Electrochemical behavior of 45S5 bioactive ceramic coating on Ti6Al4V alloy for dental applications

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Abstract. Titanium and its alloys are widely used as implant materials because of their mechanical properties and non-toxic behavior. Unfortunately, they are not bioinert, which means that they can release ions and can only fix the bone by mechanical anchorage, this can lead to the encapsulation of dense fibrous tissue in the body. The bone fixation is required in clinical conditions treated by orthopedic and dental medicine. The proposal is to coat metallic implants with bioactive materials to establish good interfacial bonds between the metal substrate and bone by increasing bioactivity. Bioactive glasses, ceramics specifically 45S5 Bioglass, have drawn attention as a serious functional biomaterial because osseointegration capacity. The EPD method of bioglass gel precursor was proposed in the present work as a new method to obtain 45S5/Ti6Al4V for dental applications. The coatings, were thermally treated at 700 and 800°C and presented the 45S5 bioglass characteristic phases showing morphology and uniformity with no defects, quantification percentages by EDS of Si, Ca, Na, P and O elements in the coating scratched powders, showed a good proportional relationship demonstrating the obtention of the 45S5 bioglass. The corrosion tests were carried out in Hank's solution. By Tafel extrapolation, Ti6Al4V alloy showed good corrosion resistance in Hank’s solution media, by the formation of a passivation layer on the metal surface, however, in the system 45S5/Ti6Al4V there was an increase in the corrosion resistance; i_corr, E_corr and corrosion rate decreased, the mass loss and the rate of release of ions, were lower in this system than in the titanium alloy without coating.

1. Introduction
Titanium and Titanium alloys are extensively used as biomaterials for implants applications, due to their excellent mechanical properties and non-toxic behavior. Unfortunately, in general, metallic implants are not bioinert at all, which means that they can release ions and they can only have mechanical anchorage with bone, leading to encapsulation with fibrous tissue inside the body. In most of the cases the osseointegration is required for orthopedic and dental applications [1, 2], so it is necessary to coat the metal in order to obtain good interfacial union between metal substrate and bone which increases the bioactivity [3]. Recently, electrochemical deposition methods (EPD) have gain increased interest due to the simplicity of their application and the possibility to obtain uniform coatings inclusive in irregular form substrates at room temperature with low cost equipment [4].
Bioactive glasses, mainly the ceramic formulation Bioglass 45S5 (45% SiO\textsubscript{2}, 24,5%, Na\textsubscript{2}O 24,5% CaO y 6% P\textsubscript{2}O\textsubscript{5} weight %), have been of interest as biomaterials because their osseointegration capacity [5, 6, 7, 8]. It has been reported that bioglass 45S5 can be inserted at high scale in bone hurted zones to help the restoration and it also brings structural support establishing hard bonding to bone [9, 10]. Elsewhere bioglass has been used for other applications as implants, to release the conductive auditory loss, for the mantenent of endosseus prosthesis and as particulate material to enhance the natural restoration process in patients with periodontal disease [10, 12]. Nevertheless, those processes imply the formation of hydroxiapatite calcium phosphate layer on the implanted glass material [13]. In this work, electrophoretic deposition method (EPD) was used to obtain 45S5/Ti6Al4V system, starting with a colloidal precursor suspension obtained by sol-gel synthesis. The obtained films were structurally characterized and the corrosion resistance in Hank's solution at 38°C was determined by potentiometric tests.

2. Experimental procedure

2.1. Ti6Al4V substrates preparation

1 x 1 cm Ti6Al4V plates were used as substrates because this alloy is the most used for implants and dental membranes, excellent mechanical properties of this alloy have been reported by different authors, fatigue strength of 707 MPa in 10\textsuperscript{7} cycles, Young's modulus of 110 GPa, creep resistance of 860 MPa and tensile strength of 930 MPa [14, 15, 16, 17, 18, 19]. Alagic et al. [20], studied the wear resistance of Ti13Nb13Zr and Ti6Al4V alloys and reported a wear volume loss of 5.19 y 0.0751 mm\textsuperscript{3}, and hardness values of 231 and 575 HV, respectively, so the Ti6Al4V presented the best mechanical behavior. Substrate plates were previously polished with SiC from 240, 320, 400 to 600 mesh then, they were ultrasonic washed in acetone bath, rinsed in distilled water and wetted in alcohol.

2.2. 45S5 bioglass coating

45S5 bioglass was synthetized by sol-gel, starting with a HNO\textsubscript{3} 1M solution in which, the precursors were hydrolized tetraetilortosilicate ((C\textsubscript{8}H\textsubscript{20}O\textsubscript{4}Si), 99.9%, Sigma Aldrich, US), 6% del trietil fosfate ((C\textsubscript{6}Hi\textsubscript{5}O\textsubscript{4}P), 99.8%, Sigma Aldrich, US), then 24.5% sodium nitrate (NaNO\textsubscript{3}, 99%, Sigma Aldrich, US) and 24.5% calcium nitrate ((Ca(NO\textsubscript{3})\textsubscript{2}.4H\textsubscript{2}O, 99%, Sigma Aldrich, US) were added. After hydrolysis and polycondensation take place, the suspension was taken to the electrophoretic cell to carried out the deposition on the Ti6Al4V substrates. The hydrolized deposits were thermally treated at four different temperatures 500, 600, 700 and 800°C to obtain the 45S5 bioglass coatings. The four samples were labeled as follows: BG500, BG600, BG700 and BG800. The heating rate (5°C/min), time at calcination temperature (120 min) and cooling rate (5°C/min) until room temperature, were the same and constant for all the samples. The obtained phases in the 45S5 bioglass coatings were characterized by X Ray Diffraction (XRD), using a SIEMENS D-5000 model difractometer with CuKa radiation. The nanostructural morphology characterization was followed by scanning electron microscopy (SEM) using a field emission scanning electron microscope JEOL JSM.7600F, The obtained coatings elemental composition was determined by EDS.

2.3. Electrochemical test

Ti6Al4V alloy and 45S5/Ti6Al4V system were evaluated by electrochemical techniques in a GAMRY potencióstate in order to know the corrosion behavior in Hank's solution at 37°C simulating the human body ambient. Tafel extrapolation technique was used applying a potential scanning from -250mV to 1500 mV with a scanning rate of 1 mV/s, over the open circuit potential (OCP). Exposition area of 0.31669 cm\textsuperscript{2} was used for all samples, equivalent weight of 11.44 g. was used for the titanium alloy, according with ASTM G102-89 (ASTM 1999) norm [21]. The electrochemical cell was conformed to a saturated AgCl electrode as reference electrode, high purity graphite electrode as counter electrode and Ti6Al4V alloy and 45S5/Ti6Al4V samples as working electrodes. Deaerated Hank's solution at pH=7.4, and at 37 °C, was the media used, the composition from SIGMA is shown in Table 1,
electrochemical tests were carried out after 1 hour of immersion in Hank’s solution in order to stabilize the open circuit potential and temperature.

| Table 1. Hank’s solution chemical composition (g/l) (ZIGMA) |
|----------------|----------------|----------------|----------------|----------------|
| NaCl           | KCl            | Na₂HPO₄        | KH₂HPO₄        | NaHCO₃         | D-Glucose     |
| 8.0            | 0.4            | 0.047          | 0.06           | 0.35           | 1.0           |

3. Results

3.1. Structural characterization
In order to study phases evolution during thermal treatment of the sol-gel electrodeposited bioglass precursors, structural characterization was carried out by X Ray Diffraction of the 45S5 bioglass xerogels thermally treated at 700, 800 and 1000°C and are shown in Figure 1. Crystalline phases peaks of Na₂Ca₃Si₆O₁₈ (JCPS #77-2189), began to appear in the xerogel treated at 700°C, in the diffractograms of the xerogels treated at 800 and at 1000°C, those peaks appear with higher intensity and also another peak, corresponding to the crystalline phase Na₂Ca₄(PO)₄²SiO₄ (JCPS #32-1053) is present. Those phases coincide with the ones reported by other authors who synthetized bioactive glasses with the 45S5 bioglass composition [4, 5, 6, 7, 10, 22, 23].

![Figure 1. X Ray diffraction patterns of the xerogels treated at 700, 800 and 1000°C](image)

Morphologies obtained by Field emission SEM of the 45S5 Bioglass xerogels, thermally treated at 700, 800 and 1000°C are presented in Figures 2a-d. Xerogel treated at 700°C presents a fiber like structure, as it was treated at higher temperature than \( T_{g1} \) and \( T_s \), the phases detected in the corresponding X Ray diffractogram, which are reach in phosphorus and silicon, are present [10]. In the micrographs of Figures 2b and 2c, corresponding to the xerogels treated at 800 and 1000°C, a growing of the particles and an evident change in the morphology is observed. This change may be due to the development of an amorphous matrix in which there are immersed crystalline phases and a great densification due to the higher temperature treatment over the \( T_{g1}, T_s \) and \( T_{g2} \) at which the phases rich in phosphorous and silicon are obtained. Figure 2d show the porous morphology of the xerogel treated at 1000°C, at lower magnification.
Figure 2. Field emission SEM micrographs of the 45S5 xerogels thermally treated at (a) 700°C (30000X), (b) 800°C (10000X), (c) 1000°C (100000X) and (d) 1000°C (5000X).

The microanalysis of the obtained 45S5 xerogels treated at 700, 800 and 1000°C, presented the signals of O, Si, Ca, Na y P, all of them are characteristic elements 45S5 bioglass. In xerogel treated 800°C, the same elements of the bioglass were detected, observing an increase in Calcium and a decrease in Sodium, because this xerogel was treated at higher temperature than $T_g$ at this temperature, it is possible to have diffusion and this occurs in the transition between the second and the third step of the 45S5 bioglass sinterization process. The microanalysis of the xerogel treated at 1000°C, showed evidence of more diffusion processes, enhancing the calcium content and decreasing the sodium content. Obtained 45S5 bioglass coatings morphologies were also observed by FESEM, at 5000X and are shown in Figure 3. Figure 3a, shows the coating treated at 500°C which presents inhomogeneities and defects due to the low thermal treatment temperature bellow the glass transition temperature $T_g$. Figure 3b, shows a more homogeneus coating treated at 600°C, which is distributed on all the substrate surface. Nevertheless it is specter that this coating is not well densifiqued because it was only treated at temperature 20°C up to the glass transition temperature $T_g$, so it is only partially dense. Figure 3c, shows the coating treated at 700°C, the change in the structure is evident appearing small and well distributed crystals, covering uniformly all the substrate surface, no defects were observed in this coating. Berbecaru et al. [23] obtained a 45S5 bioglass coating on Ti6Al4V alloy by magnetron sputtering technique and stablished that thermal treatement at 700°C by 2 hours, was adequate to obtain a glass crystallized coating according with their XRD and FTIR results which is in agreement with the present results, they also found that immersion in body simulated fluid (SBF) generates the band corresponding to Si-OH bonding. Figure 3d, shows the coating treated at 800°C, which presents a growing structure on the substrate formed by bigger aggregates originated at temperatures over the glass transition temperature $T_g$, where phases richer in phosphorus and silicon.
like Na2Ca3Si6O18 and Na2Ca4(PO)4Si2O4 crystallize, originating a substantial change in the morphology, which generates separation on that surface coating. The micrograph at higher magnification (Figure 3e), allows to see the acicular morphology of these crystals. Plewinski et al. [5] established that bioglass 45S5 crystallization allows better formation of the apatite layer in comparison with the amorphous bioglass and concluded that this vitro-ceramic should be consider as a material for coating dental implants.

Figure 3. FESEM Micrographs of 45S5 bioglass coatings thermally treated at: a) 500°C (5000X), b) 600°C (5000X), c) 700°C (11000X), d) 800°C (500X), and e) 800°C (100 000X), f) coating thickness.
3.2. Tafel extrapolation
The behavior of the potentiodynamic polarization curves at open circuit potentials, as a result of the immersion in Hank’s solution media of the Ti6Al4V alloy and the 45S5 bioglass/Ti6Al4V system are discussed here. At the beginning, the simple BG700, presents better corrosion resistance than the Ti6Al4V alloy, because it had a current intensity ($i_{corr}$) value of 0.001 A/cm$^2$ Alves et al. [25] evaluated this alloy polished with SiC 600 mesh in Hank’s solution at 25 and 37°C finding $i_{corr}$ values of 0.0877 y 0.0309 A/cm$^2$, respectively, similar value to the one obtained in this work for the Ti6Al4V alloy which was a $i_{corr}$ of 0.013 A/cm$^2$. According to this result, the bioglass obtained coating inhibits the electrochemical attack and avoid the Al$_2$O$_3$ and V$_2$O$_5$ oxides liberation, which origins Al+ and V+ liberation to the blood current and to the osseous tissue inside the body [26,27]. This effect is evident by the displacement to the left of the anodic and cathodic curves obtained for the BG700 sample. The curve displacement indicates the diminishing of the corrosion current intensity ($i_{corr}$), for the BG700 coating, in comparison with the obtained values for the Ti6Al4V alloy, which means that there are less electrochemical reactions generating the biofilm degradation than the ones for the Ti6Al4V alloy. There was also observed an important change in the corrosion potential ($E_{corr}$) taking more noble values, diminishing the activity of the 45S5/Ti6Al4V system treated at 700°C, also this system presented the lowest values of the anodic ($B_a$) and cathodic ($B_c$) slopes, which indicates the highest protection barrier in Hank’s solution (pH=7.4) at temperature of 37 - 38°C, in comparison with the other coatings and the Ti6Al4V substrate. The less noble corrosion potential ($E_{corr}$) was obtained by the Ti6Al4V alloy with a negative value of -292.9 mV, presenting the higher activity, which means that an activation process is carried out allowing the formation of a passivation layer The bioglass coating with the highest current corrosion intensity ($i_{corr}$) was BG800 due to the higher crystalline growing detected in the morphology observation leading to the formation of active sites. As it was observed in Figure 3.e. Nevertheless the increase in $i_{corr}$ value was not really important as it could be expected, since it did not presented an important activity. BG700 sample had the more noble value for corrosion potential ($E_{corr}$) of -50.32 mV, which means less activity in the system. BG500 and BG600 samples showed more negative values of corrosion potentials ($E_{corr}$), than BG700 and BG800 samples, indicating that in BG500 and BG600, first there is a higher activity and then there is stabilization. In the case of the sample BG500 there was a thermal oxidation which generated growing in the passivation layer [28], so its behavior was very similar to the one of the Ti6Al4V substrate. BG700 sample presented the lowest corrosion rate, in millimeters per year (mpy), having 1.317x10^{-3} mm/year and a weight loss of 0.028x10^{-9} g/cm$^2$, compared with Ti6Al4V alloy that had 1.161x10^{-4} mm/year and 140.9x10^{-9} g/cm$^2$, respectively. Ions liberation for sample BG700 was estimated of 1.15x10^{-9} g/cm$^2$, compared with Ti6Al4V alloy that had 11.78x10^{-9} g/cm$^2$ Balamurugan et al. [3] reported a bioactive glass coating obtained by electrophoretic deposition method with increased corrosion resistance in physiologic media. Krzakala et al. [19] anodized the Ti6Al4V alloy in Ca(H$_2$PO$_4$)$_2$ and NaOH baths obtaining bioactive films with low values of $i_{corr}$ and the activity reduction with possitive values of $E_{corr}$ in comparation with the alloy, and also reported high polarization resistance.

4. Conclusions
- 45S5 bioglass thin and homogeneous coatings on Ti6Al4V alloy were obtained by sol-gel synthesis and electrophoretic deposition methods.
- The coatings were nanostructured and had mean thickness of 1 -5 microns.
- The obtained bioglass coatings presented good protection against ionic attach of Hank’s Solution specially the one thermally treated at 700°C (BG700).
- According with the extrapolation Tafel results, there was a reduction of one order of magnitude in the current density of corrosion ($i_{corr}$), in the corrosion rate and in the weight loss of the obtained 45S5 Bioglass coating thermally treated at 700°C compared with the Ti6Al4V alloy and the other obtained coatings.
- The more noble behavior was presented by the BG700 sample, which change the corrosion potential to more positive values, reducing the 45S5/Ti6A4V system activity.
Relating the obtained extrapolation Tafel, the lowest value for ions liberation was also presented by the bioglass coating treated at 700°C (BG700).

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