

Electrophoretic deposition of a bioactive Si, Ca-rich glass coating on 316L stainless steel for biomedical applications

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ABSTRACT

This work consisted in the development and characterization of a vitroceraamic coating on 316L stainless steel by means of electrophoretic deposition (EPD). This vitroceraamic coating was obtained through a Si-, Ca-rich glass coating crystallization. The electrophoretic deposition tests were performed on 316L stainless steel mechanically polished substrates. The results suggest that the electrophoretic coatings adhered well to the metallic surfaces. The results demonstrate that the crystallized coatings are potentially bioactive, because a dense and homogeneous apatite layer, similar to a bone, makes up.

Keywords: vitroceraamics, electrophoretic deposition, biomaterials, apatite.

RESUMEN

Este trabajo consistió en el desarrollo y caracterización de un recubrimiento vitro-cerámico sobre acero inoxidable 316L, obtenido por medio de un proceso de deposición electroforética. El recubrimiento vitro-cerámico fue obtenido al cristalizar una capa de vidrio rica en calcio y silicio. Las pruebas de deposición electroforética fueron realizadas sobre sustratos de acero inoxidable 316L, pulidos mecánicamente. Los resultados sugieren que los recubrimientos electroforéticos fueron muy bien adheridos a la superficie metálica. Los resultados demuestran que los recubrimientos cristalizados son potencialmente bio-activos, debido a la formación de una capa densa y homogénea de apatita similar al hueso.

1. Introduction

Implants and prostheses, manufactured with bio acceptable metallic materials, do not stick directly to a living bone. On account of this reason, they must be clinically fixed through mechanical interlocking using screws and acrylic cements ^[1, 2]. Nevertheless, the performance and durability of this type of fixations are this based on its permanence in the body, its degradation that causes metalosis, and the intensity of the mechanical load that must resist when the patient moves. If the prosthesis fractures or wears off it is given off, it can had been able to cause damage to the adjacent tissue, hemorrhage, pain and the possibility of amputating the implanted organ ^[2].

Recently, evidence has been found that plasma-sprayed hydroxyapatite (HA) coatings on metallic substrate form have evidenced a chemical bond to the bone after its implantation ^[3]. The intention of covering a prosthesis with a material that will form an inter-phase between the bony system and the metallic prosthesis is to obtain an integrable bony chemical fixation, of great durability. The osseointegration allows a fixation of the prosthesis to naturally fixate of one natural way. The organism does not "attack" the metallic prosthesis; this prevents the liberation of with which the metallic ions liberation is prevented. Once the biomaterial is transformed into apatite, the osteogenesis process

remains stays, ensuring making sure a permanent fixation with avoiding no more surgeries operations or states pain states for the patient. The more most widely used technique for the formation of osteointegrables coatings is the fixation by the plasma-sprayed technique.

The plasma-sprayed technique is already in clinical use. The covering of hydroxyapatite by the plasma-sprayed technique, in general, becomes biomimetic apatite after 16 weeks of the implantation. For successful results, the patient must convalesce and be under medical care. Its main disadvantage is the high temperature required in this process, which leads to bioactive layers with defective structures [4] and which, in addition, damages the substrate of the prosthesis, decrements its mechanical properties as well as its life utility, and compromises the osseointegration.

An alternative material for bioactive coatings is wollastonite (W). Wollastonite (TCP/W) glass-ceramics have also shown to be highly bioactive thanks to the formation of apatite on 90% of the surfaces only after 4 weeks of implantation. This is due to the W crystals [4].

A promising technique is electrophoretic deposition (EPD), which offers some interesting advantages such as the feasibility to coat substrates of complex geometries and the ability to form homogenous layers [5, 6]. In addition, this process is simple and inexpensive. The main disadvantage of the EPD technique is the necessity of a subsequent sintering of the coatings, which may damage the metal or alloy mechanical properties. However, this can be used as part of the process to obtain a β -TCP/W glass, without coating and substrate structure thermal damage.

2. Materials and methods

Metallic substrates were grounded and polished according to the ASTM F-89 standard [4]. The substrates were gently washed, ultrasonically cleaned in ethanol, and stored in desiccators before EPD. In order to obtain a particle smaller than 2 μ m, wollastonite (Santa Anita, S. A.) was ball-milled for 5 h, changing direction every 30 minutes.

In order to obtain the glass to be subsequently crystallized in a eutectic material, 19.96 g of SiO_2 , 58.15 g of CaCO_3 , and 21.88 g of $(\text{NH}_4)_2\text{PO}_4$ were all mixed. Afterwards, this mixture was put in a platinum crucible, and thermally treated at 1450 °C with a 7 °C/min rate. When it reached 1450 °C, it was quickly cooled at room temperature. This material was then dried at 100 °C for 1 hour, whereupon it was milled in a mortar and agate balls planetary mill. The weight ratio was 4/1 (agate/ceramic). The thus-obtained dust was characterized by MEB and XRD.

Spectrophotometric-grade acetone was used as a dispersive medium for EPD [7]. The β -TCP/W glass suspension concentration was 4 g/L. The zeta potential was determined by using a Laser Zee Meter (Pem Kem, model 501); a negative value was obtained for the glass/acetone suspension (18.8 mV). This suggests that, in the electrophoretic cell, the working electrode acts as a cathode for the ceramic deposition. The distance between the electrodes was 10 mm. A direct electric current of 800 V was used for 3 min in order to obtain the single glass W/ β -TCP coating. After its characterization, the coating was crystallized in air at 900 °C for 5 h. The heating and cooling rates were 2 °C/min.

Adhesion measurement was made through a test of tension; a graphic of stress vs. the displacement was obtained. The test was performed following the ASTM F-1501 and F-1044 norms, trial 6.4. The vitroc ceramic coatings were bonded to a metallic surface with epoxy resin.

A simulated body fluid (SBF) with an ionic concentration nearly equal to that of human blood plasma was prepared according to the procedure described by Kokubo *et al.* [8-13].

Reagent grade sodium chloride (NaCl), sodium hydrogen carbonate (NaHCO_3), potassium chloride (KCl), dipotassium hydrogen phosphate trihydrate ($\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$), magnesium chloride hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$), calcium chloride dehydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$), and sodium sulfate (Na_2SO_4) were all dissolved in deionized water and buffered to pH 7.4 with tris(hydroxymethyl)-aminomethane and 1N HCl at 37 °C. The coated substrates were immersed in 250 mL of a SBF at 37 °C for 21 days.

The surface of the coatings was characterized by scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), and X-ray diffraction (XRD). The SBF remaining solutions were analyzed with inductively coupled plasma spectrometry (ICP).

3. Results and discussion

The change of W/TCP glass deposit weight per surface area, as a function of the applied voltage during EPD, is shown in Figure 1. The homogeneous deposition was obtained at 800V. As observed in Figure 1, the deposit weight increases is increased. The curve of the

figure does not show a decrease concerning the W/TCP glass deposition yield, but the glass color grew dark when the voltage was increased. After the deposition, the coatings were thermally treated at 900°C for 5 hours.

Figure 2 shows the effect of the temperature on the hardness in the steel 316L. It is observed that to 900°C, the hardness is close to 127° HB. The size of the grain before the heat treatment was ASTM 6,479 (Figure 2b), and ASTM 6,11 at the end of the heat treatment (2c). Reason why a significant change in the microstructure of the steel was not observed, so it is deduced that the mechanical properties of this steel, at such temperature, are not decremented.

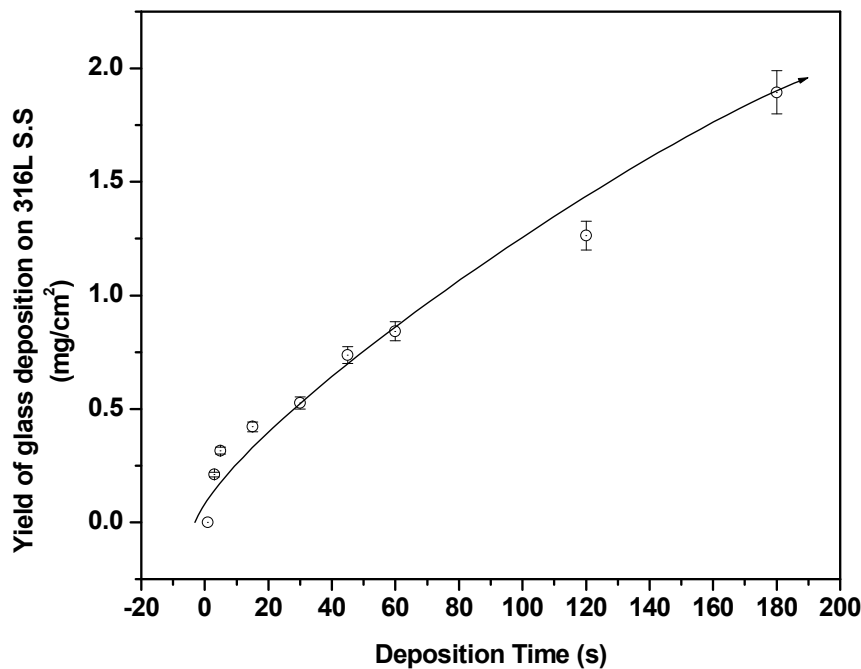


Figure 1. W/TCP glass deposition yield on 316L S.S. as a function of deposition time.

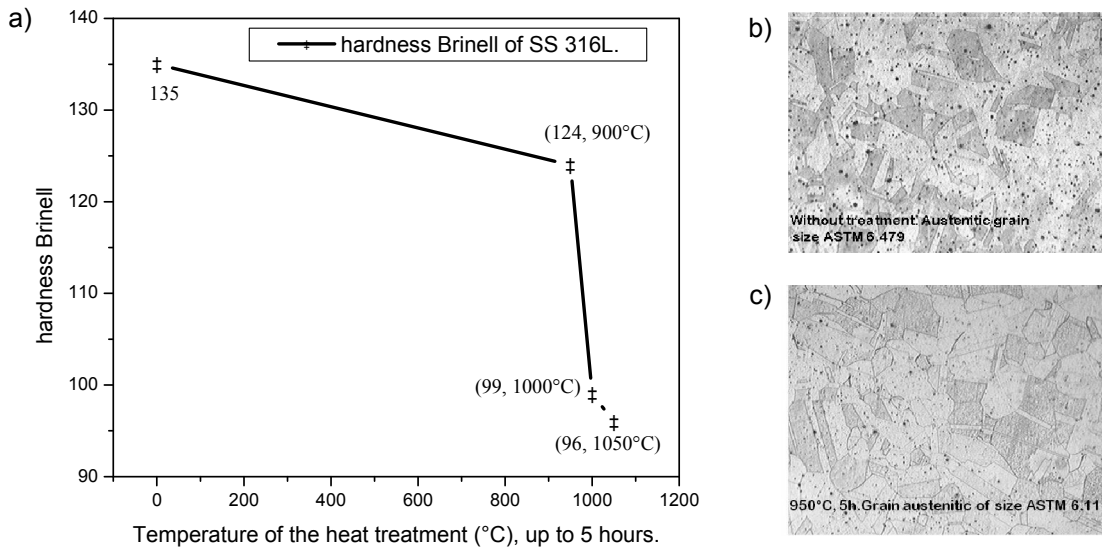


Figure 2. Test of hardness Brinell versus temperature of heat treatment for stainless steel 316L.

Figure 3a shows the vitrocereamic electrophoretical coating microstructure. It shows a homogeneous pore-free surface. After the heat treatment, the microstructure exhibited two phases. With EDX, it was determined that one was W, and the other

apatite (A), as observed in Figure 3b. This was due to the crystallization of the W/TCP glass. The roughness of the substrate was 1.9 μm , which is sufficiently high, so it allows a bio-mimetic process that enables the transformation of the vitrocereamics into apatite^[9].

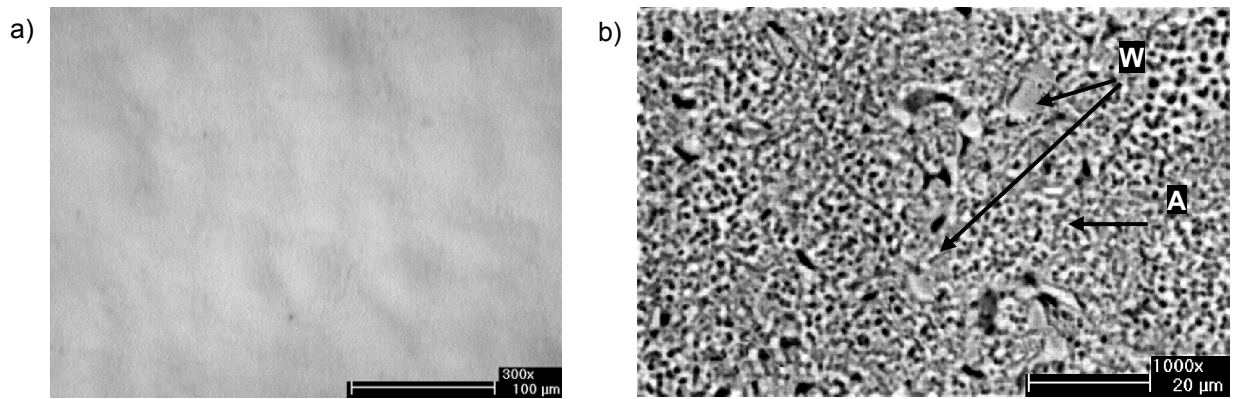


Figure 3. Crystallized coating surface on 316L steel, after thermally treated at 900°C for 5 hours, by 300 increments (a) and 1000 increments (b).

Figure 4 shows the graphic of stress vs. the displacement resulting from the adhesion measure of the coatings obtained. Surfaces of samples after running the adhesion test are observed in Figures 5a and 5b. The ceramic layer had epoxy resin residues (5a), and the epoxy resin layer shows some spherical particles in the ceramic covering (5b).

The adhesion test proved to be indeterminate, the reason being that the epoxy resin used to bond the coatings to the traction sheet became fractured after a 12.01 MPa bond stress in average. Therefore, the adhesion was acceptably good in reference to another process such as the electrophoretic and biomimetic process, which reports maximum bond stress values of 8 MPa^[8].

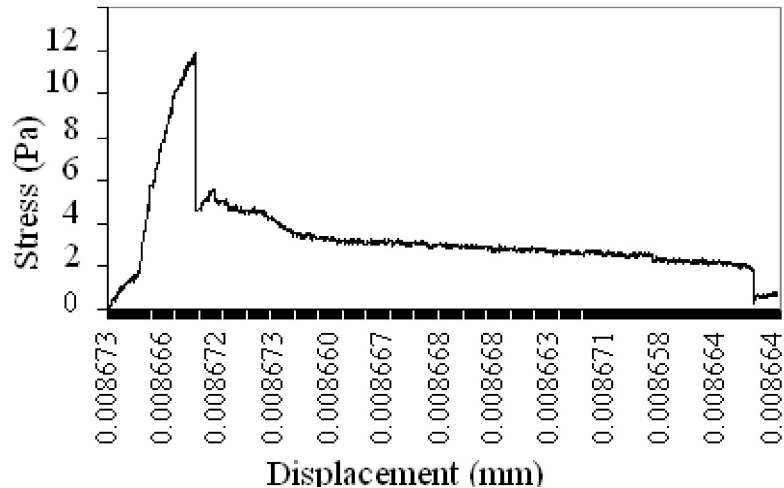


Figure 4. Diagram of stress versus displacement of the covering of vitrocereamics on steel 316L.

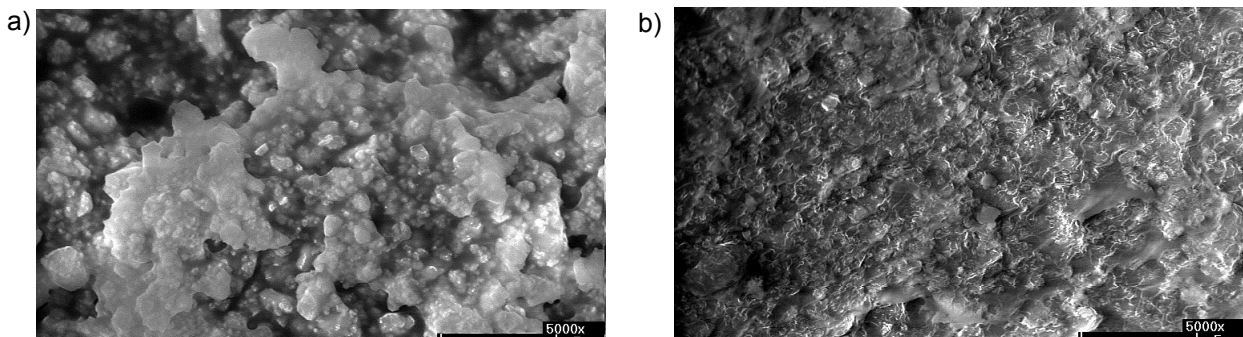


Figure 5. Images of the faces of the fracture, both surfaces are of the epoxy resin.

Figure 6 shows the surface of samples after 21 days of immersion in a SBF. The morphology of this layer is similar to that observed in existing bioactive systems after their immersion in a SBF. The cross section shows a 6.79 μm W/A layer. On this one, a second porous 43.7 μm Ca-, P-rich layer, and a compact 33.6 μm Ca-, P-rich layer appears. The EDS spectrum corresponding to the coating appears in Figure 6a. It does not show if alloying elements are present, except for magnesium. By infrastructure, it was not possible to measure micro-hardness in each one of the layers of the covering. Nevertheless, previous studies indicate that in osseointegrable coatings, the adhesion is good enough to allow the mobility of the patients, supporting bio-mechanic loads that this movement produces. This implies the necessity of making measurements on the mechanical resistance that present these coatings *in vitro* and *in vivo*.

The Ca/P atomic ratios calculated from the EDS results were 1.59 for the Ca-, P-rich coating. These

values are close to the Ca/P ratio of Ha (1.67). The peak of the lower intensity, corresponding to Mg (Fig. 7a), may be because this element is present in the SBF. According to the literature^[9], the apatite formed in the SBF is a partially substituted apatite with other ions in lower contents. Additionally, recent works^[11] have reported that when magnesium is present in a SBF, this produces Mg-containing apatite layers in bioactive systems. The partial substitution of calcium for other alkaline elements, such as Mg, leads to an apatite resembling Ha, but it shows a deficiency in calcium ions^[12-17]. Figure 7b shows the coating XRD patterns after immersion in a SBF for 21 days. The compound formed on the coating was identified as Ha. The peaks corresponding to the metallic substrate are also present in the XRD pattern. The metallic oxide registry in the test of XRD possibly indicates the oxides of anchorage of the covering that are between the metallic substrate and the covering. They may have been registered thanks to the penetrability of X-rays. With the test of EDS, it was not possible to locate these oxides on the surface.

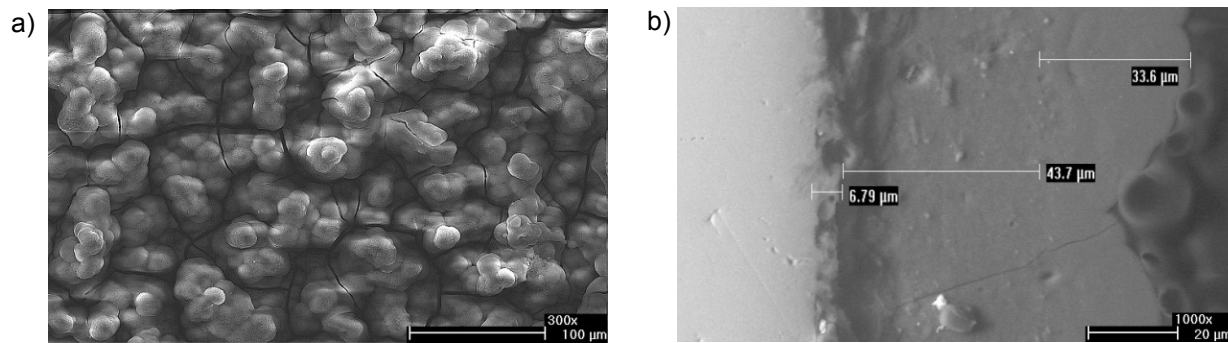


Figure 6. Crystallized coating surface on 316L steel (a) and its cross-sectional section (b) after 21 days of immersion in a SBF.

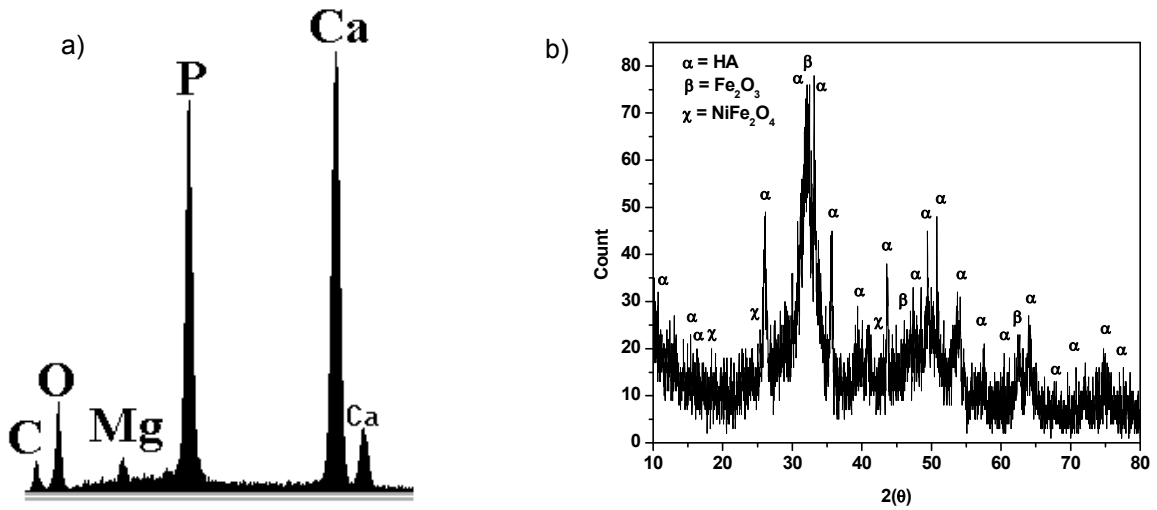


Figure 7. W/A coating EDX Spectrum on 316L steel (a), and XRD patterns of vitroc ceramic substrate surface on 316L steel (b), both after 21 days of immersion in a SBF.

According to scan-line analyses, this layer may be a metallic oxide one, produced by the heat treatment of samples. No metallic elements were

detected by scan-line analyses in the Si-, P-rich layer thickness, which formed on the cross section of the coatings.

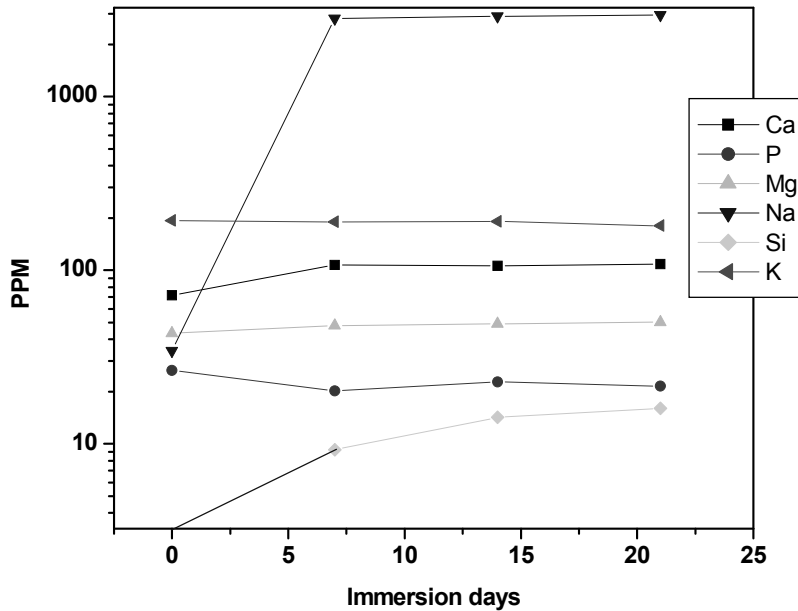


Figure 8. Chemical composition of a SBF remaining solutions diagram, diagram illustrating the bioactivity test of vitroc ceramic coatings on 316 L steel for the 7, 14, and 21 days of immersion periods.

Figure 8 shows the chemical analysis of the SBF remaining solutions as a function of the immersion time of the coated samples. The silicon concentration increases with immersion time in the SBF, which may be due to the partial dissolution of W. As expected, the phosphorous content decreases over time, which may indicate that the formation process of apatite on the materials surface is taking place^[14-19]. During the first 7 days of immersion, the calcium content increases, due to the partial dissolution of wollastonite. The potassium concentrations remain practically constant, and the sodium increment in the first 7 days, and still after, remains constant in the solution. These results agree with those obtained by EDS and XRD shown in Figure 7. A similar behavior was observed when the SBF solutions corresponding to the single wollastonite coated samples were analyzed, as shown in Figure 8. No metallic ions were found by ICP spectrometry in the SBF remaining solutions. These coatings have proved they can form apatite on their surfaces.

Further research, such as cell culture and *in vivo* testing, needs to be performed. However, this kind of coatings on 316L stainless steel, obtained by EPD, have proved to be promising bioactive materials for bone replacement and reconstruction.

4. Conclusions

These results demonstrate the possibility of obtaining bioactive vitroceraamic coating on stainless steel by electrophoretic deposition. This coating can form a dense and homogeneous apatite layer after 21 days of immersion in a SBF. During the mechanism of apatite formation, the vitroceraamic coating dissolves completely into a SBF. On the other hand, the apatite-formed coating seemed to be strongly attached after the dissolution of the vitroceraamic coating layer.

The heat treatment of the samples after electrophoretic deposition has a positive effect on bioactivity. No metallic elements were detected either on the apatite coating or in the remaining SBF solutions.

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Acknowledgments

The author gratefully acknowledges CONACYT (Mexico) and Engineer Jaime Ramírez-García from CINVESTAV-Salttillo for his contribution to the electrophoretic cell study.

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