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Hydroxyapatite Formation on CaTiO₃ Film Prepared by Metal-Organic Chemical Vapor Deposition

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Calcium titanate (CaTiO₃) films were prepared on commercially pure titanium (CP-Ti) by metal-organic chemical vapor deposition using Ca(dpm)₂ and Ti(O-i-Pr)₂(dpm)₂ precursors. The formation of hydroxyapatite (HAp, Ca₁₀(PO₄)₆(OH)₂) on CaTiO₃ film was investigated in a Hanks' solution. The formation rate of HAp was significantly affected by deposition conditions of CaTiO₃ films, particularly substrate temperature (T_{sub}). The time for the HAp formation was 3.6 Ms (42 d) on the CaTiO₃ film prepared at $T_{\text{sub}} = 873$ K, whereas that was 1.2 (14 d) and 0.3 Ms (3 d) on that prepared at $T_{\text{sub}} = 973$ and 1073 K, respectively. Octacalcium phosphate (OCP, Ca₈H₂(PO₄)₆·5H₂O) was identified on the CaTiO₃ film prepared at $T_{\text{sub}} = 1073$ K by the immersion for 21.6 ks. [doi:10.2320/matertrans.MRA2007016]

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1. Introduction

Ti and Ti alloy have been widely used as artificial bone and tooth due to its excellent mechanical property, corrosion resistance and biocompatibility.¹⁾ The reconstruction of bone on Ti substrates can be promoted by ceramic coatings, e.g. hydroxyapatite (HAp, Ca₁₀(PO₄)₆(OH)₂), tricalcium phosphate (TCP, Ca₃(PO₄)₂) and calcium titanate (CaTiO₃). So far, many kinds of processing, e.g. sputtering,²⁾ sol-gel³⁾ have been attempted to prepare these coatings. Among them metal-organic chemical vapor deposition (MOCVD) has advantages of high deposition rate and excellent microstructure controllability. We have first prepared CaTiO₃ film by MOCVD,⁴⁾ and reported that the microstructure of CaTiO₃ film changed depending on deposition conditions, particularly substrate temperature (T_{sub}). The deposition rate (R_{dep}) of CaTiO₃ films by MOCVD increased with increasing T_{sub} , showing the highest R_{dep} of 45 $\mu\text{m h}^{-1}$ at 1073 K.

The biocompatibility of CaTiO₃ film can be evaluated by immersion in several kinds of pseudo body fluid. Asami *et al.* have prepared CaTiO₃ film by sputtering, and immersed in a simulated body fluid (SBF) and a Hanks' solution to investigate the elution of CaTiO₃ film and HAp formation on CaTiO₃ film. Several percent of CaTiO₃ was dissolved into the solution and calcium phosphates having similar Ca/P ratio to HAp were formed.⁵⁻⁷⁾ Yamashita *et al.* have prepared CaTiO₃ sintered body and immersed in a 1.5 times concentrated SBF after polarizing CaTiO₃ in a DC field of 1 to 1000 V.⁸⁾ Ca²⁺ ions were mainly adsorbed to negatively charged surface (N-surface) and became a supersaturation state. The phosphate ions were attracted by the supersaturated cations and the HAp was formed faster than that without DC field. Ohba *et al.* prepared HAp/CaTiO₃ multi-layer film by a hydrothermal method and reported that the HAp formation was accelerated on the HAp/CaTiO₃ film.⁹⁾ Manso *et al.* prepared CaTiO₃ film in 4 μm thicknesses by sol-gel spin-coating process and confirmed that morphological and structural suitability of CaTiO₃ coatings for their use as buffer layers between a TiAlV alloy and a HAp is strongly

reinforced by the behavior of the CaTiO₃ surface in pseudo body fluid.¹⁰⁾ However, no studies on the HAp formation on CVD CaTiO₃ films were reported.

In this study, CaTiO₃ films were prepared by MOCVD and the HAp formation on CVD CaTiO₃ films was investigated by immersion in a Hanks' solution.

2. Experimental Procedure

CaTiO₃ films were prepared by a vertical cold-wall type CVD apparatus. Source precursors of Ca(dpm)₂ (bis-dipivaloyl-methanato-calcium) and Ti(O-i-Pr)₂(dpm)₂ (bis-dipivaloyl-methanato diisopropoxy titanium) powders were heated at 523 to 573 and 393 to 453 K to obtain objective molar ratio of Ca(dpm)₂ to Ti(O-i-Pr)₂(dpm)₂ ($R_{\text{Ca/Ti}}$), respectively. This $R_{\text{Ca/Ti}}$ was calculated by measuring the weight loss of each precursor after the deposition. The source vapors were carried into the CVD reactor with Ar gas. O₂ gas was separately introduced by using a double tube nozzle, and mixed with the precursor vapors in a mixing chamber placed above a substrate holder. The total gas flow rate ($FR_{\text{tot}} = FR_{\text{Ar}} + FR_{\text{O}_2} + FR_{\text{source vapor}}$) was fixed at $3.33 \times 10^{-6} \text{ m}^3 \text{ s}^{-1}$. The total pressure (P_{tot}) in the CVD reactor was fixed at 0.8 kPa. The substrate temperature (T_{sub}) was

Table 1 Deposition conditions of Ca-Ti-O film.

Precursor Temperature, T_{prec}	
Ca(dpm) ₂	: 323~573 K
Ti(O-i-Pr) ₂ (dpm) ₂	: 193~453 K
Total gas flow rate, FR_{tot}	: $3.33 \times 10^{-6} \text{ m}^3 \text{ s}^{-1}$
Carrier Gas	
	: Ar
Ca(dpm) ₂	: $0.83 \times 10^{-6} \text{ m}^3 \text{ s}^{-1}$
Ti(O-i-Pr) ₂ (dpm) ₂	: $0.83 \times 10^{-6} \text{ m}^3 \text{ s}^{-1}$
O ₂ gas flow rate, FR_{O_2}	: $1.2 \times 10^{-6} \text{ m}^3 \text{ s}^{-1}$
Total pressure, P_{tot}	: 0.8 kPa
Deposition temperature, T_{dep}	: 873~1073 K
Deposition time	: 0.3~0.9 ks
Substrate	: CP-Ti

Table 2 Chemical composition of Hanks' solution.

Concentration (mg/m ³)							
NaCl	KCl	Na ₂ HPO ₄	KH ₂ PO ₄	MgSO ₄	MgCl ₂	CaCl ₂	Glucose
8.00	0.40	4.79×10^{-2}	6.00×10^{-2}	4.88×10^{-2}	4.68×10^{-2}	0.14	1.00

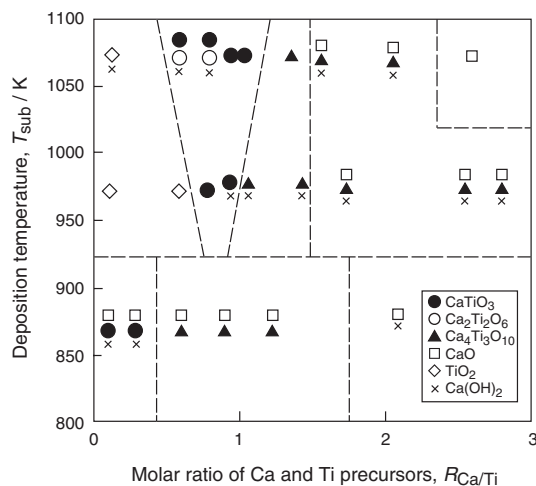


Fig. 1 CVD phase formation diagram of Ca-Ti-O film as functions of T_{sub} and $R_{\text{Ca/Ti}}$ phase at $P_{\text{O}_2} = 0.32$ kPa and $P_{\text{tot}} = 0.8$ kPa.

changed in the range between 873 and 1073 K. The deposition conditions are summarized in Table 1. Sand-blasted commercially pure titanium (CP-Ti) of $10 \times 10 \times 0.5$ mm was used as substrate. A Hanks' solution was used as a pseudo body fluid and kept at 310 K in an incubator. The composition of the Hanks' solution was listed in Table 2. CaTiO₃ coated CP-Ti was immersed in the Hanks' solution for 21.6 ks (6 h) to 3.6 Ms (42 d). Crystal phases of the immersed samples were identified by XRD and microstructure was observed by SEM.

3. Results and Discussion

3.1 Preparation of CaTiO₃ coatings

Figure 1 shows the CVD phase formation diagram of Ca-Ti-O film as functions of T_{sub} and $R_{\text{Ca/Ti}}$. The broken lines denote the boundary between the formation area of different crystal phases. CaO-rich films were obtained in a low T_{sub} region, and TiO₂-rich films were obtained in a high T_{sub} region. CaTiO₃ film in a single phase was obtained at $T_{\text{sub}} = 1073$ K, $R_{\text{Ca/Ti}} \approx 1$ and $T_{\text{sub}} = 973$ K, $R_{\text{Ca/Ti}} \approx 0.7$. CaTiO₃ film in a single phase was not obtained at $T_{\text{sub}} = 873$ K, and CaO was always co-deposited with CaTiO₃ or Ca₄Ti₃O₁₀. Ca(OH)₂ phase obtained in wide-ranged conditions may be formed by the reaction of CaO and moisture in air after the deposition, and the amount of Ca(OH)₂ phase was quite few.

Figure 2 shows the surface morphology of CaTiO₃ films prepared at $T_{\text{sub}} = 873$ to 1073 K. The CaTiO₃ and CaO mixed film prepared at $T_{\text{sub}} = 873$ K and $R_{\text{Ca/Ti}} = 0.4$ had a smooth granular surface with a grain size of 3 to 4 μm in diameter (Fig. 2(a)). The CaTiO₃ film in a single phase prepared at $T_{\text{sub}} = 973$ K and $R_{\text{Ca/Ti}} = 0.65$ had a relatively

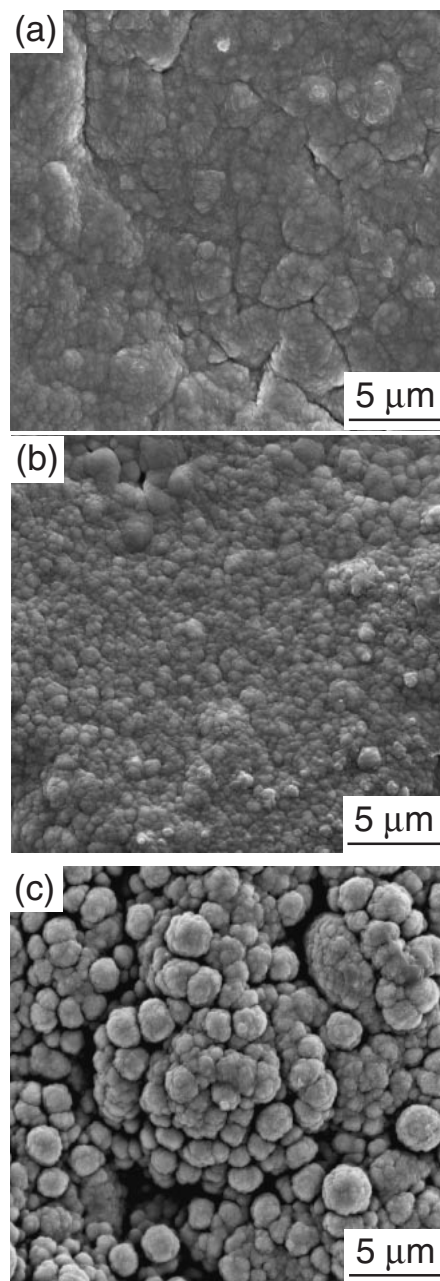


Fig. 2 Surface morphology of Ca-Ti-O film prepared at $T_{\text{sub}} = 873$ K and $R_{\text{Ca/Ti}} = 0.4$ (a), $T_{\text{sub}} = 973$ K and $R_{\text{Ca/Ti}} = 0.65$ (b) and $T_{\text{sub}} = 1073$ K and $R_{\text{Ca/Ti}} = 1.08$ (c).

smooth granular surface with a small grain size of 1 μm in diameter (Fig. 2(b)). The surface of CaTiO₃ film prepared at $T_{\text{sub}} = 1073$ K and $R_{\text{Ca/Ti}} = 1.08$ showed a cauliflower-like aggregate texture of 2 to 3 μm in diameter which consisted of fine grains of 50 nm in diameter (Fig. 2(c)).

3.2 HAp formation in a Hanks' solution

Figure 3 shows the XRD patterns of the mixture film of

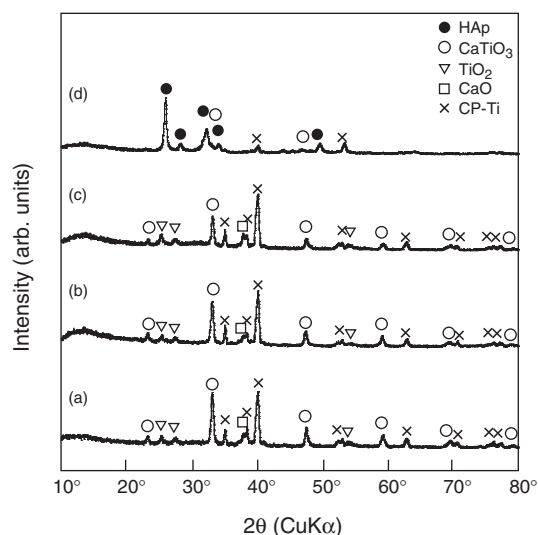


Fig. 3 XRD patterns of CaTiO₃ coated CP-Ti prepared at $T_{\text{sub}} = 873$ K after immersion in Hanks' solution. (a) 0.6, (b) 1.2, (c) 2.4 and (d) 3.6 Ms.

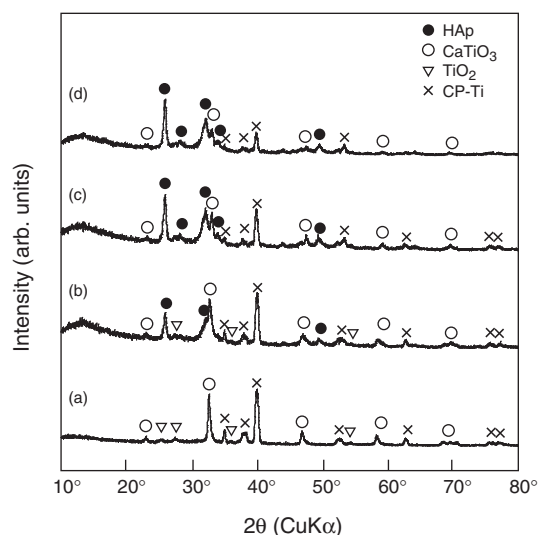


Fig. 5 XRD patterns of CaTiO₃ coated CP-Ti prepared at $T_{\text{sub}} = 973$ K after immersion in Hanks' solution. (a) 0.6, (b) 1.2, (c) 2.4 and (d) 3.6 Ms.

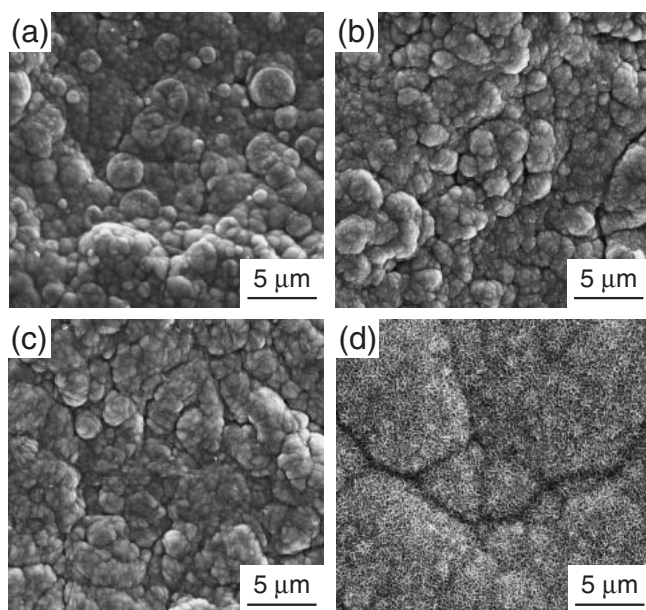


Fig. 4 Surface morphology of CaTiO₃ coated CP-Ti prepared at $T_{\text{sub}} = 873$ K after immersion in Hanks' solution. (a) 0.6, (b) 1.2, (c) 2.4 and (d) 3.6 Ms.

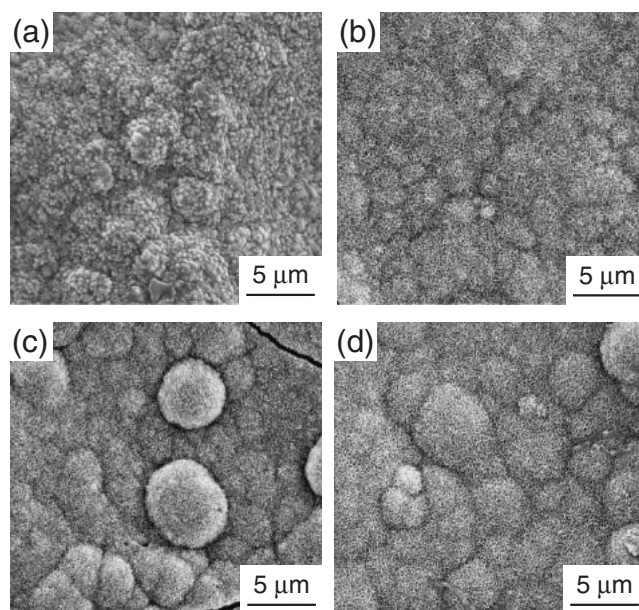


Fig. 6 Surface morphology of CaTiO₃ coated CP-Ti prepared at $T_{\text{sub}} = 973$ K after immersion in Hanks' solution. (a) 0.6, (b) 1.2, (c) 2.4 and (d) 3.6 Ms.

CaTiO₃ and CaO coated on CP-Ti substrate at $T_{\text{sub}} = 873$ K and $R_{\text{Ca/Ti}} = 0.4$ after the immersion in the Hanks' solution for 0.6 (7 d) to 3.6 Ms (42 d). No change was observed after 2.4 Ms (28 d) (Figs. 3(a) to (c)). HAp with a significant orientation of (002) was identified after 3.6 Ms (Fig. 3(d)). Asami *et al.* prepared CaTiO₃ films by sputtering and reported that (002) oriented HAp precipitated on the CaTiO₃ film. The (002) orientation of HAp can be common due to a low surface energy basal plane of hexagonal structure.

Figure 4 shows the surface morphology of the mixture film of CaTiO₃ and CaO coated on CP-Ti at $T_{\text{sub}} = 873$ K and $R_{\text{Ca/Ti}} = 0.4$ after the immersion in the Hanks' solution for 0.6 to 3.6 Ms. No change of surface morphology was observed until 2.4 Ms (Figs. 4(a) to (c)), and then a significant change of the surface was identified by the HAp

formation after 3.6 Ms (Fig. 4(d)). The HAp on the CaTiO₃ film had a cancellous texture.

Figure 5 shows the XRD patterns of the CaTiO₃ film in a single phase coated on CP-Ti at $T_{\text{sub}} = 973$ K and $R_{\text{Ca/Ti}} = 0.65$ after the immersion in the Hanks' solution for 0.6 to 3.6 Ms. HAp was identified after 1.2 Ms (14 d) (Fig. 5(b)). The XRD peaks of HAp became more significant and the peak of (002) increased with increasing the immersion time.

Figure 6 shows the surface morphology of the CaTiO₃ film in a single phase coated on CP-Ti at $T_{\text{sub}} = 973$ K and $R_{\text{Ca/Ti}} = 0.65$ after the immersion in the Hanks' solution for 0.6 to 3.6 Ms. No HAp was observed after 0.6 ks immersion (Fig. 6(a)), however, the surface of the CaTiO₃ film was wholly covered by the cancellous HAp after 1.2 Ms (Fig. 6(b)). The characteristic cancellous texture of HAp

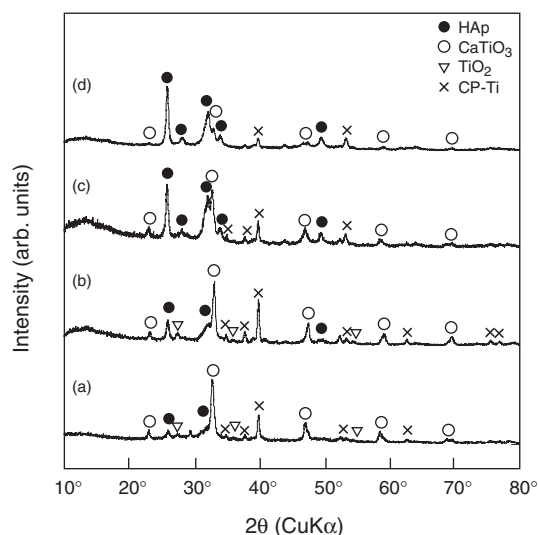


Fig. 7 XRD patterns of CaTiO_3 coated CP-Ti prepared at $T_{\text{sub}} = 1073$ K after immersion in Hanks' solution. (a) 0.6, (b) 1.2, (c) 2.4 and (d) 3.6 Ms.

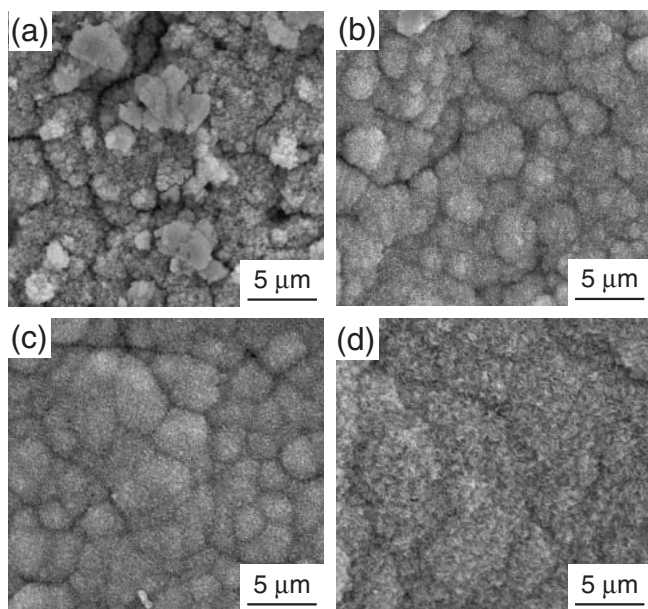


Fig. 8 Surface morphology of CaTiO_3 coated CP-Ti prepared at $T_{\text{sub}} = 1073$ K after immersion in Hanks' solution. (a) 0.6, (b) 1.2, (c) 2.4 and (d) 3.6 Ms.

became more significant with increasing the immersion time.

Figure 7 shows the XRD patterns of the CaTiO_3 film in a single phase coated on CP-Ti at $T_{\text{sub}} = 1073$ K and $R_{\text{Ca}/\text{Ti}} = 1.08$ after the immersion in the Hanks' solution for 0.6 to 3.6 Ms. The HAp formation was detected shortly after the immersion for 0.6 ks, and the (002) orientation of HAp became more significant with increasing the immersion time.

Figure 8 shows the surface morphology of the CaTiO_3 film in a single phase coated on CP-Ti at $T_{\text{sub}} = 1073$ K and $R_{\text{Ca}/\text{Ti}} = 1.08$ after the immersion in the Hanks' solution for 0.6 to 3.6 Ms. The surface of the CaTiO_3 coating was already covered with HAp after 0.6 Ms (Fig. 8(a)). The HAp formation having the cancellous texture was more significant than that prepared at $T_{\text{sub}} = 973$ K even after 0.6 Ms

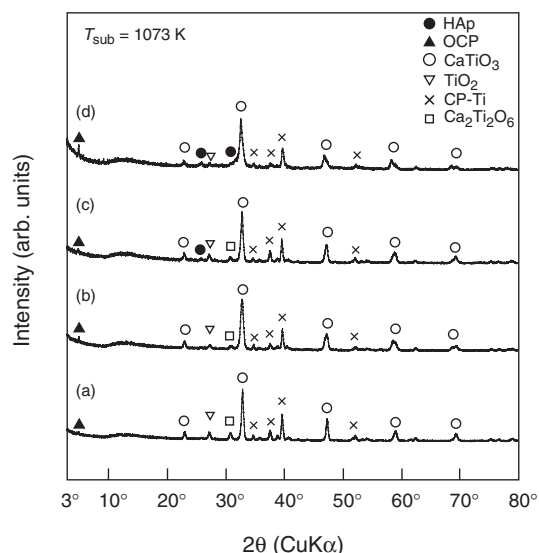


Fig. 9 XRD patterns of CaTiO_3 coated CP-Ti prepared at $T_{\text{sub}} = 1073$ K after immersion in Hanks' solution. (a) 0.02, (b) 0.08, (c) 0.3 and (d) 0.4 Ms.

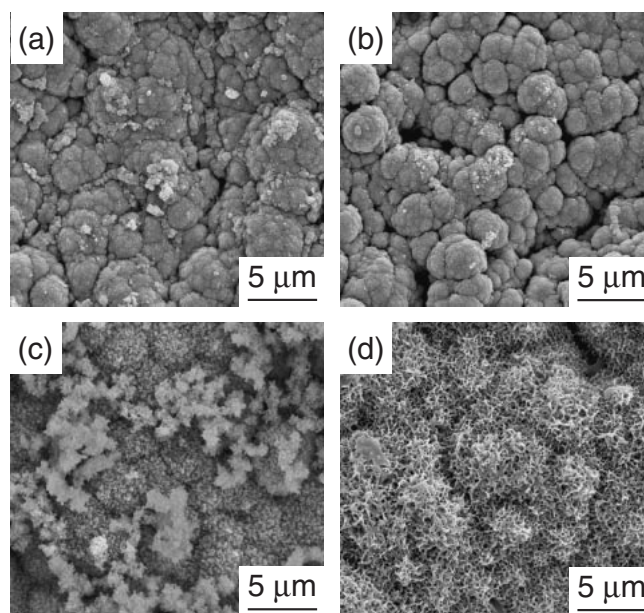


Fig. 10 Surface morphology of CaTiO_3 coated CP-Ti prepared at $T_{\text{sub}} = 1073$ K after immersion in Hanks' solution. (a) 0.02, (b) 0.08, (c) 0.3 and (d) 0.4 Ms.

(Figs. 8(b) to (d)).

The HAp formation has been proceeded significantly on the CaTiO_3 coating prepared at $T_{\text{sub}} = 1073$ K and $R_{\text{Ca}/\text{Ti}} = 1.08$ even after 0.6 ks. Figure 9 shows the XRD patterns of the HAp formation after the immersion within 0.6 Ms. The HAp formation was detected by XRD after 0.3 Ms (3 d) immersion. It is known that octacalcium phosphate (OCP, $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$)^{11,12} would be formed prior to the HAp. In this study, the OCP was detected even after 21.6 ks (6 h).

Figure 10 shows the surface morphology of the CaTiO_3 coating prepared at $T_{\text{sub}} = 1073$ K and $R_{\text{Ca}/\text{Ti}} = 1.01$ after the immersion within 0.6 Ms. Some granular precipitates were observed after immersion for 21.6 and 86.4 ks (Fig. 10(a),

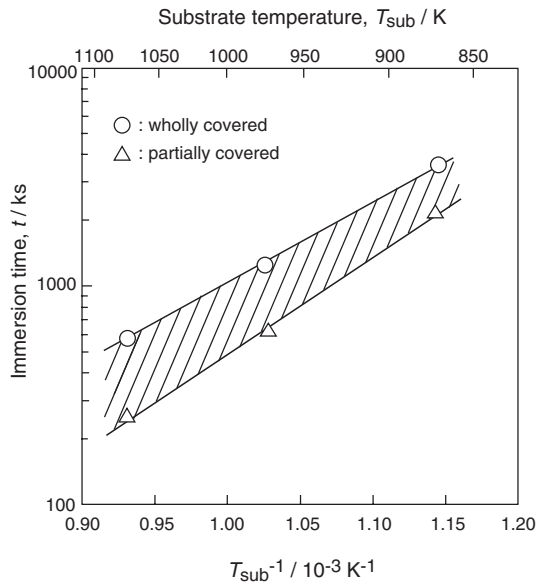


Fig. 11 Relationship between the T_{sub} of CaTiO₃ coatings and the needed immersion time for HAp formation.

(b)). They could be the particles of OCP. The characteristic cancellous texture of HAp can be seen after the immersion for 0.3 Ms, and the surface of the CaTiO₃ coating was entirely covered with HAp.

Since the HAp formation on pure Ti usually need 2.4 to 3.6 Ms,^{13,14} the CaTiO₃ film prepared at $T_{\text{sub}} = 1073$ K has an excellent capability of HAp and OCP formation. It can be understood that the T_{sub} has significant effect on the HAp formation on the CaTiO₃ coatings and the fine grains of submicron meter and the complicated surface may prompt the formation of HAp in pseudo body fluid.

Figure 11 shows the relationship between T_{sub} and time for the HAp formation in an Arrhenius format. Almost a linear relationship between $\log t$ and T_{sub}^{-1} can be observed; the higher T_{sub} , the shorter HAp formation time.

Figure 12 shows the SEM images of HAp formation formed on the CaTiO₃ film prepared at $T_{\text{sub}} = 1073$ K and $R_{\text{Ca/Ti}} = 1.01$ after the immersion for 0.3 Ms. The precipitated HAp had an acicular structure of several 100 nm in length and 50 nm in width. There can be seen two kinds of distinct HAp formation behavior as shown in Figs. 12(a) and (b), *i.e.*, an uniform HAp formation on the CaTiO₃ grains (Fig. 12(a)) and a local HAp formation at the CaTiO₃ grain

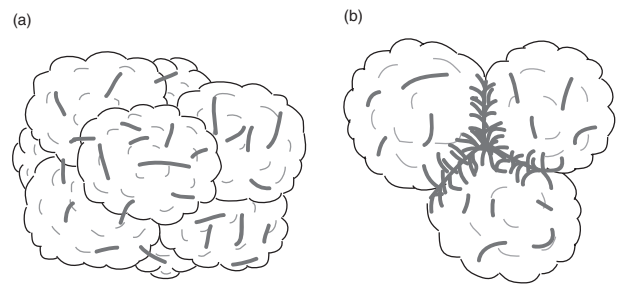


Fig. 13 Schematic diagram of HAp nucleation on CaTiO₃ film.

boundary (Fig. 12(b)). Figure 13 depicts the schematic diagram of the HAp nucleation on CaTiO₃ film. The morphology of CaTiO₃ film changed from smooth ($T_{\text{sub}} = 873$ K) to granular ($T_{\text{sub}} = 973$ K) to cauliflower texture ($T_{\text{sub}} = 1073$ K), becoming more complicated with increasing T_{sub} . Since the composition, lattice parameter and preferred orientation of CaTiO₃ films are almost the same among the CaTiO₃ films, only difference might be morphology; the more complicated, the faster HAp formation. Weng *et al.* proposed the HAp formation mechanism on CaTiO₃ film in a Hanks' solution¹⁵) as follows. CaTiO₃ film would first elute into the solution and the Ca²⁺ ions concentration might increase locally, where PO₄³⁻ ions could be attracted and reacted with Ca²⁺ ions, forming HAp. The CaTiO₃ film prepared at $T_{\text{sub}} = 1073$ K had a complicated and bumpy texture consisting of aggregated fine grains. The interface of aggregated fine grains may be preferred nucleation sites as kink or step site in common crystal growth.

Comparing to other methods such as sputtering, laser ablation, hydrothermal and sol-gel, CaTiO₃ film prepared by MOCVD had a more complicated surface morphology, causing a superior formation ability of HAp.

4. Conclusion

CaTiO₃ films were prepared on CP-Ti substrate by MOCVD using Ca(dpm)₂ and Ti(O-i-Pr)₂(dpm)₂ precursors. In a Hanks' solution, HAp formed after 3.6 Ms on the CaTiO₃ film prepared at $T_{\text{sub}} = 873$ K, 1.2 Ms for that prepared at 973 K and 0.3 Ms for that prepared at 1073 K. OCP formation was identified on the CaTiO₃ film prepared at $T_{\text{sub}} = 1073$ K after 21.6 ks of the immersion. Precipitated HAp had a cancellous texture and a significant (002) orientation. The

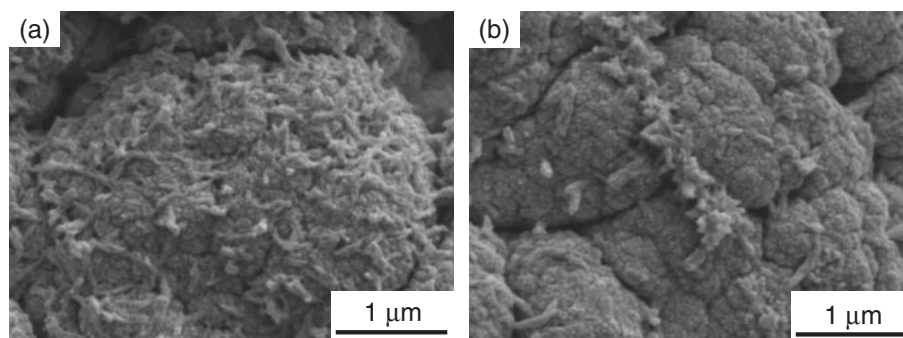


Fig. 12 SEM image of HAp nucleation on CaTiO₃ coated CP-Ti prepared at $T_{\text{sub}} = 1073$ K after immersion in Hanks' solution for 0.3 Ms.

nucleation and growth of HAp may be mainly associated with the surface morphology of CaTiO₃ film.

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