

CHARACTERIZATION AND DISSOLUTION BEHAVIOR OF SPUTTERED CALCIUM PHOSPHATE COATINGS AFTER DIFFERENT POSTDEPOSITION HEAT TREATMENT TEMPERATURES

Y. Yang, PhD
 C. M. Agrawal, PhD
 K.-H. Kim, PhD
 H. Martin, BS
 K. Schulz, PhD
 J. D. Bumgardner, PhD
 J. L. Ong, PhD

KEY WORDS

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Y. Yang, PhD, is with the Department of Restorative Dentistry, Division of Biomaterials, University of Texas Health Center at San Antonio, and C. M. Agrawal, PhD is with the Center for Clinical Bioengineering, University of Texas Health Science Center and the College of Engineering, University of Texas at San Antonio, San Antonio, TX.

K.-H. Kim, PhD, is with the College of Dentistry and Institute of Biomaterials Research and Development, Department of Dental Biomaterials, Kyungpook National University, Jung-Gu, Daegu, Korea.

K. Schulz, PhD, is with the Dave C. Swalm School of Chemical Engineering and the Biomedical Engineering Program, and J. D. Bumgardner, PhD, is an associate professor with the Biomedical Engineering Program and the Agricultural and Biological Engineering Department, Mississippi State University, Mississippi State, MS.

J. L. Ong, PhD, is professor in the Center for Clinical Bioengineering, University of Texas Health Science Center, and the Department of Restorative Dentistry, Division of Biomaterials, MSC 7890, University of Texas Health Center at San Antonio, 7703 Floyd Curl Drive, San Antonio, TX 78229-3900. Correspondence should be addressed to Dr Ong.

There is a lack of correlation between specific properties of hydroxyapatite coating surfaces, osseointegration processes, and implant success. The aim of this study was to evaluate the relationship between well-characterized structural and chemical properties of radio-frequency sputtered calcium phosphate (CaP) coatings and their dissolution behavior. Sputtered CaP coatings were evaluated as-sputtered (non-heat treated) or after 1 hour of postsputter heat treatments at 400°C or 600°C. All coatings were characterized by X-ray diffraction, X-ray photoelectron spectroscopy, Fourier transform infrared spectroscopy, and contact angle measurement. The dissolution behavior of CaP coatings in the presence and absence of proteins was also investigated. It was observed from this study that as-sputtered CaP coatings were amorphous. The 400°C heat-treated CaP coatings exhibited low crystallinity ($1.9\% \pm 0.4\%$), whereas the 600°C heat-treated CaP coatings were highly crystalline ($67.0\% \pm 2.4\%$). The increase of Ca/P ratio, PO_4/HPO_4 ratio, and the number of PO_4 peaks were observed to be consistent with the increase in heating temperature and the degrees of coating crystallinity. Phosphorus ions released from CaP coatings decreased with the increase of crystallinity of CaP coatings. In addition, immersion of CaP coatings in media containing proteins resulted in an increase in P ions released as compared with coatings immersed in media without proteins. It was concluded that the degree of CaP coating crystallinity can be controlled by varying the postdeposition heat-treatment temperature. It was also concluded that, aside from coating crystallinity, dissolution and reprecipitation of the coatings can be controlled by knowing the presence of proteins in the media and PO_4/HPO_4 ratio within the coatings.

INTRODUCTION

Hydroxyapatite (HA) and calcium phosphate (CaP) coatings are successfully used in dental and orthopedic implant therapies.^{1,2} However, there are still many concerns about the re-

sorption of HA coatings in a biological environment. It was suggested that dissolution of HA coatings may play a role in influencing early osseointegration,³ thereby resulting in the increased interfacial strength through early skeletal attachment and increased bone

contact with implant surfaces.^{4,5} However, it was also reported that exceedingly rapid dissolution may result in poor bone bonding to implant surfaces and coating disintegration, which may result in particulate debris formation.^{6,7}

Dissolution is an important variable and is affected by the characteristics of both the HA coating and the physiological solution.⁸ The critical coating specifications include purity (phase composition), crystallinity, Ca/P ratio, microstructure, porosity, surface morphology, surface roughness, coating thickness, and coating adhesion to implant surfaces. These variables, depending upon the processing parameters and the method of deposition, affect dissolution and reprecipitation of CaP materials, which will ultimately affect their short- and long-term clinical performance. Unfortunately, the performance-enhancing advantages of plasma-sprayed HA are mired by considerable controversy because of the lack of correlation between specific properties of the HA surface and implant success. This has led to many conflicting animal and clinical observations and, as a result, no consensus exists on the optimum HA coating properties required for the optimum rate of development of osseointegration.^{9,10}

Several experimental deposition processes exist for producing HA and CaP coatings, including electrophoretic codeposition,¹¹ sputter deposition,^{12,13} and high-velocity oxy-fuel combustion spray deposition.¹⁴ These experimental processes have been developed in an attempt to improve the adhesive, compositional, and structural properties of the coatings. Regardless of the deposition process used, it is the surface of the coating that is especially crucial for the fixation mechanism because of its direct contact with bone and body fluids on implantation. As such, characterization of the coatings before use is critical. In this study, the relationship between structural and chemical properties of CaP coatings and their dissolution behavior was evaluated. Char-

acterization of radio-frequency sputtered-CaP coatings after postdeposition heat treatment was performed by X-ray diffraction, X-ray photoelectron spectroscopy (XPS), Fourier transform infrared (FTIR) spectroscopy, and contact angle measurements. The dissolution behavior of sputtered coatings after different treatments was evaluated in the presence and absence of protein for a period of 12 days.

MATERIALS AND METHODS

Materials preparation

Titanium (Ti) grade 2 (Metal Samples, Munford, Ala) disks, 15.30-mm diameter and 2-mm thick, were used in this study. The Ti surfaces were prepared by wet grinding with 240-, 400-, and 600-grit silicon (Si) carbide paper to a surface roughness of $r_a = 0.37 \pm 0.01$ μm , as measured by profilometry (Surtronic 3, Taylor-Hobson, UK). These surfaces were ultrasonically degreased in acetone and ethanol for 10 minutes each, with deionized water rinsing between applications of each solvent. Passivation was accomplished by exposing the Ti samples to a 40% nitric acid solution at room temperature for 30 minutes (ASTM F86-76) and rinsing with deionized water, which was followed by air drying. The cleaned Ti disks were sputter coated with a thin CaP layer. In addition, glass slides were used as substrates for sputtering.

Sputter coating

Sputtering of CaP onto the cleaned Ti and glass slide surfaces was performed with a CMS-18 radiofrequency magnetron sputtering system (Kurt J Lesker Company, Clariton, Pa). The target used in the sputtering process was a 10.16 cm diameter sintered HA (0.635 cm thick) on a copper backing (Target Materials Inc, Dayton, Ohio). The base pressure in the sputtering chamber was $\leq 5.0 \times 10^{-6}$ torr. Sputter deposition of all samples was accomplished in a single batch with a process pressure of 1.0~1.5 mbar and a sputtering power of 200 W for 7 hours at a coating

rate of 60 nm per hour. After sputtering, the coatings of 0.42 μm thick (20 samples each group) were left as-sputtered or subjected to a postdeposition heat treatment at either 400°C or 600°C for 1 hour in a Thermolyne 48000 furnace (Barnstead International, Dubuque, Iowa).

X-ray diffraction

A D8 advanced X-ray diffractometer (Bruker, Madison, Wis) was used to characterize the structure of the CaP coatings. The X-ray diffractometer was equipped with a single Gobel mirror to yield a diffracted parallel beam while removing the $K\beta$ radiation. By using a grazing incidence attachment, a 0.35° soller slit, and a LiF (100) flat crystal monochromator to improve resolution and peak-to-background ratios, triplicate coatings were analyzed with $\text{Cu } K\alpha$ radiation at 40 KV and 30 mA. Triplicate coatings per treatment group were scanned from 25° to 35° 2θ at a scan rate of 0.1° per minute. Crystalline peak area in the range of 25° to 35° was calculated, and the crystallinity percentage of the coatings was quantified by correlating the crystalline peak area to an HA crystallinity standard curve. The HA crystallinity standard curve was derived by mixing known quantities of 100% crystalline and amorphous commercial HA powder (Hitemco Medical Applications Inc, Old Bethpage, NY). Crystallinity percentage of the coating was analyzed by analysis of variance (ANOVA), and differences in crystallinity were considered significant at $P < .05$.

X-ray photoelectron spectroscopy

Elemental and chemical composition of the surface layer of the disks was determined by XPS with a Physical Electronics Model 1600 surface analysis system (Phi, Eden Prairie, Minn). The system used an Mg electrode ($K\alpha$ radiation at 1253.6 eV) at 15 kV and 300 W as the X-ray source. Triplicate samples were positioned at a 45° take-off angle with respect to the analyzer. Two spots, approximately 800 μm in di-

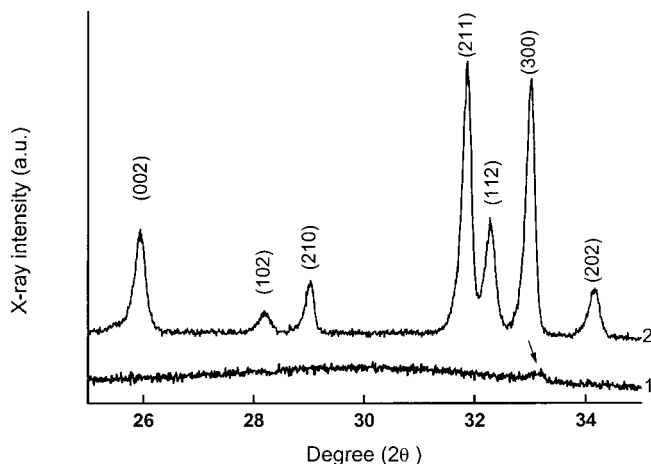


FIGURE 1. Representative X-ray diffraction patterns of sputtered calcium phosphate (CaP) coatings (1) after a 400°C heat treatment and (2) after a 600°C heat treatment. The arrow indicates the (300) peak.

ameter, were evaluated on each sample. Survey spectra were averaged from 10 scans with a pass energy of 46.95eV. Survey spectra were used to identify surface elements and to calculate their relative composition in atomic percent. High-resolution spectra of elements were averaged from 15 scans with a pass energy of 23.5eV. The high-resolution spectra were used to identify the chemical states and to estimate percentage of chemical species present. Quantitative analyses were based on peak areas and atomic sensitivity factors with the Spectral Data Processor v2.3 software (XPS International, Mountain View, Calif). The Ca/P ratio of coatings from different treatments was analyzed by ANOVA, and differences in Ca/P ratios were considered significant at $P < .05$.

Fourier transform infrared spectroscopy

Structural and molecular composition of coatings and sputtering target were evaluated with a model 550 Magna-IR FTIR spectroscopy (Thermo Nicolet, Madison, Wis). By using a resolution of 1 cm^{-1} and a scan number of 32, triplicate coatings per treatment group were analyzed from 400 cm^{-1} to 4000 cm^{-1} . Control Ti disks were used for background collection. For the CaP coatings, data collection was per-

formed with an 80° grazing-angle accessory.

Contact angles

Contact angles for 5 surfaces per group were measured with a VCA 2000 video contact angle system (Advance Surface Technology, Billerica, Mass). The contact angles, determined with drops of ultrapure distilled water, cell culture media (Dulbecco's modified Eagle's medium) and 1 mg/mL albumin solution, were measured at room temperature. The image of the water droplet was captured within 10 seconds of delivery. The results were analyzed by ANOVA, and differences in contact angles were considered significant at $P < .05$.

Dissolution study

The heat-treated and non-heat-treated CaP coatings were immersed in a 1.0 M Tris (Fisher Chemical, Fair Lawn, NJ) buffer containing $80\ \mu\text{M}$ NaCl (Fisher Chemical) in the presence and absence of 0.1 mg/mL bovine plasma fibronectin (Sigma Chemical Company, St Louis, Mo). The pH of solutions was balanced at 7.4 before the dissolution study. The experiment was performed in a sterile and humidified 95% air, 5% carbon dioxide atmosphere at 37°C . It is imperative that the pH of each solution is achieved after all chemical

components are added to the media and brought to 37°C . A Tris buffer was used to maintain a constant pH of 7.4 around each sample during the incubation period. The specimens were incubated in buffer solution at 37°C for 12 days. The buffer media were changed daily to ensure all parameters were equal with respect to the constitution of the media between each of the test specimens, especially with respect to quantities of calcium (Ca) and phosphate. As the buffer media were collected each day, the volume withdrawn and pH were recorded. Each dissolution sample was saved for subsequent analysis of phosphate release.

Measurement of inorganic phosphorus

The amount of phosphorus (P) ions released in solution each day was measured colorimetrically utilizing the reaction of ammonium molybdate and ascorbic acid with the inorganic phosphate to obtain a molybdenum blue complex. The reaction was done in a 96-well microtiter plate. Each sample was diluted 10-fold to make a $100\text{-}\mu\text{L}$ solution. Solution A was made by combining 2 parts double distilled water, 1 part 5.0 N sulfuric acid (Baker Analyzed, Phillipsburg, NJ), 1 part 0.01 M ammonium molybdate tetrahydrate (Sigma) in water, and 1 part 10% ascorbic acid (Sigma). Solution A was made fresh for each assay. To the $100\text{-}\mu\text{L}$ sample dilution, a $100\text{-}\mu\text{L}$ solution A was added. The complex was allowed to form for 1 hour at room temperature. It subsequently was read at 655 nm on a Benchmark microplate reader (Bio-Rad Laboratories Inc, Hercules, Calif). Each P concentration was calibrated with standard curve of P vs absorbance. ANOVA analyses for inorganic P ions released were carried out on the absorbance data, and differences were considered significant if $P < .05$.

RESULTS

X-ray diffraction

The as-sputtered CaP coatings were observed to be amorphous, whereas

TABLE 1

Atomic percentage (mean \pm SD; $n = 3$) of elements on the surface of Ti and CaP-coated Ti samples†

Sample	C	O	N	Ca	P	Si	Ti	Ca/P*
Ti control	58.2 \pm 4.3	34.6 \pm 3.6	1.4 \pm 2.0	1.3 \pm 1.6	—	2.7 \pm 0.6	1.9 \pm 0.6	—
CaP, not heat treated	45.7 \pm 3.5	38.2 \pm 2.4	1.1 \pm 1.4	8.4 \pm 0.8	5.43 \pm 0.9	1.1 \pm 1.1	—	1.6 \pm 0.2 ^a
CaP, heat treated at 400°C	57.8 \pm 5.2	30.1 \pm 4.5	0.4 \pm 1.1	7.6 \pm 1.3	3.0 \pm 0.7	1.0 \pm 1.1	—	2.6 \pm 0.3 ^b
CaP, heat treated at 600°C	52.2 \pm 5.7	33.1 \pm 4.6	0.3 \pm 0.8	8.6 \pm 1.2	3.5 \pm 0.6	2.2 \pm 0.7	—	2.5 \pm 0.2 ^b

†Ti indicates titanium; CaP, calcium phosphate; C, carbon; O, oxygen; N, nitrogen; Ca, calcium; P, phosphorus; Si, silicon.

*Values with the same superscript are not statistically different for the CaP-coated samples at $P \leq .05$.

crystalline peaks were observed for the heat-treated coatings (Figure 1). A single peak was observed for the 400°C heat-treated CaP coatings, whereas peaks matching apatite-type structure were observed for the 600°C heat-treated CaP coatings. Crystallinity of the 400°C and 600°C heat-treated CaP coatings were $1.9\% \pm 0.4\%$ and $67.0\% \pm 2.4\%$, respectively.

X-ray photoelectron spectroscopy

Representative XPS survey spectra of the as-sputtered CaP coatings and heat-treated CaP coatings indicated the presence of Ca, P, and oxygen (O). Adventitious carbon (C) and Si from the grinding process were also detected. The relative surface composition of the elements for the samples is shown in Table 1. The C concentrations on the surfaces of as-sputtered CaP coatings, 400°C heat-treated CaP coatings, and 600°C heat-treated CaP coatings were $45.7\% \pm 3.5\%$, $57.8\% \pm 5.2\%$, and $52.2\% \pm 5.7\%$, respectively. Significant differences in C concentrations between as-sputtered CaP coatings and 400°C heat-treated CaP coatings ($P = .0008$) and as-sputtered CaP coatings and 600°C heat-treated CaP coatings ($P = .037$) were observed.

The as-sputtered CaP coatings exhibited a near-HA stoichiometric ratio of Ca/P on the surface, whereas both of the heat-treated CaP coatings exhibited a significant enrichment of Ca relative to P ($P \leq .0001$). There was no difference between the surface Ca/P ratio for the heat-treated samples ($P > .05$).

Representative high-resolution spectra for P from the CaP coatings

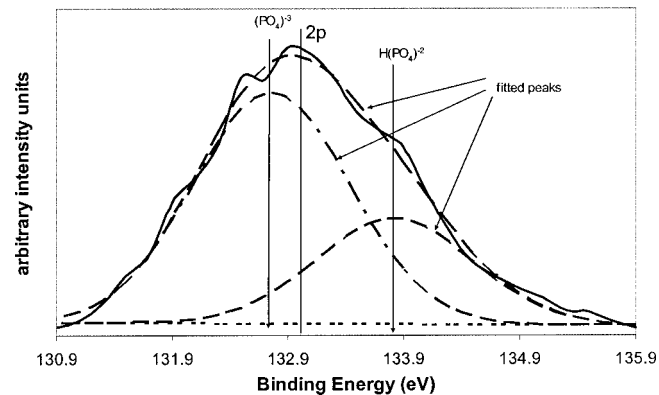


FIGURE 2. Representative high-resolution 2p spectra of calcium phosphate (CaP) coatings with X-ray photoelectron spectroscopy. The 2p were curve-fitted showing 2 peaks at 132.7 eV and 133.7 eV.

TABLE 2

Estimate of percentage (mean \pm SD; $n = 3$) of $(\text{PO}_4)^{-3}$ and $\text{H}(\text{PO}_4)^{-2}$ species from P high-resolution spectra of CaP-coated Ti samples*

Sample	$(\text{PO}_4)^{-3}$ [~132.7 eV]	$\text{H}(\text{PO}_4)^{-2}$ [~133.7 eV]	Ratio
CaP, not heat treated	67 \pm 5	32 \pm 5	2.2 \pm 0.7
CaP, heat treated at 400°C	67 \pm 12	32 \pm 12	2.5 \pm 1.4
CaP, heat treated at 600°C	72 \pm 12	28 \pm 12	3.4 \pm 2.3

*P indicates phosphorus; CaP, calcium phosphate; Ti, titanium.

showed that 2 peaks were found to fit to the 2p peak (Figure 2). The peak at approximately 132.7 eV corresponded to $(\text{PO}_4)^{-3}$ type species, and the peak at approximately 133.7 corresponded to $\text{H}(\text{PO}_4)^{-2}$ type species. As shown in Table 2, the PO_4/HPO_4 ratio increased with the heat treatment temperature. However, no statistical differences caused by the different heat treatments were found between the 2 phosphate species peak areas ($P = .7$). Significant differences in O concentrations also were observed on surfaces of as-sputtered CaP coatings as compared with

400°C heat-treated CaP coatings ($P = .003$) and 600°C heat-treated CaP coatings ($P = .037$).

FTIR spectroscopy

No hydroxyl (OH) group peak was observed in as-sputtered CaP coatings and 400°C heat-treated CaP coatings (Figure 3). For 600°C heat-treated CaP coatings, an OH peak at 3572 cm^{-1} was observed. The number of PO_4 peaks was observed to increase with increasing heat treatment temperature. Two PO_4 peaks at 547 cm^{-1} and 458 cm^{-1} were observed in as-sputtered CaP

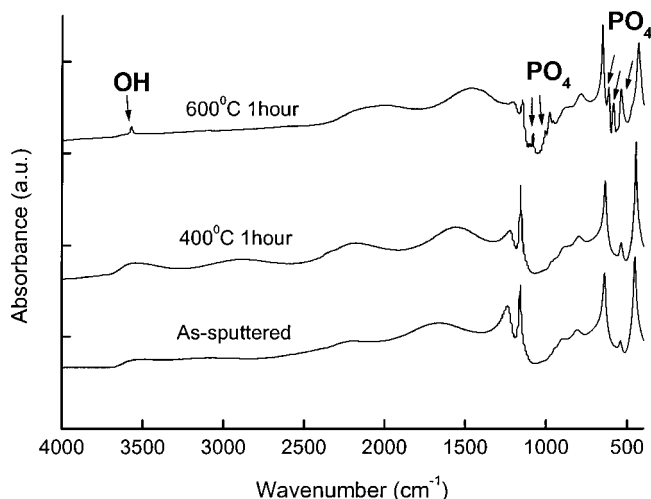


FIGURE 3. Representative fourier transform infrared spectra for as-sputtered calcium phosphate (CaP) coatings, 400°C heat-treated CaP coatings, and 600°C heat-treated CaP coatings. The arrow indicates the OH and phosphate peaks.

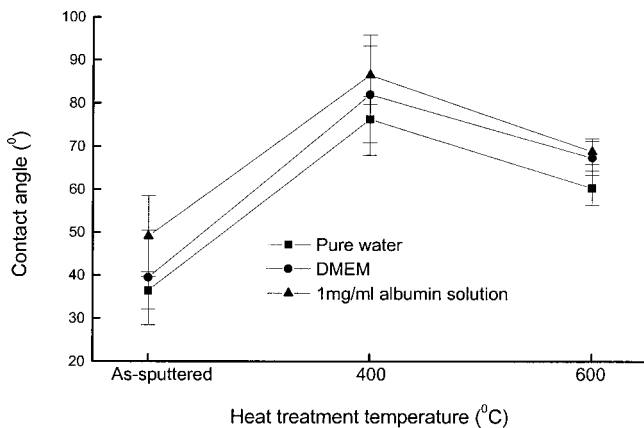


FIGURE 4. Contact angles for as-sputtered calcium phosphate (CaP) coatings, 400°C heat-treated CaP coatings and 600°C heat-treated CaP coatings.

coatings and 400°C heat-treated CaP coatings. In addition to these peaks, additional PO_4 peaks at 1084 cm^{-1} , 964 cm^{-1} , 617 cm^{-1} , and 585 cm^{-1} were observed for 600°C heat-treated coating. Other peaks (3365 cm^{-1} , 3735 cm^{-1} , 1253 cm^{-1} , 1158 cm^{-1} , 915 cm^{-1} , 812 cm^{-1} , 656 cm^{-1}) were also observed for all coatings.

Contact angle

As shown in Figure 4, significantly different contact angles were observed for as-sputtered CaP coatings, 400°C heat-treated CaP coatings, and 600°C heat-treated CaP coatings. Highest contact angle was observed for the 400°C heat-

treated CaP surfaces. Significant differences of contact angles on as-sputtered CaP coatings, 400°C heat-treated CaP coatings, and 600°C heat-treated CaP coatings were observed regardless of the media used.

Dissolution study

Phosphorous ions released in the presence and absence of protein for as-sputtered CaP coatings, 400°C heat-treated CaP coatings, and 600°C heat-treated CaP coatings are shown in Figures 5a through b. It was observed that in the presence and absence of protein, a significantly lower amount of P ions was released from the 600°C heat-treat-

ed surfaces. The 400°C heat-treated CaP coatings were observed to release more P ions compared with the 600°C heat-treated CaP coatings, and the as-deposited CaP coatings were observed to have the greatest amount of P ions released. Significant differences were found in released P ions levels on the first day between as-sputtered CaP coatings and 600°C heat-treated CaP coatings ($P = .00025$). Samples immersed in media containing proteins were observed to release significantly higher concentrations of P ions as compared with coatings immersed in media without protein.

DISCUSSION

Although HA and CaP coatings have been successfully used in dental and orthopedic implant therapies, many conflicting animal and clinical observations abound regarding their clinical outcomes.^{9,10} It is generally known that variation in the chemical and physical characteristics of the CaP and HA coating affect early bone cell activity, thereby influencing long-term success.¹ As such, it is critical to characterize the surface of the coatings before biological evaluations in vitro and in vivo.

In this study, the as-sputtered CaP coatings were observed to be amorphous, indicating that the sputtering process resulted in a loss of the apatite-type structure found on the HA target. Postdeposition heat treatment allowed CaP coatings to crystallize, forming an apatite-type structure. A significant increase in the degree of coating crystallinity was observed as the heating temperature was increased. Amorphous-to-crystalline phase transformation temperature has also been reported during the post-plasma-sprayed heat treatments of D-Gun-sprayed HA coatings.¹⁵

Surface analysis with XPS indicated the presence of adventitious C and silica contaminations on surfaces of sputtered CaP coatings. Significant differences in C concentrations between as-sputtered CaP coatings and 400°C heat-treated CaP coatings and as-sput-

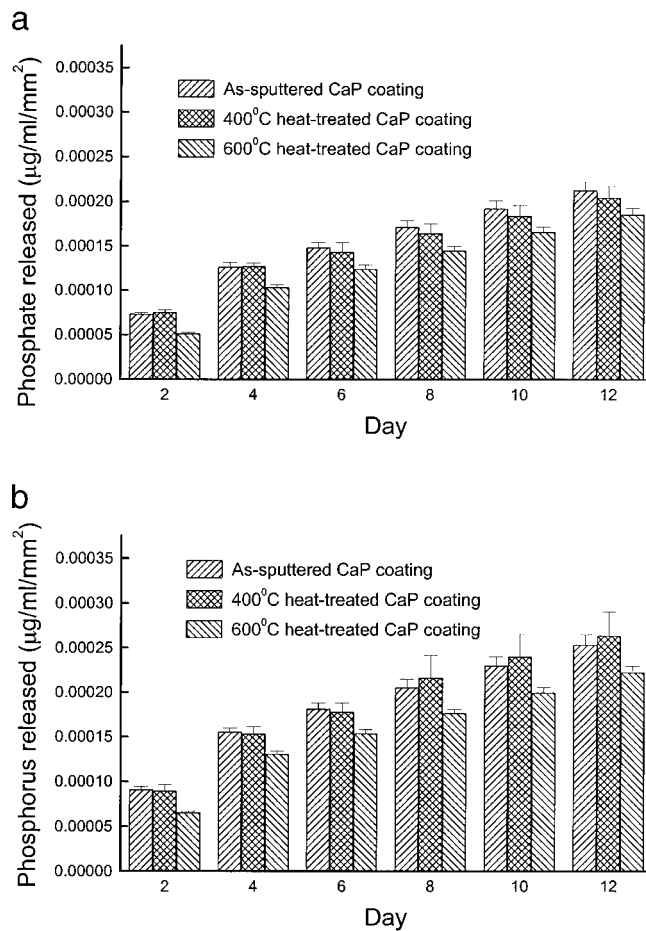


FIGURE 5. Phosphate release in a 1.0 M Tris buffer in the absence (a) and presence (b) of protein for as-sputtered calcium phosphate (CaP) coatings, 400°C heat-treated CaP coatings, and 600°C heat-treated CaP coatings.

tered CaP coatings and 600°C heat-treated CaP coatings were observed, with the highest C concentrations observed on surfaces of the 400°C heat-treated CaP coatings. It was suggested that the C contaminants were mainly in the form of carboxyl groups (CH_x) rather than the carbonate groups (CO₃).^{16–18} This observed significant concentration difference in surface carboxyl contaminant was confirmed with contact angle measurements, showing significant differences in contact angles between the different heat-treated CaP coatings. In addition, differences in contact angle measurements on coatings may be attributed to the significant differences in O concentrations on the CaP surfaces of different heat treatments.

Compositional analysis of the as-sputtered coatings with XPS also indicated a near-HA stoichiometric ratio of Ca/P on the surface, whereas heat-treated CaP surfaces were observed to exhibit a significantly enriched Ca surface. No significant difference between the surface Ca/P ratio of the 400°C and 600°C heat-treated samples was observed. It was suggested that differences in Ca/P ratio between the as-sputtered and heat-treated CaP coatings may have been the result of Ca ion (Ca²⁺) diffusion from bulk-to-surface during the heat treatments.¹⁹

XPS analysis indicated an increase of PO₄/HPO₄ ratio as postdeposition heat-treatment temperature was increased. This increase in PO₄/HPO₄ ratio was consistent with the increasing

degree of coating crystallinity as a result of increasing heat-treatment temperature. In addition, the increasing number of PO₄ peaks observed during the FTIR analysis as a result of increasing postdeposition heat-treatment temperature was also consistent with the increasing degree of coating crystallinity. It was suggested that HPO₄, to some degree, indicated crystal imperfection.^{20,21} By using high resolution transmission electron microscopy, other investigators have shown that higher annealing temperature not only increased grain size or crystallinity, but also improved crystal formation by minimizing the number or preventing the formation of crystal defects.²²

Generally, it was reported that CaP coatings immersed in media would first experience dissolution followed by achievement of a dissolution and reprecipitation equilibrium.²³ Such changes in factors influencing the equilibrium would change the dissolution behavior. In this study, the release of P ions from the coatings was measured. In the presence and absence of protein, a significantly lower amount of P ions was released from the 600°C heat-treated surfaces. The 400°C heat-treated CaP coatings were observed to release more P ions as compared with the 600°C heat-treated CaP coatings, and the as-deposited CaP coatings were observed to have the greatest amount of P ions released. Significant differences in P ions released or dissolution was suggested to be attributed to the differences in CaP crystallinity.¹⁸ In the presence of protein, coatings were observed to release significantly more P ions compared with coatings immersed in the absence of protein. It has been reported that some organic substances have a high affinity for HA or CaP surfaces and that the growth of HA crystals was often inhibited by the adsorption of these organic substances.^{23–26} As a result of the high affinity for CaP surfaces to adsorb proteins, reprecipitation of CaP is often inhibited. In addition, it was observed from XPS that the heat-treated CaP coatings ex-

hibited higher PO_4/HPO_4 , whereas the as-sputtered CaP coatings exhibited lower PO_4/HPO_4 ratio. It has been suggested that the higher the PO_4/HPO_4 ratio, the lower the dissolution rate.^{23,27} As such, it was suggested that in addition to coating crystallinity, the PO_4/HPO_4 ratio may be an additional important factor influencing CaP dissolution and reprecipitation.

CONCLUSIONS

In this study, amorphous CaP coatings were produced with radiofrequency magnetron sputtering. The increase in the degree of coating crystallinity was consistent with the increasing number of PO_4 peaks observed as a result of different postdeposition heat treatments. By varying the postdeposition heat-treatment temperature, the degree of CaP coating crystallinity was controlled. It was also concluded that aside from coating crystallinity, dissolution and reprecipitation of the coatings can be controlled by knowing the presence of proteins in the media and PO_4/HPO_4 ratio within the coatings.

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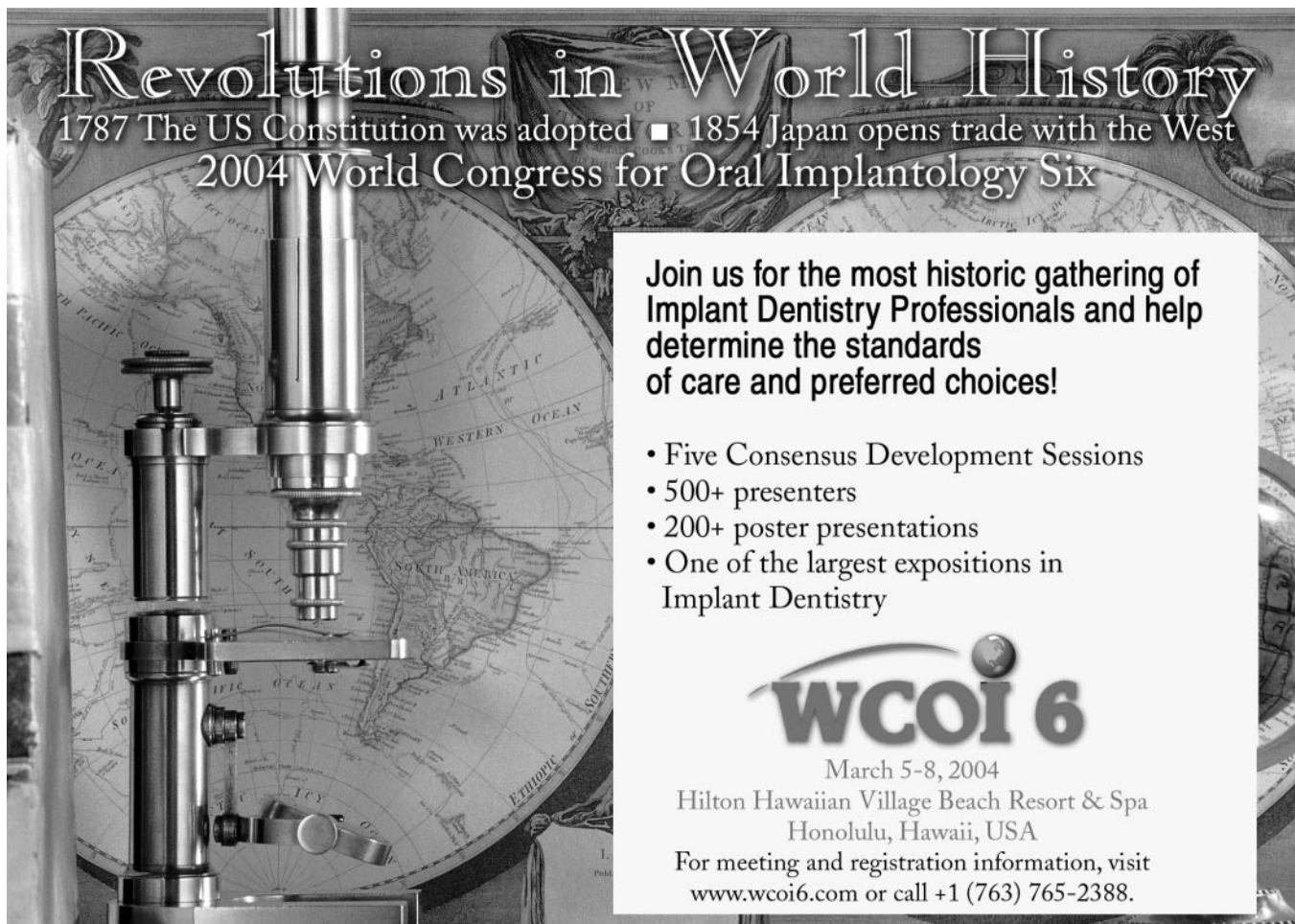
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