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Excimer laser deposition of apatite at room temperature on titanium substrates

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ABSTRACT. Highly adhesive apatite films were deposited by pulse laser sputtering of apatite target on Ti substrates at room temperature. The model of laser ablation/deposition of multi-component solids was discussed to explain the observed differences in the properties of films obtained from apatite mineral, sintered hydroxyapatite, and bone tissue targets.

INTRODUCTION

Hydroxyapatite (HA) is the mineral base of bone tissue and is used as a biologically compatible coating for medical and dental implants [1]. Plasma spraying is commonly used for HA deposition, but recently laser assisted film deposition techniques have been used successfully [2-4]. Crystalline films of HA have been obtained by manipulation of the laser fluence and the atmospheric conditions and use of high substrate temperatures, $>400^{\circ}\text{C}$ [2]. In our experiments, natural apatite [NA] samples were successfully used for film deposition of high quality coatings on Ti substrates at room temperature.

EXPERIMENTAL.

Three types of samples HA, NA and bone tissue were used as targets for apatite film deposition by KrF-excimer laser, $\lambda=248\text{ nm}$ (EMG-203, Lambda Physik). In our experiments the focused UV laser beam was scanned periodically across the target in order to avoid the formation of deep craters in the target. The laser pulse repetition rate was 5 Hz, pulse energy up to 300 mJ (controlled by attenuator), and laser pulse fluence on the target was $0.7\text{--}11\text{ J/cm}^2$. The target to substrate distances were 3.5 cm and a Ti foil target (0.05 mm thickness) was used as substrate for apatite deposition. The film thickness was varied from ~ 0.1 to $\sim 2\text{ }\mu\text{m}$ and the deposition rate was in the range $0.02\text{--}5\text{ }\text{\AA}/\text{pulse}$. Residual air pressure in the vacuum cell was maintained at $3\cdot 10^{-2}\text{ Torr}$.

The deposited apatite films were examined by SEM, FT-IR and-Raman spectroscopy. The film adhesion was determined by a scratch test; a unique quantitative method for very thin films [5]. The scratching was made by a corundum point with a $57\text{ }\mu\text{m}$ radius. The adhesive force was determined by

the maximum vertical load which could be applied to the point, without stripping the film from the substrate [5].

RESULTS

Most of our investigations were made with titanium substrates; an important implant material. The films deposited from HA and NA samples were mirror-like and scanning electron micrographs showed smooth surfaces with round shaped particles of 1-10 μm in size. Both the quantity and the size of particles controlled by increasing the laser fluence. The films deposited from bone tissue were much more spongy and round shaped particles appeared only at the fluences more than $\sim 5 \text{ J/cm}^2$.

The adhesion of films on Ti substrates vs fluence is shown in fig.1. With a substrate temperature of 400°C , both HA and NA films have excellent adhesion with a maximum fluence near $2\text{--}4 \text{ J/cm}^2$. This is in accordance with the results of [2]. Conversely, the adhesion of films obtained at room temperature from HA and bone was quite low. The most striking results were obtained with films prepared from NA at room temperature. In the fluence range $2\text{--}4 \text{ J/cm}^2$ those films have practically the same adhesion level as the films deposited at 400°C .

The films were investigated by FT-IR spectroscopy. The vibration bands of the phosphate ions (PO_4^{3-}) of HA appear in the range $550\text{--}610 \text{ cm}^{-1}$ and $1000\text{--}1100 \text{ cm}^{-1}$ respectively [6]. The film spectra, obtained from NA, and the initial spectra of HA and NA are given in fig. 2.

Fig.1. The adhesion of films obtained from different targets

Fig.2. FT-IR spectra of NA-(1), HA-(2) and NA films: at 20°C , 2 J/cm^2 -(3), 7.3 J/cm^2 -(4); at 400°C , 2 J/cm^2 -(5), 7.3 J/cm^2 -(6)

Note the close similarities between the spectra of HA and NA. The FT-Raman spectra of HA and NA films are also almost identical at the same laser fluences and substrate temperatures. As the laser fluence is increased, the maximum of the main absorption peak in the FT-IR spectra shifts to lower frequencies. A particularly striking feature of the spectra obtained at 400°C is the strong feature near 1110 cm^{-1} .

These data show that there is no direct correlation between the spectral features and the adhesion properties. However for different targets and substrate temperatures, we have shown that the mechanical properties of the films may be characterized by spectral methods without destruction of the materials.

DISCUSSION

The film adhesion at a given substrate temperature depends on the size (d) and velocity (v) of particles emitted from the target. The d and v values are determined firstly by ablation and secondly by collisional processes and other parameters. Laser irradiation of the targets results in emission of ions, atoms and micro particles of various sizes. These species reach the substrate with velocities $v \sim 10^5 - 10^6$ cm/sec. [7], and form a dense film. The particles with $d > 10 \mu\text{m}$ have $v < 10^4$ cm/sec. hence producing more spongy films with poor adhesion.

We have developed models for analysis of laser induced decomposition of multi-component materials [9-10]. Our models show that when the laser strikes the target, there is a fluence region in which the temperature front of the chemical reaction varies with time. Hence the gas pressure caused by the chemical and physical processes of ablation, also fluctuates. The pressure amplitude quickly reaches the durability limit [10, 11] resulting in mechanical destruction of the target and emission of macro-particles. The particle sizes are determined by the decomposition on the scale of reaction front distance and do not exceed the value $1/\alpha$, where α -absorption coefficient.

For HA and NA, vaporization is the main process of material ablation. However, vaporization may be accompanied by molecular decomposition. This process is a high temperature and must give the particles with the traces of melting. For bone ablation the decomposition of collagen at 350-400 °C leads to destruction before vaporization and the particles produced must show an irregular form.

Theoretical analysis [10] show that there is an optimal fluence region at which d is minimal and film adhesion is maximal. Our experimental results are in agreement with this model. For a quantitative comparison, a more precise definition of optical, thermal and mechanical parameters is

needed. The different adhesion properties of HA and NA films prepared at room temperatures may be caused by the differences in absorption coefficients or in mechanical properties of the target materials. At the high substrate temperatures, the crystallisation processes become more important [2]. Note, we estimate that the increase of substrate temperature due to the kinetic energy of evaporated particles was is less than 10K.

To ameliorate the film quality it is possible to introduce highly absorbing impurities into the initial materials. Thus increasing the energy absorbed by the targets or, one may use a laser wavelength at which the absorption of the target material itself is higher.

SUMMARY

We have developed laser sputtering techniques which allow deposition of high quality apatite films on to substrates at room temperature; the first time such low temperatures have been used successfully. We have deposited films on to titanium substrates and these show excellent adhesion characteristics. A theoretical model of laser ablation of multi-component solids was discussed to explain the differences in the experimental results obtained with different targets-HA, NA and bone tissue. We hope that these results will be useful to develop the practical technology of apatite film deposition for different medical and dental implants.

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