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Poly-crystallized hydroxyapatite coating deposited by pulsed laser deposition method at room temperature

Masahito Katto [a,*], Kou Kurosawa [a,b], Atushi Yokotani [b], Shoichi Kubodera [b], Akihiro Kameyama [b], Takeshi Higashiguchi [b], Takeyoshi Nakayama [c], Masahiro Tsukamoto [d]

[a] *Cooperative Research Center, University of Miyazaki, 1-1 Gakuen-Kibanadai-Nishi, Miyazaki 889-2192, Japan*
[b] *Department of Electrical and Electronic Engineering, University of Miyazaki, Japan*
[c] *Department of Electrical and Electronic Engineering, Kinki University, Japan*
[d] *Joining and Welding Research Institute, Osaka University, Japan*

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Abstract

We have deposited hydroxyapatite (HAp) films on Ti substrate by pulsed laser deposition using KrF excimer laser. We used HAp targets sintered at temperatures of 500, 700, 900 and 1100 °C with densities between 1.5 and 2.4 mg/mm^3. SEM images of the coating surface revealed that the deposited films had spherical structures with diameter of 5 μm. X-ray diffractometry (XRD) analysis showed that the deposited films contained amorphous HAp. Films deposited with a target sintered at 900 °C showed that poly-crystallized HAp coating was achieved at room temperature.

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1. Introduction

Hydroxyapatite (HAp), $Ca_{10}(PO_4)_6(OH)_2$, has good biocompatibility and is being widely used as a coating material to improve the durability and biocompatibility of implants. Among the various HAp coating methods, the pulsed laser deposition (PLD) technique was introduced in 1992 for high quality HAp coating deposition [1] using excimer lasers [1–5] and harmonics of Nd:YAG lasers [6,7]. The layers were deposited in water vapor atmosphere on Ti or Ti-based alloys substrates. The substrates were maintained at temperatures between 500 and 800 °C in the previous studies to generate a high degree of crystallinity [1–7]. However, high substrates temperature and water atmosphere conditions promote

* Corresponding author. Tel.: +81 985 58 7572; fax: +81 985 58 3899.
E-mail address: mkatto@opt.miyazaki-u.ac.jp (M. Katto).

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the oxidation of the Ti substrate surface prior to the growth of the HAp layer, thus degrading the adhesion of the coating to the substrate [8,9]. Therefore, crystalline HAp coatings should be deposited at lower temperatures to avoid extensive oxidation of the substrate.

Craciun et al. [10] proposed a vacuum ultraviolet (VUV) annealing method, by which they annealed a coating with a Xe_2-VUV excimer lamp in oxygen atmosphere and obtained a crystallized HAp film. We have developed a new HAp coating method using two UV excimer laser beams. This method, which we called a laser assisted laser ablation (LALA) method, is based on PLD and uses the second laser as an 'assist laser' to anneal the substrate. We found that irradiation with the assist beam improved the adhesion of the coatings [11–13]. However, the HAp was amorphous without the annealing process. If a poly-crystallized layer is obtained without the annealing process, it is possible to improve the crystallinity of the coating.

To achieve high crystallization of the deposited films, nucleation and migration processes of the particles are important. These processes depend not only on the substrate temperature but also on the energy of the ablated particles.

In this paper, we investigated the characteristics of PLD deposited coatings from HAp ceramics targets of various densities to obtain poly-crystalline HAp coating at the room temperature.

2. Experimental details

HAp targets made of HAp powder supplied from Taihei Chemical Industry Co. Ltd. were used. We made the target pellets by compressing the HAp powder by a pressure of 150 MPa. Then the ceramics targets were fabricated by sintering the pellets for 10 h in air at a temperature of 500, 700, 900 and 1100 °C using an electrical oven. The HAp targets had densities in the range from 1.5 to 2.4 mg/mm^3, proportional to the sintering temperature. The deposition was performed by an ordinary PLD scheme using a KrF excimer laser (GAM Laser, EX-10) for ablation. The laser beam was focused by a quartz lens ($f = 350$ mm) on the target surface with a fluence of 5 J/cm^2 and repetition rate of 100 Hz at a 45° angle of incidence. The ablated particles from the target were deposited on the polished Ti substrate that was positioned on the stage normal to the target at a distance of 20 mm. The target was rotated during the deposition period of 10 min. The deposition chamber had a base pressure of 10^{-3} Torr, then distilled water was supplied from a tank into the chamber. The water vapor pressure was kept at an equilibrium pressure of 1.0 Torr by adjusting the water flow valve.

The coating layer was characterized by scanning electron microscope (SEM), X-ray diffractometry (XRD) and Fourier transform-infrared spectroscopy (FT-IR). We also estimated the concentration ratio of Ca to P using the X-ray photoelectron spectroscopy (XPS) analysis.

3. Results and discussion

The characteristics of sintered targets at various temperatures were estimated by XRD and XPS analysis. We found no alteration and decomposition of the HAp phase. The Ca/P ratio after sintering at each temperature is shown in Fig. 1.

In Fig. 2a–d, SEM images of the deposited film surface are shown, deposited from targets sintered at the temperature of (a) 500, (b) 700, (c) 900 and (d) 1100 °C, respectively. Each surface had a morphology of spherical particles with diameter of 5 μm and some ablated debris. The film deposited from the target sintered at 900 °C, contained smaller grains than those present in the films deposited from targets sintered at 500, 700 and 1100 °C (see Fig. 2c).

The XRD patterns are shown in Fig. 3. Patterns from the deposited films in Fig. 3b–d exhibit a broad

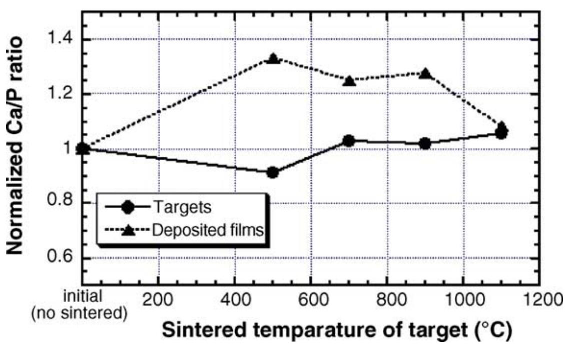

Fig. 1. Normalized Ca/P ratio of HAp targets and deposited films plotted as a function of the sintering temperature.