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Coating of $CaTiO_3$ on titanium substrates by hydrothermal reactions using calcium-ethylene diamine tetra acetic acid chelate

Y. FUJISHIRO, N. SATO, S. UCHIDA, T. SATO*
Institute for Chemical Reaction Science, Tohoku University, 2-1-1 Katahira, Sendai 980-77, Japan

Titanium plates were treated in $[Ti(O_2)EDTA]^{2-}$–$Ca(EDTA)^{2-}$ mixed solutions and/or $Ca(EDTA)^{2-}$ solutions (where EDTA is ethylene diamine tetra acetic acid) at pH 9–13 and 150–250 °C for 0.5–12 h. The film, about 50 μm thick, and consisting of mixtures of $CaTiO_3$ and TiO_2 was formed in 0.01 M $[Ti(O_2)EDTA]^{2-}$–0.01 M $Ca(EDTA)^{2-}$ mixed solution at pH 13 and 250 °C for 6 h. The film consisted of large icosahedral and hexagonal particles, of about 10 μm diameter, and small aggregated particles, of about 1 μm diameter. On the other hand, the film, about 20 μm thick, consisted of hexagonal plate-like $CaTiO_3$ particles, of about 1 μm diameter, was formed in 0.01 M $Ca(EDTA)^{2-}$ solution at pH 13 and 250 °C for 6 h. The thickness of both films increased with time, where the film formation rate in 0.01 M $[Ti(O_2)EDTA]^{2-}$–0.01 M $Ca(EDTA)^{2-}$ mixed solution was much faster. The $CaTiO_3$ film formed on the surface of titanium promoted the precipitation of hydroxyapatite on the substrate by the hydrothermal reactions in $Ca(EDTA)^{2-}$–PO_4^{3-} mixed solutions.

1. Introduction

Hydroxyapatite, $Ca_{10}(OH)_2(PO_4)_6$, is a typical biocompatible ceramic material and has received much attention for its application as an implant material. The clinical use of hydroxyapatite as a load-bearing implants, however, is limited because of its mechanical brittleness. On the other hand, although metal implants such as titanium possess excellent mechanical properties, their biocompatibility is poor. Attention has therefore been focused on the formation of hydroxyapatite coatings on titanium by several methods such as plasma spraying, sputtering, doctor blade, electrolysis, a biological process using simulated body fluid, etc. [1–6]. Hydroxyapatite films formed by methods using heat treatment such as plasma spraying, sputtering, doctor blade, etc., tend to differ from bone apatite in chemical composition [6]. The biological process using simulated body fluid is a novel technique to form a hydroxyapatite coating on various materials, but the growth rate is quite slow [4]. We reported [7, 8] that hydroxyapatite films could be formed quickly on titanium substrates by the hydrothermal reactions in $Ca(EDTA)^{2-}$–PO_4^{3-} mixed solutions around 150 °C (where EDTA is ethylene diamine tetra acetic acid). The adherence of hydroxyapatite film thus formed on titanium substrates, however, is modest because of the lack of the chemical interaction between hydroxyapatite and titanium. One solution to this problem is possibly to form an intermediate film on titanium substrates which shows excellent adherence with both titanium substrates and hydroxyapatite. Hydrothermal treatment of a metal substrate is a promising method to form strongly adherent film of metal compounds [9, 10]. $CaTiO_3$ is a candidate material for compatibility with hydroxyapatite because PO_4^{3-} may be strongly adsorbed by Ca^{2+} on the surface of $CaTiO_3$. Accordingly, in the present study, the formation of $CaTiO_3$ films on titanium substrates by hydrothermal reactions was investigated.

2. Experimental procedure

A stock solution of 0.01 M $Ca(EDTA)^{2-}$ was prepared by mixing $Ca(NO_3)_2$ solution and Na_2H_2 EDTA solution. A stock solution of 0.01 M $[Ti(O_2)EDTA]^{2-}$–0.01 M $Ca(EDTA)^{2-}$ mixed solution was prepared by mixing Ti(IV) peroxide solution, $Ti(O_2)\,(OH)_{n-2}^{(4-n)+}$, Na_2H_2 EDTA solution and $Ca(NO_3)_2$ solution where $Ti(O_2)(OH)_{n-2}^{(4-n)+}$ was prepared by mixing titanium tetraisopropoxide, 1 M HCl solution and 2 M H_2O_2 solution as reported [11]. A stock solution of 0.01 M $Ca(EDTA)^{2-}$–0.01 M PO_4^{3-} mixed solution was prepared by mixing $Ca(EDTA)^{2-}$ and Na_2HPO_4 solutions. The solution pH was adjusted with 2 M NH_3, 6 M NaOH and 2 M HCl solutions at the desired value.

Titanium plates (Niraco Co., purity > 99.9%, 5 mm × 10 mm × 0.6 mm) were used as the substrates. The surfaces of the substrates were successively washed with

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*Author to whom all correspondence should be addressed. E-mail: tsusato@icrs.tohoku.ac.jp acetone and distilled water using an ultrasonic cleaner.

After a piece of titanium plate and 15 cm^3 reaction solution were placed in a sealed SUS 304 type stainless steel tube, equipped with polytetrafluoroethylene (Teflon) cup insert of 25 cm^3 inner volume, the tube was immersed in a 50 wt % KNO_3 + 50 wt % $LiNO_3$ molten salt bath set to the desired temperature and maintained at this value for the desired time. After heat treatment, the sealed tube was taken out of the bath and cooled in air. The treated plates were washed with distilled water and dried at room temperature using a vacuum desiccator for 1 d.

The morphology of the 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 film thickness was measured from scanning electron micrographs of cross-sections of the substrate. The concentrations of calcium, titanium and phosphorus in solutions and films were determined by inductively coupled plasma–Auger electron spectroscopy (ICP-AES) and electron probe microanalysis (EPMA), respectively.

3. Results and discussion

3.1. Coating of $CaTiO_3$ film by the hydrothermal reactions in $[Ti(O_2)(EDTA)]^{2-}$– $Ca(EDTA)^{2-}$ mixed solutions

Titanium plates were treated in 0.01 M $[Ti(O_2)(EDTA)]^{2-}$–0.01 M $Ca(EDTA)^{2-}$ mixed solutions at pH 9, 11 and 13 and 150–250 °C for 2 h. No film formation was observed below 200 °C although significant amounts of precipitates were formed in the solutions. On the other hand, thin films, amorphous to X-ray, were formed on the substrate at 250 °C. XRD patterns of the precipitates formed in the solutions at pH 9–11 and 150–250 °C for 2 h are shown in Fig. 1.

The precipitates below 200 °C were amorphous as determined by X-ray. On the other hand, anatase-type TiO_2 and $CaTiO_3$ precipitated at 250 °C and pH 9–11 and pH 13, respectively. Therefore, it may be concluded that the solution pH and temperature should be greater than 13 and 250 °C, respectively, in order to form $CaTiO_3$. These results suggested that titanate ion, $Ti(OH)^{n-}_{4+n}$ which exists in alkaline solution, plays an important role for the formation of $CaTiO_3$.

The EPMA image of the cross-section of the titanium plate treated in 0.01 M $[Ti(O_2)(EDTA)]^{2-}$–0.01 M $Ca(EDTA)^{2-}$ mixed solutions at pH 13 and 250 °C for 2 h are shown in Fig. 2. The calcium concentration in the film increased with increasing the film thickness, while the titanium concentration decreased, indicating the formation of compositionally graded calcium titanate film.

As seen in Fig. 3, the film thickness increased with time, e.g. approximately 50 and 80 μm for 6 and 12 h, respectively.

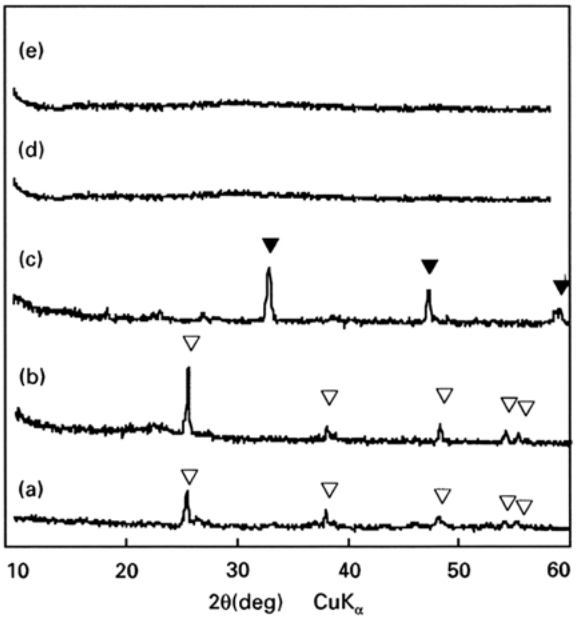

Figure 1 XRD patterns of the powders precipitated by hydrothermal reactions in 0.01 M $[Ti(O_2)(EDTA)]^{2-}$–0.01 M $Ca(EDTA)^{2-}$ solutions for 2 h. (a) pH 9 and 250 °C, (b) pH 11 and 250 °C, (c) pH 13 and 250 °C, (d) pH 14 and 200 °C, (e) pH 13 and 150 °C, (▽) TiO_2, (▼) $CaTiO_3$.

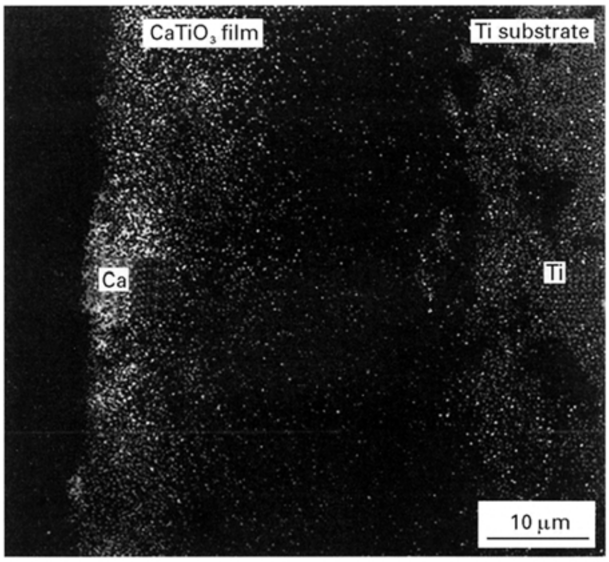

Figure 2 EPMA image of the cross-section of the titanium plate treated in 0.01 M $[Ti(O_2)EDTA]^{2-}$–0.01 M $Ca(EDTA)^{2-}$ mixed solution at pH 13 and 250 °C for 2 h.

corresponding to anatase was noticeably increased at 12 h. These results suggested that it is difficult to form $CaTiO_3$ film as single phase by the hydrothermal reaction in $[Ti(O_2)(EDTA)]^{2-}$–$Ca(EDTA)^{2-}$ mixed solutions. This may be due to the fact that the rate of decomposition of $[Ti(O_2)(EDTA)]^{2-}$ is faster than that of the dissociation of $Ca(EDTA)^{2-}$.

Fig. 5 shows scanning electron micrographs of the surface of the film formed for 6 h. The film consisted of large icosahedral and hexagonal particles, of about

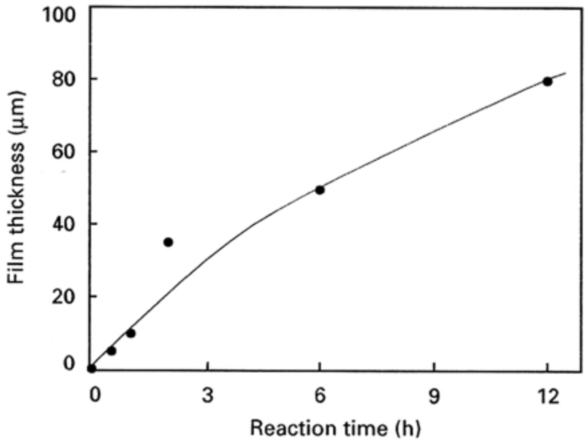

Figure 3 Time dependence of the film thickness formed in 0.01 M $[Ti(O_2)EDTA]^{2-}$–0.01 M $Ca(EDTA)^{2-}$solution at pH 13 and 250 °C.

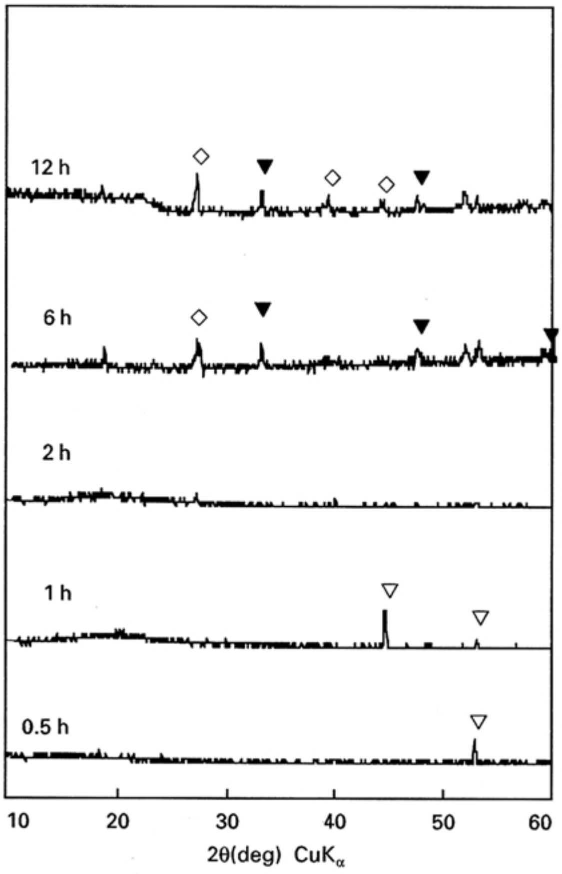

Figure 4 XRD patterns of the films formed in 0.01 M $[Ti(O_2)EDTA]^{2-}$–0.01 M $Ca(EDTA)^{2-}$ solution at pH 13 and 250 °C for various times. (◇) TiO_2, (▼) $CaTiO_3$, (▽) Ti.

solution, the large icosahedral and hexagonal particles and small aggregated particles seem to be $CaTiO_3$ and TiO_2, respectively.

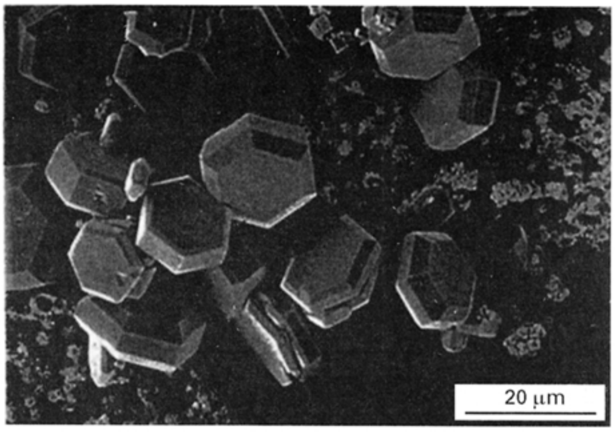

Figure 5 Scanning electron micrograph of the surfaces of titanium plates treated in 0.01 M $[Ti(O_2)EDTA]^{2-}$–0.01 M $Ca(EDTA)^{2-}$ mixed solution at pH 13 and 250 °C for 6 h.

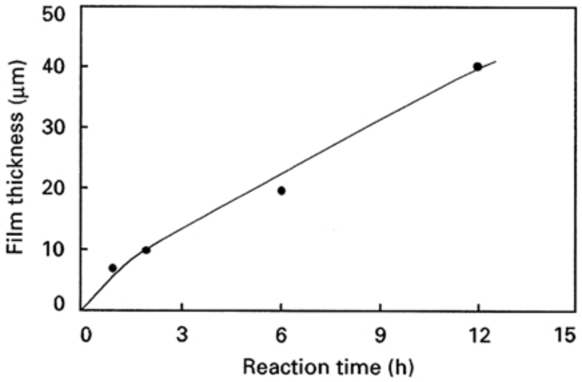

Figure 6 Time dependence of the film thickness formed in 0.01 M $Ca(EDTA)^{2-}$ solution at pH 13 and 250 °C.

3.2. Coating of $CaTiO_3$ film by the hydrothermal reactions in $Ca(EDTA)^{2-}$ solutions

Titanium plates were treated in 0.01 M $Ca(EDTA)^{2-}$ solutions at pH 13 and 250 °C for various times. Under the present reaction conditions, the reactions occurred preferentially on the surface of the substrates, i.e. the plates were uniformly coated by the film, whereas no precipitation was observed in the solution. As seen in Fig. 6, the film thickness increased almost linearly with time and was ~40 μm for 12 h, which was almost half that formed in 0.01 M $[Ti(O_2)EDTA)]^{2-}$–0.01 M $Ca(EDTA)^{2-}$mixed solutions.

XRD profiles of the surface of titanium plates treated in 0.01 M $Ca(EDTA)^{2-}$ solutions at pH 13 and 250 °C for various times are shown in Fig 7.

XRD peaks corresponding to $CaTiO_3$ were observed for the plates treated for longer than 6 h, but the formation of TiO_2 was not observed at all, indicating that the film consisted of single-phase $CaTiO_3$.

Fig. 8 shows a scanning electron micrograph of the surface of the titanium plate treated for 6 h. The substrate was entirely coated with the film, which consisted of small thin hexagonal particles, of about 1 μm diameter. The size is one-tenth of that of the icosahedral and hexagonal particles formed in 0.01 M $[Ti(O_2)(EDTA)]^{2-}$– 0.01 M $Ca(EDTA)^{2-}$ mixed solutions.

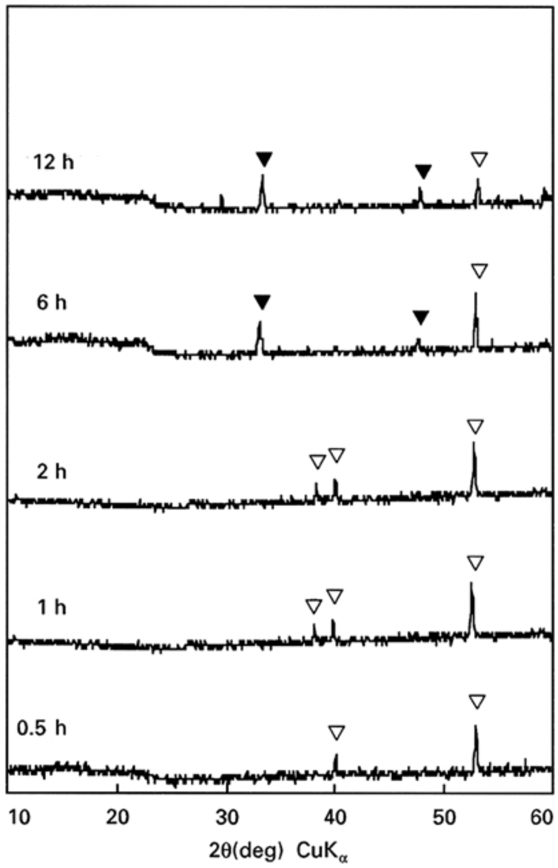

Figure 7 XRD patterns of the films formed in 0.01 M Ca(EDTA)$^{2-}$ solution at pH 13 and 250 °C for various times. (▽) Ti, (▼) $CaTiO_3$.

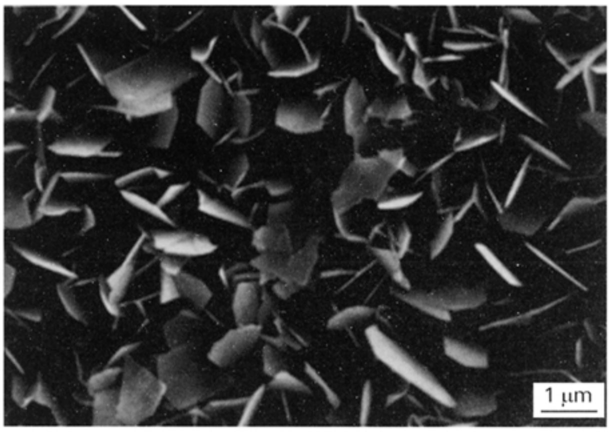

Figure 8 Scanning electron micrograph of the surface of the titanium plate treated in 0.01 M Ca(EDTA)$^{2-}$ solution at pH 13 and 250 °C for 6 h.

3.3. Reaction schemes for the formation of $CaTiO_3$ by hydrothermal reactions

The reactions of titanium substrates, $[Ti(O_2)EDTA]^{2-}$–$Ca(EDTA)^{2-}$ and/or $Ca(EDTA)^{2-}$ solutions are thought to proceed as follows.

(A) Decomposition and dissociation of chelates

$$[Ti(O_2)EDTA]^{2-} \rightarrow Ti(OH)_{4+n}^{n-} + EDTA^* \quad (1)$$

$$Ca(EDTA)^{2-} \rightleftharpoons Ca^{2+} + EDTA^{4-} \quad (2)$$

(B) Dissolution of titanium substrate

$$Ti + 2H_2O + nOH^- \rightarrow Ti(OH)_{4+n}^{n-} + 2H_2 \quad (3)$$

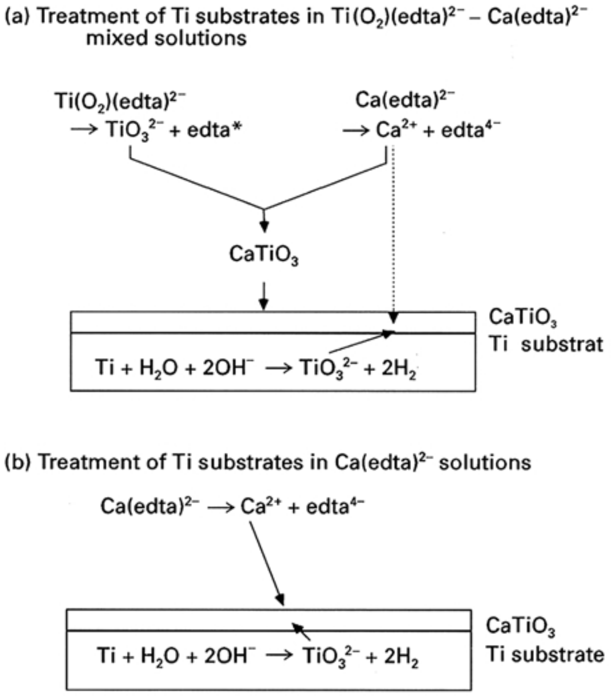

Figure 9 Reaction schemes for the coating on titanium substrates in (a) $[Ti(O_2)EDTA]^{2-}$–$Ca(EDTA)^{2-}$ mixed solution, and (b) $Ca(EDTA)^{2-}$ solution.

(C) Formation of $CaTiO_3$ and TiO_2

$$Ti(OH)_{4+n}^{n-} + Ca^{2+} \rightarrow CaTiO_3 + H_2O + 2H^+ + nOH^- \quad (4)$$

$$Ti(OH)_{4+n}^{n-} \rightarrow TiO_2 + 2H_2O + nOH^- \quad (5)$$

where EDTA* indicates decomposition products of EDTA. Reactions 1 and 2 should uniformly proceed in the solution, but Reaction 3 only occurs on the surface of the titanium substrate. Reactions 4 and 5 proceed competitively depending on the solution pH and Ca^{2+} concentration, i.e. Reaction 4 may proceed preferentially above pH 13 in the presence of Ca^{2+}, whereas Reaction 5 becomes dominant below pH 12 and/or in the absence of Ca^{2+}. Therefore, when titanium substrates are treated in $[Ti(O_2)EDTA]^{2-}$–$Ca(EDTA)^{2-}$ mixed solutions, $CaTiO_3$ and TiO_2 are formed both on the surface of substrates and in the solutions as shown in Fig. 9a. Because the film was not formed in $[Ti(O_2)EDTA]^{2-}$–$Ca(EDTA)^{2-}$ mixed solutions below 200 °C, even though significant amounts of precipitation occurred in the solution, the dissolution of titanium from the substrate seems to be essential to form films on the substrate, indicating that the dissolved parts act as nuclei for the precipitation. Further, when the rate of $[Ti(O_2)EDTA]^{2-}$ decomposition is faster than that of dissociation of $Ca(EDTA)^{2-}$, TiO_2 is formed simultaneously with $CaTiO_3$ even above pH 13. On the other hand, when titanium substrates are treated in $Ca(EDTA)^{2-}$ solutions above pH 13, $CaTiO_3$ can be formed preferentially on the surface of the substrates as shown in Fig. 9b.

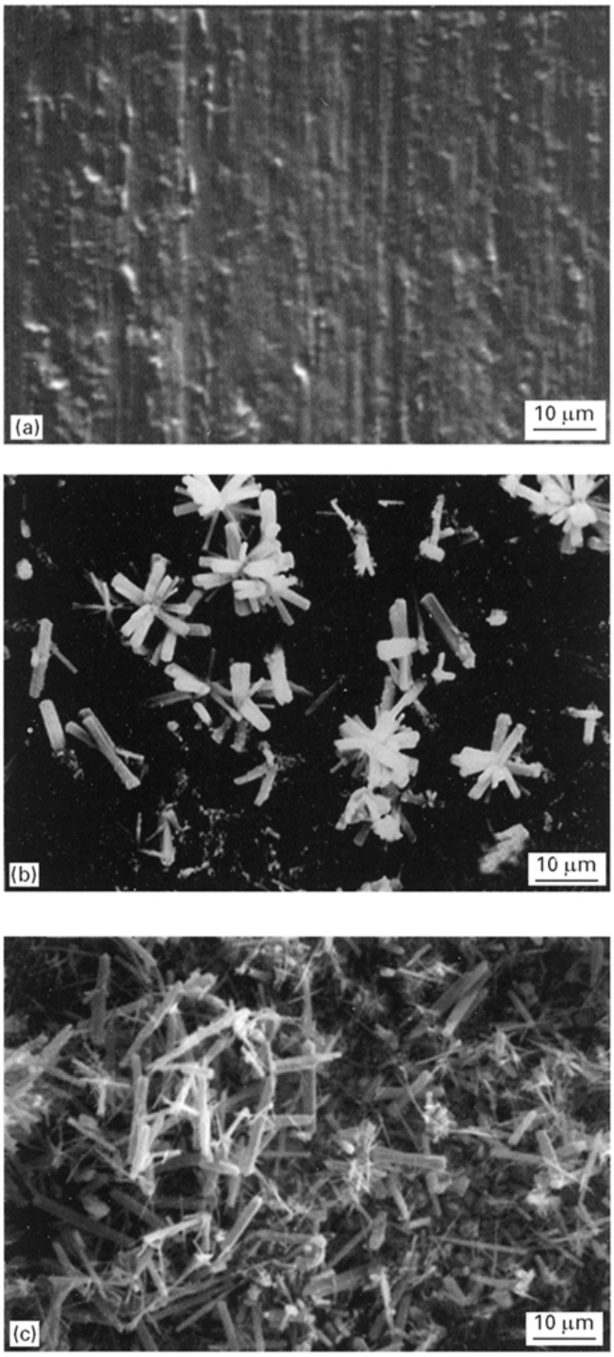

Figure 10 Scanning electron micrographs of the surfaces of the substrates treated in 0.01 M $Ca(EDTA)^{2-}$–0.01 M PO_4^{3-} mixed solutions at pH 9 and 250 °C for 6 h. (a) titanium plate, (b) $CaTiO_3/Ti$ plate treated in 0.01 M $[Ti(O_2)EDTA]^{2-}$–0.01 M $Ca(EDTA)^{2-}$ mixed solution at pH 13 and 250 °C for 6 h, (c) $CaTiO_3/Ti$ plate treated in 0.01 M $Ca(EDTA)^{2-}$ solution at pH 13 and 250 °C for 6 h.

3.4. Coating of hydroxyapatite on $CaTiO_3/Ti$ plates

Titanium plate, and $CaTiO_3/Ti$ plates (which $CaTiO_3$ coated on titanium plates by treating in 0.01 M $[Ti(O_2)EDTA)]^{2-}$–0.01 M $Ca(EDTA)^{2-}$ mixed solutions and 0.01 M $Ca(EDTA)^{2-}$ solution at pH 13 and 250 °C for 6 h) were treated in 0.01 M $Ca(EDTA)^{2-}$–0.01 M PO_4^{3-} mixed solutions at pH 9 and 250 °C for 2 h. As seen in Fig. 10, no precipitation was observed on the titanium plate, but a significant amount of hydroxyapatite precipitated on the surface of $CaTiO_3/Ti$ plates, although the morphology of hydroxyapatite precipitates was very different from each other, i.e. when $CaTiO_3/Ti$ plates formed in 0.01 M $[Ti(O_2)(EDTA)]^{2-}$–0.01 M $Ca(EDTA)^{2-}$ mixed solutions was used, rod-like hydroxyapatite, 5–10 μm long, precipitated as islands. On the other hand, rod-like and needle-like hydroxyapatite, 10–15 μm long, precipitated uniformly on the surface of $CaTiO_3/Ti$ plates formed in 0.01 M $Ca(EDTA)^{2-}$ solutions. These results suggested that the coating of hydroxyapatite on the substrates was promoted not by TiO_2 but $CaTiO_3$, indicating that $CaTiO_3$ acts as nuclei for the precipitation of hydroxyapatite.

4. Conclusions

1. The film, about 50 μm thick, consisting of mixtures of $CaTiO_3$ and TiO_2 was formed by the hydrothermal treatment of titanium substrate in 0.01 M $[Ti(O_2)EDTA]^{2-}$–0.01 M $Ca(EDTA)^{2-}$ mixed solution at pH 13 and 250 °C for 6 h. The film consisted of large icosahedral and hexagonal particles, of about 10 μm diameter, and small aggregated particles, about 1 μm long.
2. The film, about 20 μm thick, consisting of hexagonal plate-like $CaTiO_3$ particles, of about 1 μm diameter, was formed by the hydrothermal treatment of titanium substrate in 0.01 M $Ca(EDTA)^{2-}$ solution at pH 13 and 250 °C for 6 h.
3. $CaTiO_3$ formed on the surface of titanium promoted the formation of hydroxyapatite film on the substrate by the hydrothermal reactions in $Ca(EDTA)^{2-}$–PO_4^{3-} mixed solutions.

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