

The corrosion behaviour of TiN-coated powder injection molded AISI 316L steel

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Abstract: The use of AISI 316L stainless steels for biomedical applications as implants is widespread due to a combination of low cost and easy formability. However, wrought 316L steel is prone to localized corrosion. Coating deposition is commonly used to overcome this problem. Ceramic hard coatings, like titanium nitride, are used to improve both corrosion and wear resistance of stainless steels. Powder injection moulding (PIM) is an attractive method to manufacture complex, near net-shape components. Stainless steels obtained from this route have shown mechanical and corrosion properties similar to wrought materials. The literature on the use of PIM 316L steel, either coated or not, as implants is still very scarce. The aim of the present work was to study the corrosion behaviour of PIM 316L in two conditions: TiN-coated and bare. Electrochemical investigations were performed using EIS and potentiodynamic polarization techniques.

Introduction

The manufacture of complex, near-net shape components in an economical way is a leading objective in the metallurgical industry and may be achieved with powder injection molding (PIM) techniques. According to Koseski et al. [1] over 50% of the injection molded and sintered components are made from stainless steels compositions. The main drawback of these materials when compared to wrought stainless steels is the intrinsic porosity that may adversely affect their corrosion resistance [2,3]. However, there are reports in the literature of stainless steel materials processed via injection molding with similar or even better corrosion properties than wrought ones [4-5]. Although one of the major applications of PIM stainless steels are as orthodontic components and surgical devices, there are few works reporting on the corrosion resistance of these materials in simulated physiological solutions [6]. Sobral et al. [6] evaluated the electrochemical behavior of injection molded 316L in NaCl solution and observed tendency to pitting corrosion. It is well known that stainless steel medical devices manufactured from wrought materials are also susceptible to localized corrosion [7]. Corrosion products released to the human body may lead to infectious reactions that make the patient undergoes additional suffering ultimately leading to the implant failure [8]. Surface modification techniques and coatings deposition may enhance both corrosion resistance and biocompatibility of stainless steel. Titanium nitride (TiN) ceramic hard coatings are suitable for biomedical uses as

protective surface films due to their intrinsic biocompatibility and high wear and corrosion resistance [9,10].

The aim of the present study was to assess the corrosion resistance of TiN-coated and bare injection molded AISI 316L stainless steel in Hanks' solution. Electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization measurements were used as investigating techniques. The surfaces of the specimens after immersion were observed using scanning electron microscopy (SEM).

Materials and Methods

The material tested was a water-atomized 316L stainless steel powder (Pacific Metals) with a maximum particle size of 20 μm . The binder used in the production of the specimens was a mixture of stearic acid, ethyl-vinyl-acetate, polypropylene and paraffin. The specimens were pre-sintered in a tubular furnace in hydrogen atmosphere at 950° during 15 minutes. Sintering was carried out in the same furnace at 1300°C during three hours. The chemical composition of the material was obtained by mass spectroscopy and is given in Table 1. The specimens were produced by Lupatech S/A (Caxias do Sul - RS - Brazil).

Table 1. Elemental composition (mass percentage) of the PIM 316L stainless steel evaluated in this work.

C	Mn	P	S	Si	Cr	Ni	Mo	N	Cu	Fe
0.007	0.145	0.015	0.021	0.643	16.51	11.83	2.085	0.015	0.093	Bal.

Titanium nitride (TiN) coatings were deposited on the PIM 316L specimens using a physical vapour deposition technique. The deposition rate was 0.8-1.0 $\mu\text{m}/\text{h}$. The TiN film thickness was approximately 3 μm .

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. The electrolyte was a naturally aerated Hanks' solution and its composition is shown in Table 2. 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 polarization curves were obtained after 28 days of immersion, using a scanning rate of $1 \text{ mV}\cdot\text{s}^{-1}$. The measurements started at $-800 \text{ mV}_{\text{SCE}}$ and finished when the current density reached 1 mA cm^{-2} . All tests were carried out at 25 °C. The exposed area of the specimens either TiN-coated or bare to the solution was approximately 0.76 cm^2 .

SEM-analyses were performed with a Philips XL30 microscope. Two distinct surface conditions were observed: the material before immersion in Hanks' solution and after 28 days of immersion followed by potentiodynamic polarization test until the current density reached 1 mA cm^{-2} . This procedure was adopted for TiN-coated and bare specimens.

Table 2 . Chemical composition of Hanks' solution.

Component	Concentration (Mol/L)
NaCl	0.1369
KCl	0.0054
MgSO ₄ ·7H ₂ O	0.0008
CaCl ₂ ·2H ₂ O	0.0013
Na ₂ HPO ₄ ·2H ₂ O	0.0003
KH ₂ PO ₄	0.0004
C ₆ H ₁₂ O ₆ ·H ₂ O	0.0050

Results and Discussion

SEM micrographs of the TiN-coated and bare 316L PIM specimens after 28 days of immersion in Hanks' solution at 25°C are shown in Fig. 1.

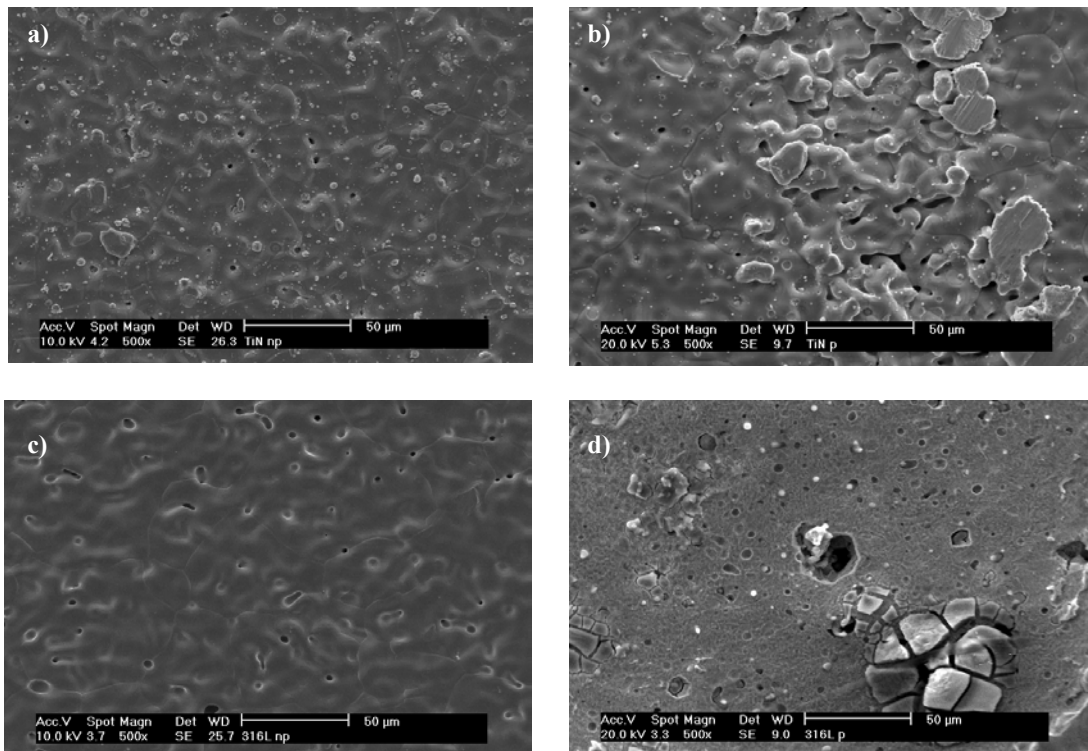


Fig.1. SEM micrographs of 316L PIM specimens: (a) TiN-coated, immersed for 28 days in Hanks' solution at 37°C, non polarized; (b) TiN-coated, immersed for 28 days in Hanks' solution at 37°C, polarized as described in the Experimental section; (c) bare steel, immersed for 28 days in Hanks' solution at 25°C, non polarized; (d) bare steel, immersed for 28 days in Hanks' solution at 25°C, polarized as described in the Experimental section.

TiN-coated and non-polarized specimen presented a surface with several pinholes smaller than 5 µm (Fig. 1a). The coating does not present cracks or pits. After the

potentiodynamic polarization measurement the coating was not removed from the surface but presented clear signs of deterioration (Fig. 1b). On the right side of the micrograph there are irregular and deep holes. These holes are surrounded by plate-like structures that were not present on the non-polarized specimen.

The bare non-polarized specimen presents small pores distributed either in the grain boundaries or inside the grains as shown in Fig. 1c. After polarization the surface is completely different. Severe deterioration occurred, as indicated by the presence of several small holes indicating pitting initiation, a large pit and cracked regions (Fig 1d). The deterioration of TiN-coated polarized specimen was less intense, suggesting that TiN coating had a beneficial protective effect on the 316L PIM surface.

Bode plots (phase angle) for bare and TiN-coated 316L PIM specimens after 1, 7, 14, 21 and 28 days of immersion in Hanks' solution at 25°C are shown in Fig. 2.

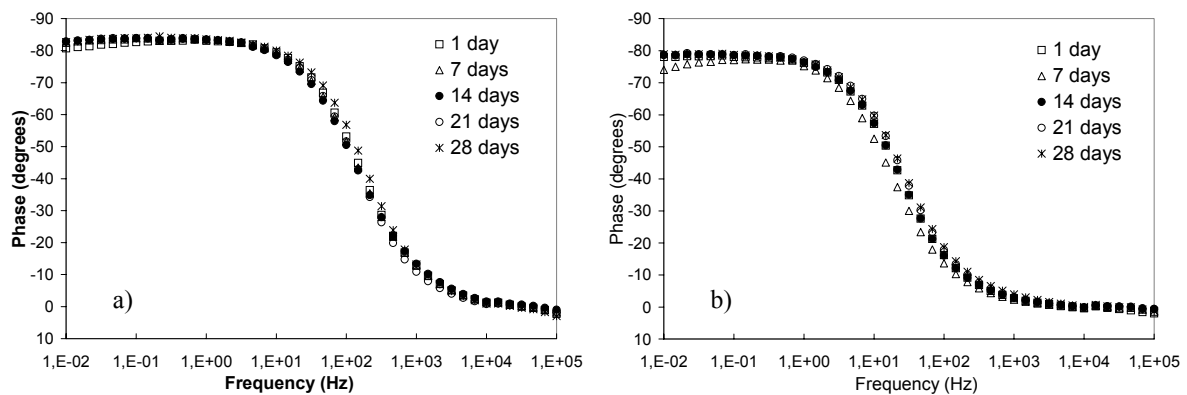


Fig. 2. Bode plots (phase vs frequency) of: (a) bare and (b) TiN-coated 316L PIM specimens after 1, 7, 14, 21 and 28 days of immersion in Hanks' solution at 25°C.

Both bare (Fig. 2a) and TiN-coated (Fig. 2b) specimens presented highly capacitive behaviour at frequencies below 1 Hz, through the whole period of immersion as indicated by the phase angle values around -80° . The diagrams did not present significant changes from the first day of immersion until the end of the test reflecting the high stability of the specimens' surfaces (bare and TiN-coated). However, if one compares the diagrams of the bare and TiN-coated specimens some small differences may be observed. One single capacitive time constant is present in the diagrams of bare and TiN-coated specimens. In the case of the bare specimen, this time constant may be ascribed to the response of the defects in the oxide layer on the surface of the stainless steel. It forms a wide plateau starting at frequencies around 10 Hz extending to 0.01 Hz. In the diagrams of the TiN-coated specimen, the time constant may be related to the response of the defects on the TiN layer and the plateau initiates at lower frequencies for this last type of specimen. These results point towards a slightly slower deterioration for the coated specimen, indicating some protective properties to the substrate.

Nyquist plots (phase vs frequency) of bare and TiN-coated 316L PIM specimens after 1 and 28 days of immersion in Hanks' solution at 25°C are shown in Fig. 3.

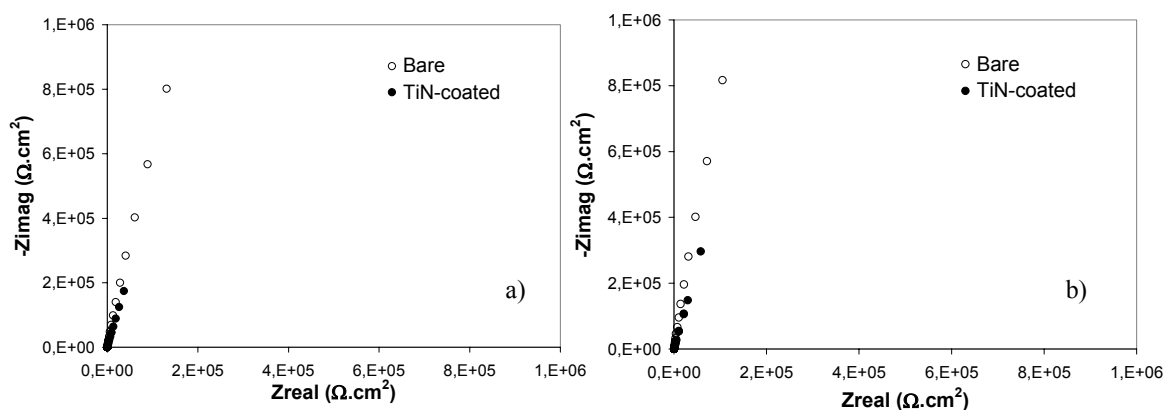


Fig. 3. Nyquist plots of bare and TiN-coated 316L PIM specimens after: (a) 1 day and (b) 28 days of immersion in Hanks solution at 25°C.

It is noteworthy that both specimens present one capacitive loop and no signs of diffusion in the low frequency region although their surfaces present several pinholes, as shown in Fig. 1. Porous materials such as those produced using powder metallurgy techniques may present diffusive behaviour and increase of capacitance as a consequence of localized attack taking place inside the pores [6]. Neither the bare or the TiN-coated specimens showed this behaviour, suggesting that the contact area of the metal with the electrolyte solution did not increase with the immersion time. Another cause for this behaviour could be the highly capacitive behaviour of the both materials tested.

Potentiodynamic polarization curves for TiN-coated and bare 316L PIM specimens after 28 days of immersion in Hanks' solution at 25°C are shown in Fig. 4.

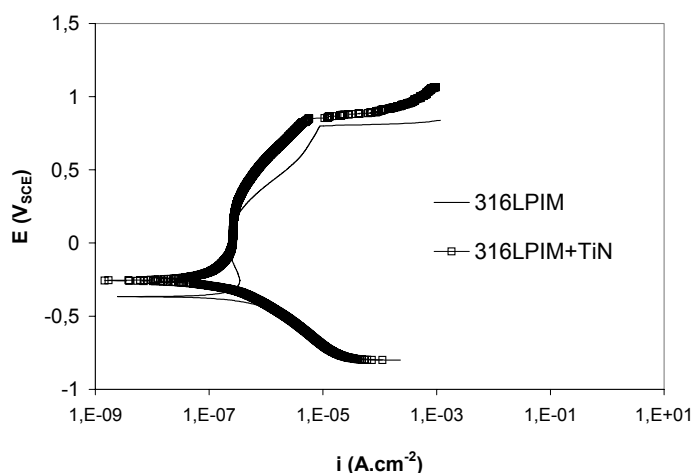


Fig. 4. Potentiodynamic polarization curves for TiN-coated and bare 316L PIM specimens after 28 days of immersion in Hanks' solution at 25°C.

The deposition of the TiN coating shifted the corrosion potential of the 316L PIM to nobler values (-0.36 V for the bare specimen and -0.25 V for the TiN-coated). Furthermore, the passive current density of the coated specimen is slightly lower when compared to the non-coated one. The onset of pitting corrosion is denoted by the breakdown potential of approximately +0.8 V in the curve of the bare specimen as indicated by the sharp increase of the current density. For the coated specimen the breakdown potential is slightly higher (around +0.85 V). It is important to note that both specimens presented very low current densities at the corrosion potential ($0.4 \mu\text{A}\cdot\text{cm}^{-2}$ and $0.1 \mu\text{A}\cdot\text{cm}^{-2}$ for the bare and TiN-

coated specimens, respectively). This is an indication of the high corrosion resistance of both materials. The results shown in the potentiodynamic polarization curves reflected a small beneficial protective effect of the TiN coating on the 316L PIM surface as already shown in the SEM micrographs (Fig. 1). The improvement in the corrosion resistance was not significant. The main contribution of the TiN coating should be on the wear resistance of the PIM 316L substrate. This property has to be evaluated to confirm if TiN may be considered a suitable coating for PIM 316L in biomedical applications.

Conclusions

The bare and TiN-coated PIM 316L specimens presented high corrosion resistance but were prone to localized corrosion. The deposition of the TiN coating only slightly increased the resistance to localized corrosion. Taking only the corrosion behaviour into account it is not possible to state that the TiN layer is an effective protection to the PIM 316L substrate.

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