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Calcium phosphate coatings prepared by electrocrystallization from aqueous electrolytes

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The concept of biological fixation of artificial joint prosthesis by using bioactive calcium phosphate coatings has generated considerable interest in recent decades. This paper reports an electrochemical route for fabricating hydroxyapatite (HA), carbonated-HA and fluoridated-HA coatings on porous and non-porous substrates at relatively low temperatures, using aqueous electrolytes. Scanning electron microscopy (SEM), X-ray diffraction (XRD) and infrared spectroscopy (IR) were used to characterize the morphology, structure and chemical composition of the coatings. The results suggest that the electrochemical route for the fabrication of bioactive calcium phosphate coatings may offer significant advantages over the currently used methods.

1. Introduction

Synthetic hydroxyapatite (HA), as well as the non-stoichiometric forms of this compound, assume substantial interest and importance because of their chemical similarity to the calcium phosphate minerals present in biological hard tissue. Hydroxyapatite, in particular, is well established as a biocompatible ceramic capable of forming a strong chemical bond with natural bone [1]. The ability to bond chemically to bone is a significant distinction between hydroxyapatite and biocompatible surgical alloys such as Ti6Al4V. However, hydroxyapatite has certain disadvantages; it is brittle, and has low tensile strength. Despite these drawbacks, hydroxyapatite can be effectively used as a coating on metallic substrates. Much effort has been directed in recent years towards the development of processing methods to deposit hydroxyapatite onto metallic substrates. Existing methods include electrophoretic deposition [2], plasma spraying [3], radio frequency sputtering [4], and pulsed laser deposition [5]. Currently, the plasma spray technique is extensively used by the implant industry. However, there are major problems associated with this method. The plasma spray technique is a line-of-sight process that produces a non-uniform coating when applied to porous surfaces. Because of the high temperature involved, this technique also has the potential of altering both the calcium phosphate ceramic coating and the metal substrate. From the economical point of view, the plasma spray process is also relatively expensive since HA powder in pure form is required. The other techniques mentioned above have more or less the same limitations. For example, with the electrophoretic technique, it is difficult, if not impossible, to obtain a uniform coating on the porous surface (e.g. multi-layer beads) of implants which have complex geometry. On the other hand this process also requires HA powder as the starting material.

We have previously reported an electrocrystallization process for fabrication of bioactive calcium phosphate coatings at relatively low temperatures using aqueous electrolytes containing Ca- and P-bearing ions [6, 7]. In this communication, we report fabrication of pure HA, carbonated-HA, and fluoridated-HA coatings on porous and non-porous substrates by this technique. The crystalline coatings resulting from the process have been identified by X-ray diffraction (XRD) and infrared (IR) spectroscopy. The morphology and the structure of the coatings were also determined by scanning electron microscopy (SEM).

2. Experimental procedure

The specimen substrates were porous-coated discs of Co–Cr–Mo (ASTM F-75) with a diameter of 30 mm and a thickness of 15 mm, and mechanically ground flat samples of Ti6Al4V (ASTM F-136) (5 cm × 1 cm). The porous coating on the disc specimens consisted of two layers of Co–Cr–Mo beads with a diameter between 500 and 700 μm. The electrolyte used for the fabrication of coatings was made by mixing 1 l 0.042 M $Ca(NO_3)_2$ and 1 l 0.025 M $NH_4H_2PO_4$ solutions. The solutions were prepared with reagent grade chemicals and deionized water. The pH of the electrolyte measured at 25 °C was 4.4. For the fabrication of pure HA coatings, CO_2-free N_2 was continuously sparged into the electrolyte during the process to minimize the risk of contamination of the coating with carbonates. For the fabrication of fluoridated-HA coatings, sodium fluoride ($[F^-] = 10^{-3}$ M) was added to the electrolyte and the pH was adjusted to 4.0 by adding nitric acid. Carbonated-HA coatings were prepared by sparging air into the electrolyte instead of nitrogen.

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The coating process was carried out at 65 ± 1 °C in a conventional electrolytic cell fitted with a saturated calomel electrode (SCE) acting as a reference electrode, and two graphite rods acting as counter-electrodes. Porous-coated Co–Cr–Mo discs and rectangular samples of Ti6Al4V were used as the cathode of the cell. A Hokuto Denko (HD) HAB-151 potentiostat/galvanostat operating in potentiostatic mode was employed to maintain the cathode potential (E_c) at a predetermined value. Coatings of HA, carbonated-HA and fluoridated-HA were deposited on the cathode (substrates) for 80 min. The coated specimen were then steam treated and subsequently calcined at 425 °C.

3. Results and discussion

3.1. Scanning electron microscopy examinations and XRD analysis

Fig. 1 shows the SEM micrograph of the surface of a typical HA coating formed on a mechanically ground titanium substrate by the electrocrystallization process. The HA coatings were formed under N_2 atmosphere at $E_c = -1.6$ V (versus SCE) for 80 min. These coatings were then steam treated at 125 °C for 4 h and finally calcined at 425 °C for 6 h. Coatings of HA prepared under these conditions were uniform, adherent and had a thickness of about 80 μm. XRD results (Fig. 2) indicated that the diffraction pattern of the coating matches the X-ray pattern of hydroxyapatite of good quality [8], having major HA peaks corresponding to 0 0 2, 1 0 2, 2 1 0, 2 1 1, 1 1 2, 3 0 0 and 2 0 2 reflections. No X-ray evidence was found for the existence of other calcium phosphate phases in the coating. It should be noted that various phases of calcium phosphate may form during the plasma spray process as a result of high temperature transformation of the starting powder [9]. The presence of calcium phosphate phases less stable than HA may adversely affect the chemical stability and the lifetime of the coating [10].

Using the XRD results, the crystal size of the HA coating was determined from the peak width at half maximum intensity of the reflection (0 0 2) using the Scherrer equation [11]. The crystallite dimension ($D_{0\,0\,2}$) was about 100 nm. The coating is therefore expected to provide a relatively large surface area, which is particularly desirable for better chemical interaction with the biological environment. Fig. 3 shows the SEM micrograph of a typical porous Co–Cr–Mo specimen coated with HA under similar conditions. It is seen that the electrocrystallization process allows the entire porous surface to be coated without clogging the pores. There is now substantial evidence that calcium phosphate ceramic coatings can increase the rate of bone tissue ingrowth and enhance the mechanical fixation of porous-coated implants in a relatively short period of time after an operation [12]. It has been suggested that this effect could be associated with the calcium phosphate coating serving as a preferred substrate, facilitating cellular activities [13]. It has also been proposed that calcium phosphate coatings may provide Ca and P ions required for calcification [14]. The positive effect of calcium phosphate coatings may also be associated with the elimination of metal ions which may act as calcification inhibitors [15]. No matter which of these phenomena is most critical, it appears that a uniform coating of calcium phosphate ceramic covering the entire porous surface would be preferable.

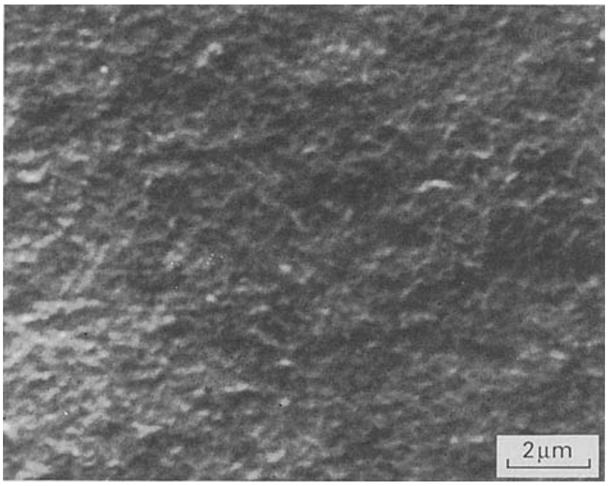

Figure 1 SEM micrograph of a typical HA coating deposited on a mechanically ground Ti sample after steam treatment at 125 °C and calcining at 425 °C.

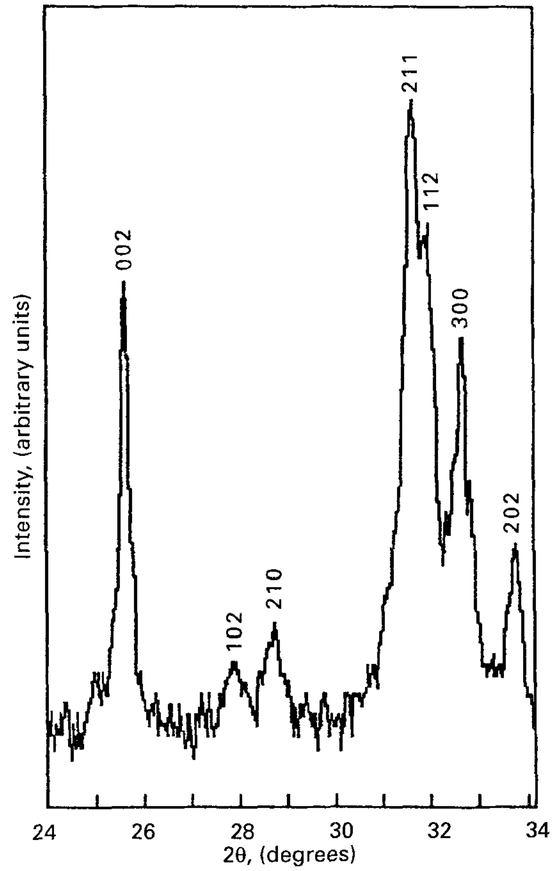

Figure 2 X-ray diffraction pattern of HA coating deposited on Ti substrate. Coating was steam treated at 125 °C for 4 h and subsequently calcined at 425 °C for 6 h.

3.2. IR spectroscopic analysis

The high purity of the HA coatings prepared under N_2 atmosphere was confirmed by the results obtained

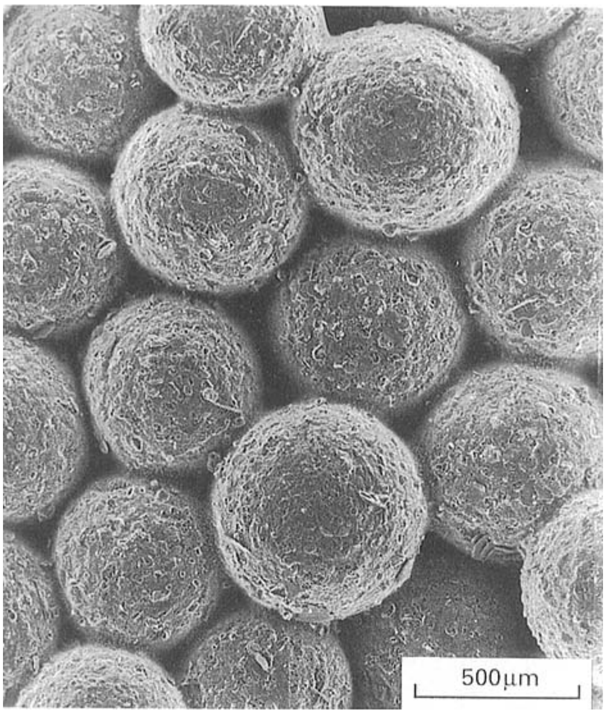

Figure 3 SEM micrograph of HA coating on a porous-coated Co–Cr–Mo substrate after steam treatment at 125 °C and calcining at 425 °C.

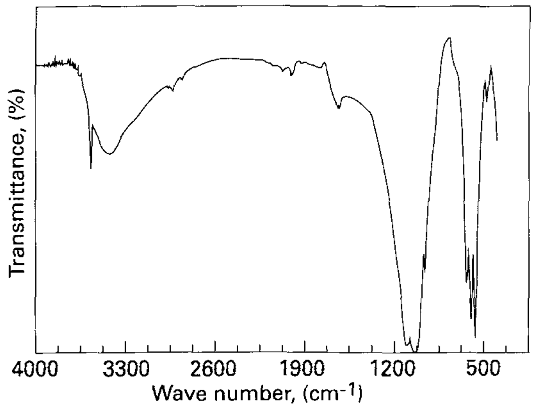

Figure 4 IR spectrum of HA coating after steam treatment at 125 °C and calcining at 425 °C.

from IR spectroscopy (Fig. 4). IR transmission spectra of the HA coatings were obtained from KBr pellets containing a fine powder of the HA removed from the flat titanium substrates. The investigated spectral region was from 4000 to 400 cm^{-1}. As seen in Fig. 4, the IR-spectrum of the coating is very similar to those reported for hydroxyapatite of high purity [16]. The bands at 3571 and 632 cm^{-1} derived from stretching and librational modes of hydroxyl in HA are very sharp, indicating that the coating is indeed well-crystallized. The bands at 1100–1032, 962, 601 and 565 cm^{-1} derived from PO_4 modes of hydroxyapatite are also apparent in this spectrum. There is also a sharp peak at 1648 and a broad band in the range 3000–3600 cm^{-1} indicative of adsorbed water.

An important aspect of the electrochemical route for fabrication of bioactive coatings is that the chemical composition of the electrolyte can be easily varied, and thus coatings with the desired chemical compositions may be tailored for specific applications. Carbonated- and fluoridated-HA coatings are of particular interest in this respect. Carbonated-HA coatings can be readily made by electrocrystallization, using electrolytes containing dissolved CO_2 and/or carbonate ions. Fig. 5 shows the IR spectrum of a typical carbonated-HA coating prepared in this work in the presence of dissolved CO_2. The IR spectrum shows both phosphate bands in the position observed for hydroxyapatite and the principal bands due to the carbonate ions in type B sites (i.e. at approximately 872, 1420 and 1460 cm^{-1}) [17]. The carbonate ions in the B sites are generally believed to replace PO_4^{-3} ions [18]. It is interesting to note that the carbonate in the biological apatites also occurs primarily in B sites [19].

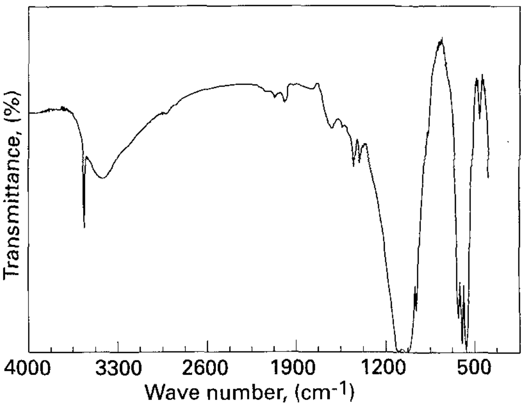

Figure 5 IR spectrum of carbonated-HA coating after steam treatment at 125 °C and calcining at 425 °C.

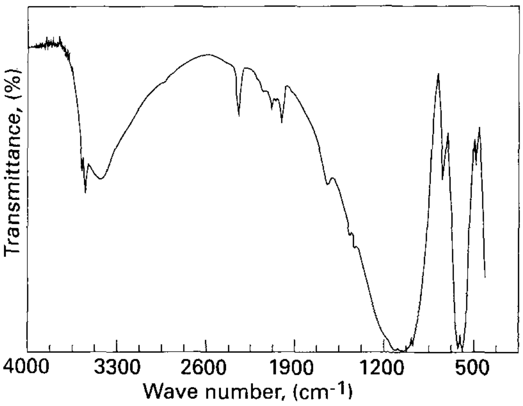

Figure 6 IR spectrum of fluoridated-HA coating after steam treatment at 125 °C and calcining at 425 °C.

Fig. 6 shows the IR spectrum of the fluoridated-HA coating obtained in the presence of fluoride ions ($[F^-] = 10^{-3}$ M). It is seen that both OH stretching and librational bands of hydroxyapatite at 3571 and 632 cm^{-1}, respectively, react to the introduction of fluoride ions into hydroxyapatite. While pure HA has only one OH stretching band at 3571 cm^{-1}, the introduction of F^- ions caused a new peak at 3540 cm^{-1}. The OH librational band at 632 cm^{-1} also shifted to 735 cm^{-1}. The bands at 3540 and 735 cm^{-1} are due to the presence of single OH in an extended fluoride chain. These peaks are the specific characteristics of fluoridated-HA, containing approximately 95%F [20].

4. Conclusions

The results suggest that the electrocrystallization process may provide an effective means for fabricating bioactive calcium phosphate coatings on porous and non-porous substrates at low temperatures. An important advantage of the technique is that the process variables can be easily monitored and controlled, and thus calcium phosphate coatings with the desired chemical compositions may be tailored for specific applications.

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