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Structural and Compositional Characterization of Ion Beam Sputtered Hydroxyapatite Thin Films on Ti-6Al-4V

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ABSTRACT

Ion Beam Sputtering (IBS) technique has been used to prepare a series of hydroxyapatite (HA) thin films on Ti and Ti alloy substrates for biomedical application. We report the effect of Post Deposition Heat Treatment (PDHT) on the structural, compositional and surface characteristics of HA films deposited on Ti-6Al-4V. The films underwent PDHT for 2 h at 300, 400, 500 and 600°C under air environment. After PDHT, the structure and the chemical composition of the films were characterized using Rutherford Backscattering Spectrometry (RBS), X-ray Diffraction (XRD), Fourier transform infrared absorption spectrometry (FTIR) and Scanning Electron Microscopy (SEM). The results showed that the crystallinity of HA increased with temperature. However, SEM results revealed that some cracks were observed if the temperature of PDHT was higher than 600°C. FTIR measurements showed that the existence of hydroxyl and phosphate bands in all films increased with temperature. RBS analysis indicated that the as-deposited films had a low Ca/P ratio which increased to stoichiometric value with increasing PDHT temperature. From this study we suggest that 600°C is probably the best PDHT temperature to obtain a better characterization and surface properties of HA film produced by IBS. It can also be concluded that IBS can be used as an alternative method for deposit HA film on titanium alloy substrate.

Key words: Ion beam sputtering, hydroxyapatite, Ti6Al4V, RBS, post deposition heat treatment

INTRODUCTION

Many techniques have been utilised to prepare hydroxyapatite (HA) coating such as plasma spraying technique (Tsui *et al.*, 1998), sol gel technique (Weng *et al.*, 2003), biomimetic (Bigi *et al.*, 2005) and magnetron sputtering (Nelea *et al.*, 2003) for biomedical applications. Some technologies developed in semiconductor industry apply to fabrication of HA coating, such as ion beam technique (Yoshinari, 2009). The ion beam techniqueis able to deposit nano-scale and dense coating which results in better adhesion strength by the formation of diffusion layer at interface (Yoshinari, 2009). Hence, there is tendency to develop a thin film HA by ion beam sputtering which offer certain benefits such as homogeneous structure and high phase stability (Yang *et al.*, 2005; Ong and Lucas, 1994; Ong *et al.*, 1992).

Categorised as one of the calcium phosphate group, hydroxyapatite (HA), $Ca_{10}(PO_4)_6(OH)_2$ has attracted much attention due to its similar chemical composition to human bone and teeth. Moreover, it has excellent bioactivity and biocompatibility. Amongst the other calcium phosphates, HA is the most desirable phase having thermal stability and low solubility (Shi, 2006). The main problem with this material is its low toughness and brittle properties which limits the applications when high mechanical strengthis required especially to non-load bearing implants (Shi, 2006). However, this problem can be overcome by applying an HA coating onto bioinert materials-commonly titanium alloys that have superior mechanical strength and stiffness. Hence, there is interest in employing HA coatings on titanium alloy in biomedical applications. In addition, biological performance of titanium alloy can be enhanced by forming a bioactive coating on the surface. For this reason, HA is widely applied as a coating on metallic prosthesis and implants in biomedical applications.

The performance of HA coating could be evaluated with two important factors. Firstly, the composition and the properties of coating should ideally conform *in vitro* and *in vivo* performance. The structure and composition of HA coating plays an important role which can affect the thermal stability, biological response, mechanical properties and dissolution potential. Secondly, HA coating should remainadherent to the substrate for the long term application. So far, the main problem associated with current HA coating is the delamination and poor adhesive bonding. Most *in vivo* and clinical studies do not concentrate on the compositional and structural characterization of the coatings (Ong and Chan, 2000) which play a major role towards the adherence of the coating to the substrate. Therefore, for the long term implant applications, all these properties should be considered and designed for practical purpose to achieve a good coating performance. The aim of this study is to investigate the structural and composition of HA coatings produced by ion beam sputtering when coatings are subjected to post deposition heat treatment at different temperature. Emphasis is placed on the RBS characterization since this technique could give more reliable analysis on HA composition.

MATERIALS AND METHODS

Sample preparation: In this study, commercial purity (Ti-6 wt% Al-4 wt% V) titanium alloy was used as substrate. The coupon samples were cut into 10×10 mm squares from 3 mm thick Ti6Al4V plate. Prior to the ion beam sputtering deposition, the coupon surfaces were mechanically ground sequentially with 240 to 1200 grit SiC paper. They were then polished with diamond paste (OPS 6 to 1 μm grit size) to a mirror like finish. All samples were cleaned ultrasonically in acetone and dried in an air environment.

Ion Beam Sputtering (IBS) process: The deposition process was conducted using our in-house built system of ion beam sputtering (Kennedy *et al*., 2008; Murmu *et al*., 2012), as shown in Fig. 1. In this study, we used commercial HA target with 99.9% purity supplied by Able Target Limited. Prior to the deposition process, the titanium coupon substrates were first fixed to a rotating stage in a vacuum chamber. The high purity argon was used as a controlled gas atmosphere while the deposition was conducted at a pressure of 2×10^{-6} m bar with 0.4 mA of current. The primary argon (Ar+) ion beams with energy of 12.5 keVbombarded the target surface and sputtered a small amount of ion. The uniformity of the coatings was controlled by rotating the sample holder to the target rotation. The deposition rate was estimated to be 40 nm h^{-1}.

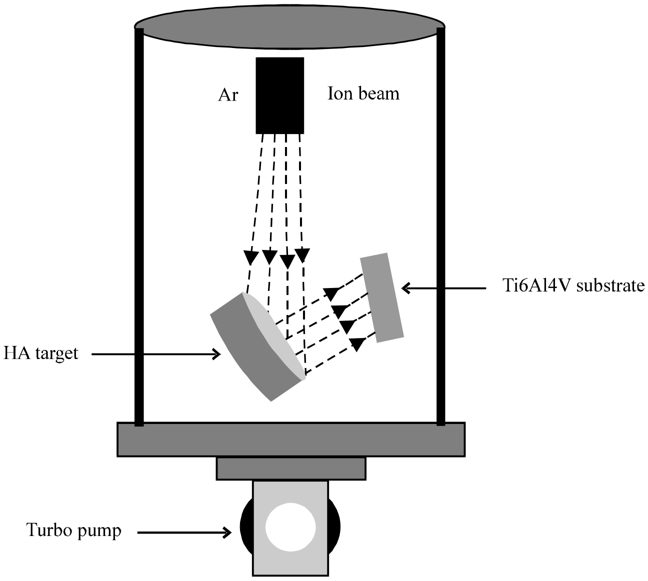


Fig. 1: Ion beam sputtering systems

Post Deposition Heat Treatment (PDHT): In order to change the amorphous phase of the as-deposited film to crystalline phase, the as-deposited samples were subjected to post deposition heat treatment in an air-circulated furnace between 300 and 600°C for 2 h with a heating rate of 10°C min^{-1}. The samples were then air-cooled to room temperature.

Characterization of HA coating: Several characterization processes were conducted after the deposition process. The phase identification was detected by using X-ray Diffraction (XRD), D2 PhaserBruker with CuK$_{\text{á}}$ radiation at 1.54056 Å. They were scanned from 20 to 35°2è angle at a step size of 0.02 and a count time of 1 s for each step. The Fourier Transform Infrared Spectroscopy (FTIR) analysis was also conducted in order to detect the functional groups present in HA films. Rutherford Backscattering Spectroscopy (RBS) was used to quantitatively profile the films composition. The morphology of the films was examined using an environmental scanning electron microscope (ESEM FEI 200 F). All the samples were coated with Pt prior to SEM analysis. The elemental analysis of the films was also performed using Energy Dispersive X-ray spectroscopy (EDS) equipped with a SiLi (Lithium drifted) detector.

RESULTS AND DISCUSSION

X-Ray diffraction: The as-deposited HA films produced in this study were amorphous. Figure 2 demonstrates the X-ray diffractions of HA films before and after PDHT. From the relative peak intensity in the XRD pattern, the existences of hexagonal HA were detected on the films after PDHT. These peaks were attributed to (200), (002), (210), (211), (300) and (202) HA crystal planes with JCPDS-ICDD card No: 01-073-1731. The growth of crystalline HA phase is signified by a more intense peak at 2O = 31.8° at higher PDHT 600°C. However, when the sample was subjected to 600°C, an extra small peak was detected at 2O = 25.1°. This was probably due to the phase transition of HA to a **β**-TCP at high temperatures. Noted that, in this studythe HA film remains amorphous at 300°C PDHT. The XRD results also showed that 400°C was the starting temperature for HA coating to start crystallisation.

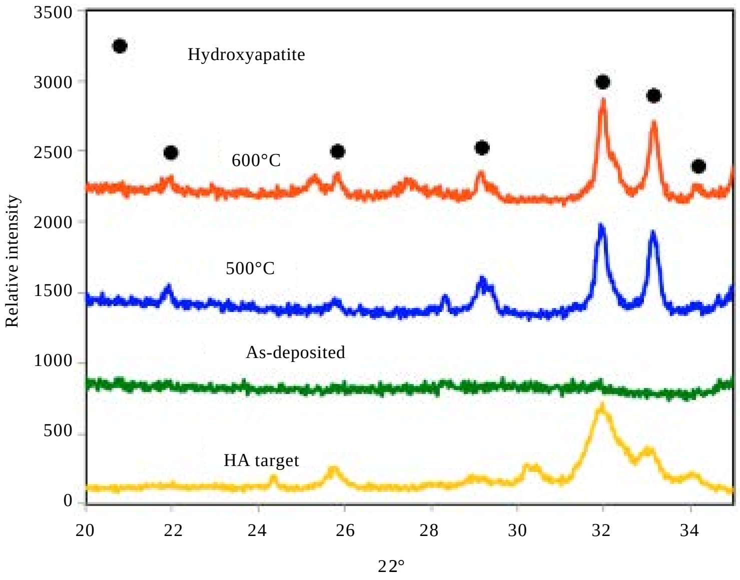
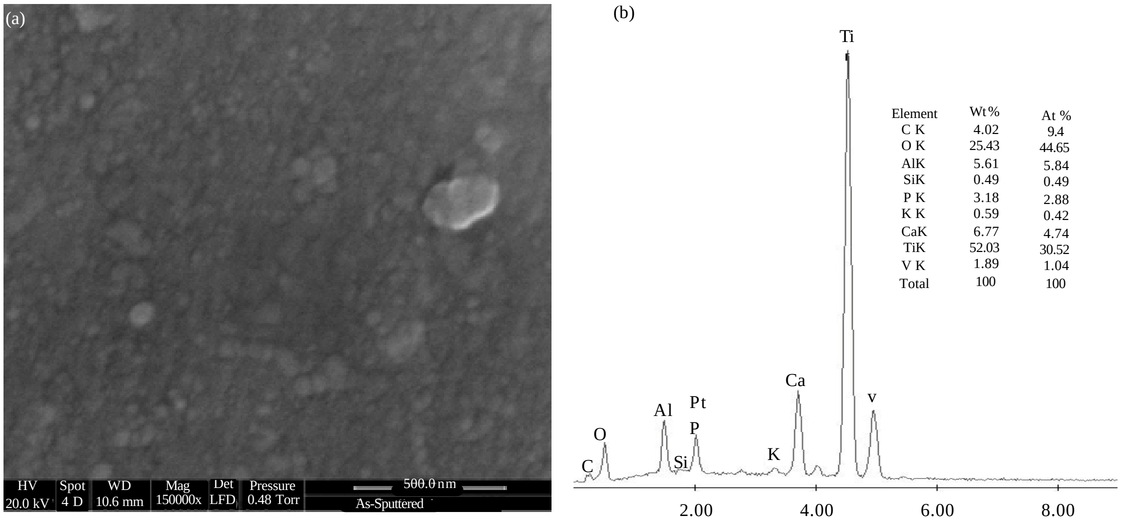


Fig. 2: XRD patterns of HA films on Ti6Al4V substrate before and after post deposition heat treatment

In support to XRD results, FTIR analysis was carried out to confirm the characteristic peaks of HA. The main band for HA target were assigned to the phosphate and carbonate group. The trend was observed at PDHT 500°C where a phosphate band and a carbonate band appeared around the same wave number. After a further PDHT at 600°C all bands became more pronounced showing the significance of PDHT. The crystallinity increased with increasing temperature, especially in the phosphate bands. Overall, all the samples exhibited the characteristic of HA on the films. These results also were in good agreement with the XRD analysis indicating the HA characteristic peaks and the transformation phase from amorphous to crystalline at higher PDHT.

Scanning Electron Microscope (SEM): Figure 3 shows the SEM micrograph of the as-deposited film. It reveals that the surface topography of the coating wasdense and homogeneous. The EDS spectra show the Ca/P ratio in the range of 1.5 to 1.7. The HA films produced were uniform and had an even distribution on the surface, Fig. 4. This figure shows the elemental mapping of distribution composition of the HA film with post deposition heat treatment at 600°C. According to this elemental mapping, the film was predominantly rich in Ca and P. The film was homogenously distributed with the presence of these elements. The fact that the Ca and P exist in the form of HA were already confirmed by the presence of HA peaks in the XRD and FTIR analysis. This elemental mapping result further confirmed that the distribution of Ca and P were continuous and uniform on the film.

In this study, the amorphous film produced by ion beam sputtering had a stoichiometric composition close to pure HA (Ca/P = 1.67) which leads to the transformation of crystallization at a lower temperature. However, during the post deposition heat treatment cracks were observed at a higher temperature of 600°C due to mis matched thermal expansion between the HA film and the substrate. Figure 5 presents an SEM image of the crack formed on the HA film subjected to PDHT at 600°C. It is noted that these cracks could be prevented by managing the heating rate during the post deposition heat treatment.



Element	Wt%	At %
C K	4.02	9.4
O K	25.43	44.65
AlK	5.61	5.84
SiK	0.49	0.49
P K	3.18	2.88
K K	0.59	0.42
CaK	6.77	4.74
TiK	52.03	30.52
V K	1.89	1.04
Total	100	100

Fig. 3(a-b): SEM micrograph of (a) surface morphology and (b) EDS spectrum of as-deposited HA film

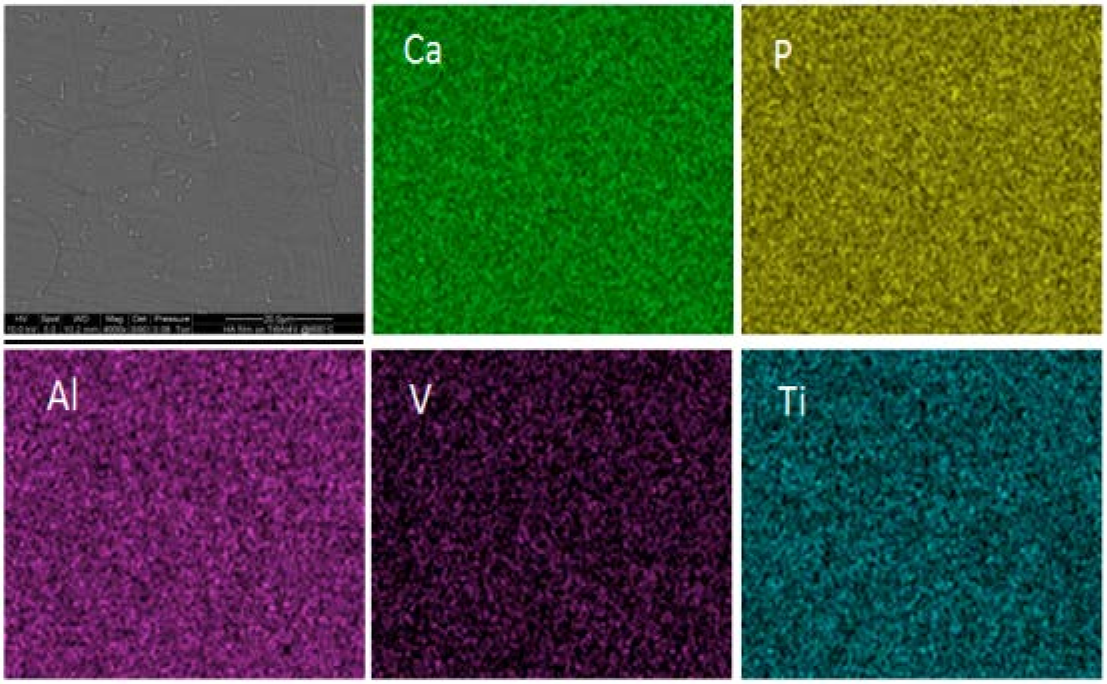


Fig. 4: Element mapping of HA film on Ti6Al4V at 600°C PDHT

Rutherford Backscattering Spectroscopy (RBS): Ion Beam Analysis (IBA) techniques such as Rutherford Backscattering Spectrometry (RBS), Particle Induced X-ray Emission (PIXE) and Nuclear Reaction analysis (NRA) were used to determine the composition and uniformity of the thin

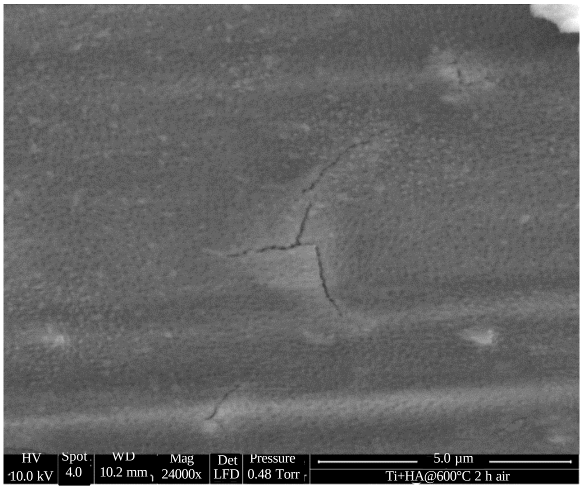


Fig. 5: Cracks were detected on HA film at 600°C PDHT

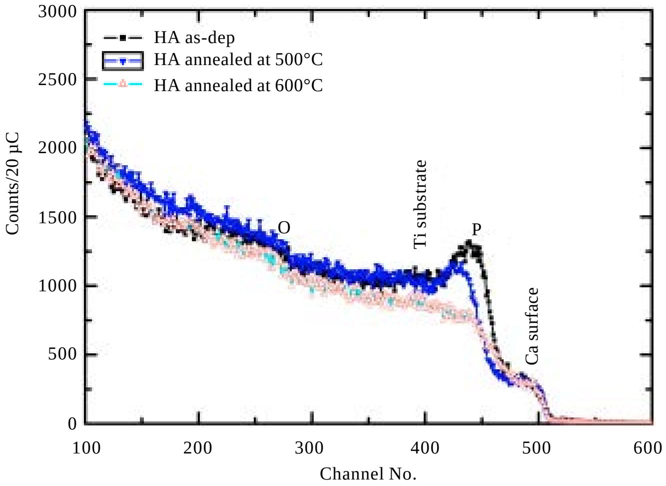


Fig. 6: RBS spectra of HA film deposited on Ti6Al4V substrate before and after post deposition heat treatment

films and to probe for impurities and to measure elemental depth profiles (Kennedy *et al*., 1999, 2001, 2006). We used a 2.0 MeV $^4He^+$ ion beam impinging on the samples under normal incidence using the 3 MV Van de Graaffaccelerator at the Institute of Geological and Nuclear Sciences, Lower Hutt, New Zealand. The surface barrier detector for measuring the energy of the backscattered particles was mounted at 165°. A low ion current density of 10 nA mm^{-2} was used to measure the samples non-destructively in short time (less than 15 min). Typical RBS spectra obtained on HA film deposited on Ti6Al4V substrate is shown in Fig. 6.

An RBS spectrum can be interpreted based on the following key principles: The energy of the elastically scattered beam is proportional to the mass of the target nuclei, the cross-section (yield of backscattered particles) is proportional to the elemental composition of the target material and the incident beam and the backscattered particles loose energy as they pass through the sample. Thus scattering events that occur at a certain depth occur at a lower energy in the spectrum. Elemental concentrations of matrix components and impurities can be investigated as well as depth profiles of almost every element of the periodic table can be measured. The RBS technique detects the number of atoms per unit area in a layer. Using the material density, the film thickness can be calculated in conventional units such as nm or μm. The energy loss of the ion contains depth information. Therefore, analysing the shape of the energy spectrum of the emitted ion yields (counts) information on the concentration profiles can be obtained. Thickness and composition information were extracted from the spectra using the data deconvolution software Rutherford Universal Manipulation Program (RUMP) (Doolittle, 1985).

It can be seen from Fig. 6, Calcium, Phosphorus and oxygen from the film can be detected and the peaks are overlapped since the substrate materials is Ti alloys which has higher mass than film elemental mass. Thickness of this particular film was 2.4×10^{18} at cm^{-2}, which corresponds to 650±20 nm by taking the HA material density into account. The composition ratio of Ca:P in as-deposited film was found to be 1.8 and has reduced to 1.6 after annealing as seen on the reduction of the P peak intensity. It was found that after annealing the HA film has diffused into the substrate as evidenced in the P peak shift observed in the annealed samples (Fig. 6 channel number from 470 to 440).

CONCLUSION

In this present study, HA films on Ti6Al4V were successfully deposited by ion beam sputtering technique. The films were subjected to different post deposition heat treatments which significantly affect the crystallinity and morphology on HA films. However, cracks were observed on the samples subjected to PDHT at 600°C due to mis match thermal expansion between the film and the substrate. RBS reveals that the film is stoichiometric after PDHT and composition of HA decreases gradually with depth inside the surface layer.

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