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Microanalyses of the hydroxyl-poly-calcium sodium phosphate coatings produced by ion beam assisted deposition

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Abstract Thin calcium phosphate coatings on titanium alloy substrates were prepared by Ar^+ ion beam assisted deposition (IBAD) from hydroxyl-poly-calcium sodium phosphate (HPPA) target. The coatings were analyzed by XRD, FTIR, XPS. These analyses revealed that the as-deposited films were amorphous or no apparent crystallinity. No distinct absorption band of the hydroxyl group was observed in FTIR spectra of the coatings but new absorption bands were presented for CO_3^{-2}. The calcium to phosphorous ratio of these coatings in different IBAD conditions varied from 0.46 to 3.36.

Keywords Hydroxyl-poly-calcium sodium phosphate, Coating, Titanium, Ion beam assisted deposition

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1 INTRODUCTION

Calcium phosphate-based biomaterials are biocompatible and bioactive materials. They are well known for their osteoconductivity.[1,2] However, the brittle nature of these ceramics limit clinical uses in load-bearing situation, for instance in the total hip replacement. Ti alloy is an implantation material and its mechanical properties are excellent. The use of different techniques to coat metallic implants with calcium phosphate-based biomaterials aims at combining mechanical properties of metals with the excellent bioactivity of these ceramics, which will improve bonding between the implants and newly

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formed bone.[3] In addition to bioactivity, a satisfactory calcium phosphate coating must be dense, hard, adherent and tough for clinical applications.[4] The ion beam sputtering deposition has been investigated as a method for producing bioactive ceramic coatings on metallic implants due to its various advantages, including the production of thin coatings of high density and superior adhesion.[5,6] In the present work, hydroxyl-poly-calcium sodium phosphate (HPPA) coatings on Ti alloy were produced by the ion beam assisted deposition (IBAD) and the structure and surface morphology of the coatings were analyzed by using XRD, FTIR and XPS.

2 EXPERIMENT

A commercially available Ti alloy substrate (cylinder of $\phi 12\,\mathrm{mm}\times 6\,\mathrm{mm}$) was mechanically polished and ultrasonically cleaned with acetone and alcohol. The hydroxyl-poly-calcium sodium phosphate (HPPA) powder with the chemical formula of $[\mathrm{NaCa_nP_mO_k}]_m\cdot \mathrm{H_2O}$ was synthesized using a wet method.[7] The HPPA powder disks, which were to be used as the ion beam deposition targets, were cold pressed following a standardized procedure. The HPPA coatings were then prepared by the ion beam assisted deposition technology.

The deposition system mainly consists of a Kaufman ion source and a Freeman ion source, a target holder, and a rotatable sample holder in the paths of both ion beams (Fig.1). The deposition chamber was evacuated to a base pressure of $(2.8\text{–}3.7)\times 10^{-4}$ Pa. Prior to the deposition, etching of substrates with 800 eV and 40 mA/cm^2 argon ions for 30 min was performed to clean the surface of titanium substrate. The energetic ion beam was produced by ionizing high purity argon gas (99.999% pure). After cleaning, the stage was rotated so that the titanium alloy substrates were placed in the path of the sputtered atoms. The calcium phosphate coatings were deposited by an $\mathrm{Ar^+}$ ion beam sputtering of 1200 eV and 40 mA/cm^2 for 60 min. The second $\mathrm{Ar^+}$ ion beam of 60 keV was used to homogenize the coatings and the dosages were 2×10^{15}, 7×10^{15} and 2×10^{16} ions/cm^2, respectively. An X'Pert-Pro-MPD-Philips X-ray diffraction (XRD) was employed to assess the structures of as-deposited HPPA coatings. The thin layer analysis technology was adopted. The incident angle of X-ray is 0.4°. Fourier transform infrared (FTIR) spectroscopy was performed on a Nicolet FTIR 20SXB machine for characterizing various functional groups of the coatings, especially the hydroxyl and phosphate groups. The FTIR spectra were obtained using the transmittance mode from 4000 to 400 cm^{-1}. Samples used for FTIR analysis had KCl crystal substrate and the coating which was deposited by sputtering from an HPPA target. For the X-ray photoelectron spectroscopic (XPS) analysis, the calcium phosphate coating/titanium samples were mounted on stainless steel stubs using double-sided adhesive and placed in a vacuum chamber. The vacuum chamber was then evacuated to minimum base pressure of 9×10^{-6} Pa. The MgK_α radiation (1253.6 eV) was used, and the coated surfaces were scanned over a range 0–1000 eV, with a pass energy of 100 eV. In order to determine the distribution of various elements in the thin Ca-P coatings, the depth profiling was accomplished by sputter-etching with various periods of time and hence the chemical composition of the coatings at different depth was obtained.

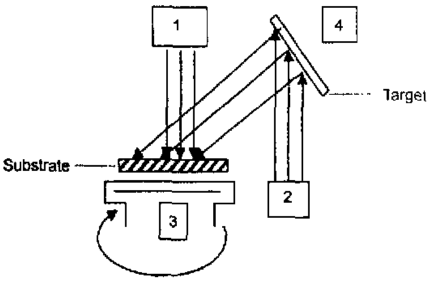

Fig.1 Schematic diagram showing the ion beam assisted deposition technique. (1) High-energy ion source for mixing, (2) Low-energy ion source for sputtering, (3) Sample holder, (4) Target holder

3 RESULTS

The XRD pattern of the as-sputtered calcium phosphate coating from the HPPA target is shown in Fig.2. As seen in this pattern, the as-sputtered coating only exhibited a broad bump between 27° and 23° and no peaks other than those of the titanium were observed, indicating that the as-sputtered coating was amorphous, or no apparent crystallines were produced.

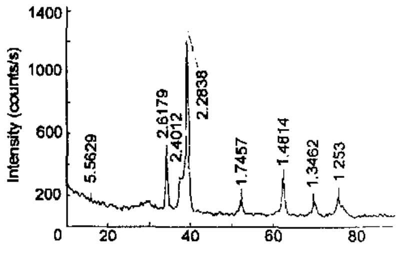

Fig.2 The XRD pattern of as-deposited coating from HPPA target

Figs.3 and 4 display, respectively, the typical FTIR spectra of HPPA target and the coating from the HPPA target that was deposited on the KCl crystal substrate. Compared with the FTIR spectrum of the HPPA target, many absorption bands disappeared in the FTIR spectrum of the as-sputtered coating. However, the absorption band at 1029 cm^{-1} was still observed, indicating the existence of PO_4^{-3} in the as-sputtered coating. No distinct absorption bands of the hydroxyl group were observed and new absorption bands at 1436 and 719 cm^{-1} were presented for CO_3^{-2}, which were brought about by the deposition process.

Table 1 lists the XPS results obtained from as-sputtered coating. The binding energies of Ca, P and O confirmed the existence of PO_4^{-3}. The binding energy of C at 284.6 eV indicated the presence of carbon contamination, and the binding energy of C at 288.6–288.9 eV indicated the existence of CO_3^{-2}, which was brought about by the deposition process.

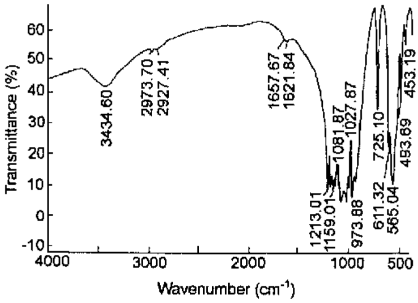

Fig.3 The FTIR spectrum of the HPPA target

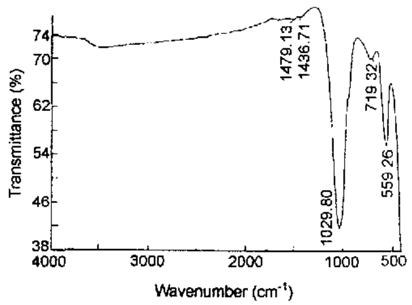

Fig.4 The FTIR spectrum of as-sputtered coating from the HPPA target

Table 1 Binding energies as a function of etching time for the as-sputtered coating

Etching time	Binding energy (eV)			
(min)	C_{1s}	Ca_{2p}	P_{2p}	O_{1s}
0	284.6/288.6	347.2	133.0	531.4
5	284.6/288.7	347.4	133.1	531.3
20	284.6/288.8	347.5	133.3	531.1
30	284.6/288.9	347.2	133.1	531.1

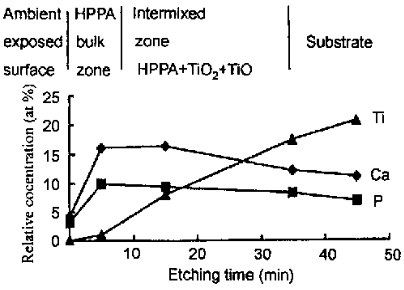

Fig.5 Depth profile of the HPPA coating produced by Ar$^+$ IBAD

Depth profiles of the HPPA coating produced is shown in Fig.5. It is found that the coating is divided into four regions. Due to Ar$^+$ IBAD, complete mixing of Ti and calcium phosphate can be achieved. Hence, the HPPA coatings on the Ti substrate possess superior adhesion. The XPS analysis reveals that the Ca/P ratio for the HPPA coatings using mixing dosages of 2×10^{15}, 7×10^{15} and 2×10^{16} Ar$^+$ ions/cm^2 are 3.36, 2.74 and 0.46, respectively.

4 DISCUSSION

The XRD analyses showed that as-deposited Ca-P coatings were amorphous. This "amorphous" appearance is a direct result of the ion beam assisted deposition technique. Because of the high vacuum and a relatively low temperature as compared with the plasma spraying coating method, there was not enough energy for the growth of nano-crystallites in the coatings during the deposition process and hence the as-deposited coatings were shown to be amorphous.

Variations for the phosphate group and the loss of the hydroxyl group in FTIR spectra were also caused by the ion beam deposition technique. During the deposition process, components of the target, such as phosphate and hydroxide or oxygen and hydrogen, may not be transferred completely to the substrate (or anchored on the substrate surface and remained in the coatings) because of the requirement of maintaining a low pressure in this particular coating method.

The variation in the Ca/P ratio among coatings is attributed to the fabrication parameter used. As phosphorus is very volatile, the low pressure during the sputtering process affects the anchoring of the sputtered phosphorus on the substrate. In addition, during the sputtering and the deposition process, the sputtering rate of calcium atoms is different from that of phosphorus atoms. On the other hand, a possible cause was the substitution of carbonate group for the phosphate groups in the HPPA molecule. The process of ion beam sputtering HPPA target was studied using theoretical analysis.[8] The results show that, because of the collision of sputtering ions and HPPA molecules, defects such as lattice displacement and vacancy are produced in the coating. Generally speaking, the higher ion energy is, the more defects are produced. These defects made it possible for the substitution of the carbonate group for the phosphate group in the HPPA molecule.

5 CONCLUSIONS

Dense and homogeneous HPPA coatings were successfully produced on titanium substrate using the ion beam assisted deposition. The results show that the as-deposited coatings are amorphous. Compared with the original HPPA target, some variations in chemical composition of the coatings were brought about in the deposition process, such as the distortion of the phosphate lattice, loss of hydroxyl groups, and the incorporation of CO_3^{-2}. However, no valence variation of the elements in the coatings was found. Depth profiling of the coatings reveals four distinct regions. The Ca/P ratios of the HPPA coatings vary from 0.46 to 3.36, which is related to the fabrication parameters.

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