Functionally graded calcium phosphate coatings produced by ion beam sputtering/mixing deposition

C.X. Wang\textsuperscript{a,b,\*}, Z.Q. Chen\textsuperscript{a}, M. Wang\textsuperscript{b}, Z.Y. Liu\textsuperscript{c}, P.L. Wang\textsuperscript{c}, S.X. Zheng\textsuperscript{c}

\textsuperscript{a}Department of Dental Materials, College of Stomatology, West China University of Medical Sciences, Chengdu 610041, Sichuan, China
\textsuperscript{b}School of Mechanical and Production Engineering, Nanyang Technological University, Nanyang Avenue, Singapore 639798, Singapore
\textsuperscript{c}Laboratory of Radiation Physics and Technology, Institute of Nuclear Science and Technology, Sichuan University, Chengdu 610064, Sichuan, China

Received 9 November 1998; accepted 20 September 2000

Abstract

\textsuperscript{32} Ar\textsuperscript{+} ion beam sputtering/mixing deposition was used to produce thin calcium phosphate coatings on titanium substrate from hydroxyl-poly-calcium sodium phosphate (HPPA) and HPPA + Ti targets. Three types of coatings (one type of monolayer coating and two types of functionally graded coating) were manufactured. It was found that as-sputtered coatings were amorphous. No distinct hydroxyl band was observed in the FTIR spectra, but new absorption bands were determined for CO\textsubscript{3}\textsuperscript{2-}, which resulted during the deposition process. Compositional gradients from the surface to the interior (i.e. adjacent to the substrate) were achieved for the functionally graded coatings. Post-deposition heat treatment indicated that the bonding strength between the coating and the substrate was improved by the use of functionally graded structures.

2001 Elsevier Science Ltd. All rights reserved.

Keywords: Ion beam sputtering/mixing deposition; Hydroxyl-poly-calcium sodium phosphate; Monolayer coating; Titanium; Functionally graded coating

1. Introduction

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 can lead to improved bonding between implants and the newly formed bone [1]. In addition to bioactivity, a satisfactory calcium phosphate coating must be dense, hard, adherent and tough for clinical applications [2]. Ion beam sputter deposition has been investigated as a method for producing bioactive ceramic coatings on metallic implants due to its various advantages, which include the production of thin coatings of high density and superior adhesion [3,4]. In this process, the ionized argon gas is used to sputter atoms from a ceramic target. These sputtered atoms build up on the metallic substrate that is placed in the path of the sputtered material.

One method to improve properties of coatings and the bond strength between the coating and the substrate is to employ a coating with a novel structure. Functionally graded materials (FGMs) have a gradient compositional change from the surface to the interior of the material. With the unique microstructure of an FGM, a specially designed material can perform specific functions and meet performance requirements. The great potential of FGMs has attracted much attention in different fields such as aerospace industry and electrical power generation [5,6]. In the field of biomaterials, several approaches have been used to develop functionally graded biomaterials for implants [2,7,8].

In this investigation, attempts were made to develop functionally graded coatings (FGCs) of calcium phosphate and titanium. These coatings would combine a strong adhesive strength to the titanium substrate with good bioactivity at the coating surface (or near-surface). Monolayer calcium phosphate coating and FGCs were produced by the ion beam sputtering/mixing deposition technique. In this paper, some preliminary results on the microstructure and adhesion strength of these coatings are presented.
2. Materials and methods

A commercially available pure titanium substrate (plates of dimensions 20 mm × 20 mm × 1 mm) was mechanically polished and ultrasonically cleaned with acetone and alcohol. Hydroxyl-poly-calcium sodium phosphate (HPPA) powder with the chemical formula of [NaCa₃P₆O₁₆]·H₂O was synthesized using a wet method [9]. HPPA powder disks and disks of HPPA powder mixed with pure titanium powder in different proportions, which were to be used as the ion beam sputtering targets, were cold pressed following a standardized procedure. Table 1 gives composition of the discs used in this investigation.

The deposition system mainly consisted of a Kaufman ion source and a Freeman ion source, a target holder, and a rotatable sample holder in the path of both ion beams (Fig. 1). The deposition chamber was evacuated to a base pressure of 2.8–3.7 × 10⁻⁴ Pa. Prior to deposition, etching of substrates with 800 eV and 40 mA/cm² 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 substrates were placed in the path of the sputtered atoms. The monolayer calcium phosphate coatings were sputter deposited by an Ar⁺ ion beam with 1200 eV and 40 mA/cm² for 60 min. The sputter deposited functionally graded coatings (FGCs) from the HPPA and HPPA + Ti disk targets were deposited by sputtering each target with a 1400 eV and 40 mA/cm² Ar⁺ ion beam for 30 min, respectively, in sequence (from the 100% Ti target to the 0% Ti target). For the sputtering/mixing deposited FGCs, after sputtering from each target with the Ar⁺ ion beam at 1400 eV and 40 mA/cm² for 30 min, the second Ar⁺ ion beam with 60 keV was used to homogenize the coating and the dosage was 1.5 × 10¹⁵ ions/cm². Samples used for Fourier transform infrared spectroscopy (FTIR) had KCl crystal substrate and the coating which was sputter deposited from an HPPA target.

X-ray diffraction (XRD) was employed to assess the structure of as-sputtered coatings. A Rigaku D/max-α X-ray diffractometer with Cu Kα radiation at 40 keV and 50–80 mA was used. FTIR was performed on a Nicolet FTIR 20SXMB machine for characterizing various functional groups of the coatings, especially the hydroxyl and phosphate groups. FTIR spectra were obtained using the transmittance mode from 4000 to 400 cm⁻¹. In order to evaluate the residual thermal stress in FGCs, post-deposition heat treatments of as-sputtered coatings were performed for 60 min at 500 and 650 °C, respectively, followed by furnace cooling to room temperature. The surface morphology of coatings was examined by using a scanning electron microscope (SEM, Hitachi X-650, Hitachi, Japan) and a scanning tunneling microscope (STM, Explorer STM/AFM, TopoMetrix Co., USA). To prevent charging, the samples for SEM observations were coated with a thin layer of carbon. Scanning tunneling microscopy (STM) is a relatively new technique for mapping a surface with high resolution. A probe can be sharpened to a few angstroms in radius at the tip and then brought to within about 2 nm above a flat surface. Piezoelectric mounts in the instrument control both lateral and up and down movements. This technique is based on the electron tunneling phenomenon, i.e., a current flow between the probe and the surface due to an overlap of the respective wave functions. The minute current, nanoamperes or less, varies exponentially with the tip–sample separation, about 10-fold per angstrom. The tunneling current is used to control the up and down movement. As the surface is scanned, a relief map (image) of the surface is obtained, with a resolution down to the atomic scale. A major advantage of STM over other imaging techniques is that the specimen does not have to be in vacuum; it can be in air or immersed in water or some other fluid. STM can be used to study conducting and semiconducting surfaces. As for X-ray photoelectron spectroscopy (XPS), the as-sputtered coatings on titanium substrate were mounted on stainless-steel stubs using double-sided adhesive and placed in the XPS vacuum chamber. The vacuum chamber was then evacuated to a minimum base pressure of 9 × 10⁻⁶ Pa. Using Mg Kα radiation (1253.6 eV), coating surfaces were scanned over a range of 0–1000 eV, with a pass energy of 100 eV. Relative atomic concentrations of all identified elements

<table>
<thead>
<tr>
<th>Ti weight percentage</th>
<th>100%</th>
<th>90%</th>
<th>70%</th>
<th>50%</th>
<th>30%</th>
<th>10%</th>
<th>0%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Actual weight (g)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti</td>
<td>200</td>
<td>180</td>
<td>119</td>
<td>65</td>
<td>30</td>
<td>10</td>
<td>0</td>
</tr>
<tr>
<td>HPPA</td>
<td>0</td>
<td>20</td>
<td>51</td>
<td>65</td>
<td>70</td>
<td>90</td>
<td>100</td>
</tr>
</tbody>
</table>

*The deposition sequence was from the 100% Ti disk target to the 0% Ti disk target.

![Fig. 1. Schematic diagram showing the ion beam sputtering/mixing deposition technique: (1) high-energy ion source for mixing, (2) low-energy ion source for sputtering, (3) sample holder, (4) target holder.](image)
were computed from multi-element data using peak areas and established elemental sensitivity factors. In addition, spectra for these elements were computer curve fitted to yield the best binding-energy values. The binding energies for the elemental photoelectron peaks were corrected for charging using the adventitious carbon (C1s) photoelectron peak at 284.6 eV as a reference. In order to investigate the distribution of elements in the deposited thin coating, depth profiling was accomplished by sputter etching the coating and obtaining chemical analysis data from the sputter-etched area. Using Ar$^+$ ions, a differentially pumped ion gun (equivalent to a sputtering rate of about 10 nm/min) with a potential of 4 kV was used to sputter etch the samples. The analysis of the sputtered surfaces was performed until the surface of the titanium substrate was reached.

3. Results

The XRD pattern of the as-sputtered monolayer calcium phosphate coating from the HPPA target is shown.
Table 2

<table>
<thead>
<tr>
<th>Etching time (min)</th>
<th>Binding energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cls</td>
</tr>
<tr>
<td>0</td>
<td>284.6/288.6</td>
</tr>
<tr>
<td>5</td>
<td>284.6/288.7</td>
</tr>
<tr>
<td>20</td>
<td>284.6/288.8</td>
</tr>
<tr>
<td>30</td>
<td>284.6/288.9</td>
</tr>
</tbody>
</table>

in Fig. 2. As can be seen in this pattern, the as-sputtered coating only exhibited a broad bump and no peaks other than those of the titanium substrate were observed, indicating that the as-sputtered coating was amorphous.

Figs. 3 and 4 display the typical FTIR spectra of HPPA powder and the monolayer coating from the HPPA target which was deposited on the KCl crystal substrate, respectively. Compared with the FTIR spectrum of HPPA powder, 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 939 cm$^{-1}$ were present for CO$_3^{2-}$, which was brought about by the deposition process.

In the present study, STM was used to investigate the surfaces of the as-sputtered monolayer coating. Fig. 5 shows typical STM images of as-sputtered coating on
titanium substrate using the HPPA target. In these STM images, a fibrous morphology (asparagus-like) can be seen. This morphology resembles the mineral component of hard tissues. The same morphology was observed in the growth of tricalcium phosphate ceramic [10].

Table 2 lists the XPS results obtained from as-sputtered monolayer 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.

The depth profiles of FGCs produced by Ar$^+$ ion beam sputtering and Ar$^+$ ion beam mixing deposition with both using HPPA + Ti targets are shown in Figs. 6 and 7, respectively. It can be seen that from the surface to the interior of the FGCs, the concentration of Ti increased, while concentrations of calcium and phosphorus decreased. In addition, compared with FGC produced by Ar$^+$ ion beam sputtering deposition alone, the composition changes in FGC produced by Ar$^+$ ion beam sputtering/mixing deposition are more gradual. Due to the Ar$^+$ ion beam mixing process, complete mixing of Ti and calcium phosphate could be achieved. Consequently, there was Ti element on the surface of the FGC produced by Ar$^+$ ion beam sputtering/mixing deposition, while no Ti element was detected on the surface of the FGC produced by Ar$^+$ ion beam sputter deposition.

Figs. 8 and 9 exhibit SEM micrographs of as-sputtered coatings and coatings after being heat treated at 500 and 650°C, respectively. It can be seen that as-sputtered coatings had smooth morphologies. When heat treated at 500°C, there were no cracks in coatings and no peel-off of the coatings was observed. When the temperature was raised to 650°C, peel-off occurred in the coatings. However, the coating peel-off in the FGC produced by Ar$^+$ ion beam sputtering/mixing deposition was slight, with the monolayer coating being the worst case.

4. Discussion

Variations for the phosphate group and the loss of the hydroxyl group were also caused by the ion beam deposition technique. During the deposition process, components of the target, such as 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 maintenance of low pressure for this particular coating method.

In FGCs, because of the compositional gradient, the residual thermal stress caused by the difference in coefficient of thermal expansion was relaxed to some extent. Therefore, during the post-deposition heat treatment, the peel-off in FGCs was minimal. Because of the relatively low temperature maintained in the ion beam sputtering/mixing deposition process as compared to that used in the plasma spraying process, there was not enough energy for the growth of nanocrystallites and hence the as-sputtered coatings were shown to be amorphous by
the XRD analysis while plasma sprayed coatings exhibited certain degrees of crystallinity. Post-deposition heat treatments can provide the energy needed for the growth of crystallites (Fig. 10). It can be seen that the crystallinity of coating increased, and the peaks for the Ca–P coating appeared, which confirmed that the as-deposited coatings were amorphous. This can also be the reason for changes in morphology of coatings after heat treatment. In the surface of the coatings, some crystalline-like morphology was apparent after heat treatments. However, due to the growth of crystallites, the formation of P–Ti compound at the coating–substrate interface and the difference in the coefficient of thermal expansion between Ti and calcium phosphate, some cracks were produced during the heat treatment process. Peel-off of calcium phosphate coatings may subsequently take place. Therefore, care needs to be taken to judiciously choose heat treatment temperature in order to improve the crystallinity of the amorphous coatings while avoiding coating peel-off.

5. Conclusions

Dense calcium phosphate-based coatings and calcium phosphate–titanium FGs can be produced by using the ion beam sputtering/mixing deposition technique. XRD analysis shows that the as-sputtered coating is amorphous. In comparison with the HPPA ceramic target, some changes in chemistry are brought about in coatings during the deposition process, such as the loss of hydroxyl groups and the incorporation of CO$_3^{2-}$. STM images reveal a fibrous morphology (asparagus-like) on the coating substrate. This morphology resembles the mineral component of hard tissues. A compositional gradient from the surface to the interior of the coating can be achieved and hence functionally graded coatings are obtained. The residual thermal stress in the coating due to the difference in coefficient of thermal expansion is relaxed in FGs.

Acknowledgements

The work reported in this paper was supported by the National 863 Program of New Technology and the National Natural Science Foundation of China. Professor W.C. Zhang of Chengdu Institute of Chemistry, Chinese Academy of Sciences, is thanked for the assistance in producing HPPA.

References


