



Deposition behavior and characteristics of hydroxyapatite coatings on Al₂O₃, Ti, and Ti6Al4V formed by a chemical bath method

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Abstract

A simple chemical bath method was used to deposit hydroxyapatite (HA) coatings on Al₂O₃, Ti, and Ti6Al4V substrates at ambient pressure by heating to 65–95 °C in an aqueous solution prepared with Ca(NO₃)₂·4H₂O, KH₂PO₄, KOH, and EDTA. The deposition behavior, morphology, thickness, and phase of the coatings were investigated using scanning electron microscopy and X-ray diffractometry. The bonding strength of the coatings was measured using an epoxy resin method. The HA coatings deposited on the three kinds of substrates were fairly dense and uniform and exhibited good crystallinity without any additional heat treatment. A coating thickness of 1–1.8 μm was obtained for the samples coated once. By repeating the coating process three times, the thickness could be increased to 4.5 μm on the Al₂O₃ substrate. The bonding strength of these coatings was 18 MPa.

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1. Introduction

The average human lifespan today has been increased remarkably owing to the development of medical technology and increased income levels. Hence, the demand for artificial substitutes for body parts such as teeth, hip joints, and hearts is currently increasing. These substitutes must necessarily be composed of biocompatible materials to replace parts of human body without inducing any side effects in surrounding tissue. Such materials, so-called biomaterials, are classified into bioactive and bioinert materials [1].

Hydroxyapatite (HA), Ca₁₀(PO₄)₆(OH)₂, is an important inorganic component of hard tissue in the human body and has long been studied as a superior bioactive material. However, its applications are limited to bone cements or fillers due to its weak mechanical properties [2]. In contrast, Al₂O₃, Ti, and Ti alloy exhibit good mechanical strength and chemical stability. However, their bioinertness causes problems such as fibrous film formation, resulting in the loose fixation of implants; or dissolution of the materials in the body, thereby damaging cells [3,4].

To solve such problems, a number of studies have been performed on the modification of bioinert material surfaces through HA coating to induce direct bonding with hard tissues. The typical methods employed in this approach include plasma spraying, CVD, sputtering, flame spraying, electrochemical deposition, sol–gel processing, pulsed laser deposition, thermal spraying, and electrophoresis. Among these techniques, only plasma spraying has been successfully commercialized. However, due to their high processing temperatures, these methods involve a deficit of phosphorus ions or the formation of an amorphous phase that can cause rapid biodegradation and reduced tissue bonding due to the formation of heterogeneous phases [5]. The implementation of a biomimetic process [6–8] that mimics the formation mechanism of natural bone tissues may be an alternative to avoid such problems. Methods of this type enable various compositions of HA coatings to be formed using a simulated body fluid at normal human body temperature (36.5 °C). However, the disadvantage of these techniques is that the coating formation rate is slow, requiring up to 4 weeks to complete [7].

A chemical bath method was reported in which HA was coated on Ti6Al4V substrates simply by heating at ambient pressure in an aqueous solution composed of Ca²⁺ and PO₄³⁻

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ions in the stoichiometric ratio of HA [9]. This method has the advantages of being simple, having no restrictions regarding substrate shape, and yielding stoichiometric HA coatings with good crystallinity at low temperatures below 100 °C.

In the present study, using the chemical bath method, HA coatings were deposited on Ti6Al4V as well as Al₂O₃ and Ti substrates. The deposition behavior, microstructure, and phases of the coatings were investigated and compared among the three kinds of substrates. The bonding strength of the coatings deposited on Al₂O₃ substrates was also evaluated.

2. Experimental procedure

2.1. Preparation of substrates and coating solutions

Al₂O₃ substrates (11 mm in diameter, 4 mm thick) were fabricated using α -Al₂O₃ powder (AKP-30, average diameter 0.4 μ m, Sumitomo, Japan) by uniaxial pressing and sintering at 1550 °C for 2 h. The sintered densities of the substrates were at least 98%. The Ti and Ti6Al4V substrates (9 mm in diameter, 5 mm thick) were prepared with commercially available rods by cutting them into discs. All of the substrates were ground with diamond wheels to a finish of 800 grit on the surfaces to be coated.

The coating solution was prepared using potassium hydroxide (KOH; Alfa, USA), calcium nitrate tetra hydrate (Ca(NO₃)₂ · 4H₂O; Aldrich, USA) as a source of Ca²⁺ ions, and potassium dihydrogen phosphate (KH₂PO₄; Alfa, USA) as a source of PO₄³⁻ ions, along with ethylenediaminetetraacetic acid (EDTA; C₁₀H₁₆N₂O₈; Alfa, USA) for chelating Ca²⁺ ions. When Ca²⁺ and PO₄³⁻ ions are mixed together in an aqueous solution, they immediately react even at room temperature to precipitate HA in the form of a powder rather than a coating. Hence, control of the reaction rate through EDTA is necessary for coating deposition. The solubility of EDTA is very low in acidic solution but high in alkaline solution.

First, a KOH solution containing PO₄³⁻ and OH⁻ ions (denoted as **Solution I**) was prepared by dissolving 0.62 mol KOH, 0.086 mol EDTA, and 0.05 mol KH₂PO₄ in distilled water, with the latter two added later. EDTA is ionized as it is dissolved in KOH. The reaction is exothermic and continues until EDTA is completely ionized. After the completion of the EDTA ionization, the solution is strongly alkaline with pH 14. No reaction occurs during the addition of KH₂PO₄. Second, a solution containing Ca²⁺ ions (denoted as **Solution II**) was prepared by dissolving Ca(NO₃)₂ · 4H₂O in distilled water in an amount corresponding to a stoichiometric Ca/P mole ratio of 1.67 when mixed with the KOH solution. Lastly, a transparent coating solution was prepared by mixing the two solutions.

2.2. Deposition and characterization of coatings

In the coating process employed, HA coatings are formed by the following reaction:

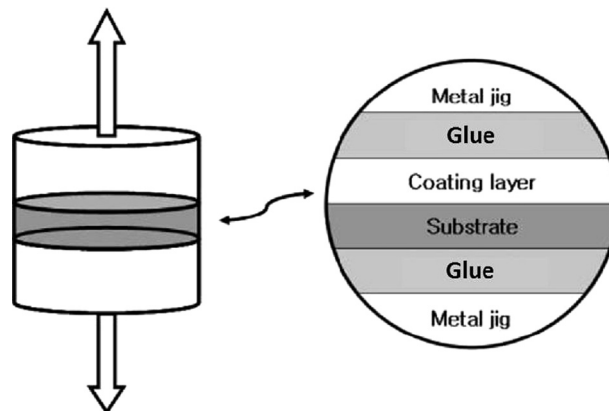


Fig. 1. Specimen arrangement for the tensile bonding strength testing of the HA coatings.

When **Solution I** and **Solution II** are mixed together in the stoichiometric ratio of HA (Ca/P=1.67), white precipitates of Ca(OH)₂ are formed momentarily and then dissolved to form EDTA–Ca²⁺ chelate compounds. As the temperature increases, Ca²⁺ ions are dissociated from the compounds and bond with PO₄³⁻ ions to form an HA coating.

The Al₂O₃, Ti, and Ti6Al4V substrates were ultrasonically cleaned, hung in a beaker containing the coating solution, and heated using a silicon oil bath to deposit the coating. The substrates were heated for 1 h from room temperature to 65 °C, for 3 h at 80 °C, and for 3 h at 95 °C. For the Al₂O₃ substrate, the coating process was repeated up to three times to increase the coating thickness. The coated substrates were washed using an ultrasonic cleaner to remove any residue on the surfaces and then dried.

The coated samples were characterized without any additional heat treatment. The thickness, microstructure, and phase of the coatings were investigated using SEM (JSM- 6300, JEOL, Japan) and XRD (D/MAX RAPID-S, Rigaku, Japan). The bonding strength of the coatings was measured using an epoxy resin method [10] for the samples coated on Al₂O₃ substrates. The test specimens were fabricated as shown in Fig. 1, with the samples coated twice. The tests were performed in tension (cross-head speed 0.5 mm/min) on a universal testing machine (H10KS, Hounsfield, UK).

3. Results and discussion

Fig. 2 shows the microstructures of the samples coated on Al₂O₃ substrates before and after deposition. Fig. 2(b) shows that the surface of the coating layer consisted of fine, rod-shaped crystals with a diameter of approximately 0.5 μ m and length of at least 1 μ m, which had grown from the substrate surface. This morphology is characteristic of HA with a hexagonal crystal structure often found in the case of hydrothermal synthesis [11–13]. This result confirms that the coating crystals grew lengthwise. Fig. 2(c) shows that the coating layer was approximately 1.8 μ m thick and bonded well with the substrate surface without delaminating.

Figs. 3 and 4 show the microstructures of the samples coated on the Ti and Ti6Al4V substrates, respectively, before and after

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