

Bioactive coatings deposited on titanium alloys

C. García^a, S. Ceré^{b,*}, A. Durán^c

^a Universidad Nacional de Colombia, sede Medellín, Colombia

^b INTEMA-Universidad Nacional de Mar del Plata, Division Corrosion, Juan B Justo 4302, B7608FDQ Mar del Plata, Buenos Aires, Argentina

^c Instituto de Cerámica y Vidrio (CSIC), Madrid, Spain

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Abstract

One of the ways to minimise corrosion products release from metallic implants to the surrounding tissue consists in applying a protective coating which may be functionalised with a bioactive material, able to generate a natural bonding to the living tissue. This work describes the development of a double layer coating obtained by the sol–gel technique containing bioactive glass, glass–ceramic or hydroxyapatite particles in hybrid methyl-triethoxysilane (MTES) and tetraethylorthosilicate (TEOS) sol on titanium alloy (ASTM F 67). Samples were electrochemically evaluated in a simulated body fluid (SBF). The application of the coating on the titanium alloy shows an improvement in the corrosion resistance in the tested period of time. This improvement could be due to the reaction of the particles with the physiological medium, which nucleates the formation of calcium phosphate crystals, and blocks the porosity of the coating.

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1. Introduction

The demand for metallic materials in medical and dental devices continuously increases being very important in the medical field mainly due to their mechanical properties [1]. However, the corrosion of the metallic implants is critical because it could affect negatively the biocompatibility and the mechanical integrity. Large concentrations of metallic cations coming from the prosthesis can result in biologically adverse reactions and might lead to the mechanical failure of the implant.

Titanium and Ti-alloys are among the most used materials for in vivo applications, due to their good physical and mechanical properties such as low density, high corrosion resistance and mechanical resistance. However, titanium and other alloying metal ions as aluminium and vanadium,

release from the implants being accumulated in the nearby tissues, due to the aggressive action of the biological fluids [2–5]. The titanium itself is not toxic and its presence in soft tissues seems not to present allergenic or adverse reactions in cellular cultures [3,6].

The aim of this work was the developing of sol–gel coatings containing different bioactive particles of glass, glass–ceramic or hydroxyapatite deposited on the Ti6Al4V alloy. The film should reduce the corrosion of the metal alloy which inhibits the metallic ions release to the living tissue as well as promote bioactivity.

2. Experimental procedure

2.1. Bioactive particles

Bioactive glass particles in the CaO–SiO₂–P₂O₅ system were obtained by melting at 1600 °C, using silica sand, calcium carbonate (Aldrich) and orthophosphoric acid

* Corresponding author. Tel.: +54 223 4816600; fax: +54 223 4810046.
E-mail address: smcere@fi.mdp.edu.ar (S. Ceré).

(Aldrich) [7]. Glass–ceramic particles were obtained from the above mentioned glass followed by a thermal treatment at 1050 °C for two hours, with the aim of obtaining hydroxyapatite and wollastonite as crystalline phases. The hydroxyapatite particles were precipitated by the reaction of ammonium phosphate and calcium nitrate at pH10 [8]. All the particles were milled in an agate planetary mill (Frizsth Pulverisette, Germany), using a speed of rotation of 1500 rpm for 4 h. After milling, the particle size distribution was measured using a laser diffraction equipment (Mastersizer S, Malvern, UK). The vitreous and the partially crystalline character of the materials were evaluated by means of X-rays diffraction, using a Siemens diffrac 5000. Density of the powder materials was determined using a N2-adsorption BET (Monosorb, Quantachrome, USA).

2.2. Sol–gel sol

The sol was prepared by acid catalysis method in one stage, using TEOS (Tetraethyl orthosilicate, ABCR), and MTES (Methyltriethoxysilane, ABCR) as silica precursors; absolute ethanol (Panreac) as solvent and 0.1 N nitric and acetic acid as catalysts. The water was incorporated from the nitric acid solution in stoichiometric ratio. The molar ratio of TEOS/MTES was 40:60. All the reagents were stirred at 40 °C during 3 h obtaining a transparent sol with a pH of 1–2, and a viscosity of 2.6 mPa [9].

2.3. Suspensions

The particle suspensions were prepared by the addition of 10% in weight of particles with respect to the solution [9]. The suspensions were stirred by a high shear mixing in a rotor–stator agitator (Silverson L2R, UK) during 6 min. After the first 3 min, 0.5% by weight on solids of tetrapropyl ammonium hydroxide (TPAH, Aldrich) was added as dispersant in the glass and glass–ceramic containing suspensions. The TPAH works as a cationic surfactant adsorbed on the surface of the glass and glass–ceramic particles, and raised the pH up to 6–7, becoming far from the isoelectric point of the particles. This, in turn, creates an electrostatic repulsion between them that avoided the segregation. In the hydroxyapatite suspension 2% by weight with respect to the solids of a phosphate ester was added as dispersant. The phosphate ester acts as an anionic surfactant adsorbed on the particles of the hydroxyapatite suspension promoting the stabilisation of the suspension.

2.4. Coatings

Mirror polished metal plates with a size of 7 × 3.5 × 0.2 cm of the titanium alloy Ti6Al4V (Goodfellow) were used as substrates. Samples were degreased, hand washed with distilled water, and rinsed in ethanol. Coatings were obtained by dip-coating at room temperature using a withdrawal rate of 28 cm min⁻¹. Double coatings consisting of

a first coating of the SiO₂ hybrid sol without particles, treated at 450 °C during 30 min, followed by a second coating deposited on the top of the first one, of the particle containing suspensions, followed by the same heat treatment were applied on the substrates. The coatings thickness was measured with a profilometer (Talystep, Taylor Hobson, USA) on a scratch made on the film after the deposition. The integrity and characteristics of the coatings were evaluated by optical microscopy (Olympus BX41, USA) and the images were analysed using appropriate software (Leyca, USA).

2.5. Electrochemical assays

Electrochemical experiments were performed using an electrochemical unit (Solartron 1280B) in a Simulated Body Fluid (SBF) at pH7.3, after 1 and 10 days of immersion at 37 °C [10,11]. A traditional three-electrode cell was used. The coated sample was used as working electrode, a platinum wire as auxiliary electrode and a saturated calomel electrode (SCE, Radiometer) as the reference electrode. Impedance tests (EIS) were carried out at the corrosion potential (E_{corr}) with amplitude of 0.005 Vrms. Frequency was swept from 20000 to 0.01 Hz. Potentiodynamic polarization curves were measured from the E_{corr} to 1.4 V at a sweep rate of 0.002 V s⁻¹. The modelling of the equivalent circuits was calculated by means of the Zplot software [12].

2.6. In vitro bioactivity tests

The capacity of the coated materials to induce apatite films on their surface was studied after immersion in SBF during different periods of time. A total of 10 specimens of 3 × 2 cm of Ti6Al4V, coated with double coatings containing the different particles systems under study (glass, glass–ceramic and hydroxyapatite) were suspended independently in sealed polyethylene jars with 16 ml of SBF. The ratio of the exposed area of the sample to the fluid volume was of 0.3 cm² ml⁻¹. Immersion was maintained up to 75 days, after that the samples were washed with distilled water and dried at room temperature. The analysis of the surface and the presence of the apatitic phases were carried out by means of Scanning Electronic Microscope (JEOL JSM5910LV).

3. Results

3.1. Particle characterization

The glass was colorless and transparent, and the glass–ceramic white and translucent [7,9]. The hydroxyapatite was white, opaque and presented good crystallinity [8].

The crystalline phases present in the glass–ceramic were identified by X-ray analysis as wollastonite and hydroxyapatite while the glass samples did not present any crystalline phase. Hydroxyapatite powders presented only hydroxyapatite as crystalline phase [8]. The average

Table 1
Average particle size and density of the particles

Particles	Average particle size (μm)	Density (g/cm^3)
Glass	10 ± 1	2.92 ± 0.05
Glass–ceramic	11 ± 1	2.99 ± 0.05
Hydroxyapatite	5 ± 1	3.11 ± 0.05

particle size of the milled materials and their densities are shown in Table 1.

3.2. Coating characterization

Fig. 1 shows the coatings obtained with the three types of particles as observed by optical microscopy. The coatings present good integrity and homogeneous particle distribution, without apparent defects. The glass and glass–ceramic particles occupy around 8% of the total area and the particle size varies of $10 \pm 1 \mu\text{m}$. The hydroxyapatite particles take up about 20% of the specimen area, and its particle size varies of $5 \pm 1 \mu\text{m}$.

EIS diagrams for the Ti6Al4V alloy, bare and with the double coating containing glass, glass–ceramic and hydroxyapatite particles after 1 and 10 days of immersion in SBF, are presented in Fig. 2 as Bode plots. The three types of coatings show very similar behaviour after 1 day immersion in SBF. The Bode diagrams (angle vs. frequency) show a capacitive behaviour in a wide range of frequencies, also showing a change of slope in the low frequency limit. The phase angle decreases gradually, but not reaching zero value; this might indicate the presence of pores in the coating and diffusion phenomena between them [13]. However, it must be pointed, that after 1 day

of immersion in SBF the impedance module of the three types of coatings is higher than that of the bare metal for frequencies higher than 0.1 Hz.

After 10 days of immersion in SBF, all the coated samples present an impedance module about one order of magnitude higher respecting to the bare metal and still higher than those of 1 day of immersion in the whole range of frequencies under study. The curves corresponding to the three kind of samples present a capacitive behaviour in a wide range of frequencies. All of them present a single maximum value at the 80° phase angle. The maximum decreases progressively without getting zero value for the specimens coated with glass and hydroxyapatite containing coatings, and the angle is kept nearly constant at the low frequencies range for the glass–ceramic coated samples.

In order to get better insights about the corrosion feature occurring on the samples, EIS spectra were analyzed using equivalent electric circuits (Fig. 3).

Fig. 4 shows the polarization curves corresponding to the double coated samples containing glass, glass–ceramic and hydroxyapatite particles, after 1 and 10 days immersion in SBF. All the coated samples show passive behaviour in the whole range of potentials tested, and their passivation currents are 2–3 orders of magnitude lower than that of the uncoated samples. After 1 day of immersion in SBF, the passivation currents are $1.1 \times 10^{-8} \text{ A cm}^{-2}$ for the glass containing coating, $9 \times 10^{-8} \text{ A cm}^{-2}$ for the glass–ceramic containing coating and $4 \times 10^{-8} \text{ A cm}^{-2}$ for the hydroxyapatite containing coating. The passive behaviour is nearly constant after 10 days of SBF immersion, with passivation currents, for 3 types of coatings, up to two orders of magnitude lower than the currents of the bare metal. The

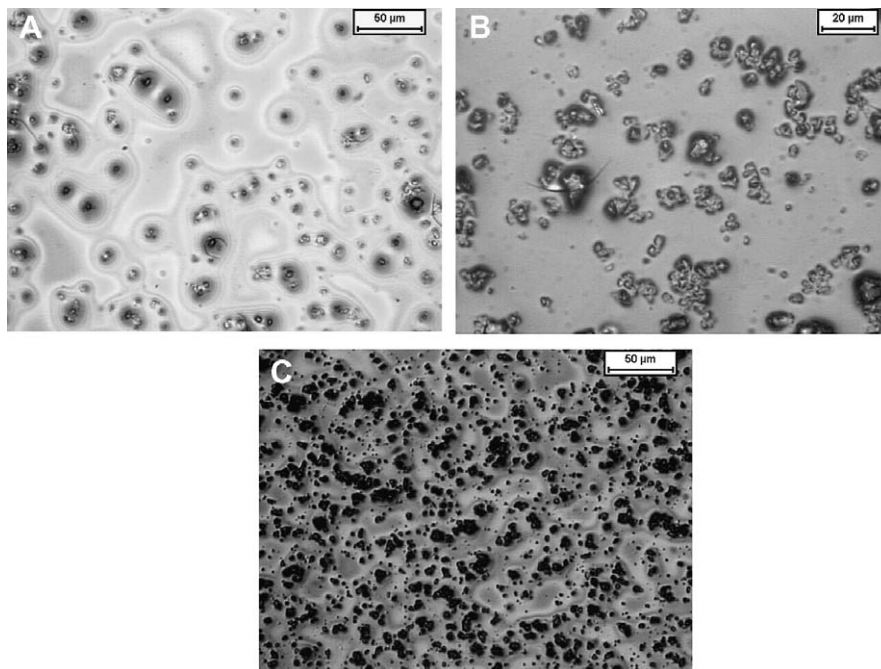


Fig. 1. Micrographs of the coatings containing the three types of particles. A: Glass, B: Glass–ceramic, C: Hydroxyapatite.

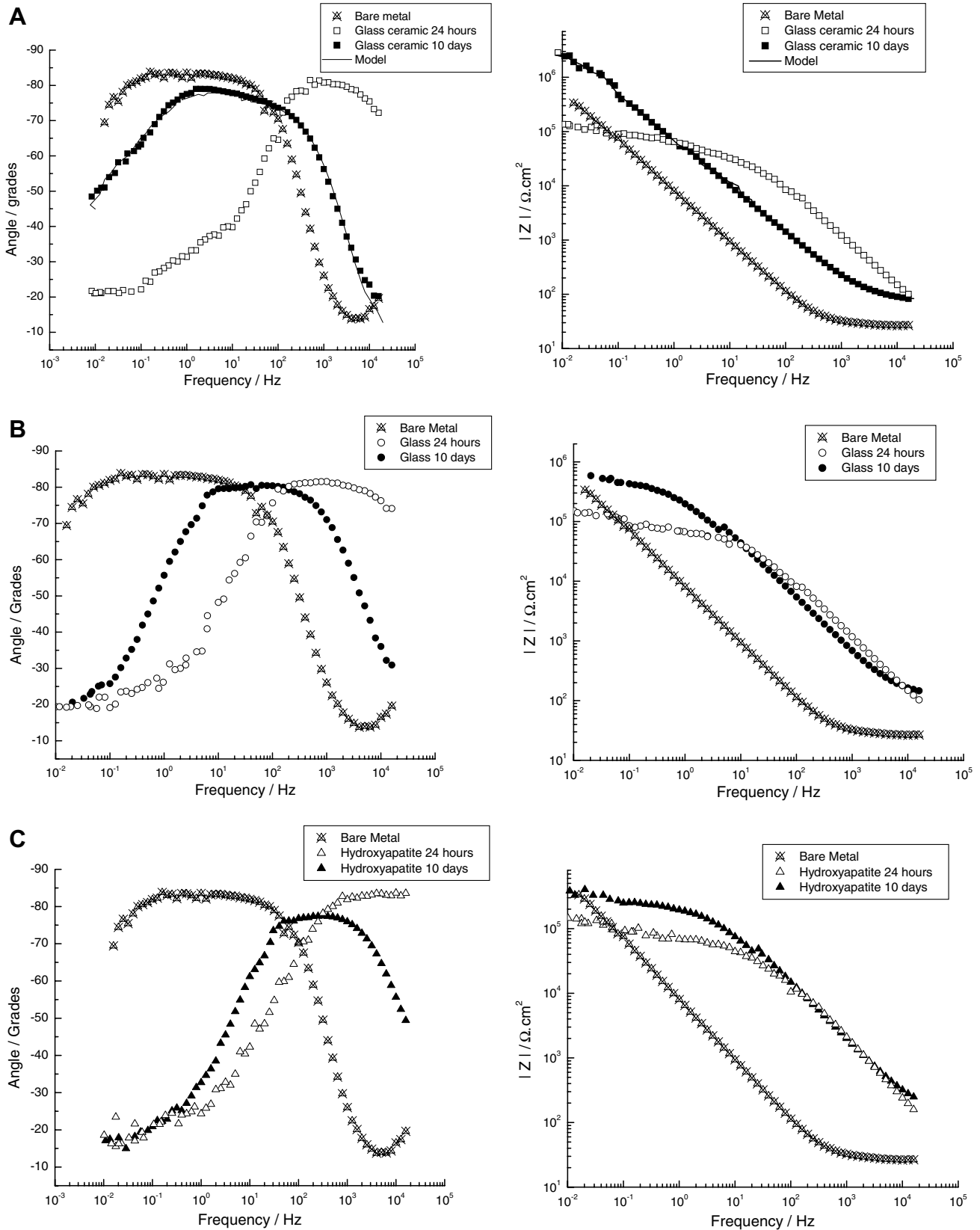


Fig. 2. Bode diagrams of the double coatings containing particles of A: Glass, B: Glass–ceramic, C: Hydroxyapatite, after 1 and 10 days of immersion in SBF.

passivation currents after 10 days immersion in SBF fluid is $1.1 \times 10^{-7} \text{ A cm}^{-2}$ for the glass containing coating,

$4 \times 10^{-8} \text{ A cm}^{-2}$ for the glass–ceramic containing coating, and $8 \times 10^{-8} \text{ A cm}^{-2}$ for the hydroxyapatite containing

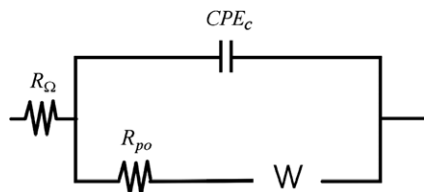


Fig. 3. Equivalent electric circuit used for the modulation of the Ti6Al4V system, coated with Glass, Glass–ceramic or Hydroxyapatite containing coatings, after 1 or 10 days immersion in SBF.

coating. It is worth noting that the glass–ceramic coatings present an improvement after 10 days of immersion, mean while hydroxyapatite and glass coatings showed a small deterioration after 10 days of immersion in SBF.

3.3. *In vitro* bioactivity test

All the coatings containing either glass, glass–ceramic, or hydroxyapatite particles formed an apatite film on the

surface after some time of immersion in simulated physiological fluid (SBF), this fact indicates that all coatings tested are potentially bioactive [10,14,15]. The apatitic composition of the superficial film was confirmed by DRX, FTIR and EDX (Fig. 5) [16]. As observed in Table 2, the deposition kinetics of the apatitic film on the coatings depends on the kind of particles present in them.

The first signals of apatite on the surface occurred after two days of immersion and were detected by means of electronic microscopy and EDX. However, the kinetics of the formation of this film is much lower in the case of the hydroxyapatite than in the glass and glass–ceramic particles and the total time required for the complete covering of the surface specimen is much longer with respect to the glass and glass–ceramic containing coatings, indicating a lower reactivity of the hydroxyapatite particles in contact with the simulated physiological fluid. Fig. 5 shows photographs of the deposits on the top of the Ti6Al4V samples that were coated with a layer containing glass particles, after 75 days of immersion in SBF and the FTIR, EDX

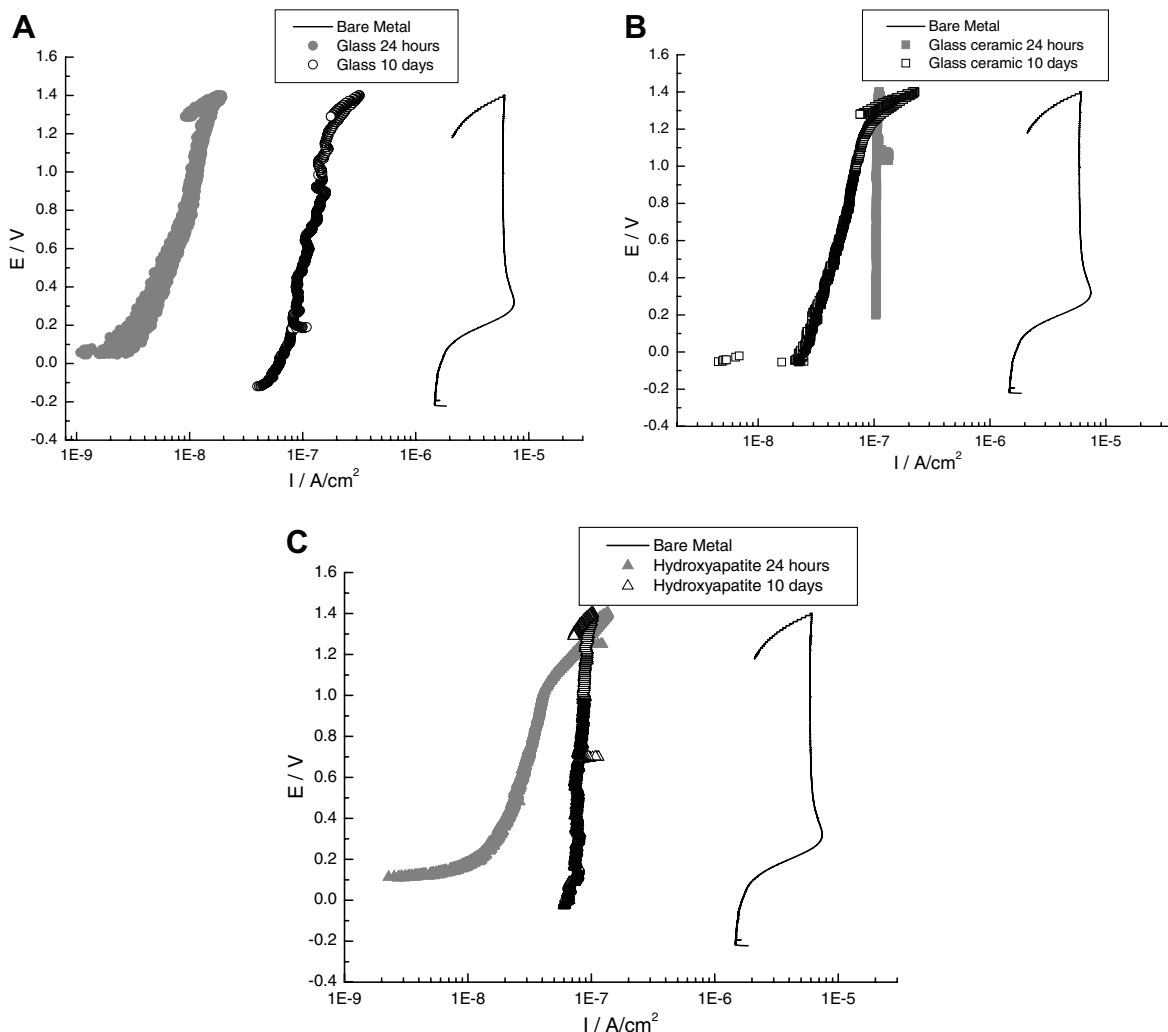


Fig. 4. Potentiodynamic polarization curves of the Ti6Al4V alloy, bare and with double coatings containing A: Glass particles, B: Glass-ceramic particles, and C: Hydroxyapatite particles, after 1 and 10 days immersion in SBF.

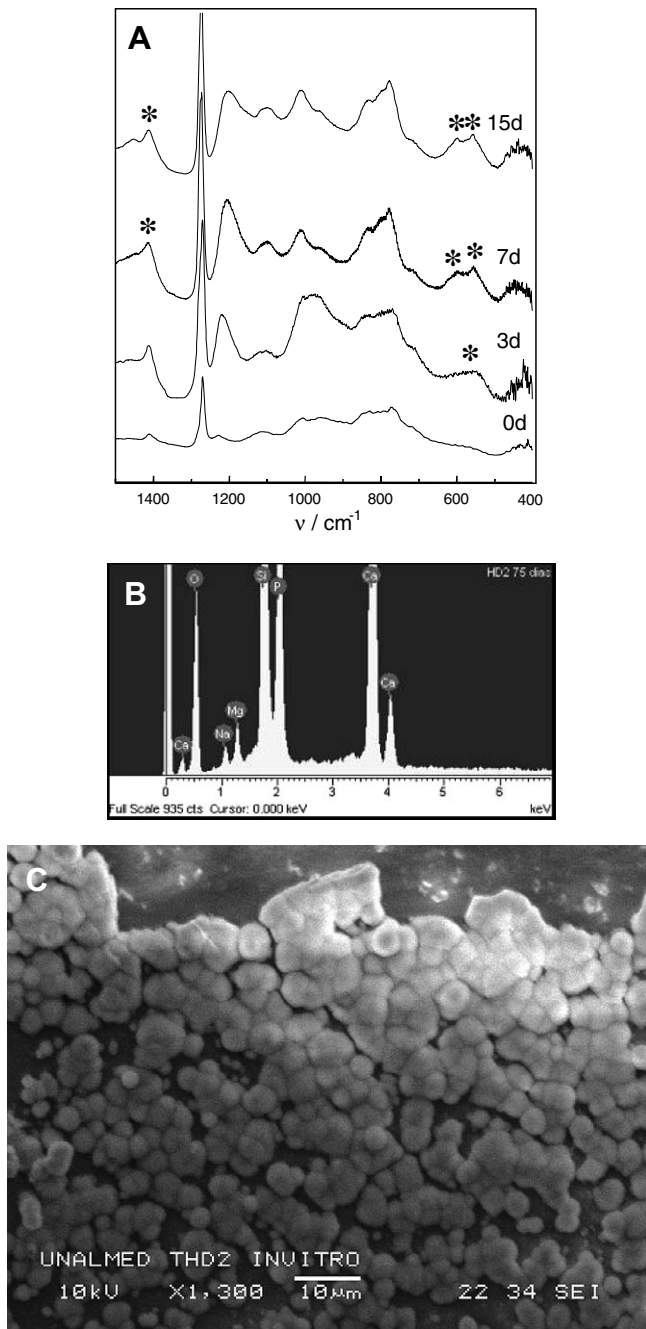


Fig. 5. A: FTIR spectra of the double coated samples containing glass at various immersion times. Y axis is shown in arbitrary units. Apatite bands are indicated with (*). B: EDX of the deposits after 75 days of immersion in SBF. C: Photomicrography of the deposits on the top of the Ti6Al4V samples that were coated with a layer containing glass particles after 75 days of immersion in SBF.

and DRX characterization of the deposits formed on the sample surface. The presence of Mg and Na in the EDX spectra can be attributed to the SBF where the samples were immersed.

4. Discussion

The procedure for preparing suspensions and coating deposition was adequate for producing homogeneous coatings and crack-free deposits with a regular distribution of particles.

Electrochemical tests show an interesting protective behaviour of the particle containing coatings. The evolution in time of the double coatings presents an increase of the impedance module after 10 days of immersion in SBF in the low frequency range. This behaviour could indicate that, although the coatings present pores and defects after 10 days of immersion in SBF, these defects could be blocked by the corrosion products of the metal or by the degradation of the particles present in the coating.

The electrochemical behaviour can be described in terms of an equivalent circuit in order to provide the most relevant parameters applicable to the corroding system. The equivalent circuit used for the adjustment of the experimental data is shown in Fig. 3. A constant phase element (CPE) was used instead of an 'ideal' capacitor, taking into account a certain degree of surface unhomogeneity, due to the deviations from -1 observed as capacities in the slope of the $\log|Z|$ vs. $\log f$ curve. In the simulation of the impedance plots, a finite Warburg impedance was included in order to account for the diffusion of the electro active species through the pores or the defects of the coating. If the material is thin, low frequencies will penetrate the entire thickness, creating a finite length Warburg element (Eq. 1) [12]

$$Z_w = \frac{R_{DO}}{(jT\omega)^n} \tanh(jT\omega)^n \quad (1)$$

where R_{DO} is associated with diffusion in the solid phase and T is related to the diffusion coefficient and the pore length. In the circuit, R_{Ω} represents the electrolyte resistance, CPE_c is related with the non ideal capacitance of the oxide film, R_{po} is the resistance presented by the porosity to the passage of the electrolyte. Parameters calculated by this type of modelling are shown in Table 3.

The analysis of these data shows that, in all cases, the resistance associated to the pores (R_{po}) and the resistance associated to the diffusion (R_{DO}) increase with the

Table 2
Bioactivity *in vitro* of the coatings containing glass, glass–ceramic, and hydroxyapatite particles

Particle	Average size (μm)	% of the area occupied by the particles	First signals of apatite on the surface of the coating (days)	Test specimen totally covered with apatite (days)
Glass	10	8	2	6
Glass–ceramic	11	8	2	7
Hydroxyapatite	5	20	2	14

Table 3

Electrochemical parameters calculated based on the modelling of the electrochemical response, for 24 h and 10 days immersion periods (double coatings with glass, glass–ceramic or hydroxyapatite particles)

Particle	Time of immersion	$R_{\Omega}/\Omega\text{cm}^2$	$\text{CPE}_0/\Omega^{-1}\text{s}^n\text{cm}^{-2}$	n	$R_{\text{po}}/\Omega\text{cm}^2$	$R_{\text{DO}}/\Omega\text{cm}^2$	$T/\text{s}^{0.5}$	n
Glass	24 h	12	4.39×10^{-7}	0.87	7.37×10^4	2.08×10^6	53.52	0.98
	10 days	17	6.47×10^{-7}	0.88	4.43×10^5	1.96×10^7	117.9	0.99
Glass–ceramic	24 h	17	4.76×10^{-7}	0.86	6.6×10^4	2.59×10^6	54.3	0.98
	10 days	15	2.93×10^{-7}	0.85	2.82×10^6	1.24×10^7	98.8	1
Hydroxyapatite	24 h	12	2.96×10^{-7}	0.86	7.05×10^4	1.85×10^6	53.9	0.98
	10 days	15	3.18×10^{-7}	0.84	2.44×10^5	1.31×10^7	117.7	0.99

immersion time. As the T parameter (directly proportional to the length of the pores and inversely proportional to the coefficient of diffusion) increase with time, it could be assumed that the length of the pores increases due to the growth of a surface thin film or, that the area of the pores decreases with time. The capacity of the coating increases with time, which might indicate a decrease in the area of the defects. This area reduction would be due to the pore and defect blocking caused by corrosion products of the metal or by reaction of the particles. Also, the reaction of the particles with the SBF could form a thin film on the coating, increasing its thickness. Therefore, the area reduction and the increase of the thickness take the value of pseudocapacity of the coating to a nearly invariant point.

The results of the EIS test for titanium alloy covered with a double coating containing any of the three different types of particles indicate that the reaction of the particles with the medium could generate the formation of a thin film on the electrode, and that this in turn could block the defects and the pores present in the coating. This blocking could cause a higher resistance to the diffusion of the electro-active species to reach the metallic substrate (which causes corrosion of the metal) increasing the apparent resistance of the system with time.

However, the comparison of these results with the polarization curves (Fig. 4) show that for glass and hydroxyapatite coatings, the passivation current density is slightly higher in all cases after the 10 days of immersion in SBF than for the 24 h of immersion, while the current density slightly decreases for the glass–ceramic containing coating after 10 days of immersion when compared with 24 h of immersion. This fact is in good agreement with that observed for the same kind of coating on stainless steel [7]. The beneficial effects of the glass-ceramic particles has also been evaluated *in vivo* on stainless steel and Cobalt alloys and this kind of particles showed the better bioactive response [17,18]. Conversely, the formation of the superficial thin film implies the reaction of the particles with the medium, generating a bigger exposed area of the substrate. Although the material is covered by a thin film that decreases the access of the electrolyte to the pores and defects, the chemical nature of this film makes it to be deposited without a good adherence to the surface. The application of an electrical potential could remove the film, leaving a bigger area of the substrate exposed to the medium and increasing the current density.

As a general result, the application of double coating on the titanium alloy causes an improvement in the corrosion resistance during the time under study. This improvement can be due to the reaction of the particles present in the coating with the physiological medium, which nucleates calcium phosphates on the surface and blocks the porosity of the coating generated.

When the rate of formation of apatitic phases film on the different particles containing coatings surface is compared, it is possible to establish the reaction kinetics of the three types of bioactive particles considered in this work. Although all the particles showed to be bioactive, the hydroxyapatite is the less reactive, followed by glass–ceramic and glass. This behaviour is probably related to the particles size and the particle crystalline grade. It is well known that the crystalline grade affects the reaction rate of the materials in the surrounding fluid [14,19]. The more crystalline the particles, the more retarded the reaction between the particles and the simulated body fluid to form apatitic phases and therefore their bioactivity is delayed. This explains the lower reactivity of glass–ceramic coatings with respect to glass containing layers. On the other hand, the smaller reactivity of hydroxyapatite particles is evident in spite of their smaller particle size when compared with the glass and glass-ceramic particles, and the higher content of particles in the coatings. Similar behaviour was observed in other studies evidencing the low reactivity of hydroxyapatite with simulated body fluid [7]. After these promising results for glass and glass–ceramic containing coatings *in vivo* test on Hokaido rats are in progress.

5. Conclusions

It is possible to obtain defect-free coatings on Ti6Al4V alloy, containing particles of glass, glass–ceramics and hydroxyapatite, using suspensions prepared with a solution of TEOS/MTES containing either glass, glass ceramic or hydroxyapatite particles.

All the coatings tested presented impedance modules higher than that of the bare metal, and also, indicating a protective role of the coating on the substrate. All the parameters calculated from the EIS experiments indicate that there is an improvement in the coating performance with the time of immersion in SBF. These results would also indicate that, in spite of the coatings showing an important pore and defect density, these defects probably

could be blocked by the detritus of the metal or by the degradation products of the particles of the coatings.

The reaction of the particles with the electrolyte generates the deposit of a superficial film on the electrode that could block the pores and the defects. This blocking result in a higher diffusion resistance for the electro active species to the metallic substrate and, therefore, it conducts to a decrease of the corrosion when increasing the immersion time.

The polarization curves showed that the double coatings, with the 3 types of particles, have a protective action on the bare metal, both, after 1 and 10 days of immersion in SBF. After 10 days of immersion in SBF, the glass ceramic double layer coating has better corrosion resistance than after 24 h. This indicates that the dissolution products are blocking effectively the electrochemical process at the pores and the defects of the coating, acting as a protective layer against corrosion and ion diffusion.

The application of double coated sample containing particles on the titanium alloy showed an improvement on the corrosion resistance in the tested period of time. This improvement could be due to the reaction of the particles with the physiological medium, which nucleates the formation of calcium phosphate crystals, and blocks the porosity of the coating (initial or post-formed).

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References

- [1] S. Roessler et al., *Colloid. Surface B* (2002) 387.
- [2] A.W.E. Hodgson et al., *Electrochim. Acta* (2002) 1913.
- [3] D. Zaffe, C. Bertoldi, U. Consolo, *Biomaterials* (2003) 1093.
- [4] T.M. Yue et al., *Mater. Lett.* (2002) 206.
- [5] B. Finet, G. Weber, R. Cloots, *Mater. Lett.* (2000) 159.
- [6] I. Milosev, M. Metikos-Hukovic, H.H. Strehblow, *Biomaterials* (2000) 2103.
- [7] C. García, S. Ceré, A. Durán, *J. Non-Cryst. Solids* (2004) 218.
- [8] C. García et al., *Key Eng. Mater.* (2005) 47.
- [9] C. García, A. Durán, R. Moreno, *J. Sol-Gel Sci. Technol.* (2005) 211.
- [10] C. Ohtsuki, T. Kokubo, T. Yamamuro, *J. Non-Cryst. Solids* (1992) 84.
- [11] T. Kokubo, *Acta Mater.* (1998) 2519.
- [12] Z. Scribner, *Plot for Windows, Electrochemical Impedance Software Operating Manual. Part I*, I. Scribner Associates (Ed.), Southern Pines, NC, 1998.
- [13] C. Liu et al., *Corr. Sci.* (2003) 1257.
- [14] T. Kokubo et al. (Eds.), *Chemical reaction of bioactive glass and glass ceramics with a simulated body fluid. Journal of Materials science: Materials in medicine*, vol. 3 (1992) 79.
- [15] T. Kasuga et al., *J. Mater. Sci.* (1987) 3721.
- [16] A. Durán et al., *J. Mater. Chem.* (2004) 2282.
- [17] C. García, *Bioactivación de metales de uso ortopédico mediante recubrimientos producidos por sol-gel*, Instituto de Cerámica y Vidrio, Universidad Autónoma de Madrid: Madrid, 2004, p. 263.
- [18] J. Ballarre et al., *J. Non-Cryst. Solids* (2002) 278.
- [19] T. Kokubo, *A/W glass-ceramic: processing and properties*, in: J. Wilson (Ed.), *An Introduction to Bioceramics*, World scientific, Singapore, 1993, p. 75.