Apatite formation behavior on bio-ceramic films prepared by MOCVD

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Calcium titanate (CaTiO3), α-tricalcium phosphate (α-TCP) and hydroxyapatite (HAp) films were prepared by metal-organic chemical vapor deposition (MOCVD) using Ca(dpm)2, Ti(O-i-Pr)2(dpdm)2 and (C2H5)2PO precursors. The phases, composition and surface morphology of these films changed depending on substrate temperature (Tsub), total pressure (Ptot) and molar ratio of each precursors (Rca/Ti, Rca/P). The surface morphology of CaTiO3 films changed from granular structure to cauliflower-like texture, and its cross-sectional morphology changed from dense to columnar structure with increasing Tsub. α-TCP and HAp films had granular surface and dense-cross-sectional morphology. CaTiO3, α-TCP and HAp films were immersed in a Hanks’ solution for 28 d. Apatite formation rate strongly depended on the surface morphology of CaTiO3 film, and apatite covered CaTiO3 film having a granular surface after 4 w while CaTiO3 film having a cauliflower-like texture after 3 d. Apatite covered α-TCP films after 14 d and HAp films after 6 h, respectively. HAp films prepared by MOCVD were promising as bone conductive materials.

Key-words: Metal organic chemical vapor deposition, Bio-ceramics, Calcium titanate, Calcium phosphate, Apatite

1. Introduction

Titanium (Ti) and its alloys have been widely applied as artificial dental implant and hip joint due to their good biocompatibility and mechanical properties. 1-3 However, Ti would take more than three months to integrate with bones. In particular, Ti implants must be kept with bones without applying mechanical force during the fixation period. It is known that the regeneration of apatite on Ti substrates can be promoted by bio-ceramic coatings such as hydroxyapatite (HAp, Ca10(PO4)6(OH)2), tricalcium phosphate (Ca3(PO4)2) and calcium titanate (Ca2TiO4). Many kinds of process have been used to prepare the bio-ceramic films, such as ion beam sputtering, 4 laser beam sputtering, 5 magnetic field sputtering, 6 sol-gel, 7 aerosol–gel, 8 electrophoretic deposition, 9 plasma spray deposition 10 and ion beam evaporation. 11 In these processes, the adherence between coatings and the substrate is the prime issue for practical applications, and therefore several techniques have been developed by modifying the surface, such as controlling surface roughness, 11 pre-oxidation of Ti surface forming TiO2 12 and CaTiO3 coating as a buffer layer. 13

Chemical vapor deposition (CVD) is advantageous to obtain wide-ranged coatings at relatively high deposition rate with good morphology controllability and well-adherence to substrates. Although many oxide and non-oxide films have been prepared by CVD, bio-ceramic films have been scarcely prepared by CVD. In the present study, Ca–Ti–O and Ca–P–O films were comparatively prepared by MOCVD, and the effect of deposition condition on the crystal phase and microstructure of Ca–Ti–O and Ca–P–O films was investigated. The apatite formation behavior on Ca–Ti–O and Ca–P–O coatings was investigated by immersing in a pseudo body fluid.

2. Experimental procedure

Ca–Ti–O and Ca–P–O films were prepared by a vertical cold-wall type CVD apparatus. 14 Source precursors of Ca(dpm)2, Ti(O-i-Pr)2(dpdm)2 and (C2H5)2PO were evaporated at 323 to 573 K, 193 to 453 K and 493 to 533 K, respectively. 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 (FRtot = FRca + FRti + FRapr) was fixed at 3.33 × 10−6 m3 s−1. The total pressure (Ptot) was changed in the range from 0.2 to 1.0 kPa. The substrate temperature (Tsub) was changed in the range of 873 to 1073 K. Quartz glass (15 × 10 × 1 mm) was used as substrate to investigate the crystal phase, morphology and deposition rate of Ca–Ti–O and Ca–P–O films and commercially pure Ti (CP–Ti) (10 × 10 × 1 mm) was also used to observe the apatite formation behavior on each coatings. The crystal structure was analyzed by X-ray diffraction (XRD). The microstructure and thickness of deposited films were examined by scanning electron microscopy (SEM). The deposition rate (Rdep) was determined by the thickness of films and deposition time. Apatite formation behavior on Ca–Ti–O and Ca–P–O coatings was investigated by the immersion test in a Hanks’ solution for 28 d. Detailed deposition condition and composition of a Hanks’ solution are summarized in Tables 1 and 2.

3. Results and discussions

3.1 CVD phase diagram of Ca–Ti–O and Ca–P–O films

Figure 1 presents a CVD phase formation diagram of Ca–Ti–O film on the quartz glass as functions of Tsub and Rca/Ti. CaO-rich films were obtained at Tsub = 873 K, and TiO2-rich films were obtained at Tsub = 973 K and 1073 K. CaTiO3 film in a single phase was obtained at Tsub = 1073 K, Rca/Ti = 1 and Tsub = 973 K, Rca/Ti = 0.7. CaTiO3 film in a single phase was not obtained at Tsub = 873 K, and CaO was always co-deposited with

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CaO phase was identified in wide-ranged conditions. This may be formed by the reaction of CaO and moisture in air after the deposition.

Figure 2 presents a CVD phase formation diagram of Ca–P–O films on the quartz glass as functions of $T_{\text{sub}}$ and $R_{\text{Ca/P}}$. CaO phase formed mainly in a low $T_{\text{sub}}$ and high $R_{\text{Ca/P}}$ region, whereas $P_2O_5$ phase formed at $T_{\text{sub}} = 1073$ K and low $R_{\text{Ca/P}}$ region. At $T_{\text{sub}} = 873$ K, no Ca–P–O phase was obtained, while a mixture phase of CaO and CaCO$_3$ was independent of $R_{\text{Ca/P}}$. At $T_{\text{sub}} = 973$ and 1073 K, the crystal structure of Ca–P–O changed depending on the $R_{\text{Ca/P}}$. $\alpha$-TCP in a single phase was obtained at $R_{\text{Ca/P}} < 0.3$, $T_{\text{sub}} = 1073$ K and $R_{\text{Ca/P}} = 0.1$ to 0.4, $T_{\text{sub}} = 973$ K and $R_{\text{Ca/P}} = 0.8$ to 1.0, $T_{\text{sub}} = 1073$ K.

3.2 Microstructure

Figure 3 depicts the surface and cross-sectional morphologies of Ca–Ti–O films on the quartz glass prepared at $P_{\text{tot}} = 0.8$ kPa. Mixture phase of CaTiO$_3$ and CaO film prepared at $T_{\text{sub}} = 873$ K had dense microstructure about 50 nm in grain size. CaTiO$_3$ film prepared at $T_{\text{sub}} = 1073$ K showed a cauliflower-like texture with agglomerated grains (Fig. 3(c)). It is generally understood that the texture changes from dense to...
columnar to dendrite to plate single crystal with increasing substrate temperature and decreasing super saturation degree of precursors in the gas phase.

Figure 4 depicts the surface and cross-sectional morphologies of \(\alpha\)-TCP at \(R_{Ca/P} = 0.4\) and HAp films on the quartz glass prepared at \(R_{Ca/P} = 0.96\), \(T_{sub} = 1073\) K and \(P_{tot} = 0.8\) kPa. Both \(\alpha\)-TCP and HAp films had a dense granular microstructure. The grain size of \(\alpha\)-TCP film was about \(1\ \mu m\) in length and \(0.5\ \mu m\) in width and that of the HAp film was about 1 to 2\,\mu m consisting of fine grains about \(0.2\,\mu m\) in diameter. The cross-sectional view of both film showed a dense microstructure.

3.3 Deposition rate

Figure 5 shows deposition rate of Ca–Ti–O and Ca–P–O film prepared at \(P_{tot} = 0.8\) kPa. Both \(R_{dep}\) increased with increasing \(T_{sub}\) and reached maximum at \(T_{sub} = 1073\) K. By further increasing in \(T_{sub}\), \(R_{dep}\) slightly decreased. This may be caused by premature reactions forming of particles in a gas phase. The highest \(R_{dep}\) of Ca–Ti–O film was \(45\,\mu m\,h^{-1}\) and that of Ca–P–O film was \(20\,\mu m\,h^{-1}\), respectively. It is well understood that the rate-controlling step in CVD can be a diffusion-limited process in a high \(T_{sub}\) region with an activation energy \((E_a)\) of a few kJ mol\(^{-1}\) and a chemical reaction limited process in a low \(T_{sub}\) region with the \(E_a\) of more than several 10 kJ mol\(^{-1}\). The \(E_a\) of Ca–Ti–O and Ca–P–O films were 70 and 80 kJ mol\(^{-1}\), implying the rate-controlling step of some kind of chemical reaction. The \(E_a\) of both films were calculated by using Arrhenius equation.

3.4 Apatite formation behavior on bio-ceramic coatings

Figure 6 shows surface microstructure of CaTiO\(_3\) coated on...
CP–Ti prepared at $T_{sub} = 1073$ K before and after immersion in a Hanks’ solution. CaTiO$_3$ film prepared at $T_{sub} = 873$ K had a dense and smooth surface (Fig. 6(a)). The surface was covered by apatite after 28 d immersion (Fig. 6(b)). On the other hand, CaTiO$_3$ film prepared at $T_{sub} = 1073$ K had a cauliflower-like texture (Fig. 6(c)), and the surface was covered by apatite after 3 d immersion (Fig. 6(d)). The morphology of CaTiO$_3$ coating changed from smooth ($T_{sub} = 873$ K) to cauliflower texture ($T_{sub} = 1073$ K), becoming more complicated with increasing $T_{sub}$. Apatite formation rate became faster depending on the change of surface morphology of CaTiO$_3$ film.

**Figure 7** shows surface microstructure of Ca–P–O coated CP–Ti before and after the immersion. While $\alpha$-TCP and HAp films had a dense and smooth surface before immersion (Figs. 7(a), (c)), apatite covered whole surface of $\alpha$-TCP coating after 2 w immersion (Fig. 7(b)) and that of HAp films after 6 h immersion (Fig. 7(d)). Since apatite formation on pure Ti usually needs more than 3 months, CaTiO$_3$ with cauliflower-like texture and also $\alpha$-TCP and HAp films prepared by MOCVD showed significantly high formation rate of apatite.

### 3.5 Mechanism of apatite formation on bio-ceramic coatings

**Figure 8** shows the surface microstructure of early stages of apatite formation on CaTiO$_3$, $\alpha$-TCP and HAp coatings. Apatite mainly formed at the hollow place of coatings. In particular, two kinds of apatite formation behavior were observed on the CaTiO$_3$ coatings as shown in Fig. 8(a). Apatite formed at boundary of cauliflower-like texture and grains, and formation rate at boundary of cauliflower-like texture was faster than that at boundary of grains. The apatite formation mechanism on the bio-ceramic coatings may be assumed as illustrated in Fig. 9. The bio-ceramic film elutes into solution (Fig. 9(a)) and the eluted ions trap at the hollow places in the film. The concentration of Ca$^{2+}$ and PO$_4^{3-}$ ion increases locally at the hollow places (Fig. 9(b)). Ca$^{2+}$ ions in the solution adsorb at the supersaturated hollow places of PO$_4^{3-}$ ions, and PO$_4^{3-}$ ions in the solution also adsorb at the supersaturated hollow places of Ca$^{2+}$ ions (Fig. 9(c)). Finally, apatite nucleates and grows as depicted in Fig. 9(d).

The apatite formation rate on CaTiO$_3$ coatings changed depending on the surface morphology of the coating, implying the surface morphology could significantly affect the apatite formation. Although both $\alpha$-TCP and HAp coatings had a smooth texture, the apatite formation rates of $\alpha$-TCP and HAp were faster than that of the CaTiO$_3$ coating having a smooth surface. Thus, the faster apatite formation rate on the $\alpha$-TCP and HAp films could be caused by the higher bone conductivity of Ca–P–O films. The apatite formation on bio-ceramic coating must have been affected by bone conductivity and surface morphology of coatings. It is known that the elution of coating, particularly calcium phosphate, would take place in advance of the formation of apatite. Since the elution rate of $\alpha$-TCP is much higher than that of HAp, the surface morphology of $\alpha$-TCP coating might have been smoother than that of HAp coating just after the immersion. This could result in the decrease of nucleation site of apatite formation for $\alpha$-TCP coating. Moreover, the adsorbed apatite nuclei would be easily detached due to the elution of $\alpha$-TCP coatings. On the other hand, the moderate elution rate of HAp coating might increase the concentration of Ca$^{2+}$ and PO$_4^{3-}$ ions in the vicinity of the HAp coating. Therefore, the apatite formation rate of HAp coating could be faster than that of $\alpha$-TCP coating.

### 4. Conclusions

Ca–Ti–O and Ca–P–O films were prepared by MOCVD using Ca(dpm)$_2$, Ti(O-i–Pr)$_2$(dpm)$_2$ and (C$_6$H$_{12}$)$_3$PO precursors. These films were immersed in a Hanks’ solution up to 28 d. CaTiO$_3$, $\alpha$-TCP and HAp films in a single phase were obtained at $T_{sub} = 973$ to 1073 K and $P_{at} = 0.8$ kPa. The surface morphology of CaTiO$_3$ films changed from dense fine grain to cauliflower-like columnar texture with increasing $T_{sub}$ and that of $\alpha$-TCP and HAp films were dense and granular microstructure. The cross-sectional morphology of CaTiO$_3$ films changed from dense to columnar structure, and that of $\alpha$-TCP and HAp films were dense structure. The apatite covered whole surface of the CaTiO$_3$ coatings with dense microstructure after 28 d, CaTiO$_3$ with cauliflower-like texture after 3 d, $\alpha$-TCP coating after 14 d, HAp coating after 6 h immersion, respectively. The nucleation of...
apatite occurred preferentially at hollow places of coatings, implying that the surface morphology of coatings could promote the apatite formation on the bio-ceramics coating.

Acknowledgements This study was partially supported by the Japan Society for the Promotion of Science (JSPS), by Grant-in-Aid for Scientific Research (B), 18360310, by Grant-in-Aid for JSPS fellows, by the Asian CORE program and by Tohoku University Global COE project on material integration.

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