CRYSTALLIZATION OF RF-MAGNETRON SPUTTERED AMORPHOUS CALCIUM PHOSPHATE

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Keywords: magnetron sputtering, calcium phosphates, crystallization, hydroxyapatite, high resolution transmission electron microscopy

Abstract: Crystallization of amorphous calcium phosphate (Ca-P) coating on Ti substrate has been investigated by Fourier transform infrared absorption spectroscopy and transmission electron microscopy (TEM). High resolution TEM was also used to elucidate crystal structure of the crystallized grains. The Ca-P coating on Ti substrate was performed by radio frequency magnetron sputtering of a sintered hydroxyapatite (HAp) target. As-sputtered Ca-P coating having 1.95 of Ca/P ratio was amorphous. Annealing the as-sputtered amorphous coating at 600 °C resulted in crystallization of the coating. Crystallized coating mainly consisted of tetracalcium phosphate (TTCP) and HAp grains. Grain sizes of TTCP and HAp were about 10–100 nm in diameter. CaO grains were also observed only near surface of annealed coating.

(Received June 30, 2004; Accepted August 25, 2004)

INTRODUCTION

Titanium and its alloys are widely recognized as candidates for bone replacement materials. However, they do not directly connect with living bones since Ti and Ti-alloys will be encapsulated by a fibrous tissue in the body. A pure titanium and its alloys with calcium phosphate (Ca-P) coating, such as hydroxyapatite (Ca5(PO4)3OH: HAp) and tricalcium phosphate (Ca3(PO4)2: TCP), can directly bond with living bones. Plasma-spraying method (PSM) is widely used for deposition of Ca-P coating. Although PSM possesses high productivity, the coating made by PSM would lose their cohesion with the substrate materials after implantation.1 Therefore, other deposition technique, such as radio frequency (RF) magnetron sputtering, is developed for the deposition of calcium phosphate coating. Some studies2-14 have shown that RF magnetron sputtering is one of efficient methods for deposition of thin calcium phosphate coatings on substrates. Bioactivity of Ca-P coatings on titanium by RF magnetron sputtering has been demonstrated by J. E. G. Hulshoff et al.2 They showed that rat bone marrow cells cultured on RF magnetron sputtered Ca-P coatings stimulated the formation of extra cellular matrix. In vitro experiments of bioactivity of RF magnetron sputtered Ca-P coatings also clarified the preferential growth of HAp in simulated body fluid.13 The Ca-P coating by RF magnetron sputtering is usually kept amorphous.2,5,7,9,11,13 Although amorphous Ca-P coating by RF magnetron sputtering has ability of cell attachment and proliferation almost same as a crystallized Ca-P coating5, the dissolution rate of amorphous Ca-P coating in Gomori's buffer, especially within a week, is lager three times than that of crystallized Ca-P coating.2 Thus, the heat treatments of amorphous Ca-P coating are usually performed for crystallization, being expected to enhance the long-term reliability of Ca-P coatings on Ti substrate. K. van Dijk et al. have studied effects of annealing time, temperature and water vapor on the structural and compositional changes of as-sputtered Ca-P coatings.4 They showed from X-ray results that amorphous Ca-P coatings annealed at 600, 800–1000 and 1200 °C in an argon flow crystallized into HAp, HAp+CaO and HAp+TCP, respectively. K. Yamashita et al.7 also have reported the crystallization of amorphous Ca-P coating at temperatures between 200 and 1200 °C. They confirmed the formation of several calcium phosphates, HAp, TCP, dicalcium phosphate and tetracalcium phosphate (Ca4P2O9: TTCP) depending on the composition of amorphous Ca-P coatings.

The studies on crystallization of amorphous Ca-P coatings conducted so far were examined mainly by X-ray diffractometry and Fourier transform infrared spectroscopy (FTIR). These experimental apparatus can not reveal the details of crystallized grains whose diameter is order of submicron. Therefore, the purpose...
Crystallization of RF-Magnetron Sputtered Amorphous Calcium Phosphate of the present study is to examine the crystallized grains of RF magnetron sputtered Ca-P coating mainly using transmission electron microscopy (TEM).

EXPERIMENTAL PROCEDURES

Pure titanium plates, 4×4×0.6 mm², were polished by using alumina powder of 0.05 μm in size. They were electropolished in a 10%HClO₄-2%CH₃OH-88%CH₃OH solution at -50 °C and 50 V, cleaned with acetone and rinsed with purified water in an ultrasonic bath. Ca-P coating on titanium plates was performed by RF magnetron sputtering (SVC-RFU, SANYU ELECTRON Co. Ltd.). Sintered hydroxyapatite plate (PENTAX Co. Ltd.) of 2 mm thick was used for target. The sputtering was done at power density of 5.1 W/cm² under Ar (99.9999%) gas pressure of 3 Pa. The as-sputtered coating was annealed at 600 °C for 3.6 ks in air. Chemical compositions of the target, as-sputtered coating and annealed coating were examined by X-ray Photoelectron Spectroscopy (XPS) (XPS-1600E, ULVAC-PHI Inc.). The XPS experiment was performed after Ar ion sputtering for 5min. Chemical bonds were examined with Fourier transform infrared spectrometer (FT/IR-430, JASCO Inc.). Microstructures were examined by both a conventional and a high resolution transmission electron microscopes, JEM2000EX and JEM3010, operating at 200 and 300 kV, respectively. The high resolution TEM images were recorded in imaging plate (FDL-UR-V, Fuji film Co. Ltd.) and were Fourier transformed by using software, "L Process" by Fuji Film Co. Ltd., for analysis of crystal structure of the grains in the coating. Thin foils for TEM to observe a cross-sectional view of the interface between Ca-P coating and Ti substrate were prepared with a focused ion beam (FB2000K, HITACHI Ltd.) equipment.

RESULTS AND DISCUSSION

Ca/P ratios of the HAp target, as-sputtered coating and annealed coating were 1.72, 1.95 and 2.09, respectively. The Ca/P ratio in the as-sputtered coating was higher than that in the target. This indicates that a deposition rate of phosphorous ions on the substrate during sputtering was lower than that of calcium ions. Since mass of phosphorus is smaller than that of calcium, phosphorus ions rather than calcium ions would more diverge by collisions with Ar ions. Such the divergence is expected to suppress a deposition rate of phosphorus ions, resulting in the higher value of Ca/P in the as-sputtered coating rather than that in the target.

Figure 1 shows the FTIR spectra of (a) the target HAp, (b) as-sputtered Ca-P coating and (c) Ca-P coating annealed at 600 °C for 3.6 ks. The spectrum of HAp target exhibits absorption bands at 440, 586, 603, 960, 1024, 1090, 1117 and 3580 cm⁻¹. Although some bands between 419 and 1117 cm⁻¹ correspond to those in the HAp target, the ν3 bands, at 1024 and 1117 cm⁻¹, are close to those detected in TTCP. Since the Ca/P ratio of annealed coating was about 2.1, which is close to the stoichiometric value of 2.0 for TTCP rather than 1.5 for β-TCP, the bands at 1024 and 1117 cm⁻¹ could be attributed to TTCP. The shoulder of the spectrum at 3580 cm⁻¹ indicates a little recovery of the O-H vibration in HAp during annealing. The FTIR spectrum of Fig.1(c) indicates that crystallization of the amorphous Ca-P coating into HAp and TTCP occurred.
Figure 2  TEM micrographs for the as-sputtered sample: (a) bright field image at/around the interface between coating and Ti substrate, (b) selected area diffraction (SAD) pattern taken from the Ti substrate and (c) SAD pattern taken from the coating, respectively.

Figure 3  TEM micrographs for the annealed sample at 600 °C for 3.6 ks: (a) bright field image at/around the interface between coating and Ti substrate, (b) dark field image taken with the reflection indicated by a white arrow in (c), and (c) selected area diffraction pattern.
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Table 1 (a) List of interplanar spacing (Å) of grains in the annealed coating evaluated from Fig. 3(c). Lists of interplanar spacing (Å) for the lattice plane (h, k, l) of (b) HAp (ICDD No. 9-432), (c) TTCP (ICDD No. 25-1137) and (d) β-TCP (ICDD No. 9-169).

<table>
<thead>
<tr>
<th>(a) Annealed coating</th>
<th>(b) HAp</th>
<th>(c) TTCP</th>
<th>(d) β-TCP</th>
</tr>
</thead>
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<tr>
<td>5.1</td>
<td>5.260 (1,0,1)</td>
<td>5.210 (1,1,0)</td>
<td></td>
</tr>
<tr>
<td>4.7</td>
<td>4.720 (1,1,0)</td>
<td>4.739 (0,0,2)</td>
<td>4.800 (1,1,3)</td>
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<td>3.473 (1,3,0)</td>
<td>3.450 (1,0,10)</td>
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<tr>
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<td>3.210 (2,1,4)</td>
<td></td>
</tr>
<tr>
<td>3.1</td>
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<td>3.160 (2,1,1)</td>
<td>3.110 (1,2,5)</td>
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<tr>
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<td>2.811 (-1,3,2)</td>
<td>2.880 (0,2,10)</td>
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<td>2.724 (2,1,2)</td>
<td>2.7570 (1,2,8)</td>
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<td>2.674 (1,1,12)</td>
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</tr>
<tr>
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<td>2.528 (3,0,1)</td>
<td>2.534 (2,2,2)</td>
<td>2.520 (2,1,10)</td>
</tr>
</tbody>
</table>

Figure 4  A series of high resolution TEM micrographs of the annealed coating. Magnified images of the regions 1 to 3 are shown in Figs. 5, 7 and 8.

substrate of as-sputtered specimen. Selected area diffraction (SAD) patterns taken from the Ti substrate and the coating are shown in Figs. 2(b) and (c), respectively. The SAD pattern in Fig. 2(c) shows a halo ring, indicating that as-sputtered coating is an amorphous state. This is consistent with the fact that the absorption bands in FTIR spectrum of as-sputtered coating were broadened. Figure 3 shows TEM micrographs for a specimen annealed at 600 °C for 3.6 ks: (a) bright field image, (b) dark field image taken with the reflection indicated by an arrow in (c), and (c) SAD pattern. Figure 3(c) shows Debye rings from the coating, indicating the crystallization of amorphous coating by the annealing. Dark field image in Fig. 3(b) shows that fine grains of about 10–100 nanometers in diameter formed in the coating. Interplanar spacing of the grains evaluated from Fig. 3(c) are tabulated in Table 1. Lattice spacing of HAp (ICDD No.9-432), TTCP (ICDD No.25-1137) and β-TCP (ICDD No.9-169), whose values are close to those obtained in the experiment, are also listed in Table 1. Table 1 indicates that since interplanar spacing shown in the table are very close to each other, it is difficult to identify the crystal structure of grains from the ring diffraction pattern in Fig. 3(c). In order to examine the crystal structure of...
Each grain, high resolution TEM (HRTEM) observation was carried out. Figure 4 shows a series of HRTEM images. In order to elucidate the crystal structure of the grains, we divided the image into three parts, the regions ① to ③, from the coating surface to the Ti substrate. Figure 5 shows HRTEM images of the coating close to the surface (in the region ① of Fig. 4). The area indicated by dotted rectangle is CaO.

Figure 6 (a) Magnified image of the area indicated by white-dotted rectangle in Fig. 5. (b) Fourier transformed pattern taken from the area indicated by square in (a). Key diagram of (b) revealed that the squared area in (a) is CaO.
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Figure 7 Magnified image of the region ② in Fig. 4. Fourier transformed pattern taken from the area indicated by arrows (a) and (b) are inserted in the figure. Areas indicated by open and solid squares indicate the areas having HAp and TTCP, respectively.

Figure 8 Magnified image of the region ③ in Fig. 4. Fourier transformed pattern taken from the area indicated by arrows (a) and (b) are inserted in the figure. Areas indicated by solid and crossed squares indicate the areas having TTCP and Ti, respectively.
Fourier transformed (FT) pattern taken from the area in the square is CaO. FT patterns are taken from all areas enclosed by the three kinds of squares in Fig. 5. Figures 5(a) to (c) show typical FT patterns taken from the areas of (a) to (c) in the HRTEM image. Key diagrams of Figs. 5(a) to (c) reveal that the areas (a) to (c) are HAp, TTCP and CaO, respectively. The areas of HAp, TTCP and CaO are marked with open, solid and centrally-dotted squares, respectively. It should be noted that CaO formed only in the vicinity of surface. A lack of phosphorus near surface due to evaporation during annealing would result in a preferential formation of CaO near surface. HRTEM images taken from region in Fig. 4 are shown in Fig. 7. Figures 7(a) and (b) are FT patterns taken from the areas indicated by arrows (a) and (b) in the HRTEM image. Key diagrams of Figs. 7(a) and (b) reveal that the areas (a) and (b) are Ti and TTCP, respectively. HRTEM observations reveal that the annealed coating mainly consists of TTCP and HAp grains. Since the Ca/P ratio in the as-sputtered coating was 1.95, which is close to the stoichiometric value of 2.0 for TTCP, TTCP would form in the as-sputtered coating during crystallization. By comparison between CaO-P2O5 quasi-binary phase diagram and CaO-P2O5-H2O quasi-ternary phase diagram, HAp is considered to be more stable rather than TTCP in the existence of H2O. H2O molecules in air might interact with the amorphous Ca-P coating to form HAp. If it occurs, large amounts of HAp grains should form near the coating surface. However, the distribution of HAp in the coating was relatively homogeneous through the coating. H2O molecules in air seem not to effect the formation of HAp. Although FTIR spectrum for as-sputtered coating exhibits an absence of absorption bands for structural OH vibration, hydroxyl ions coming from the HAp target probably exist in the as-sputtered coating. Such the hydroxyl ions in the amorphous Ca-P coating would promote a crystallization of HAp grains. The amount of hydroxyl ions in the amorphous coating, however, should be small since most hydroxyl ions would pump away or collide with Ar ions during sputtering, resulting in small absorption band for structural OH vibration in the FTIR spectrum as shown in Fig. 1(c).

CONCLUSION

Crystallization process of the amorphous Ca-P coating by RF magnetron sputtering has been investigated. As-sputtered Ca-P coating on Ti substrate was amorphous. Crystallization occurred by annealing at 600 °C for 3.6 ks was confirmed by the TEM and the FTIR experiments. The crystallized coating consists of HAp and TTCP grains of 10–100 nanometers in diameter. They were distributed in the coating homogeneously. Since Ca/P ratio in the as-sputtered coating was close to that of stoichiometric TTCP, TTCP was crystallized during annealing. Crystallization of HAp would be attributed to an existence of hydroxyl ions in the amorphous Ca-P coating. However, CaO formed near surface probably due to evaporation of phosphorus.

ACKNOWLEDGEMENTS

This work was supported in part by a Grant-in-Aid (No.14750565) for Scientific Research, Ministry of Education, Culture, Sports, Science and Technology, Japan. Thanks are also due to the INCS, Ehime University for using transmission electron microscope. This work was partly supported by "Nanotechnology Support Project" from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

REFERENCES

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