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Electrophoretic deposition of bioactive wollastonite and porcelain–wollastonite coatings on 316L stainless steel

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Abstract

Wollastonite and porcelain–wollastonite coatings on stainless steel were obtained by electrophoretic deposition using acetone as dispersive medium. A direct electric current of 800 V for 3 min was used for obtaining the single wollastonite coating. A well-sintered layer was observed after heat treatment at 1050 °C for 1 h in air. The two-layer coating was obtained by depositing dental porcelain at 400 V for 30 s followed by the deposition of wollastonite at 400 V for 3 min. After forming the two layers, this complex coating was heat treated at 800 °C for 5 min. Under these conditions, strong bonds of both the interface wollastonite–porcelain and that of porcelain–metallic substrate were observed. The *in vitro* bioactivity assessment of the coatings was performed by immersing the deposited substrates in simulated body fluid (SBF) for 21 days. All the materials showed to be highly bioactive through the formation of a homogeneous apatite layer.

Keywords: D. Porcelain; D. Apatite; Electrophoretic deposition; 316L stainless steel

1. Introduction

Implants and prostheses fabricated from metallic biomaterials, such as stainless steels and cobalt alloys, do not form a direct bond to living bone. Thus, they must be clinically fixed by mechanical interlocking using screws and cements [1,2]. Recently, hydroxyapatite (HA) coatings on metallic materials have shown to promote a chemical bond to bone within 16 weeks of implantation [3]. After this time, 80% of the surface of the HA coating is bonded [3]. Apatite/wollastonite (A/W) glass–ceramics have also shown to be highly bioactive through the formation of apatite on 90% of its surface after only 4 weeks of implantation due to the wollastonite crystals [3]. An alternative material for bioactive coatings is wollastonite ceramics.

Among the methods developed for obtaining ceramic coatings, the plasma-sprayed technique is already in clinical use. However, the main inconvenient is the high temperature required in this process, which leads to bioactive layers with defective structures [4]. Other promising technique is electrophoretic deposition (EPD) that offers interesting advantages, such as the feasibility to coat substrates of complex geometries and the ability to form homogenous layers [5,6]. Furthermore, this process is simple and inexpensive. The main disadvantage of the electrophoretic deposition technique is the necessity of a subsequent sintering of the coatings, which may lead to detrimental mechanical properties of the metal or alloy.

In this work, wollastonite was deposited by electrophoreses obtaining a single bioactive layer on 316L stainless steel. Furthermore, in order to decrease the sintering temperature, a complex coating was processed by the same technique obtaining a double layer coating consisting of porcelain and wollastonite. The *in vitro* bioactivity characterization was performed by immersing samples in simulated body fluids (SBF) for 21 days. Substrates with non-sintered wollastonite coatings were also tested.

2. Materials and methods

2.1. Specimen preparation

Metallic substrates were ground and polished according to the ASTM F-89 standard [4]. The substrates were gently

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washed, ultrasonically cleaned in ethanol and stored in a desiccator before EPD. To obtain a particle size minor than 2 μm, wollastonite (Santa Anita, S.A.) and dental porcelain (Ceramco® II, Body A1), were ball-milled for 5 and 6 h, respectively. Spectrophotometric-grade acetone was used as dispersive medium for EPD [7]. The concentration of wollastonite suspension was 1 g/L, while that of porcelain was 2 g/L. The zeta potential was determined using a Laser Zee Meter (Pem Kem, model 501), a positive value was obtained for the wollastonite/acetone suspension (23.1 mV), whereas for that of dental porcelain/acetone a negative zeta potential was obtained (−33 mV). This indicates that in the electrophoretic cell, the working electrode acts as an anode for the porcelain deposition and as a cathode for the wollastonite deposition.

2.2. Electrophoretic deposition and sintering of the coatings

Two different coatings were obtained: (i) wollastonite and (ii) porcelain/wollastonite. In all the cases, the distance between the electrodes was 10 mm. A direct electric current of 800 V for 3 min was used for obtaining the single wollastonite coating. The two-layer coating was developed by depositing dental porcelain powder at 400 V for 30 s followed by the deposition of wollastonite powder at 400 V for 3 min. The wollastonite coatings were sintered in air at 1050 °C for 1 h. The dental porcelain–wollastonite coatings were heat treated in air at 800 °C for 5 min. Both the heating and cooling rates were 2 °C/min.

2.3. In vitro bioactivity assessment

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 ($K_2HPO_4{\cdot}3H_2O$), magnesium chloride hexahydrate ($MgCl_2{\cdot}6H_2O$), calcium chloride dihydrate ($CaCl_2{\cdot}2H_2O$) and sodium sulfate (Na_2SO_4) were dissolved into 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 SBF at 37 °C for 21 days. In the aim to evaluate the effect of the sintering process on the bioactivity, substrates with non-sintered wollastonite coatings were also immersed in SBF under the same conditions.

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

3. Results and discussions

The change of the deposit weight of porcelain and wollastonite per surface area as a function of the applied voltage during EPD is shown in Fig. 1. As observed, the deposit weight increases as voltage is increased. In the case of the wollastonite coating, the deposition rate was higher during the first 400 V. At higher voltage, the deposition rate decreases significantly. This may indicate that thicker coatings increase the electrical resistivity of the working electrode, which decreases the current flow [5,6].

Fig. 2 shows an SEM image of the non-sintered wollastonite coating after 21 days of immersion in SBF and its EDS spectrum. In addition to the elements corresponding to the metallic substrate and those of wollastonite, phosphorous was also detected by EDS. The presence of phosphorous may indicate the formation of a calcium phosphate however, not a significant change was observed between the surfaces before and after immersion in SBF. This can be explained taking into account that the adherence of the non-sintered coating was poor and part of the coating was peeled off during the immersion period.

Fig. 3 shows the surface of the samples after 21 days of immersion in SBF. A homogeneous Ca, P-rich layer has been formed on the surface of both the wollastonite (Fig. 3a and c) and the porcelain–wollastonite (Fig. 3b and d) coatings. The EDS spectrum corresponding to the single wollastonite coating shows the presence of the alloying elements. This may indicate

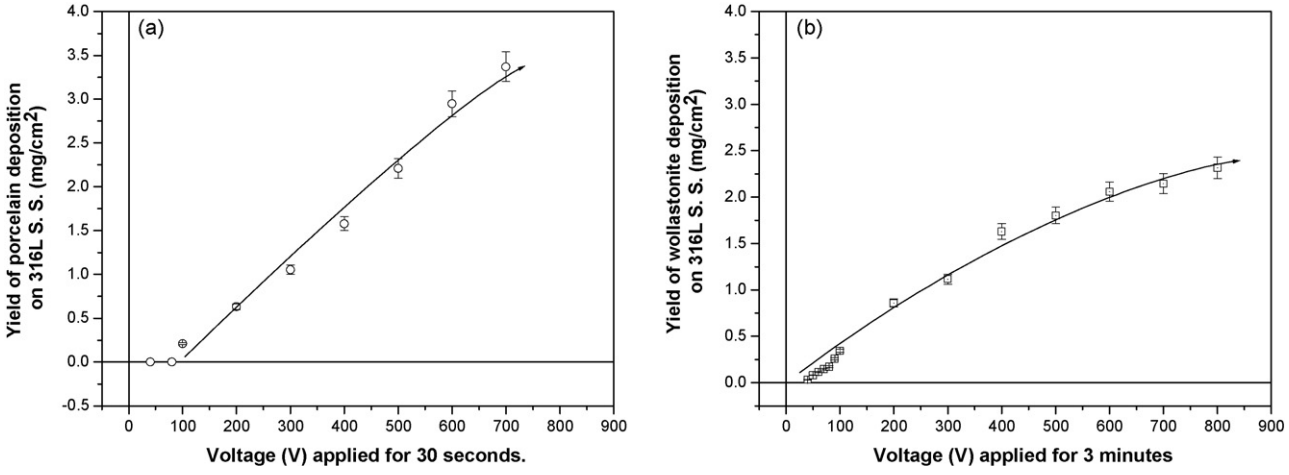

Fig. 1. Yield of (a) porcelain and (b) wollastonite (mass per surface area) deposited during EPD as a function of applied voltage.

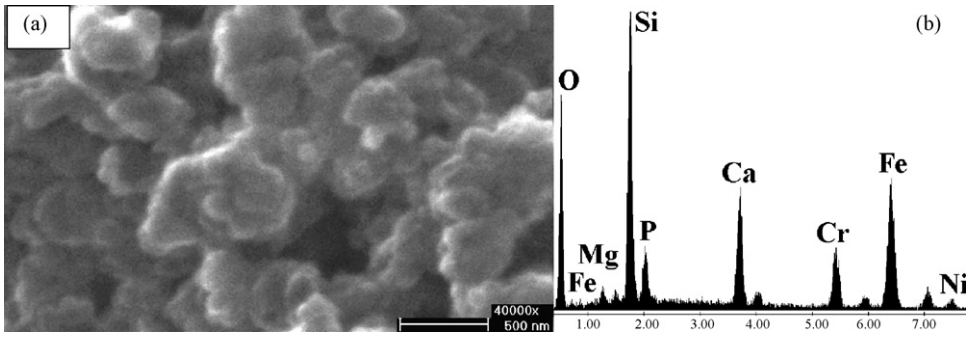

Fig. 2. Non-sintered wollastonite coating after 21 days of immersion in SBF: (a) SEM image and (b) corresponding EDS spectrum.

that this Ca, P-rich layer is thinner than the bioactive layer obtained on the porcelain–wollastonite coating. As observed in Fig. 3, the morphology of these layers is similar to that observed on the existing bioactive systems after their immersion in SBF. Larger agglomerates (19.3 and 36 μm) were formed on the dental porcelain–wollastonite coating (Fig. 3b) in comparison to those observed on the single wollastonite coating (17–22 μm, Fig. 3a).

The Ca/P atomic ratios calculated from the EDS results were 1.59 and 1.61 for the Ca, P-rich layer formed on the single wollastonite and the porcelain–wollastonite coatings, respectively. These values are close to the Ca/P ratio of hydroxyapatite (1.67). The peak of lower intensity corresponding to Mg (Fig. 3b) may be due to the presence of this element in SBF, according to the literature [9] the apatite formed in SBF is a partially substituted apatite with other ions in minor contents. Additionally, recent works [10–12] have reported that the presence of magnesium in SBF leads to Mg-containing apatite layers on bioactive systems. The partial substitution of calcium for other alkaline elements, such as Mg, leads to an apatite similar to hydroxyapatite, but with a deficiency in calcium ions [13–17].

Fig. 4 shows the XRD patterns of the wollastonite (Fig. 4a) and porcelain–wollastonite (Fig. 4b) coatings after immersion in SBF for 21 days. The compound formed on both coatings was identified as hydroxyapatite. Peaks corresponding to the metallic substrate are also present in the XRD pattern, while the electrophoretic coatings were not detected by this technique.

Fig. 5 shows the cross-section of the sintered coatings before and after immersion in SBF. In the sample corresponding to the complex coating (Fig. 5a), apart from the porcelain and wollastonite layers, other two regions identified as (e) and (f), were observed. In region (e) metallic elements, such as Fe, Cr, Al and Ni, were detected by scan-line analysis indicating that this region may correspond to a complex oxide formed as a result of the heat treatment. Region (f) corresponds to a layer between the porcelain and wollastonite electrophoretic coatings. In the layer (∼12 μm) Na, K, Si, Mg and Ca elements were detected. This may indicate that a reaction between porcelain and wollastonite is taking place at the sintering

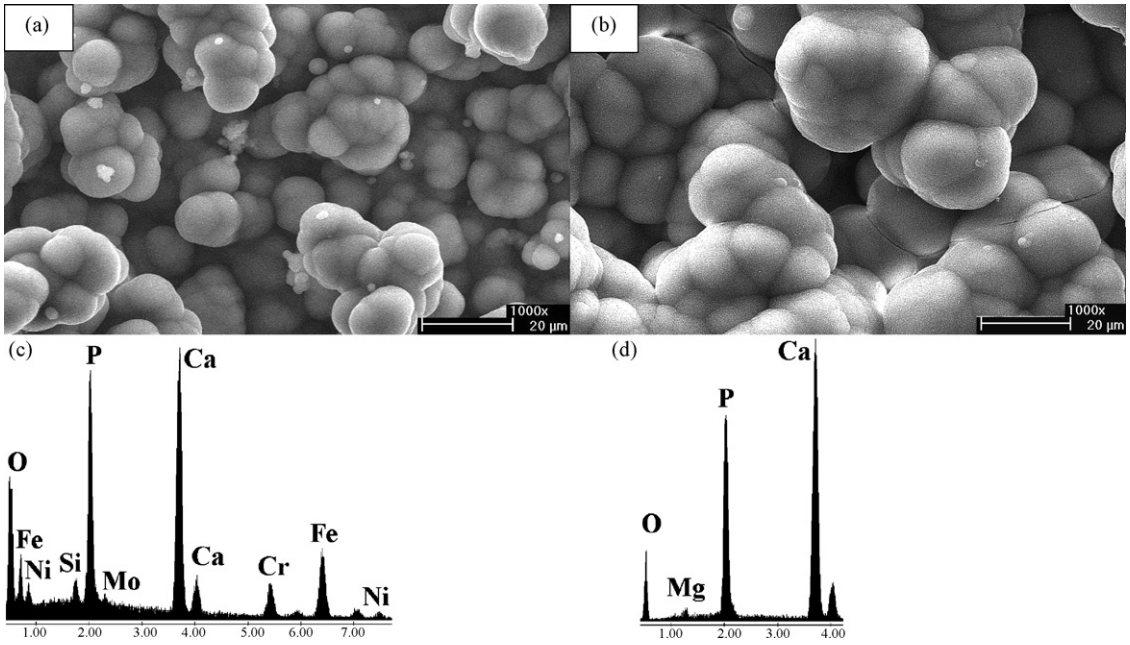

Fig. 3. Sintered wollastonite (a, c) and porcelain–wollastonite (b, d) coatings after 21 days of immersion in SBF: (a, b) SEM images and (c, d) EDS spectra.

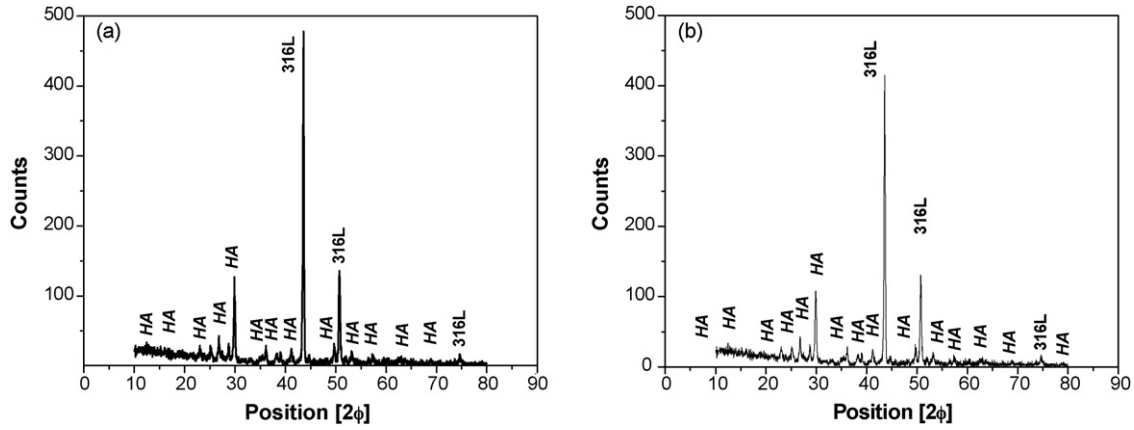

Fig. 4. XRD pattern of the samples after immersion in SBF for 21 days: (a) wollastonite coating and (b) porcelain–wollastonite coating.

temperature. The overall thickness of the porcelain–wollastonite coating was 72.4 μm. After 21 days of immersion in SBF (Fig. 5b) only two ceramic layers were observed: one corresponding to porcelain and an external Ca, P-rich layer. As described previously, the layer formed after immersing samples in SBF was identified as apatite by XRD. After bioactivity testing, the wollastonite coating is no longer present. According to the literature [17,18], wollastonite dissolves partially in SBF promoting the formation of apatite. The thickness of the Ca, P-rich layer was nearly 80 μm and the overall thickness of the coating after immersion in SBF was 97.6 μm.

Fig. 5c shows the sintered wollastonite coating. A thin layer (∼2 μm) was observed between the metallic substrate and the wollastonite electrophoretic coating. According to scan-line analyses, this may be a metallic oxide layer due to the heat treatment of the samples. The wollastonite coating showed a thickness of 50 μm. After 21 days of immersion in SBF (Fig. 5d) a dense Ca, P-rich layer of nearly 60 μm was formed. In contact with SBF, the wollastonite electrophoretic layer was dissolved and the apatite was formed directly on the metallic substrate.

No metallic elements were detected by scan-line analyses along the thickness of the apatite layer performed on the cross-section of both the single wollastonite and the porcelain–wollastonite coatings.

Regarding the adherence of apatite layers, a stronger bond is obtained when using porcelain (Fig. 5b), while in the case of the single wollastonite coating (Fig. 5d) a clear separation between the apatite layer and the metallic substrate can be observed.

Fig. 6 shows the chemical analysis of the SBF remaining solutions as a function of immersion time of the porcelain–wollastonite coated samples. The silicon concentration increases with immersion time in SBF, which may be due to the partial dissolution of wollastonite. As expected, the phosphorous content decreases with time, which may indicate that the formation process of the apatite on the surface of the materials is taking place. During the first 7 days of immersion,

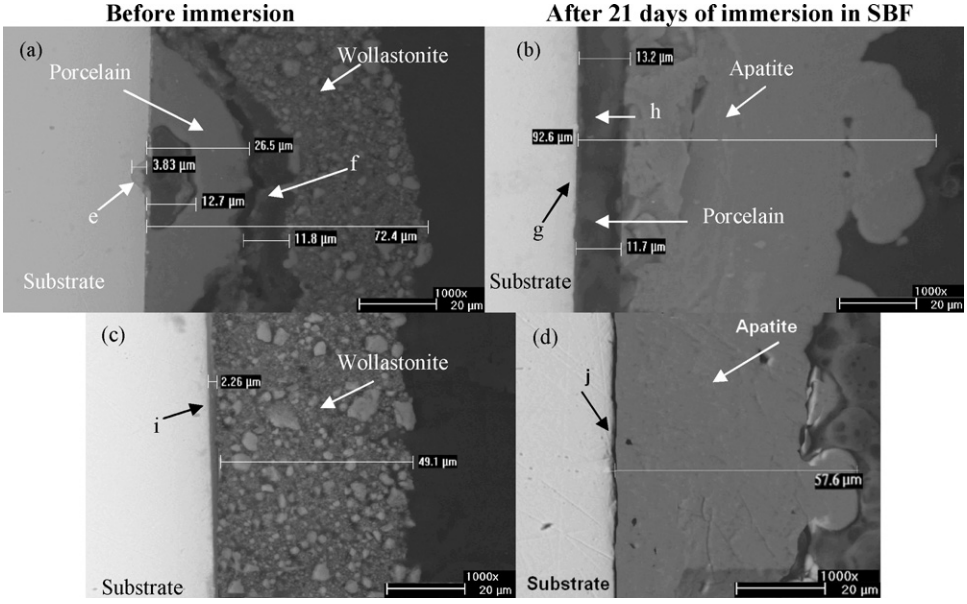

Fig. 5. Cross-section images of the coated samples before (a, c) and after 21 days of immersion in SBF (b, d); porcelain–wollastonite coating (a, b), single wollastonite coating (c, d).

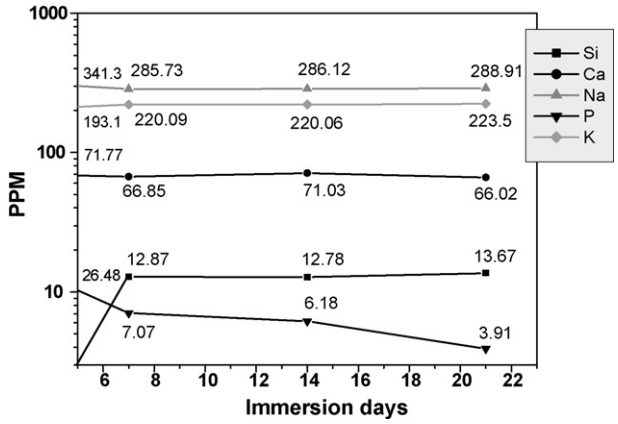

Fig. 6. Si, Ca, Na, P and K concentration in the remaining SBF solutions with time of immersion of the porcelain–wollastonite coated samples.

the calcium content increases due to the partial dissolution of wollastonite then, after 14 days, the content of this element decreases again due to the formation of the calcium phosphate on the electrophoretic coating. The potassium and sodium concentrations practically remain constant. These results are in agreement with those obtained by EDS and XRD. A similar behavior was observed when the SBF solutions corresponding to the single wollastonite coated samples were analyzed. No metallic ions were found in the SBF remaining solutions by ICP spectrometry.

The results obtained indicate that the porcelain layer has not an inhibitory effect on the bioactivity of the wollastonite coating, since both the single and complex electrophoretic coatings have demonstrated to be able to form apatite on their surfaces. Further investigation, such as cell culture and *in vivo* testing, needs to be performed however, sintered wollastonite and porcelain–wollastonite coatings on 316L stainless steel obtained by electrophoretic deposition are promising bioactive materials for bone replacement and reconstruction.

4. Conclusions

These results demonstrate the possibility of obtaining bioactive wollastonite layers on stainless steel by electrophoretic deposition. Both the single wollastonite and the porcelain–wollastonite coatings are able to form a dense and homogeneous apatite layer after 21 days of immersion in SBF. During the mechanism of apatite formation, the wollastonite layer dissolves completely into SBF. Thus, in the case of the single wollastonite coatings, the apatite forms directly on the metallic surface after immersing the samples in SBF leading to a poor-adhered apatite layer. On the other hand, the apatite formed on the porcelain coating after the dissolution of the wollastonite layer, seemed to be strongly attached. The heat treatment of the samples after electrophoretic deposition has a positive effect on the bioactivity, since no apatite was formed on the non-sintered wollastonite coated samples. No metallic elements were detected either on the apatite coating or in the SBF remaining solutions.

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