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Microstructure of ceramic coating on titanium surface as a result of hydrothermal treatment

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Hydroxyapatite coating on commercially pure titanium has been produced by a biomimetic method in order to improve osteointegration for medical implant purposes. A specific chemical treatment by etching titanium substrate with different concentrations of NaOH aqueous solution at 130 °C in an autoclave, followed by heat treatment at 600 °C was selected to obtain an activated titanium substrate. The microporous surface obtained has allowed the nucleation and growth of a calcium phosphate layer by soaking the substrate in a simulated body fluid (SBF). Scanning electron microscopy (SEM) together with energy dispersive analyzer for X-ray (EDS), X-ray diffraction (XRD) as well as Fourier transform infrared spectroscopy (FT-IR) were employed to evaluate the hydroxyapatite coating. A homogeneous structure coating without cracks defined the chemical treatment condition of the substrate.

1. Introduction

As the human immunological system tends to expel foreign materials found in the body, several researches have been performed in order to enable the application of synthetic materials, which should perform similar to natural bone. Therefore, the research of calcium phosphate ceramics has drawn much attention because of its similarity to the bone tissue [1].

Hydroxyapatite coatings on metal implants have been employed to improve their osteointegration property. Recently, biomimetic processes have been used to induce the nucleation and growth of calcium phosphate layers on different substrates. This process is based on the bone tissue formation which occurs through precipitation of calcium and phosphate ions on collagen (heterogeneous precipitation) [2–4]. The activation of the substrate surface by a chemical treatment before the coating was identified as a relevant condition for the process achievement [5, 6].

In order to coat a metal, a mechanical treatment has been applied to the surfaces of the materials to increase the contact area and enhance adhesion. This procedure has just furnished a physical nature bond between the substrate and the coating commonly obtained by the plasma spray coating process [7, 8]. A chemical pretreatment instead of a mechanical one allows the formation of a new compound in the interface between substrate and coating, improving the bond [9].

The development of calcium phosphate coating on metals has been studied because monolithic calcium phosphate ceramics lack mechanical properties. Furthermore it provides bioactivity to the metal and avoids or minimizes the release of metallic ions from the implant.

Several coating processes have been proposed in order to overcome the limitations of the coating methods available on the market [10–15]. These processes, which promote the formation of chemical bonding between the substrate and the coating, have been widely researched in the last few years [9].

The bone tissue growth on the implant's surface has been proved by the formation of an apatite layer when the biomaterial was implanted *in vivo* (the bioactivity of the material is evaluated by the rate of this layer formation). Substrates that allow the nucleation as well as growth of calcium phosphate layer on its surface are considered feasible for coating through the biomimetic technique [3].

The purpose of this work was to select a hydrothermal treatment of the titanium metal surface, transforming its TiO_2 layer [16–18] (always presented when titanium is exposed to oxygen) into a more active one. This titania active layer may be generated by a chemical treatment prior to the nucleation step, resulting in good adhesion between the substrate interface and the coating due to the formation of a chemical bond. The choice of the best condition was established through the observation of the microstructure of the final coating layer.

2. Experimental procedure

Samples of pure titanium were chemically treated with several aqueous solutions of varying NaOH concentrations (1, 5 and 10 M at 130 °C in an autoclave, for 1 or 6 h reaction time. Afterwards, these attacked samples were heated at 600 °C for 1 h in an electric furnace and then cooled to room temperature inside the furnace.

After that, the substrate was soaked in simulated body fluid (SBF) and pH over 7.0 at 37 °C for four weeks with the SBF solution replaced every two days. The SBF solution was prepared with the following ion concentrations: $[Na^+] = 142.00$ mM, $[K^+] = 5.00$ mM, $[Mg^{2+}] = 1.50$ mM, $[Ca^{2+}] = 2.50$ mM, $[Cl^-] = 147.80$ mM, $[HCO_3{}^-] = 4.20$ mM, $[HPO_4^{2-}] = 1.00$ mM and $[SO_4^{2-}] = 0.05$ mM.

Before and after the immersion experiments, the treated titanium surface was coated with thin gold film for SEM morphological observation.

Scanning electron microscopy; (SEM, Zeiss-DSM 940A), energy dispersive spectroscopy, (EDS, Oxford-link EXL II), X-ray diffraction from thin films, (XRD, Simens D 500) and Fourier transform infrared spectroscopy, (FT-IR, Nicolet Spectrometer Serie 520G) were the methods used to characterize the obtained coating.

A series of mixtures, (hydroxyapatite (HAP) 0%+TiO_2 100%, HAP 25%+TiO_2 75%, HAP 50% +TiO_2 50%, HAP 75%+TiO_2 25%, HAP 100%+TiO_2 0%), were prepared to build a calibration curve by choosing a characteristic peak of calcium phosphate at 1030 cm^{-1}. A titanium oxide (TiO_2) 99.8% P.A. (Riedel-dehaen) and HAP P.A. (Merck) with Al 0.0005% were used.

3. Results and discussion

Fig. 1 shows a significant variation of the texture on the titanium surface after the sodium hydroxide etching treatment, under six different conditions. The following chemical pre-treatment condition (NaOH, 1 M for 1 h) resulted in a larger number of smaller pores than the others shown in Fig. 1a. Different morphologies of the calcium phosphate coating after the nucleation on the chemically etched substrates were observed in Fig. 2. A crack-free and homogeneous coating on the titanium surface is the desired end product. From a microstructure standpoint, the sample in Fig. 2a was considered the best one. This result corresponds to the pre-treatment condition showed in Fig. 1a. Cracks can be observed on the surface of other coatings (Fig. 2b–f). Fig. 3 compares the EDS spectra of two coatings obtained by different surface treatments. Peaks of calcium, phosphorus and titanium can be seen, confirming the presence of calcium phosphate on the substrate surface. Another important observation is a significant difference in the titanium peak intensity. The coating without cracks (Fig. 2a) pointed out a spectrum with higher a titanium peak in relation to the others although the same EDS analytical conditions were maintained. The XRD film formed on the substrate of Fig. 2a is shown in Fig. 4a. The existence of a crystalline coating was confirmed. By comparison with Fig. 4a it can be seen that the intensity of the HAP peaks in Fig. 4b are higher. It seems that the coating thickness is increasing, allowing crack formation. It is important to remember that in Fig. 2b the coating is lightly cracked. The crystallinity of the coating structure was detected by decreasing the angle of incidence (6°) of the incoming X-ray beam [19]. This condition furnished a better X-ray penetration in the coating and detected crystalline HAP and TiO_2. Fig. 5a and b show the infrared spectra of the coating of Fig. 2a and b, respectively. These spectra show the maximum absorbance peaks of the vibrational mode of the groups that form the coating at 1466, 1422, 606, 567 and 466 cm^{-1}, which confirm the presence of a calcium phosphate with a relevant crystallinity and carbonated-apatite [20–23]. Therefore, these results together with XRD support that the coating phases are carbonated-apatite with hydroxyapatite.

The concentration of HAP coating formed on TiO_2 was determined by means of a semi-quantitative analysis. The HAP peak at 1030 cm^{-1} was chosen in order to plot a calibration curve as its points corresponded to mixtures of different percentages of HAP and TiO_2. The outer surface of the coating contained 18.72% HAP in one of the samples (Fig. 5a, without cracks) and 31.85% HAP in the other sample (Fig. 5b, with cracks). Therefore, these results confirm ''the thinner the coating the lesser its crack content''. Although the correlation coefficient obtained was not precise (0.9576) it is coherent with the other results from X-ray diffraction and EDS spectra.

The TiO_2 formed on the metal surface tends to be transformed into sodium titanate when treated hydrothermally with sodium hydroxide, allowing the formation of a network of titanate anions equilibrated by sodium cations [9]. It is already quite well known that heterogeneous precipitation of carbonated hydroxyapatite occurs on negatively charged surfaces, like those found on silica and on collagen surfaces [24]. The alkaline chemical pretreatment considered in the present work provides similar negatively charged ions on the titanium surface. This is necessary but not enough to induce and assure the heterogeneous precipitation of the apatite. Porous substrates with negative charges are the main requirement for calcium phosphate heterogeneous precipitation, and for the living bone growth on implants. Different porous structures on the surface of the chemically pre-treated titanium substrates are observed in Fig. 1. These porous structures led the coating formation, as shown by their morphologies in Fig. 2. Therefore, it can be defined that the porous structure of the titanium surface determines the nature of the resultant coating.

4. Conclusions

a. The concentrations of NaOH solution as well as the time of alkaline attack in an autoclave at 130 °C have strong effects on the morphology of the titanium metal surface.

b. The morphological differences referred to in turn (a) remarkably determine the characteristics of the calcium phosphate coating on the titanium surface after soaking for 4 weeks in SBF.

c. The infrared technique was very useful to detect carbonated apatite in all coatings. Besides, it was possible to estimate the coating thickness by means of semi-quantitative analyses.

d. Among all coatings, the thinnest one did not

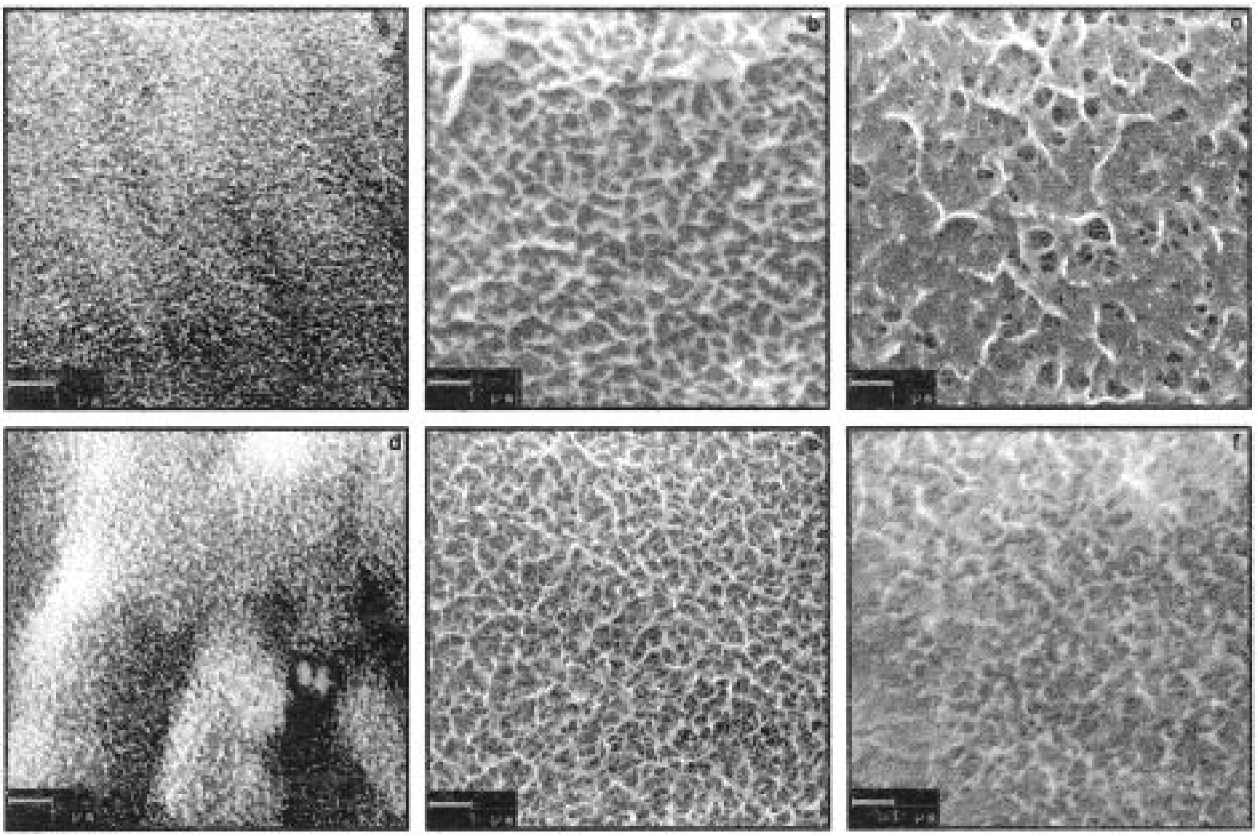


Figure 1 SEM micrograph of the titanium surface etched with 1 M sodium hydroxide for 1 h (a) and 6 h (d); 5 M sodium hydroxide for 1 h (b) and 6 h (e) and 10 M sodium hydroxide for 1 h (c) and 6 h (f) at 130 °C.

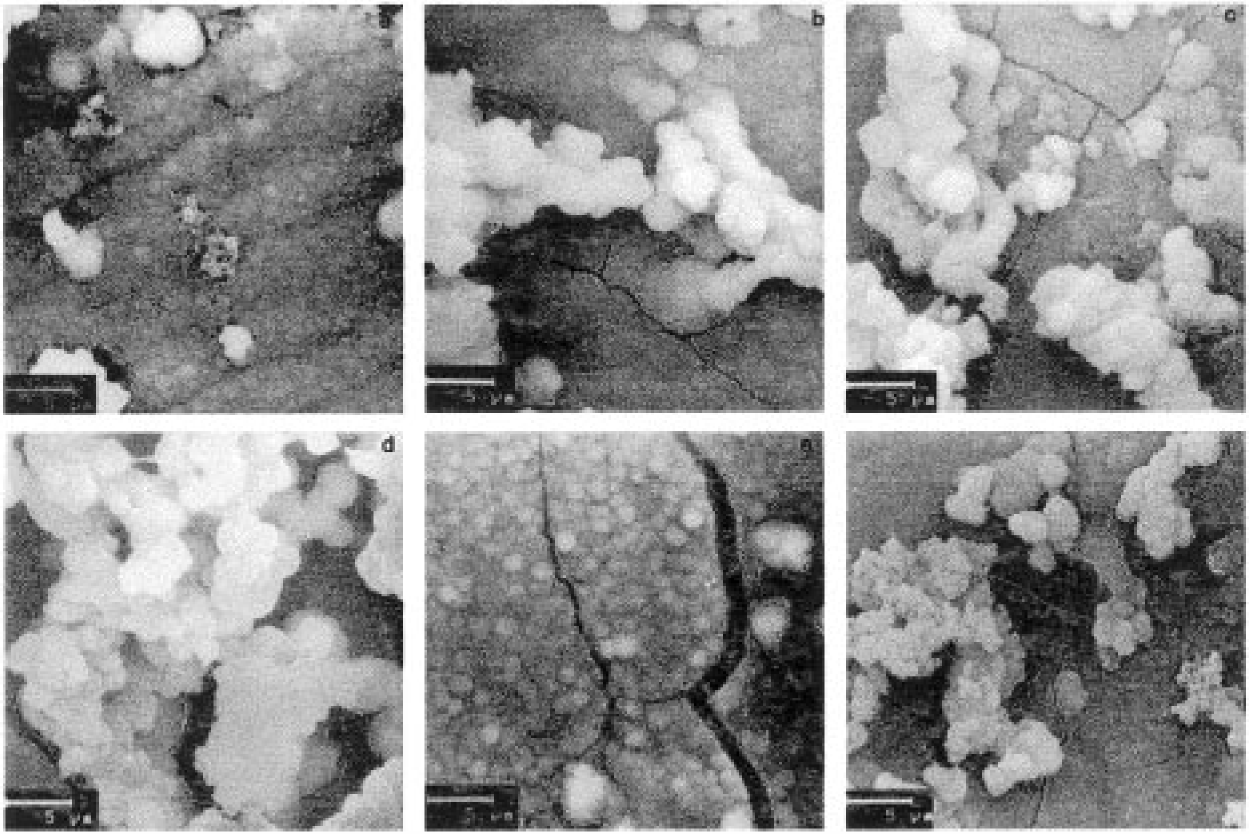
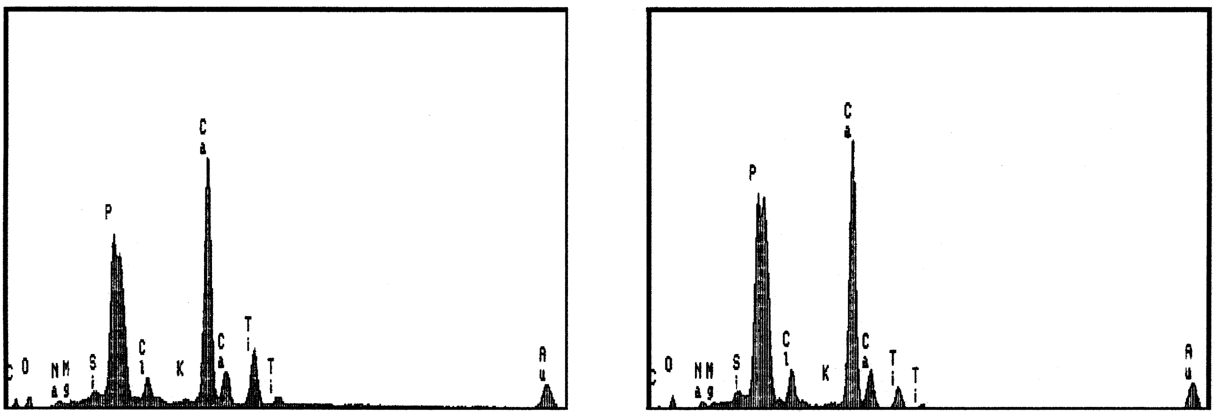


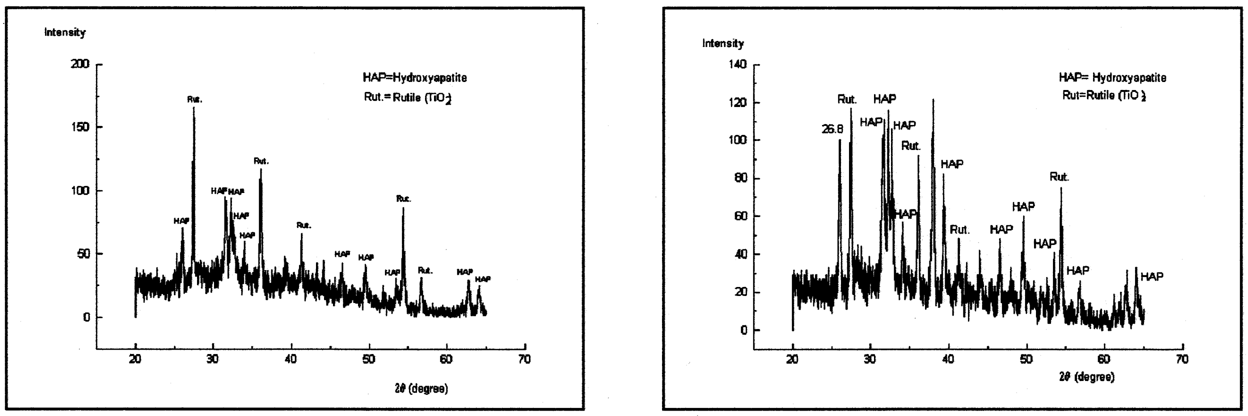
Figure 2 SEM micrograph of the calcium phosphate coating on titanium surface after four weeks soaking in SBF solution. The titanium activation etching conditions in a, b, c, d, e and f correspond to those of a, b, c, d, e and f in Fig. 1, respectively.



3a

3b

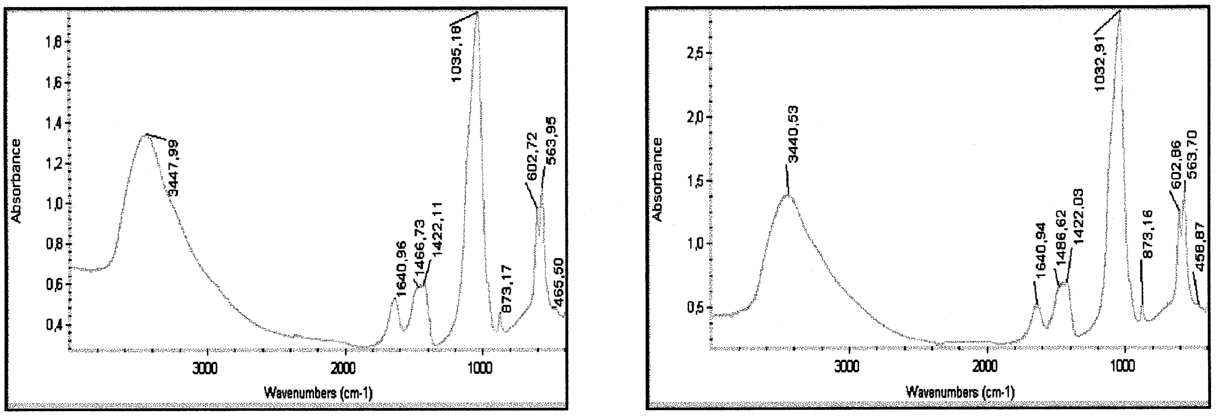
Figure 3 Intensites of characteristic X-ray spectra from EDS analysis of coating of Fig. 2a (a) and 2b (b).



4a

4b

Figure 4 Thin film X-ray diffraction of the calcium phosphate coatings of Fig. 2a (a) and 2b (b).



5a

5b

Figure 5 FT-IR spectra of the calcium phosphate coating of Fig. 2a (a) and 2b (b).

present cracks, meaning "the thinner the coating the lesser the crack content".

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