Corrosion resistance of multilayer hybrid sol-gel coatings deposited on the AISI 316L austenitic stainless steel

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Abstract. In the present work multilayer hybrid sol-gel coatings were synthesized on the AISI 316L austenitic stainless steel employed in the fabrication of orthopaedic implants. Hybrid sols were obtained from a mixture of inorganic precursor, TEOS, and organic, GPTMS, using ethanol as solvent, and acetic acid as catalyst. The characterization of the sols was performed using pH measurements, rheological tests and infrared spectroscopy (FTIR) for different ageing times. On the other hand, the coatings were characterized by scanning electron microscopy (SEM), while the corrosion resistance was evaluated using anodic potentiodynamic polarization in SBF solution at 37±2°C. The results confirmed that sol-gel synthesis employing TEOS-GPTMS systems produces uniform and homogeneous coatings, which enhanced the corrosion resistance with regard to the parent alloy. Moreover, corrosion performance was retained after applying more than one layer (multilayer coatings).

1. Introduction
The AISI 316L austenitic stainless steel has been widely used in fabrication of orthopaedic implants and biomedical internal fixation devices such as bone plates, spinal fixations, screws, etc., due to its good mechanical properties, acceptable biocompatibility, and low cost compared with those of other metallic materials used for implants, allowing it to be affordable to everybody in developing countries [1]. Nevertheless, this material is prone to suffer pitting corrosion in physiological environments, inducing the release of metallic ions, i.e. as Ni²⁺, Fe²⁺, Mo³⁺ and Cr⁶⁺, which can develop different diseases such as allergy, arthritis, cancer, or genotoxic and mutagenic activities, if these exceed the limit concentration in the human body [2,3].

One way to provide corrosion protection is to coat the surface to prevent contact with the aggressive environment. In this sense, hybrid sol-gel coatings (mixture of organic and inorganic precursors) have arisen as one of the most promising alternatives due to their convenient adhesion to the metallic substrate, low cracking susceptibility and flexibility. The latter has been associated with the presence of organic precursors, which promote crosslinking of the sol-gel network and reduces both temperature and time during the curing process. Furthermore, it is possible to obtain greater layer thicknesses, even design multilayer coatings [4-6].

Therefore, the aim of this work was to perform hybrid sol-gel multilayer coatings for improving the corrosion resistance of the AISI 316L stainless steel employed in fabrication of orthopaedic implants. It is should mentioned that the present work takes part of a large-scale research project, which final purpose is the design of multilayer sol-gel coatings with dual (barrier-bioactivity) properties on different metallic materials used for biomaterial devices.
2. Experimental procedure
Hybrid sols were prepared from a mixture of the inorganic precursor tetraethoxysilane, TEOS, and the organic precursor 3-glycidoxypropyltrimethoxysilane, GPTMS, in 3:1 molar proportion, employing ethanol as a solvent and acetic acid as catalyst. Sols were characterized by pH measurements, rheological tests and Fourier Transform Infrared (FTIR) spectroscopy for different ageing times in order to study the hydrolysis and condensation process. Later, sol-gel monolayer and multilayer (two layer) coatings were deposited the sol on the AISI 316L stainless steel (SS) following the dip-coating route and then were cured in two steps where temperature was increased progressively to prevent cracking: 60°C (4 hours) and 120°C (2 hours). Hybrid sol-gel coatings were characterized by scanning electron microscopy (SEM). Finally, their corrosion resistance was evaluated by anodic polarization test in simulated body fluid (SBF) solution at 37±2°C.

3. Results
3.1. Characterization of hybrid sols

![Figure 1](image)

Figure 1. (a) Evolution of viscosity and pH of the sol synthetized. Evolution of the FTIR spectra: (b) General spectra. Deconvolution analysis of the region 1250-1000 cm⁻¹: (c) 1 day and (d) 28 days.

Evolution of viscosity and pH versus the aging time, up to 28 days, are presented in Figure 1(a). Hybrid sols showed a progressive increment of viscosity ranging from 3.50 cP (initial) to 13.43 cP (final) (the gelation state was reached at 60 days of aging). Also it is observed that the pH of the sol remained invariant in a value of 4, during the whole gelation process, probably due to the presence of acetic acid (weak organic acid) as a catalyst. Complementary, Figure 1(b) shows FTIR spectra of sols where the O-H absorption bands, associated with the presence of solvent/water, can be observed at 3400 and 1645 cm⁻¹. Similarly, precursors distinctive bands are located at 3000-2800 cm⁻¹ and 1500-
1300 cm$^{-1}$ related to C-H bands by methyl (-CH$_3$) and methylene (-CH$_2$-) groups, which lose intensity as the ageing time increases, fact attributed to the progress of the hydrolysis reactions of the precursors [7]. In order to study hydrolysis and condensation reactions that occurred in the sol, deconvolution analysis was carried out for the region of the spectra around 1250-1000 cm$^{-1}$ (this region is related to the silicon chemistry) (Figures 1(c)-(d)). It can be noticed that the intensity of the stretching vibrations bands concerned to the Si-OH groups (1200 and 1170 cm$^{-1}$) increased, while that for the Si-O-C groups (1100 y 1080 cm$^{-1}$) declined, both as the ageing time progressed. This result is indicative of hydrolysis reaction of the precursors during the gelation process. Likewise, characteristic Si-O-Si band at 1040 cm$^{-1}$ attributed to the condensation reaction was also observed [8].

3.2. Characterization of hybrid coating

Electron micrographs of the coatings synthesized on the SS at different aging times are shown in Figure 2. As general result, the longer ageing time the more uniform coatings were obtained. In this regard, lines resulting of the surface preparation of substrate, which were initially evident for short ageing time, were completely covered when the coating was deposited under ageing longer than 7 days. This behaviour can be explained as a result of evolution of the hydrolysis and condensation reaction, which allow: i) the release of silanol groups necessary to ensure wettability and coating adhesion, ii) and the increase of the viscosity of sol required to generate continuous and uniform coatings. Further, cross-sectional analysis revealed that both monolayer and multilayer coatings were continuous and virtually free of cracks, with a thickness about 1.9 and 4.2 µm respectively (Figure 3). In addition, multilayer coatings exhibited an apparent good adhesion between layers.

![Figure 2](image_url)

**Figure 2.** Surface electron micrographs of the hybrid sol-gel coatings for different aging times: (a) 1 day, (b) 7 days and (c) 28 days.

![Figure 3](image_url)

**Figure 3.** Cross-sectional SEM micrographs of coatings obtained at 7 days of aging time: (a) monolayer and (b) multilayer.
3.3. Evaluation of the corrosion resistance of the coatings

Figure 4 shows the anodic polarization curves of the SS and monolayer coatings at different aging times and multilayer coating (obtained under ageing of 7 days). Polarization curves are presented with relative potential units to facilitate their visual analysis. In general, an increase of the aging time resulted in coatings with enhanced corrosion resistance. Thus, the corrosion current density of the coatings gradually decreased until reach a value around 2.0E-8A/cm² (about one order of magnitude lower with regard to the base material (1.6E-7A/cm²)) at seven days of aging, and remained virtually constant for longer times (Figure 4(a)). The latter can be related with the progressive formation of SiO₂, as a result of the advance of the condensation reaction, which confers a hydrophobic character and therefore good protection properties to the coating. Moreover, multilayer deposition did not show significant influence on the anodic polarization response when compared to the monolayer coating, indicating that the corrosion performance of the coating was retained (Figure 4(b)).

![Figure 4](image1)

**Figure 4.** Anodic polarization curves of the SS and the hybrid sol-gel coatings obtained at different conditions: (a) by variation of aging time and (b) by variation of the number of layers.

4. Conclusions

The results confirmed that TEOS-GPTMS sol-gel systems allow obtaining uniform coatings, with no evidence of cracking. Longer ageing times resulted in coatings with better barrier properties, so that the corrosion current density was reduced up to one order of magnitude with regard to the SS for ageing of seven days. Moreover, multilayer coatings showed good adhesion between films, increased thickness, without affecting the corrosion performance of the monolayer coatings.

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