JOURNAL OF MATERIALS SCIENCE: MATERIALS IN MEDICINE 9 (1998) 297–300

Calcium phosphate coating on titanium substrate by a modified electrocrystallization process

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Modification of ethyl alcohol added aqueous electrolyte for depositing calcium phosphate on titanium substrates by a electrocrystallization method is described. Film coated in the electrolyte with ethyl alcohol addition is more homogeneous and the growth rate is higher. The optimum quantity of ethyl alcohol added is 50% of the electrolyte. Although the pH value of electrolyte varies as ethyl alcohol is added, the phases of the deposited film remain the same, and are hydroxyapatite and brushite. The development of the microstructure of the coated film during deposition is discussed. © *1998 Chapman & Hall*

1. Introduction

Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, abbreviated as HAp) as well as non-stoichiometric forms of this compound are of considerable interest because of their chemical similarity to the calcium phosphate mineral present in biological hard tissue. HAp has been established as a bioactive ceramic because of its capability of forming chemical bonding. However, despite much effort to improve the bending strength and fracture toughness, HAp ceramic is still inferior to human bone and teeth in mechanical properties [1–3]. HAp film coatings on mechanically superior materials, including metals and ceramics, have been developed in order to overcome the shortcomings.

Many methods have been investigated to deposit HAp on metallic substrates (mainly titanium) including electropheric deposition [4, 5], plasma spray [6] and ion beam coating [7].

The electrocrystallization process for fabricating calcium phosphate coatings was introduced by Redepenning *et al.* [8] and Shirkhanzadeh [9, 10] who successfully prepared calcium phosphate coatings on titanium alloy at relative low temperature using an aqueous electrolyte containing Ca–P bearing ions. It was indicated that the electrocrystallization process may provide an effective means for fabricating bioactive calcium phosphate coatings on porous or non-porous substrates at low temperature. In this method, calcium phosphate is thought to be deposited on the cathode as a result of pH increase in the vicinity of the cathode, by reduction H^+ ion accompanying the generation of H_2 gas and OH^- ions. The mechanism is not suitable if dense film is needed. The generation of H_2 on the surface of cathode inhibits the nucleation or absorption of calcium phosphate on the cathode. Ethyl alcohol was added to the electrolyte in an effort to resolve this problem and results are reported here.

2. Experimental procedures

The electrolyte used for fabrication of the coating was prepared by mixing 1 l 0.042 M $Ca(NO_3)_2$ and 0.025 M $NH_4H_2PO_4$ solutions with a magnetic stirrer for 30 min and sedimenting for 24 h. The pH of the electrolyte measured at 25 °C was 4.1.

The anode electrode was a platinum plate of dimensions 1.5 × 2 mm. Rectangular samples of Ti (1.5 × 1.5 mm) were mechanically ground with 200 grit and used as substrates (cathode) for deposition. The substrate was cleaned with 1 M NaOH, HNO_3 and washed with deionized water then dried at 100 °C for 24 h.

The coating process was carried out at 40 °C with a DC power supply at a voltage of 5 to 25 V. Various ratios of ethyl alcohol were added to the electrolyte to increase the electrical resistance.

The resulting samples after coating were washed with deionized water and dried for 24 h at 100 °C. The structures of the samples were analysed by X-ray diffraction (XRD), and the morphologies were observed by scanning electron microscopy (SEM)

3. Results and discussion

Fig. 1 shows the variation of morphologies as the electric voltage is increased. The Ti substrate cannot be fully covered with calcium phosphate until the voltage is increased to 20 V. Deposition is mainly a result of the attractive electric forces. The current density is higher near the edge of the substrate and therefore calcium phosphate can be deposited at lower voltage near the edges. A higher voltage is necessary to provide sufficient attractive force over the whole substrate to precipitate calcium phosphate to form a film.

Although calcium phosphate film is formed in purely aqueous electrolyte, defects including cracks and pores, as shown in Fig. 2a, are present in the coated film, caused by H_2 gas bubbling during coating. Fig. 2b indicates that coating defects are decreased when 25% ethyl alcohol is added to the electrolyte, but cracks and pores are still obvious. As the amount of ethyl alcohol addition is increased to 50%, large cracks are diminished and the pore size is decreased, as shown in Fig. 2c. Fig. 2d shows the morphology of coated film as ethyl alcohol addition is increased to 66.7%, and indicates no apparent difference between 66.7% and 50% additions. However, efficiency of coating at 66.7% alcohol addition is lower than that at 50%. Therefore 50% ethyl alcohol addition in the electrolyte is thought to be the optimum composition.

The possible process of calcium phosphate deposition on the cathode comprises two main steps. First, calcium phosphate particles precipitate from the solution because the pH value increases in the vicinity of the cathode. The second step is precipitate absorption on the cathode due to culombic force. The absorption step is thought to be the rate controlling step because excess precipitates falls down to the bottom of the container during coating, which indicates that formation of precipitate is faster than absorption. The most

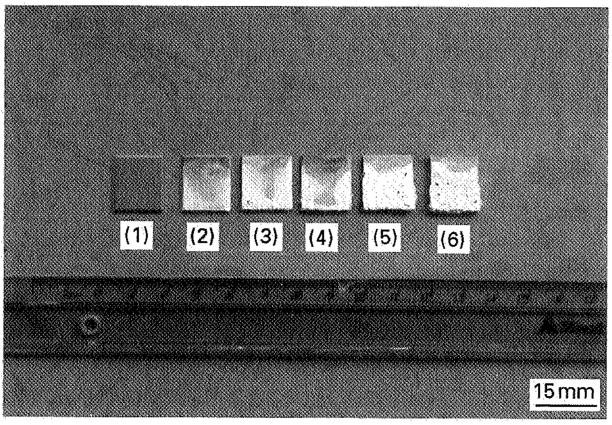

Figure 1 Morphologies of calcium phosphate deposited on Ti substrate at voltage 5 V(2), 10 V(3), 15 V(4), 20 V(5) and 25 V(6). Temp. = 40 °C, time = 60 min. (1) Blank Ti substrate.

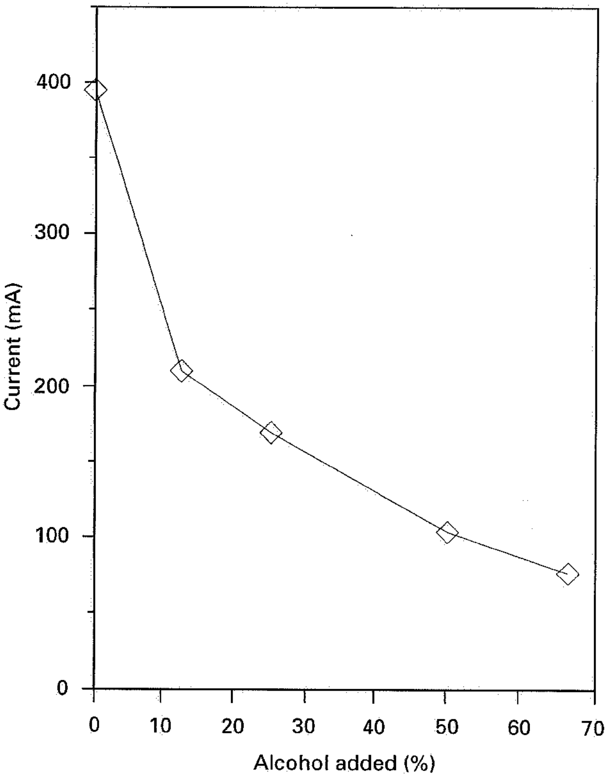

Figure 3 Current in the electrolyte at various levels of ethyl alcohol addition.

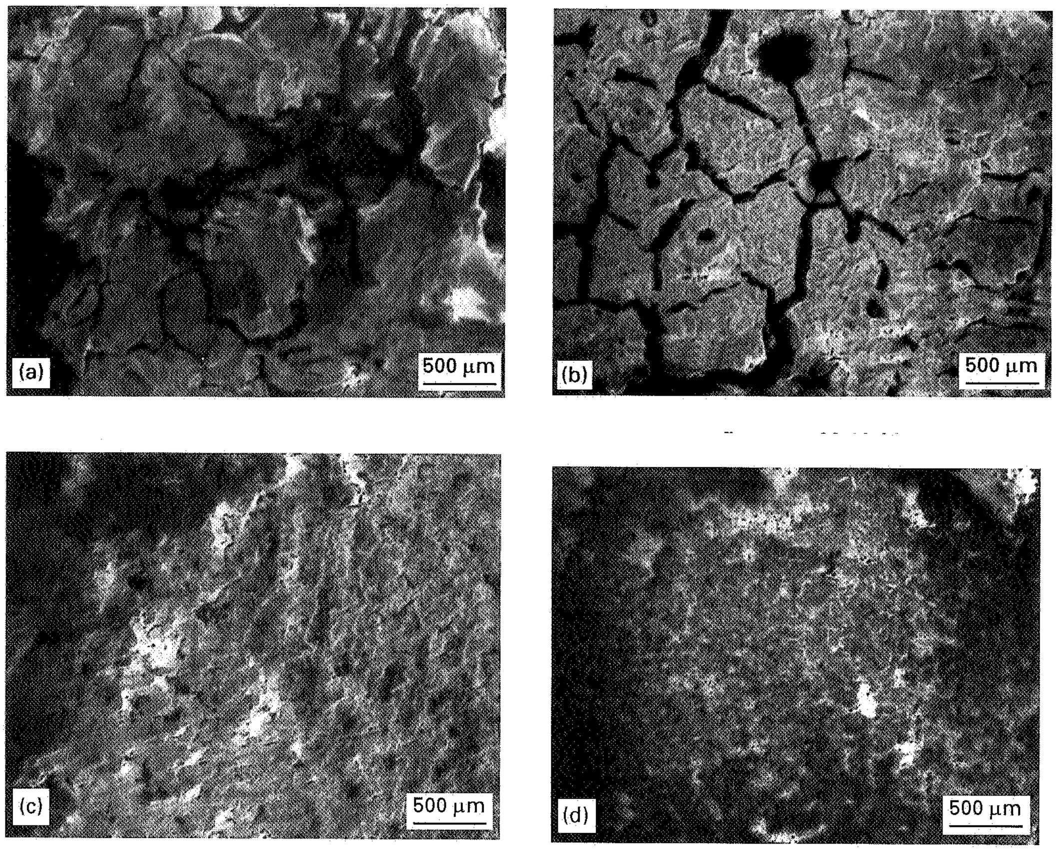

Figure 2 SEM morphologies of coated calcium phosphate film (a) without ethyl alcohol addition; (b) with 25%; (c) 50% and (d) 66.7%.

important factor effecting the rate controlled step is H_2 bubble formation. The object of the alcohol addition is to inhibit the formation of H_2 bubbles to improve the efficiency of absorption. Although the rate of forming precipitates is reduced, the compromise still results in increased deposition rate.

The addition of ethyl alcohol has two effects on the aqueous electrolyte. First, the measured current in the electrolyte is decreased as shown in Fig. 3, which indicates that the electric resistance is increased (Ohm's law). Second, the pH value of electrolyte is decreased from 4.1 to 3.4 at an alcohol addition of 50% due to hydrolysis of the alcohol in water according to the following reaction [5]:

$$RCH_2\text{-}H + H_2O \rightarrow RCH_2O^- + H_3O^+ \quad (1)$$

The variation of pH value does not change the phase formation of the film. Fig. 4 compares the XRD patterns of calcium phosphate film deposited in electrolyte with and without ethyl alcohol addition. The main phases obtained under both conditions are hydroxyapatite and brushite ($CaHPO_4$; $2H_2O$).

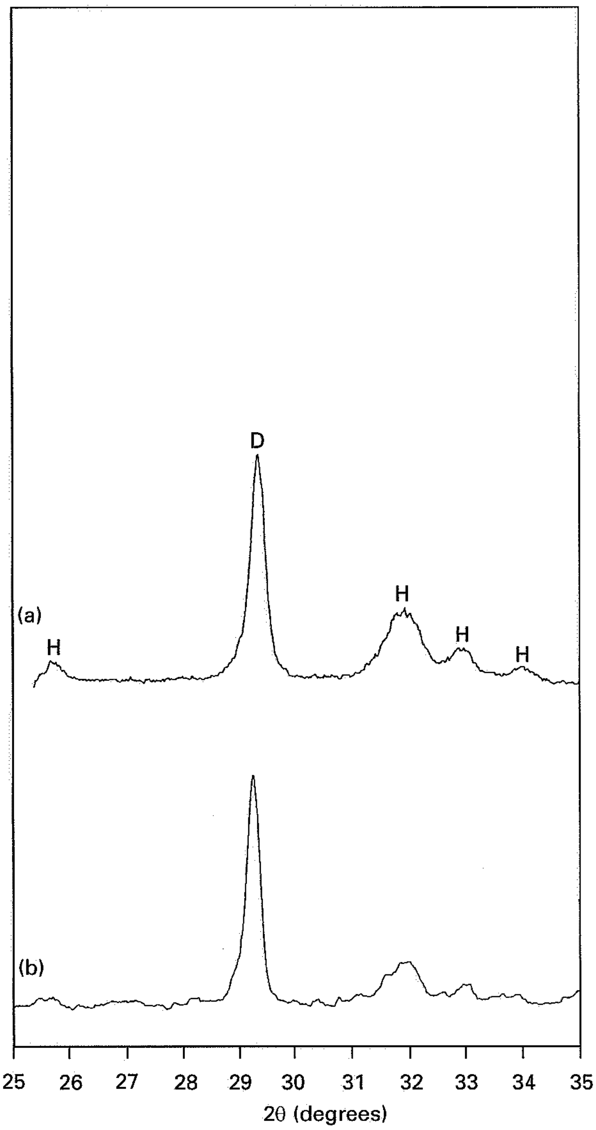

Figure 4 XRD patterns of coated calcium phosphate film (a) with and (b) without ethyl alcohol addition. (D = brushite, H = hydroxyaphalite)

Fig. 5 shows the deposition rate of calcium phosphate film in electrolyte with and without ethyl alcohol addition. The deposition rate in electrolyte with 50% ethyl alcohol addition is much higher than that without any addition and that obtained in other research [9], which is considered to be due to improvement of absorption efficiency by ethyl alcohol addition as described above. The cross-section of the film after 180 min deposition is illustrated in Fig. 6, showing a thickness of about 800 μm.

The development of microstructure in the calcium phosphate film as deposition time increases is shown in Fig. 7a to d. Absorption of individual precipitates on the Ti substrate is observed 3 s after starting deposition. The absorbed precipitates are sphere-like with average size about 1.5 μm. After 30 s of deposition the precipitates connect to form a porous film. The surface

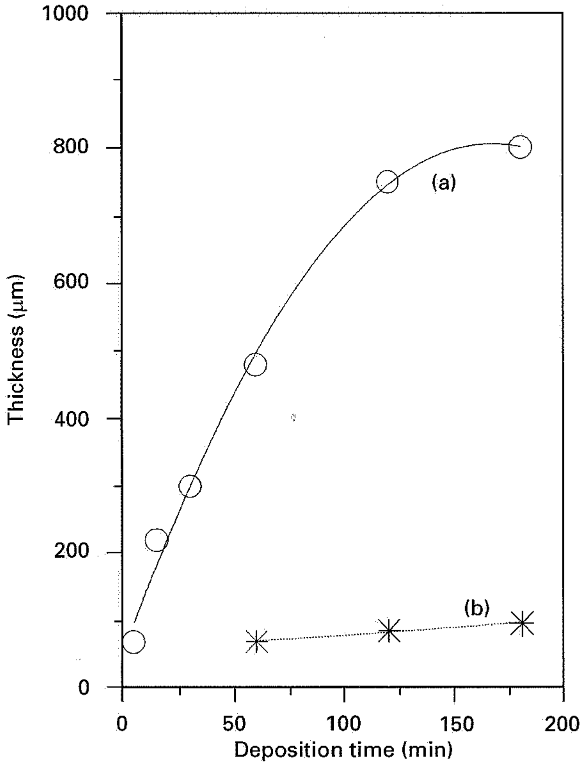

Figure 5 Deposition rate of calcium phosphate in electrolyte (a) with and (b) without 50% ethyl alcohol addition at temperature 40 °C and voltage 20 V.

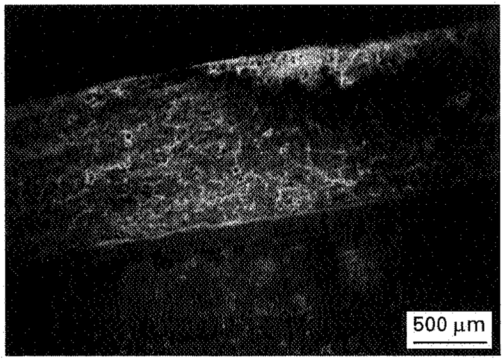

Figure 6 Cross-section of calcium phosphate film coated for 180 min on titanium substrate in electrolyte with 50% ethyl alcohol addition.

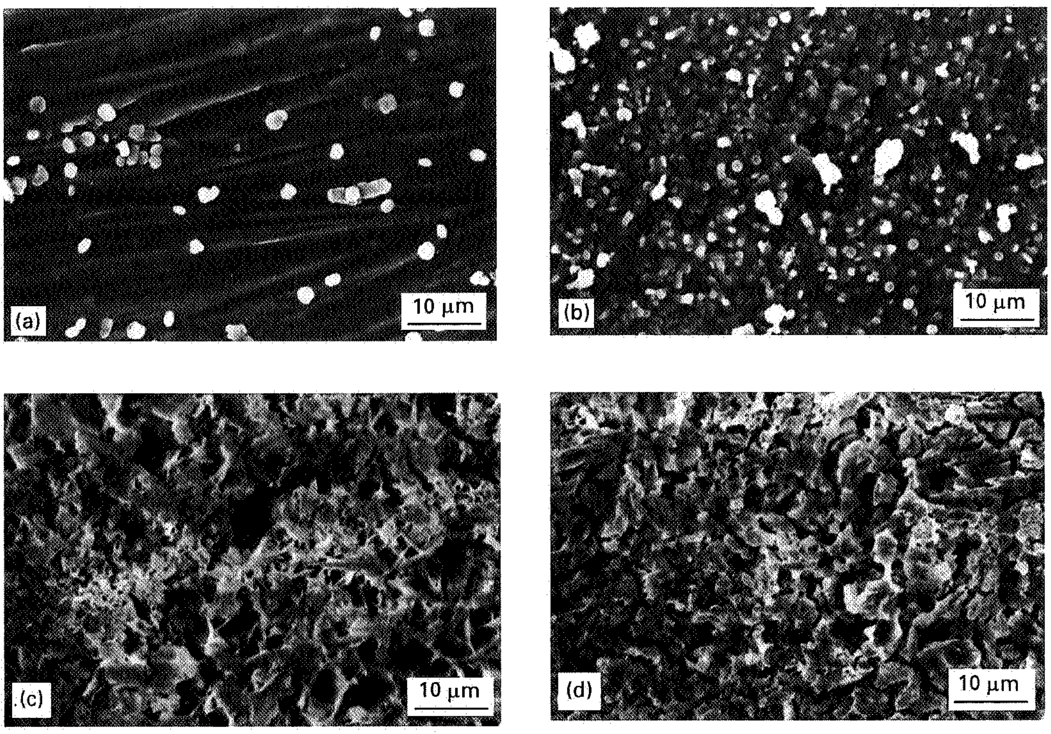

Figure 7 Morphologies of calcium phosphate on Ti substrate deposited for (a) 3 s; (b) 30 s; (c) 5 min; and (d) 180 min.

become rougher with time; plate-like crystals are formed after 5 min of deposition. The deposition rate in this early period is higher, as indicated in Fig. 5. Faster deposition rate also means more H_2 bubbling and greater porosity in the film microstructure. During deposition over 180 min, the deposition rate slows down and H_2 formation becomes less. The microstructure of the film from this period is mainly densifying rather than thicknening.

4. Conclusions

Calcium phosphate deposition on titanium substrate has been performed by electrocrystallization of 0.042 M $Ca(NO_3)_2$ and 0.025 M $NH_4H_2PO_4$ solutions with and without ethyl alcohol addition at a voltage 20 V. The film coated in electrolyte with ethyl alcohol addition is more homogeneous and the growth rate is also higher. Although the pH value of the electrolyte varies as ethyl alcohol is added, the phases of the deposited film remain the same, and are hydroxyapatite and brushite.

Calcium phosphate film is formed by accumulating individual spherical precipitates in the electrolytes. The microstructure of the coated film becomes denser as deposition times increases.

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Received 24 June
and accepted 7 August 1996