Electrochemical Deposition of Calcium-Deficient Apatite on Stainless Steel Substrate

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カルシウム欠損アパタイトのステンレス基板上への電気化学的析出

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The electrochemical deposition of calcium-deficient apatite on a stainless steel substrate was conducted by electrolyzing $0.02\text{--}0.21\text{ mol/dm}^3\text{ Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ [MCP] solutions added with and without NaNO_3 and NaF at a cathode current of 6 mA/cm^2 at $20\text{--}90^\circ\text{C}$. The formation of apatite from F^- -free MCP solutions was limited in a dilute MCP concentration region. At relatively high MCP concentrations brushite ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) or monetite (CaHPO_4) was deposited. The addition of NaNO_3 and/or NaF was effective for the formation of apatite. Deposited apatite layers were composed of ellipsoidal grains, needles or very fine granules depending on electrolysis conditions. Apatites deposited from F^- -added MCP solutions were calcium-deficient apatites with Ca/P molar ratios near 1.50, and contained F^- , HPO_4^{2-} and Na^+ ions.

Key-words: Electrochemical deposition, Apatite deposition, Calcium-deficient apatite

1. Introduction

Hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) and related calcium phosphates are of considerable interest because of their biocompatible properties, and calcium phosphate coatings have been extensively studied for the surface biocompatible treatment of bio-inert metallic and ceramic materials. Many coating methods such as plasma-spraying, sputtering, electrophoresis, spark discharge in electrolyte, spontaneous deposition in solution, and dipping- or spray-pyrolysis have been employed for the purpose. Recently, Redepenning and McIsaac,¹⁾ and Shirkhanzadeh²⁾ reported electrolytic depositions of brushite ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) and hydroxyapatite, respectively, on prosthetic alloys from acidic calcium phosphate solutions. The apatite deposited had a so-called calcium-deficient composition expressed generally as $\text{Ca}_{10-x}(\text{HPO}_4)_x(\text{PO}_4)_{6-x}(\text{OH})_{2-x} \cdot n\text{H}_2\text{O}$; $0 \leq x < 1$ (referred to as DAp). Similarly, Ban et al.³⁾ prepared apatite films on Ti from a simulated physiological solution ($\text{pH}=7.2$). The author also studied on the electrolytic depositions and characteristics of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ and CaHPO_4 , and in addition discussed about the deposition of apatite.⁴⁾ In this

paper, the influences of electrolyte concentration, temperature and additives on the electrolytic depositions of calcium phosphates were investigated focusing on particularly the apatite deposition.

2. Experimental

Electrolysis runs were carried out by electrolyzing $0.02\text{--}0.21\text{ mol/dm}^3\text{ Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ (referred to as MCP) solutions (50 ml) added with and without NaNO_3 (7.0 g) and/or NaF (0.05 g) at a constant cathode current of $6 \pm 1\text{ mA/cm}^2$ at $20\text{--}90^\circ\text{C}$. Exceptionally, a saturated solution of sparingly water-soluble $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ was used instead of the MCP solutions. Electrodes used were a Pt plate with $0.1 \times 35 \times 40\text{ mm}$ as an anode and a SUS304 stainless steel plate with $0.1 \times \text{ca. } 15 \times \text{ca. } 20\text{ mm}$ as a cathode. The resulting deposits on the cathode were washed in distilled water, dried in air, and analysed with a Philips PW1700 X-ray diffractometer (XRD), Digilab FTS-60 infrared spectroscope equipped with a reflection-absorption accessory for thin films (RAS-IR), Akashi ISI-DS130 scanning electron microscope (SEM) and a Philips PV9900-ECON3 energy dispersive X-ray spectrometer (EDX). Table 1 lists apatite deposition samples prepared for characterization.

3. Results and discussion

3.1 Deposition products

Figure 1 shows deposition products from MCP solutions with and without NaNO_3 and/or NaF at various temperatures. From the F^- -free solutions $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ and CaHPO_4 were deposited at low and high temperatures, respectively. The apatite

Table 1. Preparations of apatite deposition samples.

Sample	Electrolyte		Electrolysis ^{c)}		
	Solu- tion ^{a)}	Additive ^{b)}	T ($^\circ\text{C}$)	Dc (mA / cm^2)	t (min)
DAp1	MCP	$\text{NaNO}_3 + \text{NaF}$	37	6	30
DAp2	MCP	$\text{NaNO}_3 + \text{NaF}$	40	6	80
DAp3	MCP	$\text{NaNO}_3 + \text{NaF}$	65	6	10
DAp4	B	NaF	65	20	30

a) MCP: 0.21 mol/dm^3 MCP, B: Saturated solution ($\sim 0.5\text{ mmol/dm}^3$) of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$.

b) NaNO_3 (7.0g) + NaF (0.05g) to 50ml solution.

c) Dc: Cathode current density ($\pm 1\text{ mA/cm}^2$).

Fig. 1. Deposition products from MCP solutions added with and without NaNO_3 and/or NaF at various MCP concentrations and temperatures ($6 \pm 1 \text{ mA/cm}^2$).

● Apatite+probably ACP, ○ ACP, △ $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, □ CaHPO_4

deposition was observed only at low MCP concentrations. The addition of NaNO_3 was effective for the depositions of apatite and amorphous calcium phosphate ($\text{Ca}_3(\text{PO}_4)_2 \cdot n\text{H}_2\text{O}$,^{5,6}) ACP). These calcium phosphates are thought to be deposited as a result of pH increases in the vicinity of the cathode surface. The pH increases would be induced by probably the reduction $\text{H}_2\text{O} + \text{e}^- \rightarrow 1/2\text{H}_2 \uparrow + \text{OH}^-$. As $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ and CaHPO_4 generally precipitate at lower pH's than those for apatite and ACP precipitations, no formations of apatite and ACP suggest insufficient pH increases for their depositions. The use of relatively dilute MCP concentrations was considered to be effective for increasing pH near the cathode. A similar effect was obtained also by using high electrolysis currents.⁴

From the F^- -added solutions, the deposition of apatite occurred in wide ranges of the combination of temperature and MCP concentration, accompanying diminutions of the deposition regions of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ and particularly CaHPO_4 . The preferential diminution of CaHPO_4 was considered to be related to the ease conversion into apatite of CaHPO_4 than $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ in the presence of F^- .⁷

3.2 XRD and IR characteristics of apatite deposits

Typical XRD patterns and the corresponding RAS-IR spectra of apatite deposition layers are shown in Figs. 2 and 3, respectively. The intense diffraction from the (002) or (300) plane suggested

Fig. 2. XRD patterns of apatite deposition layers.

Fig. 3. RAS-IR spectra of apatite deposition layers.

the crystal growth to the [001] direction and oriented depositions of apatite crystals. IR bands at $1100\text{--}1000$ (ν_3), 960 (ν_1), 600 (ν_4), 570 (ν_4) and 470 cm^{-1} (ν_2) are assigned to PO_4 vibrations in apatite. The band around 870 cm^{-1} is characteristic of HPO_4 and CO_3 in apatite, however in this case the band should be due to only HPO_4 since no other bands assigned to CO_3 in apatite are observed in the range of 1400 to 1550 cm^{-1} .⁸ The splitted bands 600 and 570 cm^{-1} are also characteristic of apatite. No bands due to O-H (stretch: 3570 cm^{-1} for $\text{O-H}\cdots\text{O-H}$ and 3540 cm^{-1} for $\text{O-H}\cdots\text{F}$, libration: 630 cm^{-1})^{9,10} suggested the fluoridation of OH groups. The OH sites were presumed to be occupied by F^- ions and H_2O molecules such as $(\text{F}, \text{H}_2\text{O})_2$, from analogy with an expression $(\text{OH}, \text{H}_2\text{O})_2$ for DAP deposited from F^- -free MCP solutions.^{4,11}

3.3 Morphology of apatite deposits

Figure 4 shows SEM micrographs of apatite

Fig. 4. SEM photographs of apatite deposition layers. Bar : 3 μm .

Fig. 5. EDX spectra of DAp deposits and standards.

deposits corresponding to the XRD patterns (Fig. 2). The deposit DAp3, which showed an intense XRD diffraction from the (300) plane, was composed of ellipsoidal grains. The deposits DAp1 and DAp2 having intense diffractions from the (002) plane were composed of very fine grains with obscure shapes. The DAp4 is another example having an intense (002) diffraction. In this case, it corresponded to the

oriented deposition of apatite needles elongated apparently to the *c*-axis direction. The crystallinity and grain size of the apatite deposits increased with increasing temperature.

3.4 EDX analysis of apatite deposits

Figure 5 shows EDX spectra of DAp samples and standards. The DAp's were estimated to have calcium-deficiencies near to 1.50 in Ca/P molar ratio, and contained small amounts of Na. The presence of Na was reasonable because the substitution of Na for Ca is generally observed in apatites precipitated from Na^+ -containing solutions.

4. Conclusions

The electrolytic depositions of calcium phosphates on a stainless steel substrate were carried out by electrolyzing 0.02–0.21 mol/dm³ $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ (MCP) solutions added with and without NaNO_3 and/or NaF at a cathode current of 6 mA/cm² at 20–90°C. The formation of apatite from F^- -free MCP solutions was limited in a region of dilute MCP concentrations, and at relatively high concentrations brushite ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) or monetite (CaHPO_4) was deposited. The addition of NaNO_3 and/or NaF was effective for the formation of apatite, and enlarged remarkably the formation region. Apatite deposits were composed of ellipsoidal grains, needles or fine granules depending on temperature and current. Apatite deposited from F^- -containing solutions were fluoridated calcium-deficient apatites having a composition like $(\text{Ca}, \text{Na})_9(\text{HPO}_4)(\text{PO}_4)_5(\text{F}, \text{H}_2\text{O})_2 \cdot n\text{H}_2\text{O}$ with Ca/P molar ratios near 1.50.

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