate that the immersion of 17-4PH steels in a phosphate buffer solution leads to the increase in corrosion resistance of their surfaces.

Conclusions

The 17-4PH steels tested in this study showed a passive behavior under open circuit potential but also susceptibility to pitting corrosion. Slightly lower pitting resistance is associated to the PIM steel comparatively to the conventional one. None of the tested steels showed cytotoxicity despite the presence of low amounts of Co in the corrosion products obtained. Consequently, the results indicated potential applications of the PIM steel as biomaterial.

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References

- [1] H.J. Chuang, S.Y. Chen and S.L.I. Chan: *Corr. Sci.* Vol. 41 (1999), p.1347.
- [2] F. El Hilali, M. Habashi and A. Mohsine: *Ann. Chem. Sci. Mat.* Vol. 24 (1999), p. 169.
- [3] A.U. Malik, N.A. Siddiqi, S. Ahmad and I.N. Andijani: *Corr. Sci.* Vol. 37 (10) (1995), p.1521.
- [4] A.V.C, Sobral, A.M. Maliska, G. Tosi, J.L.R. Muzart, A.N. Klein and C.V. Franco: *Adv. Powder Metall. Particul. Mater.* Vol. 3 (11) (1995), p. 57.
- [5] A.V.C. Sobral, A.C.B. Parent, J.L.R. Muzart and C.V. Franco: *Surf. Coat. Tech.* Vol. 92 (1997), p. 10.
- [6] E. Maahn, S.K. Jensen, R.M. Larsen and T. Mathiesen: *Adv. Powder Metall. Particul. Mater.* Vol. 7 (1994), p. 253.
- [7] L. Fedrizzi, F. DeFlorian and A. Tiziani: *Adv. Powder Metall. Particul. Mater.* Vol. 7 (1994), p. 273.
- [8] T. Raghu, S.N. Malhotra and P. Ramakrishnan: *Brit. Corros. J.* Vol. 2 (1988), p. 109.

- [9] A. Tremblay and R. Angers: Adv. Powder Metall. Particul. Mater. Vol. 7 (1995), p. 225.
- [10] E. Otero, A. Pardo, M.V. Utrilla, F.J. Pérez and C. Merino: Corros. Sci. Vol. 39 (1997), p.453.
- [11] E. Klar and F.K. Samal: Adv. Powder Metall. Particul. Mater. Vol. 11 (1995), p. 11.
- [12] R.L. Sands, G.F. Bidsmesd and D.A. Oliver: Mod. Dev. Powder Metall., Vol. 2 (1966), p. 73.
- [13] A.V.C. Sobral, W. Ristow Jr., D.S. Azambuja, I. Costa and C.V. Franco: Corros. Sci. Vol. 43 (6) (2001), p. 1019.
- [14] A.V.C. Sobral, W. Ristow Jr., O.V. Correa, C.V. Franco and I. Costa: Key Eng. Mater. Vol. 189-191 (2001), p. 667.
- [15] I. Costa, C.V. Franco, C.T. Kuniوشي and I. Costa: Corrosion Vol. 62 (4) (2006), p. 357.
- [16] T. Mathiesen and E. Maahn: Adv. Powder Metall. Particul. Mater. Vol.3 (1995), p. 45.
- [17] ISO document 10993-5 Biological evaluation of medical devices, Part 5, Tests for cytotoxicity: in vitro methods (1992).
- [18] C.P. Ossa, S.O. Rogero and A.P. Tschiptschin: J. Mater.Sci. Mater. Med. Vol. 17 (2006), p. 1095.
- [19] S.O. Rogero, O.Z. Higa, M. Saiki, O.V. Correa and I. Costa: Toxicol. in Vitro Vol. 14 (2000), p. 497.
- [20] L.A. Currie: Anal. Chem. Vol. 40 (1968), p. 586.