

Molecular precursor method for thin calcium phosphate coating on titanium

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Abstract

Carbonate-containing hydroxyapatite was deposited onto titanium using a molecular precursor method, which is a novel technique for coating metal oxide film. The molecular precursor solution was prepared by the addition of dibutylammonium metaphosphate salt to an ethanol solution of Ca-ethylenediamine-*N,N,N',N'*-tetraacetic acid/amine complex. The molecular precursor solution was applied to titanium and fired at different temperatures from 300 to 700 °C for 2 h using a furnace under ordinary atmospheric conditions. A firing temperature below 400 °C did not produce an apatite film on the titanium. Firing at 600 or 700 °C formed a crystalline carbonate-containing hydroxyapatite film on the titanium substrate. Thermal analysis confirmed that a firing temperature above 500 °C is necessary to form calcium phosphate films on titanium substrates. The coating thickness and Ca/P ratio determined by electron probe microanalysis were about $0.44 \pm 0.01 \mu\text{m}$ and 1.56 ± 0.04 , respectively. After immersion of coated specimens in phosphate buffered saline (PBS) solution for periods of 1 week and 1 month, the formation of slight cracks in the coated films was observed. The tensile bond strength measurement and scratch test showed an excellent degree of adhesion of the coated film on the titanium after the PBS immersion. Finally, we concluded that a firing temperature of 600 °C is suitable for producing an adherent carbonate-containing apatite film on titanium.

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1. Introduction

In the last decade, physical vapor deposition (PVD) techniques such as ion plating [1], magnetron sputtering [2], and ion beam dynamic mixing [3] have been introduced to deposit thin calcium phosphate coatings on medical implants, especially oral implants. The PVD methods can avoid some intrinsic shortcomings of plasma-sprayed calcium phosphate coatings [4–6]. For example, PVD deposited calcium phosphate coatings are more adherent

to the underlying titanium surface and less prone to form cracks than are plasma-sprayed coatings [2,3]. Frequently, these coatings initially appear to be amorphous, which can easily be improved by rapid heat treatment with infrared radiation [7]. The main component of the crystalline structure of these heat-treated films is hydroxyapatite. Previous cell cultures and animal experiments have indicated the biological feasibility of this type of coating [8–11].

The deposition of carbonate apatite film on a titanium substrate is interesting because of its chemical resemblance to bone mineral. Recently, Leeuwenburgh et al. [12,13] reported a new coating technology referred to as electrostatic spray deposition (ESD), which was originally

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developed to synthesize thick ceramic films for solid electrolytes [14]. They found that crystalline carbonate apatite coatings were formed after heat treatment of as-deposited ESD coating. Siebers et al. [15] assayed the cell proliferation, alkaline phosphatase activity, and osteocalcin concentration of osteoblast-like cells on such calcium phosphate coatings deposited by ESD.

A disadvantage of the ESD technique is that it is a line-of-sight technique, which makes it difficult to apply uniform coatings on complex implant surface geometries or inside porous scaffold materials, such as titanium fiber mesh [16].

Liu et al. [17] deposited a thin hydroxyapatite film on stainless steel using a water-based sol-gel technique. A dense and adhesive apatite coating can be produced through water-based sol-gel technology after short term annealing at around 400 °C in air. Kim et al. [18] used a sol-gel method to coat a fluoro-hydroxyapatite film on a zirconia substrate. The use of the sol-gel technique has the potential for applying uniform coatings to porous substrates.

However, in the conventional sol-gel process alkoxides are employed and the rigorous exclusion of water from the system is essential for the synthesis and conservation of the precursor alkoxides and their solutions since the process is based on partial or complete hydrolysis of such metal alkoxides [19].

Sato et al. [20–22] also developed a novel method for coating ceramics and metal materials with metal oxide film. They called their method the molecular precursor method. The principle of the method is the application of an alcoholic precursor solution of an ethylenediamine-*N,N,N',N'*-tetraacetic acid (EDTA)–metal complex on the substrate and then firing the material at around 500–700 °C. Film formation can be attained by a combination of anionic species involving metal ions and adequate alkylammonium cations without a polymerization process. Thin films of TiO₂, Co₃O₄, and SrTiO₃ were coated onto a glass substrate using a Ti–EDTA or Co–EDTA complex by the molecular precursor method. The molecular precursor method was also used to produce SrTiO₃ thin film using a mixture of the Ti–EDTA and Sr–EDTA complex.

Recently, Sato et al. [23] found that hydroxyapatite can be deposited on titanium by using a precursor solution of a Ca–EDTA complex. Two types of precursor solutions, i.e., those with or without water, were evaluated. It was found that the Ca–EDTA precursor solution without water is more stable during storage. Thus, the recommended precursor solution is the ethanol solution reported here. To examine the possibility of applying this method to the dental and orthopedic fields, a detailed analysis of the effects of firing temperatures on titanium and a more comprehensive characterization of the deposited films should be made.

In the present study, we aimed to deposit carbonate-containing hydroxyapatite on titanium using the molecular precursor method. We investigated the influence of firing temperatures on the fabrication of carbonate-containing hydroxyapatite coating on titanium as well as some physical

properties of the deposited carbonate–apatite film for implant use.

2. Experimental details

2.1. Preparation of molecular precursor solution

The molecular precursor solution for the carbonate-containing hydroxyapatite coating was obtained by adding metaphosphate salt to a Ca–EDTA/amine ethanol solution. The general procedure for the preparation of the molecular precursor solution is shown in Fig. 1.

2.1.1. Step 1: Ca–EDTA/amine ethanol solution

To a suspended solution of 20.46 g of EDTA (Kanto Chemicals, Tokyo, Japan) in 900 ml deionized water (18MΩcm), 12.38 g of Ca(CH₃COOH)₂ was added with stirring at 75 °C for 1 h, and then the reaction mixture was cooled to room temperature. After that the reaction mixture was allowed to stand overnight. CaH₂(edta)·2H₂O was obtained as a white precipitate. The white precipitate was collected by filtration and rinsed with deionized water and ethanol, then dried in a vacuum. The yield of CaH₂(edta)·2H₂O was about 67%, and the structure was confirmed by elemental analysis of carbon, hydrogen and nitrogen (Perkin Elmer 2400 Series II CHN-analyzer, Norwalk, CT, USA) and Fourier transform infrared (FT-IR) spectra (FT-210 spectrophotometer, Horiba, Tokyo, Japan).

The Ca–EDTA/amine ethanol solution was prepared from the reaction of 4.00 g of CaH₂(edta)·2H₂O and 3.26 g of dibutylamine in 43 g ethanol under reflux conditions. A clear Ca–EDTA/amine ethanol solution was obtained.

2.1.2. Step 2: Metaphosphate salt

An ethanol solution of 10 g containing 5.8 g of phosphoric acid (85 mass%, Kanto Chemicals, Tokyo, Japan) was added to 10 g of ethanol solution of 19.4 g of dibutylamine, and the mixed solution was stirred for 5 min

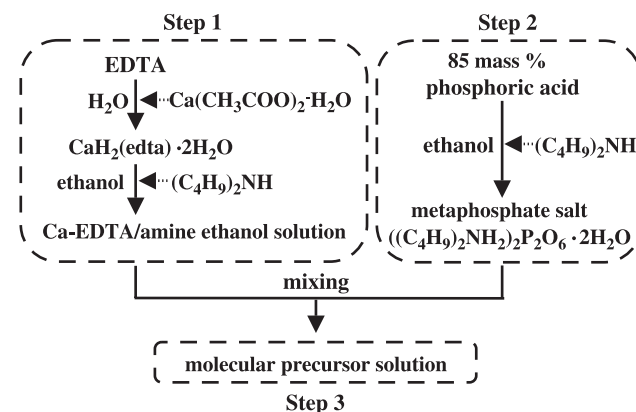


Fig. 1. Schematic presentation of preparation of precursor solution.

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