

## Hydroxyapatite Coating on Al<sub>2</sub>O<sub>3</sub> by Hydrothermal Process

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### ABSTRACT

Hydrothermal deposition of hydroxyapatite coatings on Al<sub>2</sub>O<sub>3</sub> substrates was studied using aqueous solutions of Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O and (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> containing EDTA disodium salt as a chelating agent for Ca<sup>2+</sup> ions. For the precipitation of the coatings, the EDTA-Ca<sup>2+</sup> chelates were dissociated thermally at 200°C or decomposed by oxidation with H<sub>2</sub>O<sub>2</sub> at 90°C. Scanning electron microscopy and X-ray diffraction were used to investigate the deposition behavior and the phase of the coatings. Hydroxyapatite coatings were not deposited with the thermal dissociation method, whereas uniform deposition of the coatings (about 0.7 μm thickness) was obtained with the oxidative decomposition method. The coatings consisted of fine rod-like hydroxyapatite crystals (hexagonal structure) with 60–80 nm diameters, having some preferred orientation with their length (i.e., the c axis) perpendicular to the substrate.

**Key words :** Hydrothermal deposition, Hydroxyapatite coatings, Al<sub>2</sub>O<sub>3</sub> substrates, EDTA-Ca<sup>2+</sup> chelates, Thermal dissociation, Oxidative decomposition, Preferred orientation

### 1. Introduction

Because of its high strength, low friction and wear, corrosion resistance, and biocompatibility, Al<sub>2</sub>O<sub>3</sub> has been used widely as orthopedic and dental implants.<sup>1)</sup> Commonly, bioinert Al<sub>2</sub>O<sub>3</sub> and Ti implants are encapsulated by a dense fibrous tissue that prevents direct bonding to soft and hard tissues in the body, leading to loosening of the implants.<sup>1,2)</sup> An effective way to overcome this problem is to impart bioactivity to the implant surface through a hydroxyapatite coating. Hydroxyapatite, Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>, the main mineral constituent of bone and teeth, can enhance growth of tissues around the implant, thereby promoting bonding with the implant.<sup>2)</sup> When compared with coating methods such as plasma spraying and sputtering, the hydrothermal process has a significant advantage in that it can produce crystalline, compositionally homogeneous hydroxyapatite coatings without the need for high temperature calcinations.<sup>3)</sup>

The hydrothermal processes for hydroxyapatite coatings involve heat treatments of substrates in an aqueous solution containing Ca<sup>2+</sup> and PO<sub>4</sub><sup>3-</sup> ions in an autoclave normally above 100°C. Although there are various sources of Ca<sup>2+</sup> and PO<sub>4</sub><sup>3-</sup> to make the solution, Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O or CaCl<sub>2</sub> and (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub>, NaH<sub>2</sub>PO<sub>4</sub> or Na<sub>2</sub>HPO<sub>4</sub> are commonly used to form hydroxyapatite coatings on various substrates of Ti, Ti alloy, ZrO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub>.<sup>4-8)</sup> In this case, Ca<sup>2+</sup> ions are chelated with EDTA (Ethylene Diamine Tetra Ace-

tic acid) in order to prevent immediate reaction with PO<sub>4</sub><sup>3-</sup>, which will precipitate hydroxyapatite powders rather than coatings before reaching desired hydrothermal conditions during the process. For the precipitation of hydroxyapatite coatings, the EDTA-Ca<sup>2+</sup> chelates are dissociated thermally<sup>4,7)</sup> or decomposed by oxidation with H<sub>2</sub>O<sub>2</sub>.<sup>8)</sup>

In the present work, both the thermal dissociation and the oxidative decomposition methods were used to deposit hydroxyapatite coatings on Al<sub>2</sub>O<sub>3</sub> substrates under hydrothermal conditions with the solutions prepared using Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O and (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub>. The deposition behavior of the coatings by the two methods is discussed with the results of scanning electron microscopy and X-ray diffraction studies.

### 2. Experimental Procedure

Solutions for the hydrothermal reaction were prepared using reagent-grade chemicals (Aldrich, Milwaukee, USA). Two solutions with Ca/P atomic ratios of 1 and 1.67 were prepared and named **A** and **B**, respectively. The value of Ca/P atomic ratio for stoichiometric hydroxyapatite is 1.67. The composition of the solution **A** was 0.05 M Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O, 0.05 M (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub>, and 0.05 M EDTA. The composition of the solution **B** was 0.072 M Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O, 0.043 M (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub>, and 0.086 M EDTA. The two solutions were prepared using the same procedure as follows. Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O was dissolved in deionized water and then EDTA in the form of disodium salt dihydrate was added to chelate the Ca<sup>2+</sup> ions. After stirring the solution for 10 min, (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> was added to make stock solutions of 140 ml for the solutions **A** and **B**. The pH value was adjusted with NH<sub>4</sub>OH to 6.7 and

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10.6 for the solution **A**, and 9.8 for the solution **B**. With the solution **A**, the EDTA- $\text{Ca}^{2+}$  chelates were dissociated thermally to precipitate hydroxyapatite coatings during hydrothermal treatments. With the solution **B**, they were dissociated thermally or decomposed by oxidation with  $\text{H}_2\text{O}_2$ .

$\text{Al}_2\text{O}_3$  substrates were prepared by slip casting an  $\text{Al}_2\text{O}_3$  powder (A-1000; mean particle size  $\approx 0.4 \mu\text{m}$ ; Alcoa, USA), followed by sintering for 2 h at  $1550^\circ\text{C}$  to give disc-shaped substrates (10 mm in diameter by 2.5 mm) with a relative density of 98%. The substrate surfaces were ground with SiC paper down to 600 grit.

The hydrothermal treatments were performed in a Teflon-lined autoclave (45 ml; Parr Instrument Co., USA). In the experiments, 23 ml of the stock solution was loaded into the reaction vessel. In the runs using the oxidative decomposition method, 3 wt%  $\text{H}_2\text{O}_2$  was added into the solution. The substrates were placed on the bottom of the vessel with the horizontal position of the surface to coat or suspended in the solution with the vertical position of that. The reaction vessel was heated at  $2^\circ\text{C}/\text{min}$  to  $200^\circ\text{C}$  (in the case of the thermal dissociation method) or  $90^\circ\text{C}$  (in the case of the oxidative decomposition method) and held for 3 h. After the hydrothermal treatment, the substrates were washed with deionized water using a squeeze bottle or an ultrasonic bath and dried at room temperature.

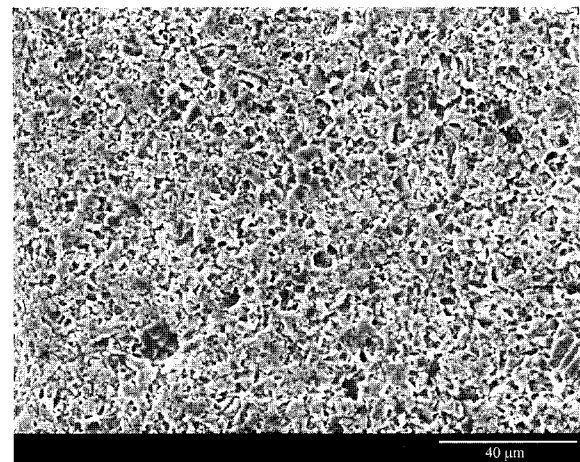
The microstructures of the top surfaces and fracture surfaces of the treated substrates were observed by scanning electron microscopy (SEM; JEOL T330A & Hitachi S4700). The crystalline phase of the coatings deposited was identified by Thin-Film X-Ray Diffraction (TF-XRD; Scintag 2000) with a grazing incidence angle of  $1^\circ$ . Powder precipitates were collected along with the treated substrates in some cases and were analyzed using SEM and XRD.

### 3. Results and Discussion

Fig. 1 shows the scanning electron micrographs of the surfaces of the substrates treated with the solution **A** of pH 6.7 by the thermal dissociation method. The position of the surface to coat was horizontal. In the case of the sample washed with deionized water using a squeeze bottle, Fig. 1(a), some needle-like particles were observed on the surface. However, in the case of the sample washed with deionized water using an ultrasonic bath, Fig. 1(b), such particles were not observed. Fig. 2 shows the scanning electron micrograph of the powder precipitate collected along with the treated substrates, which settled on the bottom of the reaction vessel. It can be seen that the precipitate consisted of long plate-like and needle-like particles similar to those observed on the substrate surfaces. XRD revealed the phase of this precipitate was crystalline hydroxyapatite as shown in Fig. 3(a). Therefore, it can be concluded that the needle-like particles observed on the substrate surface were not an adherent coating but a part of the hydroxyapatite crystals precipitated, just sitting on the surface without any adherence.



(a)



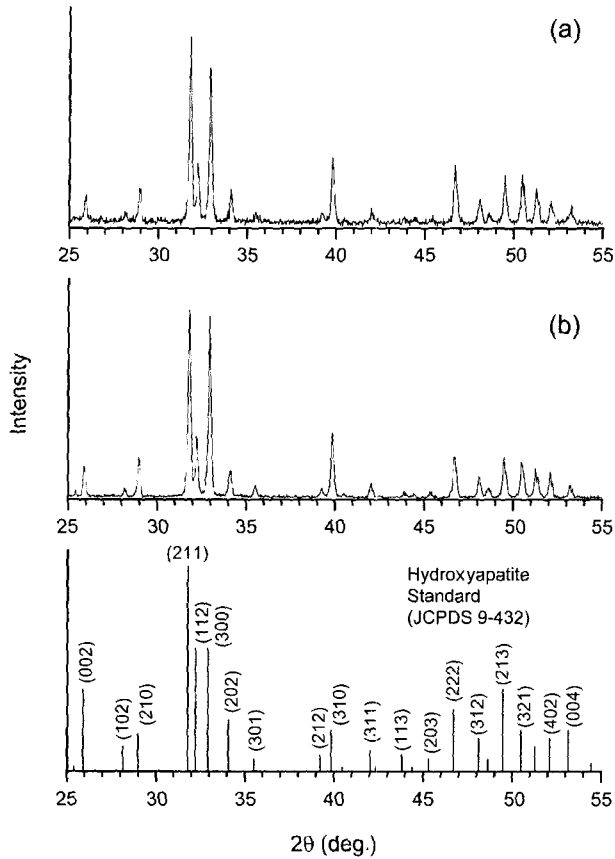
(b)

**Fig. 1.** Scanning electron micrographs of the surfaces of the substrates treated with the solution **A** of pH 6.7 by the thermal dissociation method with the horizontal position of the surface to coat: (a) the sample washed with deionized water using a squeeze bottle and (b) the sample washed with deionized water using an ultrasonic bath.



**Fig. 2.** Scanning electron micrograph of the powder precipitate collected along with the substrate treated with the solution **A** of pH 6.7 by the thermal dissociation method.

In order to avoid such confusion in the observation of coatings, the substrates were suspended in the solution with the vertical position of the surface to coat, and after hydrothermal treatments, they were washed with deionized water using an ultrasonic bath for the rest experiments consistently.

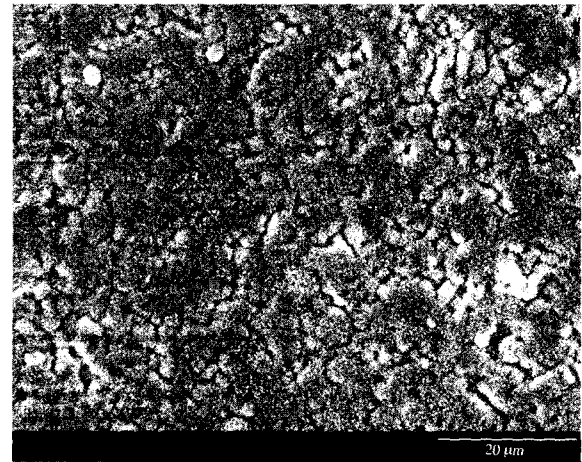


**Fig. 3.** XRD patterns of the powder precipitates collected with the substrates treated with the solution **A** of (a) pH 6.7 and (b) pH 10.6 by the thermal dissociation method, indicating their phases are hydroxyapatite.

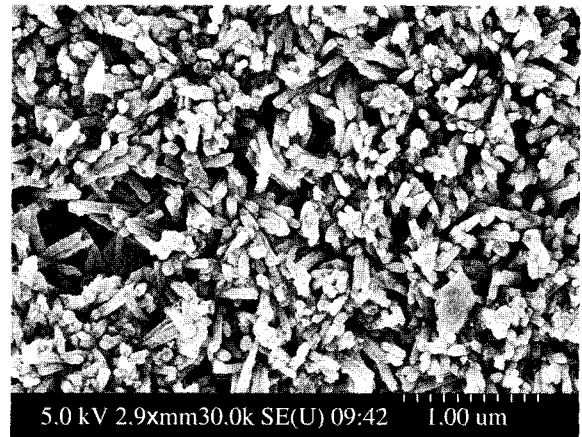


**Fig. 4.** Scanning electron micrograph of the powder precipitate collected along with the substrate treated with the solution **A** of pH 10.6 by the thermal dissociation method.

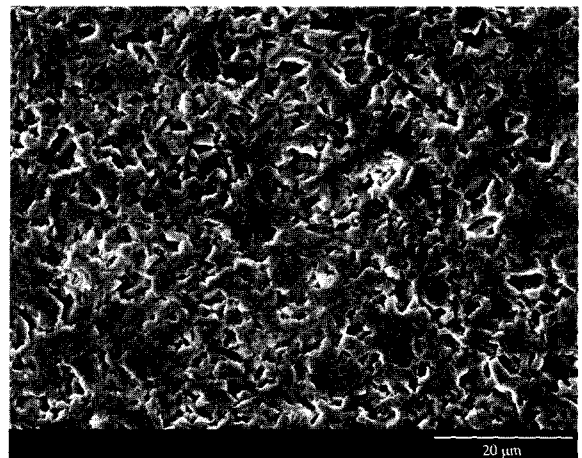
No hydroxyapatite coating was also deposited on the substrates treated with the solution **A** of pH 10.6 and with the solution **B** by the thermal dissociation method. A powder precipitate was formed in the former case but not in the lat-



(a)



(b)



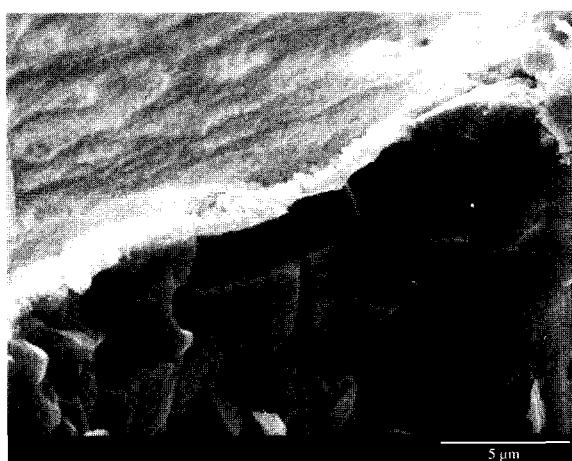
(c)

**Fig. 5.** Scanning electron micrographs of the surface of the substrate treated with the solution **B** by the oxidative decomposition method, showing the coating morphology: (a) low, (b) high magnifications, and (c) untreated substrate for comparison.

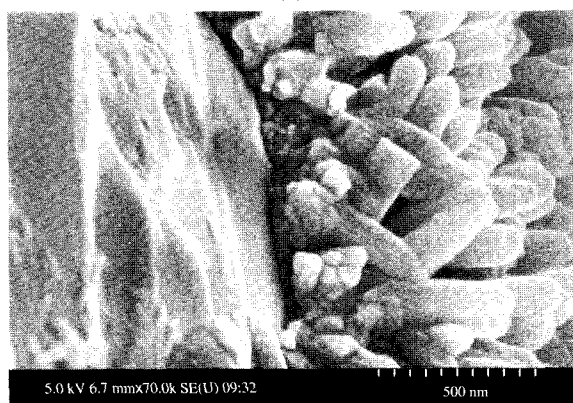
ter case. Figs. 3(b) and 4 are the XRD pattern and an SEM observation of the precipitate for the former, respectively. It also consisted of needle-like crystals of hydroxyapatite, but finer than in the case of pH 6.7 in Fig. 1(a).

Fig. 5 shows the scanning electron micrographs of the surface of the substrate treated with the solution **B** by the oxidative decomposition method. Uniform deposition of the coating was obtained in this case, Fig. 5(a) and (b), as compared with the untreated substrate, Fig. 5(c). The coating consisted of fine rod-like crystals with 60–80 nm diameters, Fig. 5(b). It is notable that many of these crystals were deposited with their length upward. Fig. 6 shows the scanning electron micrographs of the fracture surface of the sample. In Fig. 6(a), we can clearly see the coating layer with a thickness of about 0.7  $\mu\text{m}$ . In Fig. 6(b), the observation at a higher magnification, it is evident that the rod-like crystals had a tendency to grow vertically to the substrate. XRD revealed the phase of the coating to be hydroxyapatite

(Fig. 7). Hydroxyapatite has a hexagonal crystal structure, and the elongated direction of its rod-like crystals is known to be the *c* axis.<sup>3,9)</sup> Therefore, the SEM result above indicates

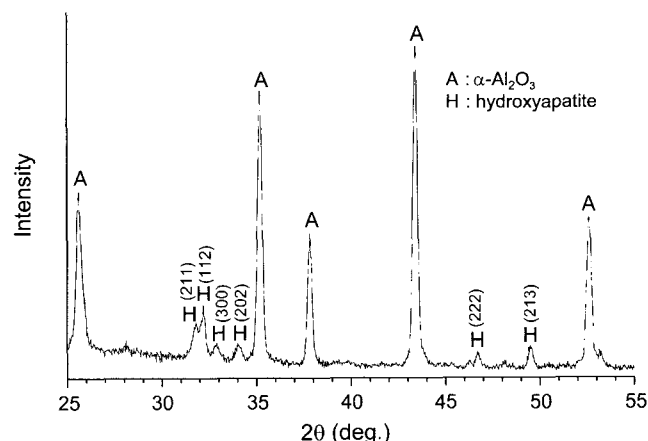


(a)



(b)

**Fig. 6.** Scanning electron micrographs of the fracture surface of the substrate treated with the solution **B** by the oxidative decomposition method, showing the coating layer: (a) low and (b) high magnifications.



**Fig. 7.** TF-XRD pattern of the substrate treated with the solution **B** by the oxidative decomposition method, showing hydroxyapatite peaks from the coating and  $\text{Al}_2\text{O}_3$  peaks from the substrate.

some preferred orientation of the hydroxyapatite crystals with the *c* axis perpendicular to the substrate. With this orientation, we expect the (002) reflection at  $2\theta = 25.9^\circ$  stronger than in the standard XRD pattern of hydroxyapatite (JCPDS 9-432; see Fig. 3). However, the (002) reflection is too close to one of the  $\text{Al}_2\text{O}_3$  peaks in position to confirm this fact as shown in Fig. 7. Instead, we can see from Fig. 7 that the (112) reflection at  $32.2^\circ$  had higher peak intensity than the (211) reflection at  $31.8^\circ$ , which has the strongest peak in the standard pattern, as a result of the preferred orientation of the hydroxyapatite crystals. The preferred orientation in the [002] direction was also reported in some other works on hydroxyapatite coatings on metal substrates formed under hydrothermal conditions.<sup>7,10)</sup> It is also found in the coating on an  $\text{Al}_2\text{O}_3$  substrate and the reaction layers of hydroxyapatite on Bioglass produced using simulated body fluids,<sup>11,12)</sup> and in the coating on a mild steel by a thermal spraying technique.<sup>13)</sup>

#### 4. Conclusions

The thermal dissociation method failed to attain the deposition of hydroxyapatite coatings on  $\text{Al}_2\text{O}_3$  substrates under hydrothermal conditions from aqueous solutions of  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and  $(\text{NH}_4)_2\text{HPO}_4$  containing EDTA. With the oxidative decomposition method using  $\text{H}_2\text{O}_2$ , uniform deposition of the coating was obtained with a thickness of about 0.7  $\mu\text{m}$  by the hydrothermal treatment at  $90^\circ\text{C}$  for 3 h. The coating consisted of fine rod-like crystals with 60–80 nm diameters, having some preferred orientation with the *c* axis perpendicular to the substrate.

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