

Characterization of Calcium Phosphate Films Grown on Surgical Ti-6Al-4V By Ion Beam Assisted Deposition

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Abstract

The plasma-spray technique is currently the most frequently used method to produce calcium phosphate coatings. Hydroxyapatite(HAp), one form of calcium phosphate, is preferred by its ability to form a direct bond with living bone, resulting in improvements of implant fixation and faster bone healing. Recently, concerns have been raised regarding the viable use and long-term stability of plasma-spray HAp coatings due to its nature of comparatively thick, porous, and poor bonding strength to metal implants. Thin layers (maximum of few microns) of calcium phosphate were formed by an e-beam evaporation with and without ion bombardments. The Ca/P ratio of film was controlled by either using the evaporants having the different ratio of Ca/P with addition of CaO, or adjusting the ion beam assist current. The Ca/P ratio had great effects on the structure formation after heat treatment and the dissolution behavior. The calcium phosphate films produced by IBAD exhibited high adhesion strength.

Introduction

Hydroxyapatite(HAp) is well known as a biocompatible material. It has the ability to bond to osseous and epithelial tissue and is accepted by muscle tissue. The reason for its acceptability lies in a composition similar to the mineral phase of bone. However, synthetic HAp has poor mechanical properties, thus, is commonly applied to metallic implants as a coating material.¹ Of the various coating methods²⁻¹⁵, plasma spraying technique is currently the primary method used commercially to produce HAp coatings on metallic implants. However, problems such as low bond strength and non-uniformity in coating density are often observed with this coating technology. Accordingly, the need for improvement of HAp coatings with a thin and adherent film without defects were suggested.^{12-13, 15-16}

Variation of the material properties of calcium phosphate coatings have an effect on the bone-bonding mechanism and the rate of bone formation.¹⁷ It was suggested that local supersaturation of the constituent ions of the bone mineral phase (calcium and phosphate) arising from ion exchange between the coating surface and surrounding physiologic fluid could be a cause for the increased bone growth. Both the Ca/P ratio and the crystallinity of the HAp coatings are important parameters which determine its chemical dissolution characteristics. Existing methods of obtaining coatings of HAp have demonstrated a lack of control over the Ca/P ratio of the resultant coatings. The ability to accurately control the Ca/P ration is very important in determining the biocompatibility and the life time of the HAp coatings. In this study, electron beam evaporation with and without ion bombardment was investigated as a

means for producing calcium phosphate coatings on metallic implants. Since evaporation of compounds results in the difference in chemistry of coating,¹⁴ sintered granules of calcium phosphate with different ratio of Ca/P were used as an evaporation source. The films were characterized with SEM equipped with EDS and XRD. The effects of crystallinity on dissolution rates and bonding strengths were investigated.

Materials and Method

Ion Beam Assisted Deposition

Samples of 1" in diameter of ELI grade Ti-6Al-4V with thickness of 2mm were cut from annealed rod and polished through 1 μm with diamond paste. The different ratio of Ca/P evaporant was prepared by the addition of CaO powder (Cerac, Milwaukee, WI, USA) to HAp powder (Alfa, Ward Hill, MA, USA). The weight percent of 12, 18, 25 CaO powders were mixed with HAp powder by ball milling in ethanol for 24 hr with alumina ball. The slurry was dried in oven maintained at 70°C while stirring vigorously. The powder mixtures were hot-pressed at 1200°C for 2hr in atmosphere.

For the ion beam assisted deposition of calcium phosphate, an electron beam evaporator (15KW rated power supply, Telemark, USA) and an end-hall type ion gun (Commonwealth Scientific, USA) were employed, and the system is schematically shown in Figure 1.

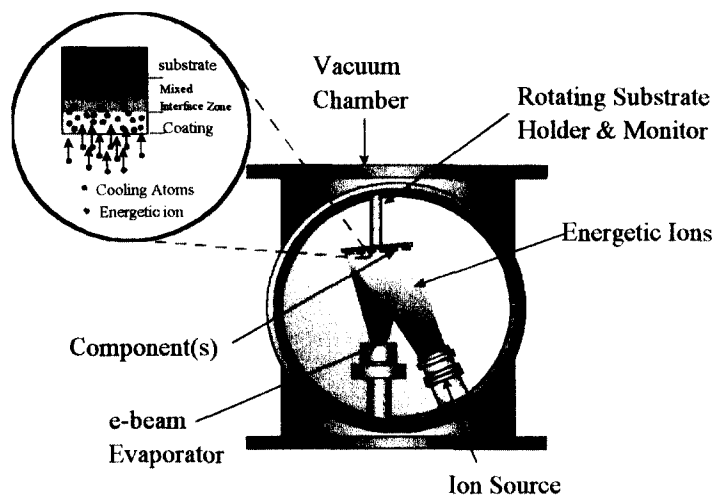


Figure 1. Schematic representation of IBAD system

Once a suitable vacuum (the usual base pressure for the system was 2×10^{-7} torr) was attained the ion gun was turned on and used for precleaning the substrate before deposition. The Ar ion beam was generated from the ion gun set to 120 V and 0.6 A. After 20 mins of precleaning, vapor fluxes of evaporants were generated with an electron beam evaporator and deposited on a rotating substrate to the thickness of approximately 6000 Å. The calcium phosphate coating were done with and without Ar ion assist, and Table 1 summarizes the deposition parameters

Table 1. Deposition parameters

Code	target	e-beam	Ion Beam	Phase
HA	HA	8.5 KV	×	β -TCP
IB06	HA	8.5 KV	130V 0.6A	β -TCP
IB08	HA	8.5 KV	130V 0.8A	HA
IB10	HA	8.5 KV	130V 1.0A	HA
CaO12	HA12CaO	8.5 KV	×	HA
CaO18	HA18CaO	8.5 KV	×	HA
CaO25	HA25CaO	8.5 KV	×	HA

Characterization of the Film

X-ray diffraction (Cu K_{α} , 50 KeV, 100 mA) was used to evaluate the structure of the as-deposited and heat treated condition. Since as-sputtered calcium phosphate films are amorphous, post deposition heat treatment was conducted in the vacuum of 3 mmTorr to obtain crystallinity. Samples were heated to 630°C with the heating rate of 5°C/min, and held for 1 hr, and then cooled in the furnace. The surface morphology and the Ca/P ratio was determined with a SEM (JEOL 5310, Japan) equipped with a EDS system (Oxford, UK).

Dissolution and Adhesion test

A Sebastian Five adhesion testing apparatus (Quad Group, Spokane, WA, USA) was used to measure the bonding strength of the film. An epoxy pre-coated aluminum stud (3.6 mm ϕ x 12mm) was vertically set to the sample. After curing at 150°C for 1 hr, the sample was inserted into the machine platen and gripped as shown in Figure 2. When activated, the stud was pull down against the platen support ridge until failure was occurred, and the tensile force required to cause failure was registered. The dissolution test was conducted in isotonic saline solution. The step between exposed area and unexposed area was measured by surface profiler (P-10TM, Tencor, USA).

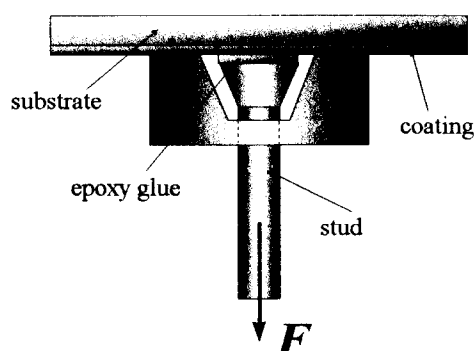


Figure 2. Schematic representation of adhesion test

Results and Discussion

Figure 3 shows the XRD patterns of the film (a) deposited with Ar ion bombardments, and (b) deposited using the evaporants of different Ca/P ratio.

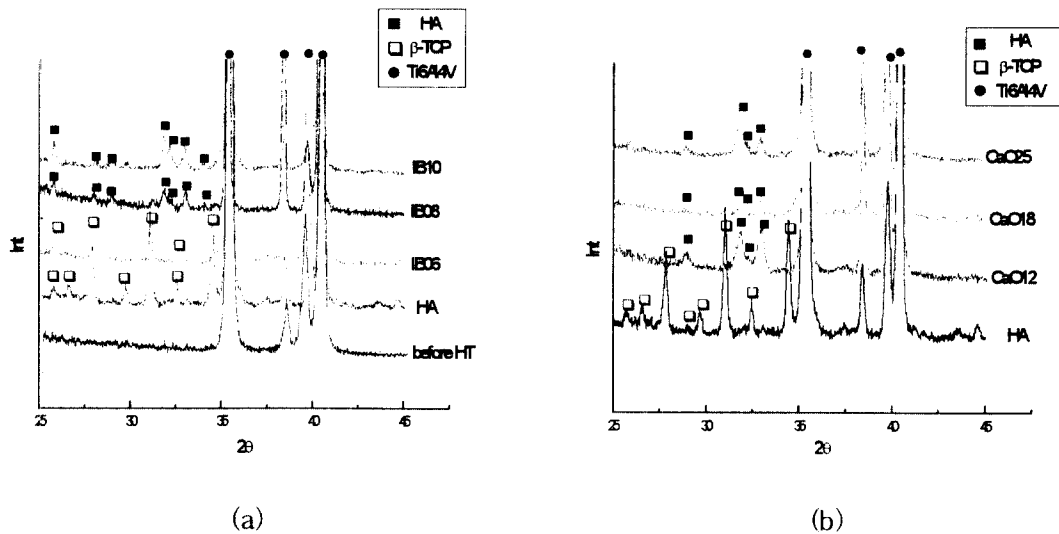


Figure 3. X-ray diffraction patterns of films deposited with (a) ion beam assist, and (b) different Ca/P ratio of evaporants

The as-deposited films did not produce any crystalline diffraction peaks other than for the substrate indicating amorphous structures. Heat treatment at 630°C for 1 hr changed the amorphous structure into β -TCP for the HA sample deposited using pure HAp evaporant and for the sample IB06 (Ar ion beam assist, 0.6A). But, the peaks were shifted to HAp with increasing ion beam assist currents (IB08, IB10). The structure formed after heat treatment is related to the Ca/P ratio of film (Figure 4)

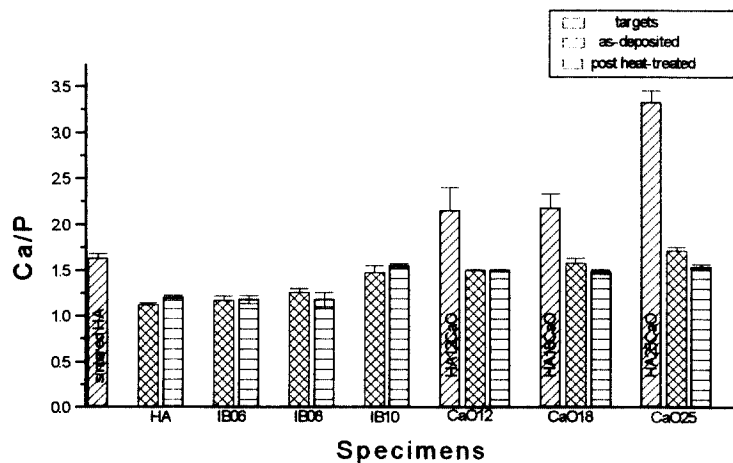


Figure 4. Ca/P ratio

The low Ca/P ratio of the sample HA and IB06 produces β -TCP, on the other hand the peaks of the high Ca/P ratio of the sample IB08, IB10, CaO12, CaO18, and CaO25 are comparable with the XRD patterns of HAp. The value of Ca/P ratio determined by EDS was calibrated with inductively coupled plasma atomic emission spectroscopy measurements (ICP-AES). Heat treatment process does not much affect the Ca/P ratio of films.

Figure 5 shows the dissolution behaviors of the as-deposited films. The sample HA ($t = 5730 \text{ \AA}$) dissolved completely within 8 hrs, while the same CaO12 (Ca/P = 1.5) dissolved only 150 \AA in 48 hrs. The solubility of the coatings is largely dependent on whether the coatings are crystalline or amorphous, and amorphous structure generally dissolve fast. However, it is very surprising that the amorphous structure of the sample CaO12 (Ca/P = 1.5) has such low dissolution rate. The reason for this is remains unclear at the present time, but it is speculated when calcium phosphate has the Ca/P ratio of 1.5, the radical of Ca^{+2} and $(\text{PO}_4)^{3-}$ are combined with electric neutrality, and the compound is the most stable form. This might be a reason why the sample CaO12 has very low dissolution rate. The dissolution rate of CaO25 is in between of HA and CaO12. More studies with samples of different Ca/P ratios and the heat treatment effects are currently conducting.

The bonding strengths of the as-deposited films are shown in Figure 6. The bonding strength are in the range of $35\sim 70 \text{ MPa}$ which is significantly higher than the plasma sprayed coating of 6.7 MPa .¹⁸ The failure mode was studied with reflected light microscope and is shown in Figure 7. Typical Wallner lines are shown in (a) radiating out from the center of the fracture surface. The failure started at the interface of substrate and film, and then proceeded to the fracture of film, which is typical fracture mode for high bonding strength. On the other hand, the films having low bonding strength debonded mostly at the interface as shown in Figure 7(b). Heat treatment usually reduces the bonding strength of coatings by inducing internal stresses caused by changing the density of the film, and the creation of an oxide layer from the substrate.¹² Heat treatment of calcium phosphate films formed by other methods is inevitable to improve dissolution rates, but is not necessary for the film deposited by e-beam evaporation with and without ion bombardments since the dissolution rate of the as-deposited film is very low and is controllable.

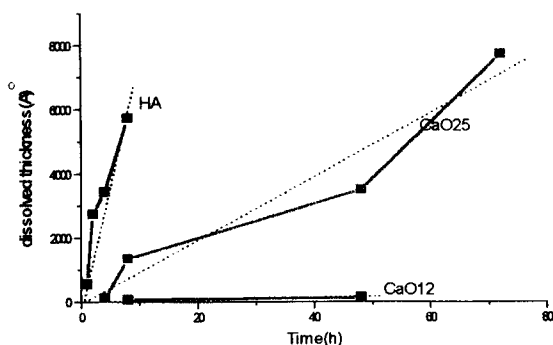


Figure 5. Dissolution behaviors

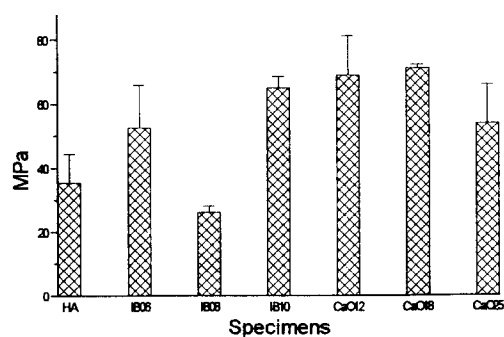


Figure 6. Bonding strength of as-coated



(a)

(b)

Figure 7. Photomicrographs of the debonded area

Conclusions

The calcium phosphate films having different ratio of Ca/P can be successfully formed by e-beam evaporation with and without Ar ion assist, and the following conclusions are drawn from this still on-going research.

1. The Ca/P ratio of calcium phosphate film is controlled by either evaporating the different Ca/P ratio of evaporants or by adjusting the ion beam assist current.
2. The as-deposited films having the Ca/P ratio of 1.1~1.2 produces β -TCP, while the Ca/P ratio of 1.5~1.7 crystallize to HAp upon heat treatment.
3. The sample CaO12 (Ca/P = 1.5) exhibits a very low dissolution rate even in the amorphous phase, and the dissolution rate is varied with the Ca/P ratio of film.
4. The calcium phosphate films deposited by ion beam assisted deposition have high bonding strength of 35~70 MPa.

Acknowledgement

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