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Calcium phosphate growth on sintered α-alumina treated with piranha solution using a wet-chemical procedure

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ABSTRACT

Two alumina samples, a high surface powder γ-alumina and a sintered α-alumina have been studied as substrates for apatite growth. In the first case, the initial stage was the calcium adsorption in an alkaline solution, followed by phosphate uptake. On the other hand, the α-alumina was firstly subjected to an acid piranha treatment at 80 °C for four hours, before alternate immersions on calcium and phosphate solutions. Next, the alumina samples were immersed repeatedly in a glycine buffer, pH 10.2, and then in tris buffer solutions, pH 7.4 at 32 °C. The resultant solids were studied by means of XRD, TEM or SEM. Calcium phosphate growth was observed in both cases. An almost uniform and continuous layer was formed on the sintered α-alumina. The results suggest that pretreatment with piranha solution seems to be a fast and efficient alternative to bioactivate the α-alumina surface.

1. Introduction

Alumina has been used in orthopedic surgery for nearly 40 years. It shows excellent corrosion resistance, high wear resistance and high strength [1]. Although alumina shows also excellent biological tolerance, it is an inert material and does not bond to the surrounding bone directly. To improve alumina bioactivity and osseointegration a number of methods have been proposed. Examples are the elaboration of composites [2–6], ion-implantation [7], surface functionalization [8–10] or coating with bioactive glasses [11] or hydroxyapatite [12]. Apatite growth on alumina using biomimetic surface treatments have also been studied [13–15]. These bioactive techniques consist of solutions that usually resemble the human plasma employing low processing temperatures [16]. On the other hand, it has been reported that hydroxylation of alumina after treatment with sodium hydroxide improves bioactivity in cell culture tests, compared with untreated alumina, without deteriorating effects on the mechanical properties [17].

Unlike well-known bioactive materials, fundamental understanding of the mechanism and factors influencing bone-like apatite nucleation and formation on alumina in vivo or in vitro remain limited. Studies on apatite nucleation and growth on substrates such as bioglasses, and sol-gel derived silica and titania have proposed that factors such as porosity, topography, surface area and surface charge are related to the apatite-forming ability of the surfaces [18,19]. Besides, it seems that an atomic or structural arrangement is also necessary for the growth of the apatite phase, such as the presence of trisiloxane rings, or certain type of structural unit of silanol groups, for silica [19,20]. In the case of titania, it seems that an amorphous phase prevents apatite formation [21]. For alumina, it is generally agreed that its lack of bioactivity is due to its positive surface charge at pH 7.4. This hinders Ca adsorption, which is widely accepted as the first step for apatite nucleation in vitro [22,23], although it has been proposed that the initial presence of phosphate on a surface can also contribute to the apatite nucleation [10,24]

In this paper we report the nucleation and growth of apatite using mild conditions on a high surface powder γ-alumina and on a sintered α-alumina subjected to acid piranha treatment. This pretreatment generates a greatly hydroxylated surface, which increases the α-alumina capacity for Ca adsorption. Besides, seemingly, an alteration on the surface structure is observed. Apparently, both modifications are important conditions for calcium phosphate nucleation and apatite growth on alumina in vitro.

2. Materials and methods

Two different substrates for apatite growth were used: powder γ-

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alumina and sintered α-alumina. γ-alumina (−325 mesh) was obtained from the thermal treatment of pseudoboehmite, synthesized according to the procedure described in a previous work, at 600 °C for two hours. α-alumina blocks were obtained via slip casting from alumina powder, Alcoa A16-SG, as raw material. A slip of 60 wt% of solid charge was prepared with that powder and distilled water. It was mixed for 24 h in a ball mill of nylamid and alumina balls. A pH of 4 was adjusted with few milliliters of nitric acid at which the suspension was stable. Dry green samples were sintered at 1600 °C for 1 h, using a heating rate of 5 °C/min. The bulk density and porosity of alumina according to the ASTM C373 were 3.874 g/cm^3 and 2.82%, respectively.

Additionally, α-alumina powder, with and without piranha treatment, was used for the FT-IR and XRD analysis. It was obtained by heating the precursor Alcoa A16-SG at 1400 °C for 1 h and a heating rate of 5 °C/min. For the piranha treatment, 0.1 gr of the powder α-alumina was immersed in 8 mL of a piranha solution (3:1 concentrated sulphuric acid/H_2O_2 35% v/v) at 80 °C for 2 h.

2.1. *Apatite growth on powder γ-alumina*

2.1.1. *Pretreatment of the samples*

Prior to use, alumina was washed with 10 mM NaOH (1 g, Al_2O_3 / 10 mL, NaOH). After stirring for 1 h, the suspension was centrifuged, and the solid was washed with deionized water to a constant conductivity of the supernatant. Finally, the solid was filtered, dried for two hours at 110 °C, and ground using an agate mortar and pestle.

Next, 0.1 g of alumina were placed on 10 mL of deionized water. After 5 days at room temperature, the suspension was centrifuged and water was discarded. Then, the solid was resuspended in a 2 mM $CaCl_2$ solution having an initial pH 11.3. After stirring for 2 h, pH was raised around 11 and the suspension was kept under stirring overnight at room temperature. The suspension was centrifuged, and the solid was washed three times with deionized water having similar pH to that of the suspension (approximately 8.5–9.5). After that, the solid was added to 5 mL of a 4 mM Na_2HPO_4 solution. The suspension was stirred for 5 h at room temperature, centrifuged, washed twice with deionized water and resuspended in 5 mL of a glycine buffer solution, pH 10.2 having the next composition: 0.5 mM $CaCl_2$ and 0.15 M NaCl. pH was adjusted with a 0.1 M NaOH for all the solutions. After stirring overnight at 32 °C, the suspension was centrifuged and washed twice with deionized water.

2.1.2. *Immersion in Ca/PO_4 buffered solutions*

The resultant solid was resuspended into a glycine buffered Ca/PO_4 solution having the next composition: glycine buffer solution, pH 10.2 (at 32 °C), 0.5 mM $CaCl_2$, 0.2 mM Na_2HPO_4 and 0.15 M NaCl. The alumina was resuspended in 15 mL of the solution for 6 h at 32 °C. Then, the sample was centrifuged, washed once and resuspended again 10 times in the same conditions. Finally, the samples were immersed 10 times in 10 mL of a tris buffer solution pH 7.4 having the next composition: 2.5 mM $CaCl_2$, 1 mM Na_2HPO_4 and 0.14 M NaCl at 33 °C for 12 h periods.

2.2. *Apatite growth on sintered alumina*

2.2.1. *Pretreatment of the samples*

Six sintered alumina specimens (approximately 1 cm^2) were treated with 8 mL of a piranha solution (3:1 concentrated sulphuric acid/H_2O_2 35% v/v) at 80 °C for 4 h. Then, the samples were rinsed with water, and washed five times ultrasonically with deionized water, immersed twice in 10 mL of a 0.1 M NaOH solution and sonicated for five minutes. Later, the samples were resuspended overnight twice in 10 mL of a 2 mM $CaCl_2$ solution at pH 11.3, at room temperature, rinsed with deionized water and immersed in 10 mL of a 2 mM Na_2HPO_4 solution for 6 h, at room temperature. Then, the samples were washed, and alternately resuspended 5 times, at room temperature for 60 min periods, into a 12.5 mM $CaCl_2$ solution and a 10 mM Na_2HPO_4 solution. In each case the solutions had pH 10. The samples were rinsed thoroughly with deionized water after each immersion.

2.2.2. *Immersion in Ca/PO_4 buffered solutions*

The samples were immersed 5 times, for 6 h periods, in 5 mL of a glycine buffered solution pH 10.2 (at 32 °C), with the next composition: 0.5 mM $CaCl_2$, 0.2 mM Na_2HPO_4 and 0.15 M NaCl. Then, the samples were resuspended 10 times, for 6 h periods, in a glycine buffered solution pH 9.9 (at 32 °C), with composition: 0.5 mM $CaCl_2$, 0.4 mM Na_2HPO_4 and 0.15 M NaCl. Finally the samples were immersed 5 times in 5 mL of a tris buffer solution pH 7.4 (at 32 °C), having the next composition: 2.5 mM $CaCl_2$, 1.5 mM Na_2HPO_4 and 0.14 M NaCl at 33 °C for 12 h periods. The samples were rinsed thoroughly with deionized water after each immersion.

2.3. *Characterization techniques*

For Scanning Electron Microscopy (SEM) analysis, a high-performance Analytical Scanning Electron Microscope Jeol JSM-6010PLUS/LA was employed. Energy Dispersive Analysis of X-rays (EDAX) was carried out in a Jeol detector. Samples used in scanning electron microscopy were coated with a thin layer of gold-palladium alloy to improve their conductivity. X-ray diffraction analysis (XRD) was carried out in a Rigaku X-ray Diffractometer Ultima IV model. XRD patterns were measured using Cu Kα1 radiation. Transmission electron microscopy (TEM) was performed in a Zeiss microscope Leo EM 910 at 120 kV.

3. Results

Fig. 1(a) shows the X-Ray Diffraction (XRD) pattern for the highly crystalline sintered alumina which matches with JCPDS 001-1243 for α-alumina. On the contrary, γ-alumina is partially amorphous and nanocrystalline, as can be deduced from the broadening of the peaks in its XRD pattern (Fig. 1(b)) that corresponds to the γ-alumina JCPDS file 010-0425. In order to observe possible structural or chemical modifications in α-alumina subjected to piranha treatment, powder α-alumina samples, which have higher surface areas, were studied by means of XRD and Fourier transform infrared spectroscopy (FTIR). The XRD patterns for the α-alumina powder samples before (solid lines) and after the piranha treatment (dashed lines), are shown in Fig. 2. It can be seen that the peaks in the pattern after the piranha treatment are slightly displaced to lower diffraction angles compared with the position of the pristine alumina peaks.

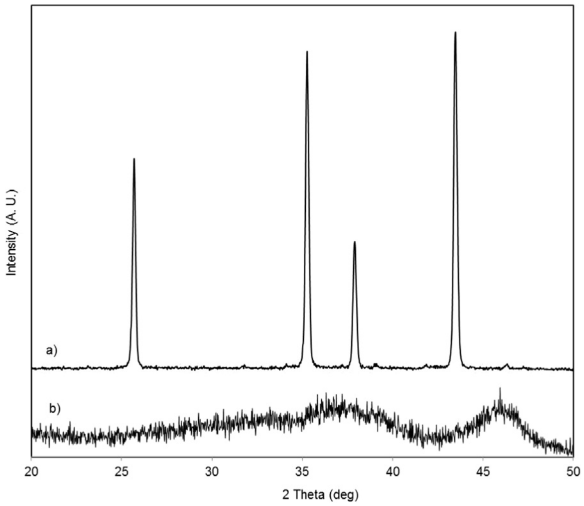

Fig. 1. XRD patterns for the sintered α-alumina (a), and the powder γ-alumina (b).