

## Hydroxyapatite Coating on Titanium by Thermal Decomposition

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**Abstract:** Hydroxyapatite (HA) coatings on Ti implants are made by the physical methods, mainly plasma spraying. We have developed a new chemical coating technique, thermal decomposition method. This method consisted of applying HA or perovskite (CaTiO<sub>3</sub>) coating solution containing organometals, phosphate ester (only in HA solution), and organic solvents onto the surface of Ti and then sintered it at 650°C. The process was repeated several times. The thin and homogeneous layer included an initial CaTiO<sub>3</sub> layer with a thickness of 0.6 μm followed by an HA layer (2.4 μm) on top. The underlying CaTiO<sub>3</sub> layer reduced oxidation of the Ti substrate and enhanced stability of the coating.

**Keywords:** hydroxyapatite coating, thermal decomposition method, perovskite.

### Introduction

Hydroxyapatite (HA) has been widely used in medicine because of its favorable biocompatibility. However, sintered HA has disadvantages such as shaping and low mechanical properties. Many studies have been conducted using HA as a coating on metal and one of the best materials discovered has been the combination of HA and titanium (Ti). The biocompatibility and mechanical properties of HA are excellent when coated on Ti. There are a variety of techniques for HA coating and one of the most common methods is plasma spraying<sup>1-2)</sup>. However, it has numerous drawbacks: 1) application requires an expensive large system; 2) it is difficult to apply on a convoluted surface; 3) HA decomposes into b-TCP and the other second phases under the high temperatures during spraying; 4) the interface between HA and Ti is fragile; and 5) a thin stable layer (less than 20 mm) cannot be obtained. We have developed a new chemical coating technique, called thermal decomposition method<sup>3-5)</sup>. This method consists of applying a solution containing organometal, phosphate ester, and organic solvent onto the surface of the Ti and then sintering it at 650°C. The thin and homogeneous coating with a thickness of 4 mm is demonstrated<sup>5)</sup>. This paper describes a methodology to form a thin and homogeneous layer which includes an initial perovskite (CaTiO<sub>3</sub>) layer followed by an HA layer on top.

### Materials and Methods

#### CaTiO<sub>3</sub> and HA Coating Solution

High purity CaCO<sub>3</sub> was heated at 1050°C for 2 h to yield CaO. A solution of 2-ethylhexanoic acid was heated at 100~120°C, and the CaO powder was added slowly into the solution. The solution was stirred at this temperatures until all the CaO was dissolved. After cooling, the resulting calcium 2-ethylhexanoate was dissolved in 1-butanol. Ti tetra-isopropoxide was added to the solution and stirred to form a transparent solution. Thus the CaTiO<sub>3</sub> coating solution was made up.

The HA coating solution was prepared with a method similar to

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that used for CaTiO<sub>3</sub>. Bis(2-ethylhexyl) hydrogen phosphate and distilled water were added to the above noted calcium 2-ethylhexanoate solution in 1-butanol, and then the HA coating solution was made up.

#### Coating Techniques on Ti plates

Grade 2 Ti plate 35×35×0.7 mm<sup>3</sup> was etched in a boiling 1N HCl solution for 15 min and washed in distilled water three times. The Ti plate was dipped into the CaTiO<sub>3</sub> coating solution for 5 min. The coated plate was centrifuged at 1500 rpm (400 g) for 1 min. Then it was left at room temperature for 10 min, dried at 110°C for 20 min, and sintered at 650°C for 10 min. The above cycle was repeated three times. The Ti plate was then dipped into the HA coating solution and treated the same way as the CaTiO<sub>3</sub>. This process was repeated for ten times.

### Results and Discussion

X-ray diffraction (XRD) pattern of the CaTiO<sub>3</sub> coated Ti plate (Fig. 1a) indicated that the surface layer contained well-crystallized CaTiO<sub>3</sub> and rutile (TiO<sub>2</sub>) due to oxidation of the Ti substrate which showed intense peaks from a-Ti. The relative intensities from rutile were 1/10 compared to those from non-coated Ti plate heated at 650°C for 30 min. Thus the CaTiO<sub>3</sub> coating reduced oxidation of the Ti substrate.

XRD pattern of the HA/CaTiO<sub>3</sub> coating on the Ti plate (Fig. 1b) exhibited well-crystallized HA and CaTiO<sub>3</sub> and the double layer consisted of HA and CaTiO<sub>3</sub> was confirmed. Weak diffraction peaks from TiO<sub>2</sub> due to oxidation of the Ti and intense peaks from a-Ti were also present in the pattern. No b-TCP was present in this diffraction pattern. In the previous studies<sup>4-5)</sup> their HA layer included 30% b-TCP.

The coating thickness was calculated from the weight increase and surface area of the Ti plate before and after coating. The theoretical densities of HA and CaTiO<sub>3</sub> were assumed to be 3.16 and 4.04 g/cm<sup>3</sup>, respectively. Thus, thicknesses of the HA and the CaTiO<sub>3</sub> layers were calculated to be 2.4 and 0.6 mm, respectively.

Scanning electron microscopy (SEM) showed that after coating of the CaTiO<sub>3</sub> and HA, a uniform film was formed on the Ti surface and morphology of the etched Ti surface was well preserved (Fig.

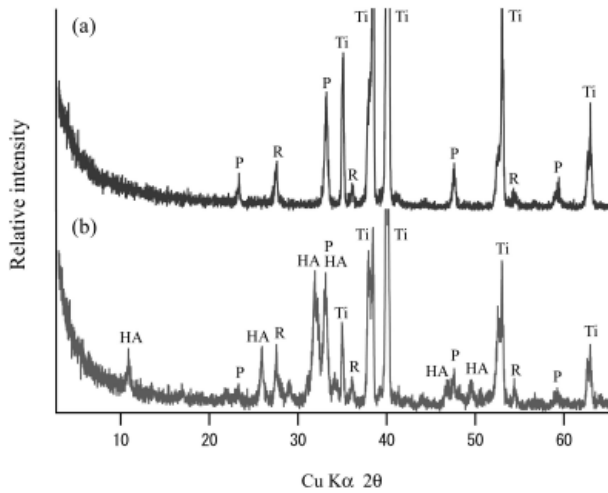


Fig. 1 X-ray diffraction patterns of (a)  $\text{CaTiO}_3$  and (b)  $\text{HA/CaTiO}_3$  coating on the Ti plates (Ti: a-Ti; HA: hydroxy-apatite; P: perovskite; R: rutile).

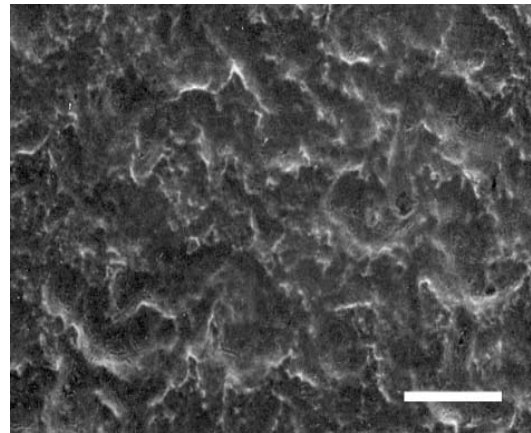


Fig. 2 SEM of the surface of the  $\text{HA/CaTiO}_3$  coated Ti plate. Bar = 50  $\mu\text{m}$ .

2). A cross-sectional view of the coated sample showed that thickness of the coating film was 3~6  $\mu\text{m}$  which was thicker than the calculated value. The HA/Ti interface had intimate contact, but distinction between  $\text{CaTiO}_3$  and HA was not clear.

Fig. 3 shows an example of the  $\text{HA/CaTiO}_3$  coating applied to commercial dental Ti implants. The double layer which consisted of HA and  $\text{CaTiO}_3$  could ensure enhanced stability and compatibility.

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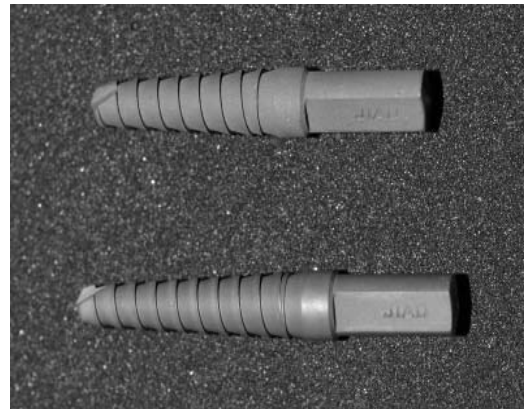


Fig. 3 Example of the  $\text{HA/CaTiO}_3$  coating applied to commercial dental Ti implants.