JOURNAL OF MATERIALS SCIENCE: MATERIALS IN MEDICINE 6 (1995) 172–176

Coating of hydroxyapatite on metal plates using thermal dissociation of calcium-EDTA chelate in phosphate solutions under hydrothermal conditions

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Coating of hydroxyapatite on various metal plates was carried out by a homogeneous precipitation technique using hydrothermal reactions in $Ca(edta)^{2-}$–NaH_2PO_4 at 140–200 °C and pH 3.4–10.0. Hydroxyapatite films were formed on the surface of the iron plates in solutions at an initial pH above 4.7, whereas aggregates consisting of needle-like hydroxyapatite crystal radiating from a point in the form of flower deposited as islands on the surface of aluminum, copper and titanium plates. The upper part of the film formed on the surface of the iron plates consisted of needle-like hydroxyapatite particles whereas the bottom of the film consisted of spherical hydroxyapatite particles. The length of the needle-like hydroxyapatite particles increased with decreasing concentration of $Ca(edta)^{2-}$.

1. Introduction

Hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, is an attractive material for prosthetic devices, tooth and bone implants, chromatographic separation, catalysis, ion-exchange, etc. Much effort has been expended to develop implant materials made of hydroxyapatite, but the clinical use of hydroxyapatite as a load-bearing implant is limited because of its mechanical brittleness [1–3]. On the other hand, although metal implants possess excellent mechanical properties, their biocompatibility is poor. Attention has therefore been focused on the formation of hydroxyapatite coatings by several methods such as plasma spray, sputtering, doctor blade, electrolysis, biological process using simulated body fluid, etc. Hydroxyapatite films formed by methods using heat treatment such as plasma spray, sputtering, doctor blade, etc. tend to be different from bone apatite in chemical composition. The biological process using simulated body fluid [4] is a novel method to form a hydroxyapatite coating, possessing high bone-bonding ability on various materials, but the growth rate of the hydroxyapatite film is not fast. In a previous paper [5], we reported that needle-like hydroxyapatite could be fabricated by the homogeneous precipitation method using the reaction between $Ca(edta)^{2-}$ chelate and PO_4^{3-} under hydrothermal conditions around 150 °C within 1 h. The homogeneous precipitation reaction can be expressed as follows, and seems to be applicable to the prompt formation of hydroxyapatite film on various substrates:

$$Ca(edta)^{2-} \rightarrow Ca^{2+} + edta^{4-} \quad (1)$$

$$10Ca^{2+} + 6PO_4^{3-} + 2OH^- \rightarrow Ca_{10}(PO_4)_6(OH)_2 \quad (2)$$

In the present study, a series of tests was conducted to investigate the reaction conditions during formation of hydroxyapatite film on various metal substrates.

2. Experimental procedure

Aluminum plate, copper plate, iron plate and titanium plate, 20 mm × 5 mm × 5 mm, were used as substrates. The purity of these metal plates was higher than 99.99%. The surface of the substrate was successively polished with emery papers No. 800 and No. 1000, degreased with acetone and washed with water using an ultrasonic cleaner. All other reagents were analytical grade and used without further purification. $Ca(edta)^{2-}$ solution was prepared by dissolving an equal number of moles of ethylenediaminetetra-acetic disodium salt, Na_2H_2EDTA, and $CaCl_2$ in distilled water. The typical experimental procedures were as follows: a metal substrate and 20 cm^3 of a mixed solution of $Ca(edta)^{2-}$ and NaH_2PO_4 (pH adjusted to the desired value with NaOH) were placed into a sealed Pyrex-glass tube prior to immersion into a silicone oil bath. The temperature of the bath was raised to the desired temperature at a heating rate of 1.5 °C min^{-1}, and maintained for the desired time; the sealed tube was removed from the bath and cooled quickly in air. After that the substrate was recovered and dried at room temperature using a vacuum desiccator. The morphology of the coated film was observed by scanning electron microscopy. The crystalline phase of the film was identified by X-ray diffraction analysis using nickel-filtered CuK_α radiation. The concentrations of Ca, Fe and P in the solution were determined by ICP.

3. Results and discussion

The time dependence of the degree of precipitation of phosphate ion in 0.04 M $Ca(edta)^{2-}$–0.04 M NaH_2PO_4 solutions at pH 5 in the presence of an iron plate is shown in Fig. 1.

The degree of precipitation of phosphate ion was less than 4% at 120 °C, but significant amounts of phosphate ion precipitated above 150 °C. This may be due to the decrease of the solubility of calcium phosphates and/or the promotion of dissociation of $Ca(edta)^{2-}$ shown by Equation 1 with increasing temperature. Various metal substrates were put into solutions containing 0.05 M $Ca(edta)^{2-}$–0.05 M Na_2HPO_4 at various pH and temperatures for 4 h to investigate the formation behaviour of hydroxyapatite film.

In the preliminary experiments no noticeable precipitation was formed on the surface of substrates placed into hydroxyapatite sol solutions adjusted to similar pH and temperatures. As shown in Table I, however, monetite, $CaHPO_4$, and/or hydroxyapatite precipitated on the substrates immersed in $Ca(edta)^{2-}$ and NaH_2PO_4 solutions under various conditions. These results indicated that the homogeneous precipitation of hydroxyapatite in $Ca(edta)^{2-}$–NaH_2PO_4 solution is essential for the formation of hydroxyapatite coating on a metal substrate. Hydroxyapatite and monetite precipitated on the surface of the titanium plate at 150 °C and pH above 5.0 and below 5.0, respectively, without noticeable change in solution pH. These results agree with the solubility diagram for calcium phosphates indicating that the stable phase of calcium phosphate is monetite at low pH and hydroxyapatite at high pH [6, 7]. On the other hand, when iron plates were used as substrates, the final solution pH increased to 6.2–6.7 even though the initial solution pH was less than 6, and the formation of hydroxyapatite was observed at an initial pH above 4.7. The increase of the solution pH might be due to dissolving iron as follows:

$$\mathrm{Fe} + \mathrm{Ca(edta)}^{2-} + 2\mathrm{H_2O} \rightarrow \mathrm{Fe(edta)}^{2-} + \mathrm{Ca}^{2+} + \mathrm{H_2} + 2\mathrm{OH}^- \quad (3)$$

It was notable that no precipitation was formed on the surface of the iron plate at pH 10.0 and 160 °C, but hydroxyapatite precipitated at pH 10.0 and 200 °C. These results suggested that the dissociation of $Ca(edta)^{2-}$ is depressed by increasing solution pH but promoted by increasing temperature.

Scanning electron micrographs of the hydroxyapatite precipitated on the surface of the iron and titanium plates in 0.05 M $Ca(edta)^{2-}$–0.05 M NaH_2PO_4 solutions at pH 6.0 and 150 °C for 4 h are shown in Fig. 2a and b, respectively. It is seen that hydroxyapatite precipitated uniformly on the surface of the iron plate to cover the surface entirely, whereas aggregates consisting of needle-like crystal radiating from a point in the form of a flower precipitated separately as islands on the surface of the titanium plate. The precipitation behaviours of hydroxyapatite on the aluminum and copper plates were similar to that on the titanium plate. Therefore, it appears that the mechanism of hydroxyapatite formation on the surface of the iron plate is different from that on aluminum, copper and titanium plates.

The dissolution behaviours of metal substrates were investigated in 0.05 M $Ca(edta)^{2-}$–0.05 M Na_2HPO_4 solutions at pH 6.6 at 150 °C. Time dependence of the concentration of aluminum, copper, iron and titanium dissolved from the substrates are shown in Fig. 3.

It is notable that a significant amount of iron dissolved in the initial stage of the reaction, i.e. the concentration of iron in the solution attained 7 mm

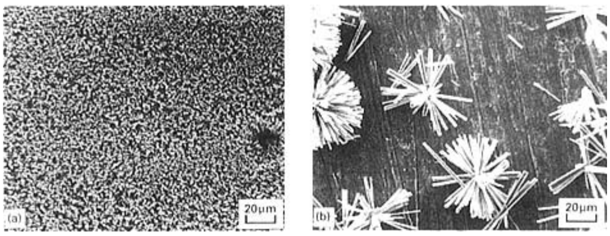

Figure 2 Scanning electron micrographs of the hydroxyapatite precipitated on the surface of (a) the iron plate and (b) the titanium plate in 0.05 M $Ca(edta)^{2-}$–0.05 M NaH_2PO_4 solutions at pH 6.0 and 150 °C for 4 h.

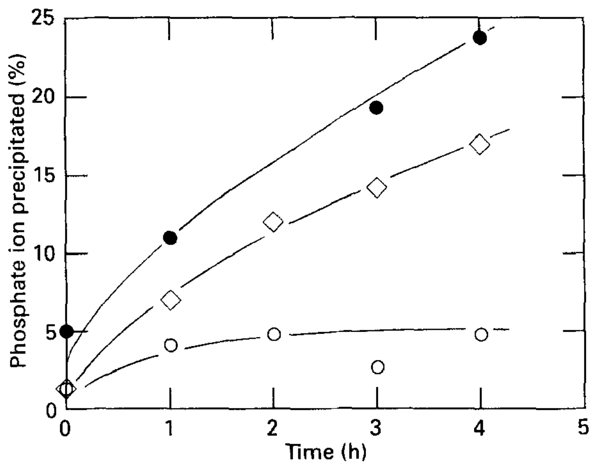

Figure 1 Time dependence of the degree of precipitation of phosphate ion in 0.04 M $Ca(edta)^{2-}$–0.04 M NaH_2PO_4 solutions at pH 5 in the presence of the iron plate: ○: 120 °C, ◇: 150 °C, ●: 180 °C.

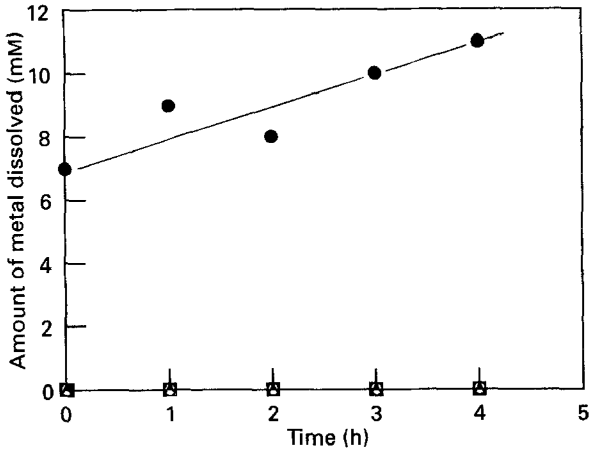

Figure 3 Time dependence of the concentration of aluminum, copper, iron and titanium leached from the substrates in 0.05 M $Ca(edta)^{2-}$–0.05 M NaH_2PO_4 solutions at 150 °C: ○: Al, □: Cu, ●: Fe, △: Ti.

until the temperature was set at 150 °C and then slightly increased with time. On the other hand, no noticeable dissolution of aluminum, copper and titanium was observed. Thus the dissolution of iron, which proceeded rapidly in the initial stage of the reaction, seemed to play an important role in the formation of hydroxyapatite film. It is suspected that the dissolution of iron resulted in the formation of nuclei for the precipitation of hydroxyapatite film. On the other hand, in the case of the precipitation of hydroxyapatite on the surface of aluminum, copper and titanium plates the surface flaws randomly formed by polishing might act as nuclei.

A scanning electron micrograph of a cross-section of the iron plate placed in 0.050 M $Ca(edta)^{2-}$–0.05 M NaH_2PO_4 solution at pH 6.0 and 150 °C for 4 h is shown in Fig. 4a. It is seen that the film consists of needle-like particles about 2.5 μm in length growing vertically to the plate. On removal of the film consisting of needle-like particles, spherical particles around 1 μm in diameter were observed between the needle-like particle layer and the iron substrate as shown in Fig. 4b.

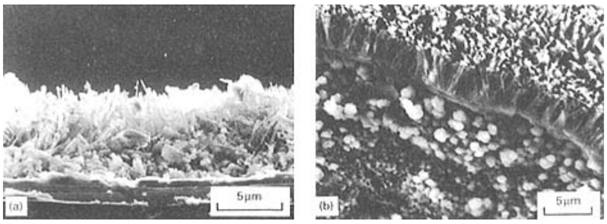

Figure 4 Scanning electron micrographs of (a) a cross-section and (b) surface of the iron plate placed in 0.05 M $Ca(edta)^{2-}$–0.05 M NaH_2PO_4 solution at pH 5.0 and 150 °C for 4 h.

X-ray diffraction patterns of the film (A) as-prepared on the surface of the iron plate immersed in 0.05 M $Ca(edta)^{2-}$–0.05 M NaH_2PO_4 solution at pH 6 and 150 °C for 4 h and (B) calcined at 500 °C for 1 h are shown in Fig. 5.

All diffraction peaks were identified as hydroxyapatite of space group $p6_3/m$ and iron, although the peak intensity ratio of hydroxyapatite was not the same as that of JCPDS 9-432. A diffraction peak corresponding to iron compounds such as iron phosphate, ion hydroxide, iron oxide, etc. was not detected. Therefore, both needle-like particles and spherical particles might be hydroxyapatite. The lattice parameters of hydroxyapatite precipitated on the surface of the iron plate were $a = 0.9424$ nm and $c = 0.6892$ nm, and agreed well with the values of JCPDS 9-432 ($a = 0.9418$ nm and $c = 0.6884$ nm). The major difference was that the hydroxyapatite film prepared in the present study showed a larger peak intensity ratio for (0 0 2)/(2 1 1) than that of JCPDS 9-432.These results suggested that the needle-like particles grown vertically to the iron plate were stoichiometric hydroxyapatite elongated in the [0 0 1] direction. Because of the significant amount of iron dissolved during the initial stage of the reaction, it is suspected that hydroxyapatite precipitated on the surface of the iron plate first by the reactions shown in Equations 3 and 2. The dissolution of iron proceeded rapidly during the initial stage of the reaction, so that the precipitation of hydroxyapatite should also have proceeded rapidly, and consequently resulted in the formation of hydroxyapatite film consisting of small spherical particles. It is likely that hydroxide ions

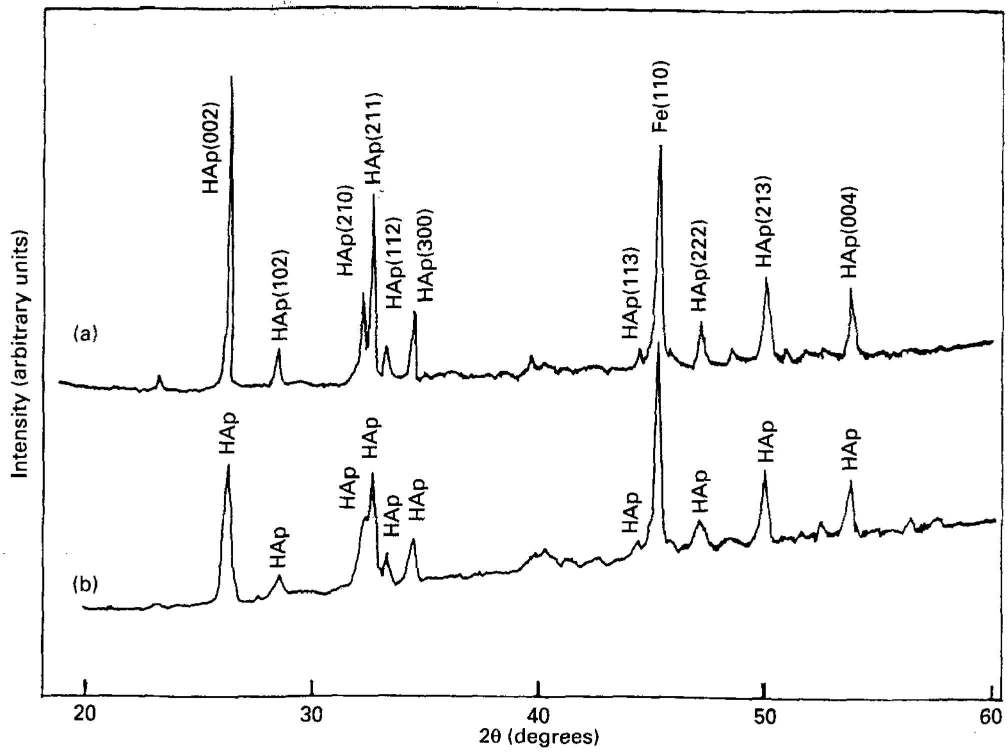

Figure 5 X-ray diffraction patterns of the film (a) as-prepared on the surface of the iron plate immersed in 0.05 M $Ca(edta)^{2-}$–0.05 M NaH_2PO_4 solution at pH 6 and 150 °C for 4 h and (b) calcined at 500 °C for 1 h.

formed by the reaction shown in Equation 3 promote the formation of hydroxyapatite. A similar mechanism is reported in the case of the formation of phosphate coating on steel [8]. It is also probable that the etch pits uniformly formed on the surface by the dissolution of iron acted as nuclei for the precipitation of hydroxyapatite. Further study is necessary to clarify the reaction mechanism. The hydroxyapatite film thus formed might prevent the further dissolution of iron, then hydroxyapatite gradually precipitated by the reactions shown in Equations 1 and 2 to develop needle-like particles. The proposed mechanism for the formation of hydroxyapatite film consisting of particles of two different morphologies on the surface of iron substrate by the hydrothermal reactions in $Ca(edta)^{2-}$–NaH_2PO_4 is schematically illustrated in Fig. 6a.

On the other hand, the precipitation of hydroxyapatite on the surface of aluminum, copper and titanium plates seemed to proceed by the reactions 1 and 2 at the surface flaws formed by polishing, as illustrated in Fig. 6b.

Scanning electron micrographs of the hydroxyapatite films formed on the surface of the iron plates in various concentrations of $Ca(edta)^{2-}$–NaH_2PO_4 solutions at pH 5 and 150 °C for 4 h are shown in Fig. 7. The length and diameter of hydroxyapatite particles and the porosity of the hydroxyapatite film increased with decreasing concentration of $Ca(edta)^{2-}$. These results indicate that the number of nuclei used for the crystal growth of needle-like hydroxyapatite decreased with decreasing $Ca(edta)^{2-}$ concentration. Therefore, it may be concluded that the concentration of $Ca(edta)^{2-}$ is one of the most significant factors controlling the morphology of hydroxyapatite film.

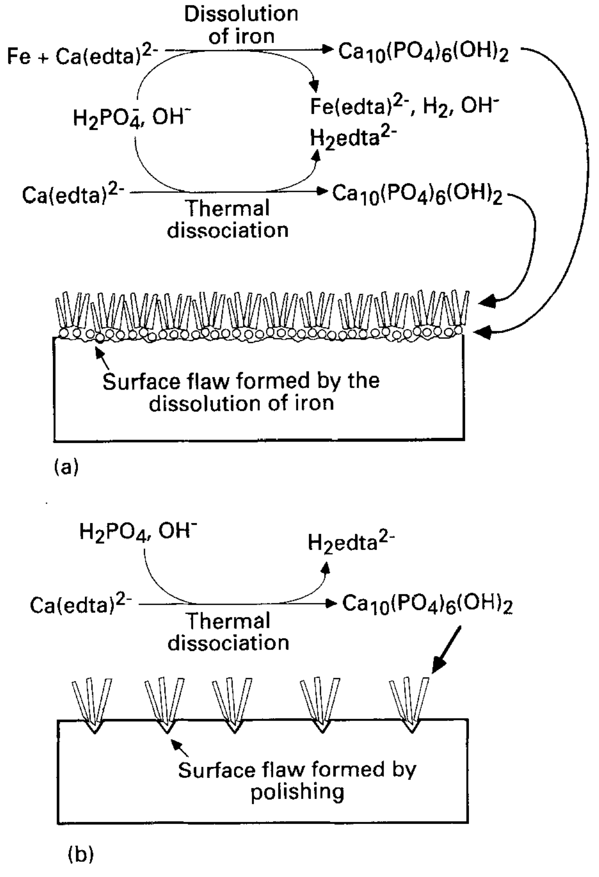

Figure 6 Schematic illustration for the mechanism of hydroxyapatite deposition on (a) the iron plate and (b) the titanium plate in $Ca(edta)^{2-}$–NaH_2PO_4 solutions.

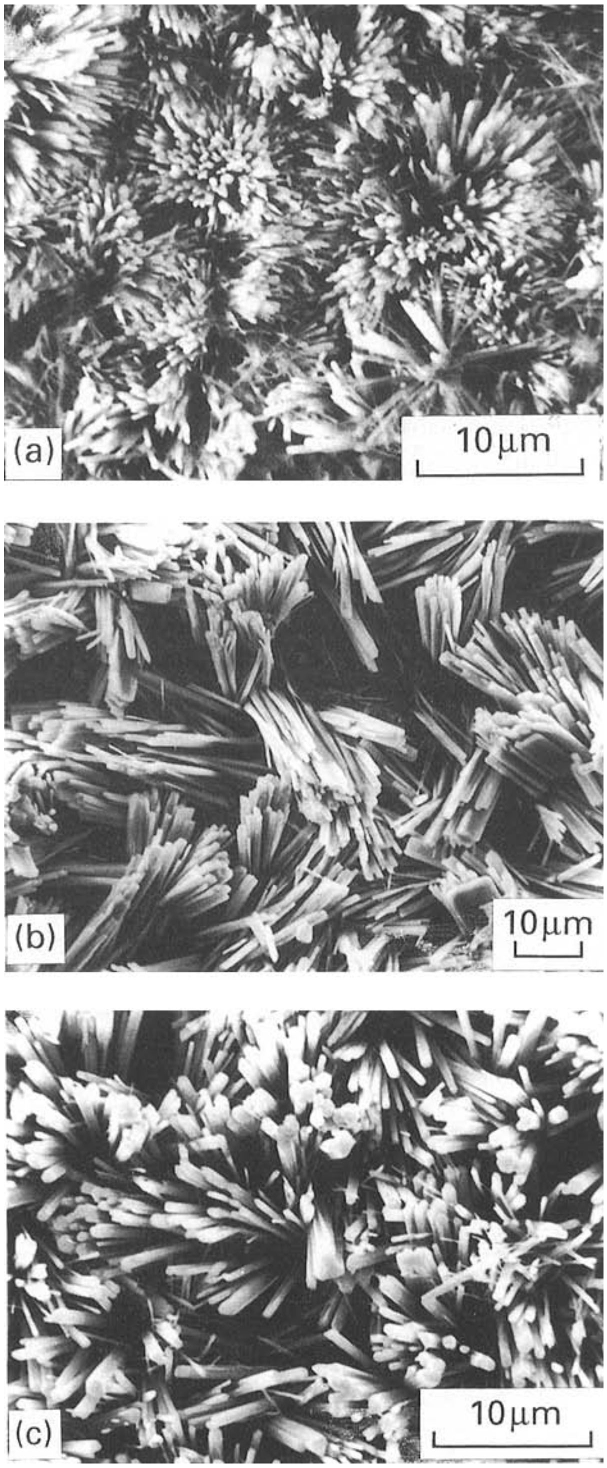

Figure 7 Scanning electron micrographs of the hydroxyapatite films formed on the surface of the iron plates in various concentrations of $Ca(edta)^{2-}$–NaH_2PO_4 solutions at pH 5 and 150 °C for 4 h: (a) 0.09 M $Ca(edta)^{2-}$–0.01 M NaH_2PO_4; (b) 0.07 M $Ca(edta)^{2-}$–0.03 M NaH_2PO_4; (c) 0.04 M Ca $(edta)^{2-}$–0.06 M NaH_2PO_4.

4. Conclusions

From the present results, the following conclusions may be drawn:

1. Hydroxyapatite films were formed on the surface of the iron plates by hydrothermal reaction in $Ca(edta)^{2-}$–NaH_2PO_4 solutions above initial pH 4.7 and 150 °C, whereas aggregates consisting of needle-like hydroxyapatite crystals radiating from a point in the form of a flower were separately deposited as islands on the surface of the aluminum, copper and titanium plates.

2. The upper part of the hydroxyapatite film formed on the surface of the iron plates consisted of needle-like particles, whereas the bottom of the film consisted of spherical particles.

3. The length of the needle-like hydroxyapatite particles increased with decreasing concentrations of $Ca(edta)^{2-}$.

Acknowledgement

This work was partly supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture in Japan.

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Received 2 June 1993
and accepted 27 April 1994