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Corrosion in 316L porous prostheses obtained by gelcasting

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Abstract

Gelcasting (GC) process, usually used for ceramic moulding, is adapted for producing spongy or porous metal osteosynthesis components destined to bone void filling. The main objective of the interconnected porosity is to improve the osteoconductive of metal matrix by ingrowth of bone. Further, porosity reduces metal density and Young module, which causes bone resorption, leading to implant failure, phenomenon known as stress shielding. The employed GC is based on the formulation of AISI 316L stainless steel powder suspension in an aqueous solution of organic polymers. This suspension is cast into porous ceramic shells, like those used in lost wax technique, wherein the polymer crosslinking is induced by heating. The shells, containing the resulting hydrogel–metal composite, are subjected to thermal cycle in order to dry, burn the organic phase, sinter the metal particles at 1200 °C, and cool down to room temperature under dry hydrogen permanent flow. The susceptibility to corrosion of 50-60 % porous pieces was analyzed. The results indicated that the lower relation between the open porosity and the total porosity, the lower the corrosion rate.

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1. Introduction

Stainless steel (ASTM F138, F139 or F745, AISI 316L grade steel), Co-Cr-Mo (ASTM F75, F562 or F799) and Ti-6Al-4V (ASTM F620) are used for load bearing applications in partial or total joint replacement, due to their satisfactory mechanical properties, corrosion resistance and biocompatibility. The latter property is related to biological response of human body, particularly referred to the ability of bone cell proliferation (osteoblasts) onto metallic surface, with minimal or any fibrous tissue (formed by fibroblasts), ensuring the implant mechanical fixation to bone. The metal surface topography may improve the fixation, by increasing roughness and open porosity. The degree of integration to bone seems to reach a maximum, when interconnected porosity is in 50 % to 80 % (in volume) range, and composed by 100 to 500 μm pores. These features favor angiogenesis (the growth of blood vessels), and thus, the proliferation and colonization of osteoblasts within the pores. At the same time, porosity promotes the reduction of density and elastic modulus of mentioned alloys (between 110 and 210 GPa), tending to a bone-like magnitude (≈ 30 GPa). This allows a better transference of the mechanical load on the bone, avoiding the accumulation of stress onto the implant, phenomenon known as *stress shielding*. This process can occur when the initial implant fixation is deficient, leading to the relative displacement of metal-bone interface (in teens of microns), thus, triggering the osteopenia process, with the consequent loss or bone resorption, tissue inflammation and/or infections. This second phenomenon, known as *aseptic loosening*, leads to bone and metal debris generation promoted by wear. The final implications are the loss of the bone-implant interface, the implant failure and the need for revision surgery. The need to favor angiogenesis, osteointegration and avoid stress shielding, has driven the development of porous or cancellous structure implants, based on Ti, Ta or Ni-Ti alloys, when mechanical performance is the leading requirement. These are applied to fracture fixation, providing a scaffold for bone tissue regeneration in orthopedic and maxillofacial surgeries [Medlin et al. (2003), Ryan et al. (2006), Li et al. (2008), and Chen et al. (2009)]. Controlled porosity can be obtained by means of gelcasting (GC) technique, widely employed for molding ceramic components. Gelcasting is based on the formulation of slurry constituted by ceramic or metallic particle dispersion in water or organic solution of monomers, polymers or proteins. The slurry is cast into polymeric, metal or ceramic molds, wherein the crosslinking of polymers or proteins is induced by heating. The product is a composite of a hydrogel with metal particles homogeneously distributed, and with sufficient toughness to withstand further handling and sintering processes. This technique has been used for manufacturing Ti and stainless steel implants [Li et al. (2008a), Li et al. (2008b), Ozols et al. (2008), Ozols et al. (2009a), Ozols et al. (2009)b]. However, the corrosion resistance of these porous alloys may differ from that of full density, when they are implanted in physiological medium. Therefore, these materials must be evaluated to ensure their safety for long-term clinical applications.

This paper refers to the corrosion resistance of porous AISI 316L implant obtained by gelcasting. This work is a continuation of previous studies, which have shown the feasibility of producing implants of various geometries for bone fixation, and assessing their osteointegration capability by in *vivo tests* [Ozols et al. (2009a)].

2. Experimental procedure

Gelcasting suspension was formulated with 75 % (in wt.) of AISI 316L particles (smaller than 45 μm) dispersion in 20 % (in wt.) and egg albumin devolved in warm distilled water. The slurry was cast in water permeable ceramic shells, similar to those used for investment casting process. These shells were wrapped in PVC films and heated in thermal water bath at 90 °C for 1 hour, in order to promote the protein gelation. The dried pieces were heated at 600 ºC/h rate, up to the sintering of 1200 ºC, where remained for 2 hours, and cooled down to room temperature under constant flow of dry hydrogen flow into a AISI 316L gas heated muffle.

Total porosity (P) was calculated from the relative density (δ_{rel}), determined by the relationship between bulk density (δ_{ap}), measured by immersion water method, and the AISI 316 L theoretical densities of (7.96 g/cm^3), according to the following relationship:

$$\delta_{rel} = 1 - \frac{P}{100} \tag{1}$$

Open porosity (P_0), defined as the ratio between open pore volume and specimen volume, was determined as follows:

$$P_0 = \frac{G_W - G}{V} \tag{2}$$

Being G the dry weight of the specimen, G_W its water saturated weight, and V its apparent volume, including pore volume.

Corrosion resistance was evaluated by means of electrochemical polarization tests in the potential range between -0.20 and 0.45 V/SCE, respect to the open circuit potential of the system, where SCE refers to saturated calomel electrode potential. The corrosion cell was assembled with the test material, as the working electrode (1 cm^2 of area), SCE as reference and a Pt electrode as auxiliary. Tests were performed using aqueous solution of 0.9 % (in wt.) of NaCl, with pH between 7.0 and 7.4, kept at 37 ºC, to simulate the human body environment. The solution was deaerated by N_2 bubbling during the tests. The samples were kept in a stabilization period of 1 hour at open circuit condition (*Eoc*). Later, the potential scans were performed at 0.167 mV/s in the anodic direction.

3. Results and discussion

3.1. Porosity measurements

Table 1 shows the density and porosity of three different samples extracted from the femoral stem obtained by gelcasting.

Table 1. Analyzed AISI 316L sample porosity.

Sample	δ_{ap} (g/cm^3)	δ_{rel} (g/cm^3)	P (%)	P_0 (%)	P_0 /P
M1	3.07	0.38	62.0	60.4	0.95
M2	3.46	0.44	56.5	55.4	0.98
M3	2.96	0.37	62.8	50.9	0.81

M1 and M2 samples show a P_o/P ratio close to 1.00, evidencing that most of the porosity is interconnected, with greater exposed surface area than in isolated porosity situation. In the case of M3 sample, its total porosity was similar to that of M1 sample, while the open porosity was significantly lower.

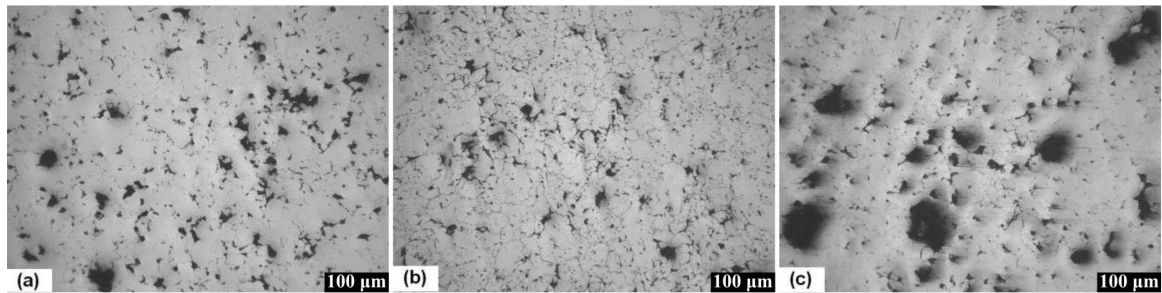Fig.1 illustrates the analyzed sample pore irregular geometry and size dispersion.

Fig. 1. Porosity: (a) sample M1; (b) sample M2; (c) sample M3.

M1 and M2 samples, whose *Po/P* ratios were similar and close to 1.00, exhibited greater uniformity of pore size distribution, while sample M3 showed higher dispersion.

3.2. Corrosion behavior

Corrosion behaviour of porous samples was compared with that of dense AISI 316L, the results are shown in Fig. 2.

The analysis of the curves shows that dense AISI 316L exhibited a lower corrosion rate and a wider passive region (about 450 mV/SCE) than porous samples. The higher corrosion rate in these samples, at least by one order of magnitude, could be ascribed not only to the increased electrochemical activity of the material, but also to the higher exposed specific area, resulting from porosity. This was not taken into account in the calculation of the current density, determined as a function of the geometric area of the sample. Another feature is the different behaviour observed in anodic potential region. Sample M1 showed a large area ($\approx$ 400 mV/SCE) at which the electrochemical activity of the material is lower, while sample M3 is active throughout the defined anodic sweep. Sample M2 shows an intermediate behaviour respect to M1 and M2 samples. The reasons for these behaviours have not yet been elucidated.

Table 2 reports the electrochemical parameters obtained from the tests.

From the results exposed in Tables 1 and 2, the variation of the corrosion rate with δ_{rel}, δ_{ap} and P_o/P can be determined, as shown in Fig. 3.
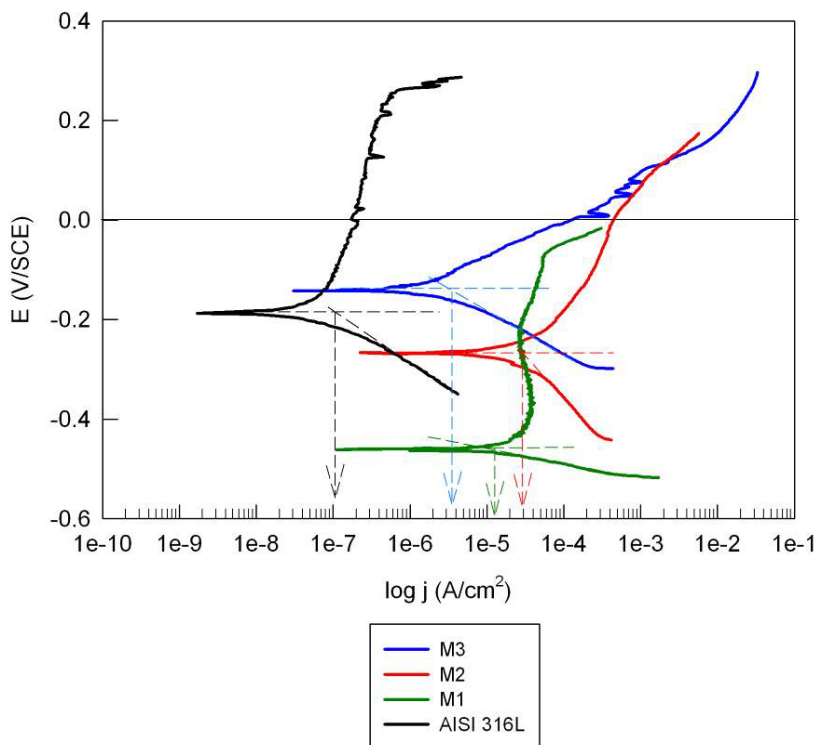

Fig. 2. Curves obtained from the electrochemical tests.

Table 2. Results of electrochemical tests.

Sample	E_{corr} (V/SCE)	j_{corr} (A/cm^2)
M1	-0.460	1.3×10^{-5}
M2	-0.267	3.0×10^{-5}
M3	-0.143	3.7×10^{-6}
Dense AISI 316L	-0.190	$1.0. \times 0^{-7}$

The lowest corrosion rate was observed for sample M3, which reported smaller δ_{rel}, δ_{ap} and P_0/P values, and bigger total porosity. While corrosion rate decreased with those parameters, open porosity has the greatest influence, because of the lower exposed specific area. In general, j_{corr} variation is directly correlated with variation of these parameters, as also shown in Fig. 3.
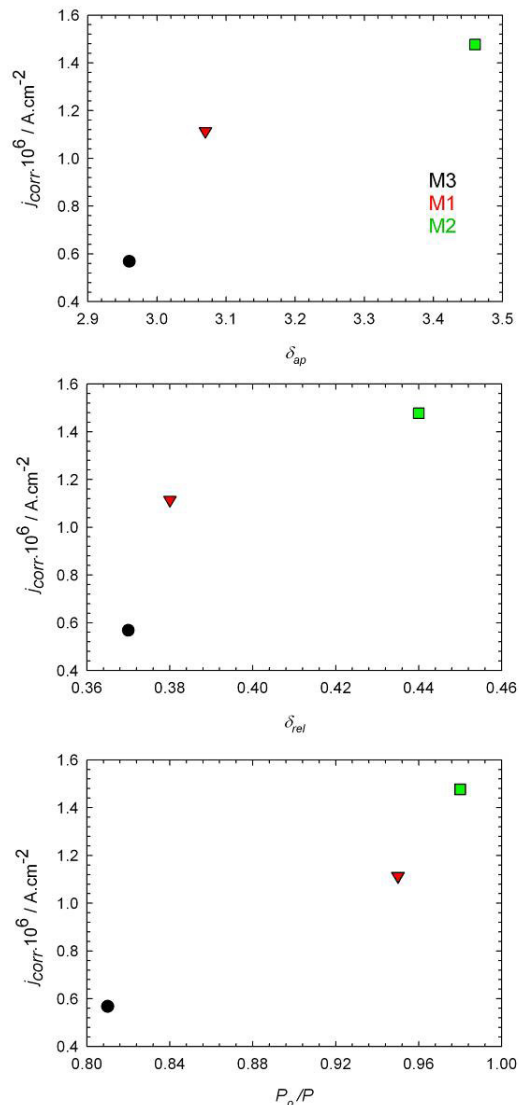
Fig. 3. Variation of corrosion rate respect to δ_{rel}, δ_{ap} and P_0/P.

4. Conclusion

The results from the electrochemical tests indicated that corrosion rate is higher in porous AISI 316L respect to the dense material. Regarding the influence of the type of porosity, it could be established that there is a significant effect of open porosity and the total porosity on the corrosion rate. The smaller open porosity implies lower corrosion rate. This behaviour can be related to the lower exposed surface area produced when open porosity decreases.

These results highlight the need to find an optimal degree of porosity that allows reconciling corrosion resistance with stress shielding on the implant and its biocompatibility.

Acknowledgements

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