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# A simple method to prepare calcium phosphate coatings on Ti6Al4V

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A two-step chemical treatment followed by immersion in a supersaturated calcification solution (SCS) was found to be a simple way to prepare calcium phosphate (Ca–P) coatings on Ti6Al4V. The Ca–P deposition on the treated metallic surfaces could be accelerated by employing a pre-calcification (Pre-Ca) procedure prior to immersion in SCS. The two-step treatment was performed by etching the metallic plates with a mixture of HCl and $H_2SO_4$ followed by ageing in boiling diluted NaOH solution at 140 °C. Pre-Ca was carried out by incubating the two-step treated plates in $Na_2HPO_4$ solution and then in saturated $Ca(OH)_2$ solution. The formation of a bioactive microporous surface oxide layer on Ti6Al4V by the two-step treatment was most probably responsible for the induction of Ca–P precipitation. The deposition rates and compositions of Ca–P coatings in two different SCSs were investigated by means of scanning electron microscopy, X-ray diffraction and infrared spectrophotometry.

## 1. Introduction

A number of simple chemical treatments have been reported to be useful to improve titanium implant surfaces for their biological applications [1–5]. A noteworthy approach was the treatment of titanium implants with highly concentrated NaOH or $H_2O_2$ solution to produce bioactive titanium dioxide ($TiO_2$) hydrogel surface layers, which could induce the precipitation of calcium phosphate (Ca–P) from supersaturated calcification solution (SCS) [4–6].

*In vitro* low-temperature ($<100$ °C) SCS immersion can be an easy way to prepare Ca–P coatings on the titanium implants with bioactive surfaces. This method mimics the natural process of biological apatite formation and has or may have the following advantages over conventional techniques like plasma spraying: (1) a biomimetic Ca–P coating is expected to show a higher bone-bonding ability; (2) conformal coatings can be produced on complex-shaped and/or microporous implants; (3) no adverse effects of heat on substrates occur; (4) a potential drug delivery system can be made by co-precipitation of protein medicines; (5) it is simple and cost-effective approach.

Efforts are being made in our group to develop a simple and controllable chemical method to prepare Ca–P coatings on metallic implants. Recently, a two-step chemical treatment was developed; for instance, etching with acid followed by ageing in dilute alkali solution at 140 °C, has been found to be effective to prepare bioactive microporous commercially pure titanium (cpTi) surfaces allowing fast Ca–P deposition during immersion in an SCS [7]. Meanwhile, it was observed that a pre-calcification step prior to immersion, comprising incubations in $Na_2HPO_4$ solution and then in saturated $Ca(OH)_2$ solution, could dramatically speed up the Ca–P precipitation on the two-step treated titanium surfaces [8]. In the present work, the effectiveness of the two-step chemical treatment and/or Pre-Ca, together with SCS immersion for the preparation of Ca–P coatings on Ti6Al4V, are further investigated.

## 2. Materials and methods

### 2.1. Cleaning and chemical treatment

A total of 100 annealed Ti6Al4V blocks with size 10 mm × 10 mm × 1.5 mm were used as samples. All the samples were ultrasonically cleaned in 70% alcohol solution and distilled water. Ten of them were not treated for control experiments. The others were

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TABLE I List of ion concentrations (mM) of FCS and HBSS

| | $Na^+$ | $K^+$ | $Mg^{2+}$ | $Ca^{2+}$ | $Cl^-$ | $HPO_4^{2-}$ | $SO_4^{2-}$ | $HCO_3^{2-}$ |
|---|---|---|---|---|---|---|---|---|
| FCS | 137 | 4.64 | – | 3.10 | 145 | 1.86 | – | – |
| HBSS | 142 | 5.81 | 0.898 | 1.26 | 146 | 0.779 | 0.406 | 4.17 |

subjected to the two-step chemical treatment, i.e. etching with the mixture of 18% HCl and 48% $H_2SO_4$ for 1 h followed by ageing in 0.2 N NaOH boiling solution at 140 °C in a pressure canner for 5 h.

### 2.2. Pre-Ca and immersion experiments

The Pre-Ca procedure, including incubations in 0.5 N $Na_2HPO_4$ overnight and then in saturated $Ca(OH)_2$ solution for 5 h, was applied on half the treated and untreated samples. Three baths of distilled water were used to rinse the samples before and after $Ca(OH)_2$ incubation. The ion concentrations of two sorts of SCSs for *in vitro* immersion, i.e. fast calcification solution (FCS) and Hanks' balanced salt solution (HBSS), are listed in Table I. Each sample was immersed in 15 ml SCS in a sealed polystyrene vial in a water bath at 37 °C. The HBSSs were refreshed every 2 days. The two-step treated surface samples with Pre-Ca were taken out of the FCS solutions at immersion times of 1, 2, 4, 8 and 16 h successively, to investigate the detailed process of Ca–P deposition. All the samples after immersion were thoroughly rinsed with distilled water and then dried in an oven at 50 °C.

### 2.3. Characterization

Scanning electron microscopy (Philip SEM525, at 20 kV) with energy-dispersive X-ray analysis (Voyager system), X-ray diffraction (Philips at normal and thin-film measuring conditions) and infrared spectrophotometry (Perkin–Elmer 783) were employed for the characterization of all the sample surfaces before and after immersion. The Ca–P coatings deposited on the side faces of the samples were peeled off to check the approximate thickness of the coatings under SEM and to estimate the deposition rate of the Ca–P coating.

## 3. Results and discussion

### 3.1. Bioactive Ti6Al4V surface

The two-step chemical treatment was found to be effective for the preparation of the bioactive cpTi

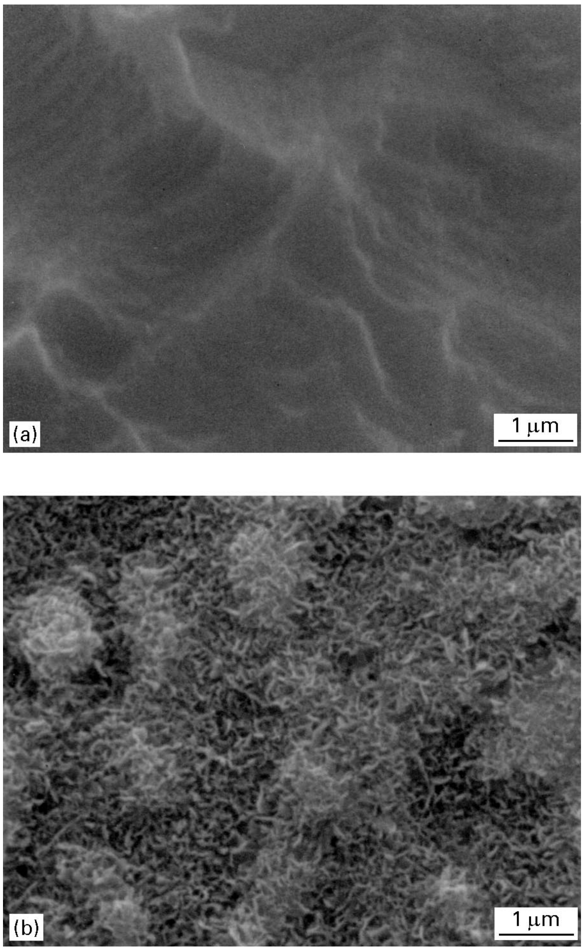

*Figure 1* Scanning electron micrographs of (a) untreated and (b) two-step treated Ti6Al4V surfaces.

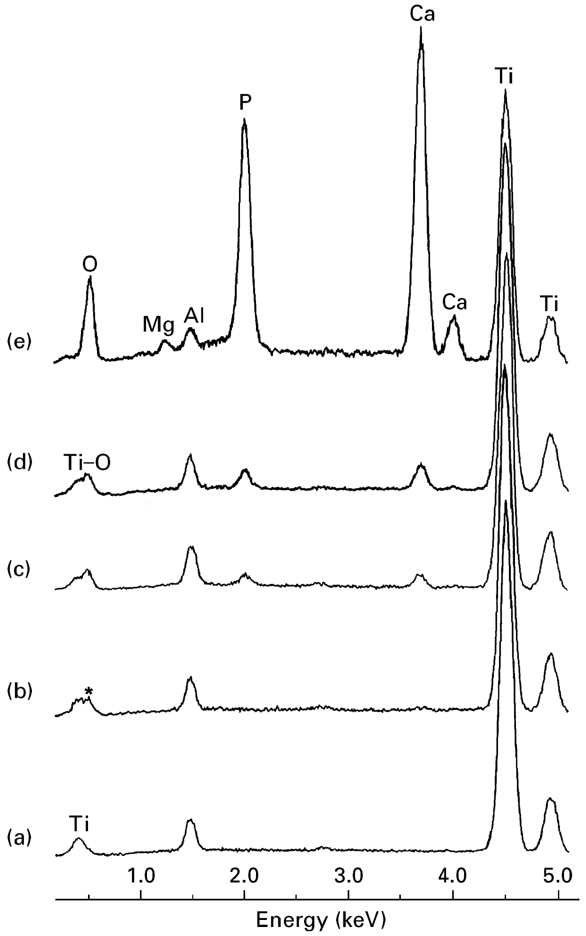

*Figure 2* The EDX spectra of the Ti6Al4V surfaces: (a) untreated; (b) two-step treated, (∗) oxygen shoulder; (c) 1 h immersion in FCS with Pre-Ca; (d) 2 weeks immersion in HBSS without Pre-Ca; and (e) 1 week immersion in HBSS with Pre-Ca.

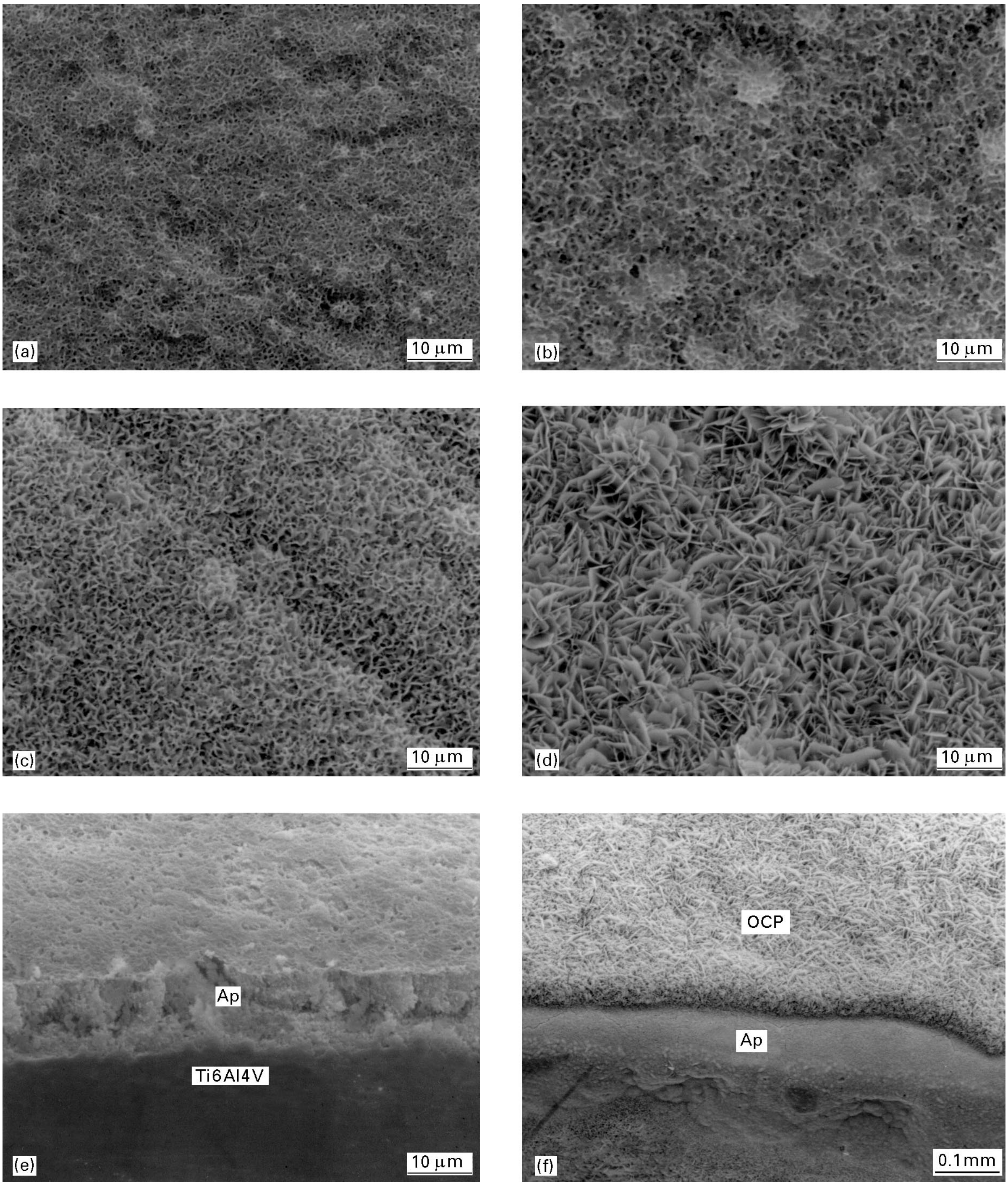

*Figure 3* Scanning electron micrographs of the Ca–P coatings formed on the two-step treated Ti6Al4V surfaces after immersion in FCS with Pre-Ca for (a) 1 h, (b) 2 h, (c) 4 h, (d) 8 h, (e) 2 h with the coatings on side faces peeled off, and (f) without Pre-Ca for 3 days. Ap, apatite; OCP, octacalcium phosphate. The photos in (e) and (f) were taken with the electron beam at a 30° angle to the sample surface.

surface which could induce Ca–P precipitation from SCS [7]. In this work, its effectiveness to Ti6Al4V was further verified. It was observed that Ca–P was deposited on all the two-step treated samples, with or without Pre-Ca, after immersion in both FCS and HBSS. Pre-Ca dramatically accelerated the Ca–P precipitation on the two-step treated samples. No precipitation was seen on any untreated samples up to day 14 of immersion in FCS or HBSS, even with Pre-Ca.

The bioactivity of Ti6Al4V most likely arose from the significant modification of surface morphology and composition by the two-step treatment. Fig. 1 shows that the originally dense Ti6Al4V surfaces became completely porous at a submicrometre scale. A relatively thick titanium oxide (usually in $TiO_2$ form [9]) layer was formed on the treated sample as indicated by EDX analyses, because the oxygen shoulder is clearly seen in the spectrum of the two-step treated surfaces and absent in that of the untreated surfaces.

It is generally accepted that a $TiO_2$ surface is always negatively charged in an aqueous environment due to amphoteric $OH^-$ groups and this could be advantageous to the induction of Ca–P precipitation from SCS [6]. It is interesting to note that such a negatively charged microporous structure just meets the requirement for an ideal bioactive biomaterial surface suggested by de Groot [10]. Both the adsorption of $HPO_4^{2-}$

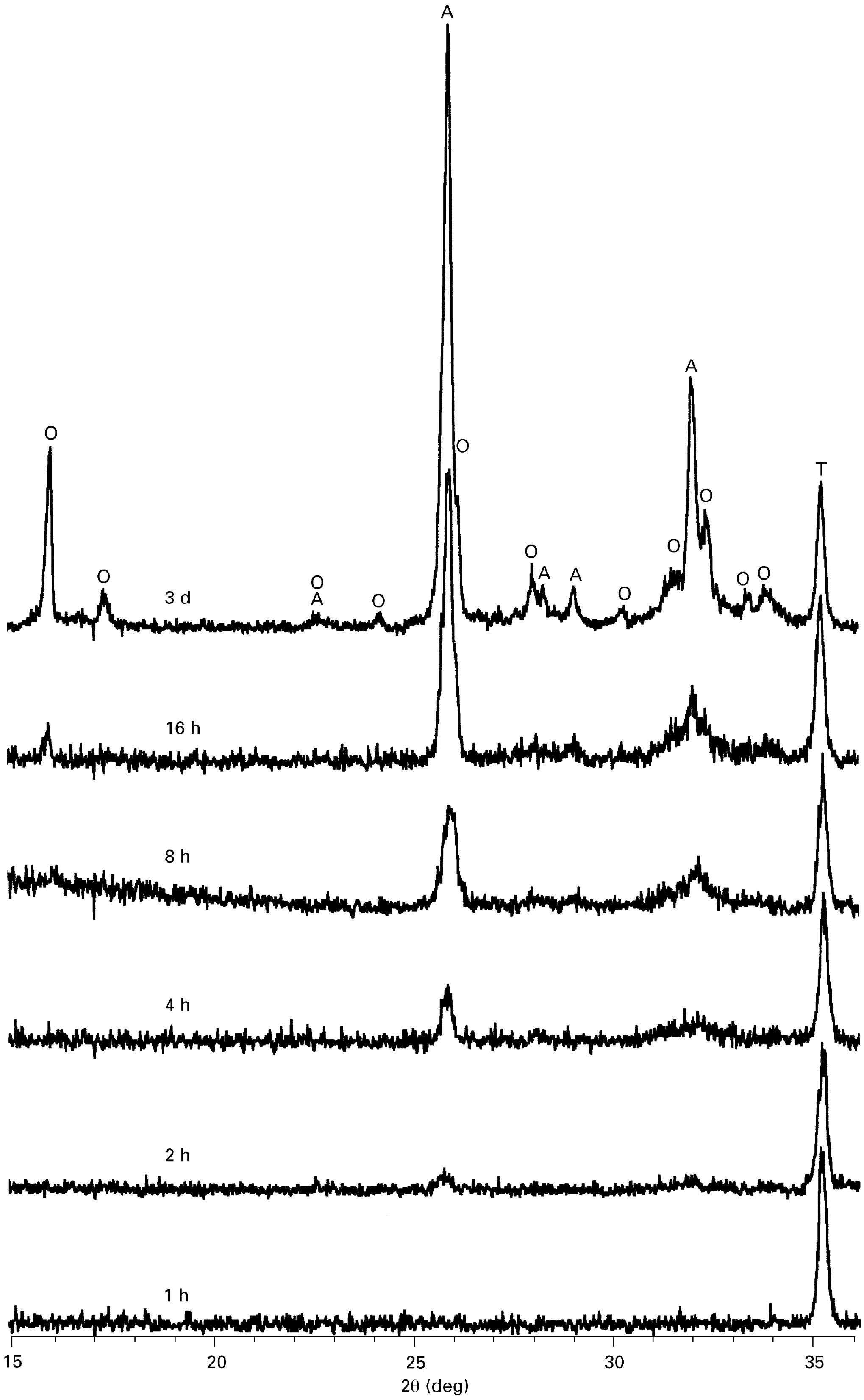

*Figure 4* The XRD patterns of the Ca–P coatings formed on the two-step treated Ti6Al4V surfaces after immersion in FCS with Pre-Ca for 1, 2, 4, 8, 16 h and without Pre-Ca for 3 days. Ap, apatite; O, OCP; T, Ti6Al4V.

ions and $Ca(OH)_2$ on $TiO_2$ surfaces has been reported in previous work [11]. The Pre-Ca procedure may have promoted Ca–P nucleation and growth from the SCSs by sufficient adsorption of $Ca^{2+}$ and/or $HPO_4^{2-}$ ions on the microporous Ti6Al4V surfaces.

### 3.2. Ca–P coatings from FCS

The Ca–P coatings were rapidly deposited on the two-step treated samples during immersion in FCS. The deposition rates of Ca–P coating without Pre-Ca and with Pre-Ca was estimated by SEM observation

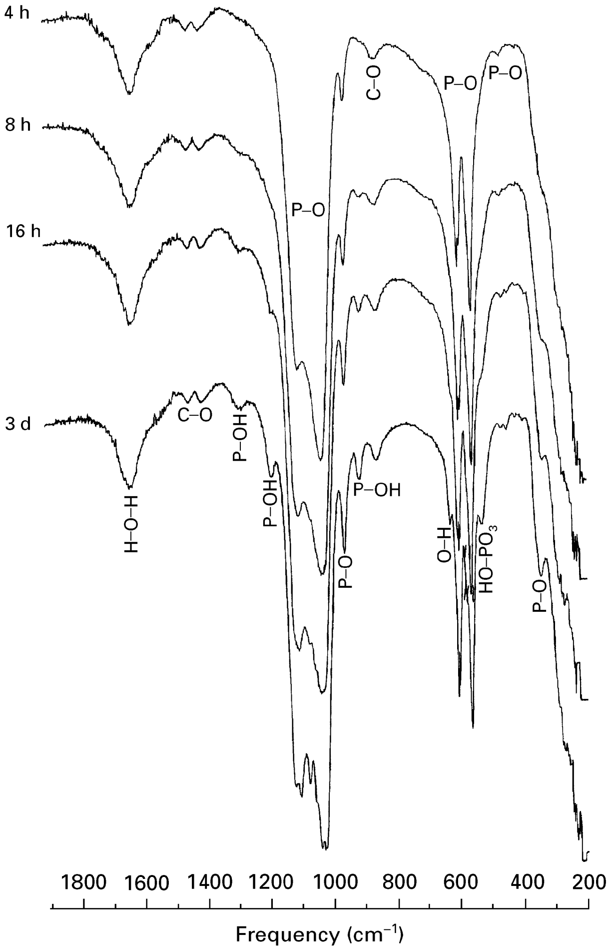

*Figure 5* The infrared spectra of the Ca–P coatings deposited on the two-step treated Ti6Al4V surfaces after immersion in FCS with Pre-Ca for 4, 8, 16 h and without Pre-Ca for 3 days.

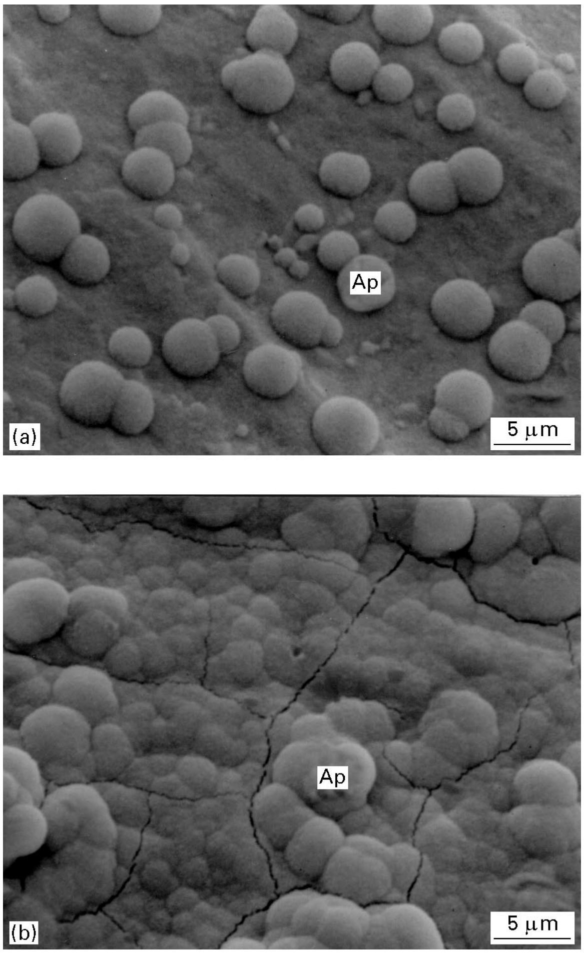

*Figure 6* The scanning electron micrographs of the apatite (Ap) deposited on two-step treated Ti6Al4V surfaces after immersion in HBSS (a) without Pre-Ca for 2 weeks and (b) with Pre-Ca for 1 week.

to be 0.5 and 2 $\mu m\,h^{-1}$, respectively. The Ca–P deposition on samples with Pre-Ca was already detectable by EDX (Fig. 2) after 1 h immersion in FCS.

Morphological features of the Ca–P coatings deposited from FCS are shown in Fig. 3. On the samples with Pre-Ca, a dense Ca–P layer, containing some tiny holes, was formed within 4 h and then small crystal plates were formed, the sizes of the crystal plates becoming larger with increasing immersion time. The thickness of the coating formed at 2 h was seen to be more than 4 μm. The Ca–P coating deposited on the samples without Pre-Ca at day 3 was observed to be composed of two different layers, i.e. a dense bottom layer and a well-crystallized top layer.

Crystallographic features of the Ca–P coatings deposited from FCS are demonstrated by their XRD patterns (Fig. 4). For the samples with Pre-Ca, the Ca–P precipitate was mainly bone-like apatite phase during the first 8 h immersion, octacalcium phosphate (OCP) phase being formed at longer immersion times. The Ca–P deposited on the samples without Pre-Ca at day 3 is a mixture of apatite and OCP. Further information on Ca–P composition can be obtained from the infrared spectra of the coatings (Fig. 5). The 4 h spectrum is basically consistent with that of carbonated apatite reported in previous research [12]. After 4 h, the contents of OCP in the coatings seemed to increase gradually as indicated by the intensity of several P–OH absorption bands which should be from the $HPO_4$ groups of OCP. The absorption bands of the $HPO_4$ group and O–H are clearly seen in the spectrum of the Ca–P deposited on the samples without Pre-Ca after 3 days immersion in FCS.

It is inferred from the results mentioned that the Ca–P coating deposited from FCS is composed of a dense bone-like apatite bottom-layer and a well crystallized top-layer mainly consisting of OCP crystal plates.

### 3.3. Ca–P coatings from HBSS

The two-step treated Ti6Al4V surface was bioactive enough to induce Ca–P deposition but insufficient to induce a uniform layer covering the entire sample surface after 2 wk immersion in HBSS. Pre-Ca significantly promoted the formation of uniform Ca–P coatings on the samples (Fig. 6). The deposition rate of Ca–P from HBSS after Pre-Ca was estimated to be 2 $\mu m\,wk^{-1}$ under SEM.

The thin-film XRD measurement indicated that the Ca–P deposited from HBSS is also apatite (Fig. 7). But two differences are noted between the apatite deposited from HBSS and from FCS: (1) more diffraction peaks of apatite were detected in the HBSS coating than in the FCS coatings deposited at early immersion stage; (2) obviously a magnesium impurity is present in the HBSS coatings as indicated by EDX analyses (Fig. 2).

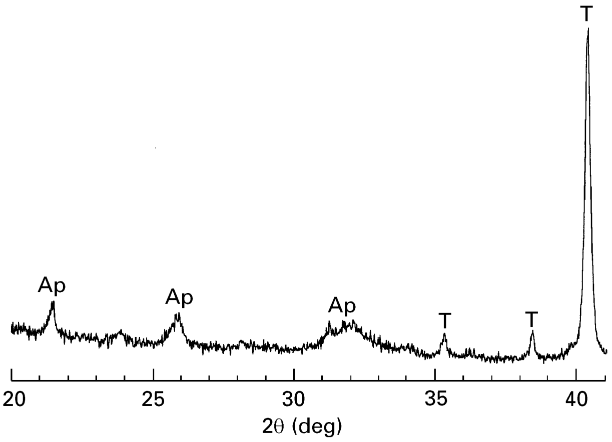

*Figure 7* The thin-film XRD patterns of the Ca–P coating deposited on the two-step treated Ti6Al4V surfaces after immersion in HBSS with Pre-Ca for 1 week. Ap, apatite; T, Ti6Al4V.

## 4. Conclusion

The two-step treatment followed by SCS immersion is a simple and effective method to prepare Ca–P coatings on Ti6Al4V. Pre-Ca can accelerate the coating deposition. The Ca–P deposition rate and composition can be easily controlled by adjusting the components of the SCS employed for immersion.

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