Influence of rapid heating with infrared radiation on RF magnetron-sputtered calcium phosphate coatings

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Abstract: This study evaluated the effect of rapid heating with infrared radiation on the physico-chemical and morphological properties of radio frequent (RF) magnetron-sputtered calcium phosphate (Ca-P) coatings. About 2.5 μm thick Ca-P coatings were deposited on titanium disks and cylinders. These specimens were left untreated or were heat treated by infrared radiation at 300, 400, 500, 600, and 700°C for 4, 7, 11, 17, and 24 s. Subsequently, the specimens were immersed in simulated body fluid (SBF) for 1 day, 1 week, and 5 weeks. X-ray diffraction measurements showed that heating at 500°C or higher resulted in an increase of coating crystallinity. In addition, FT-IR measurements revealed the appearance of OH peaks in the spectra of samples treated at 500-700°C. Electron probe microanalysis showed that after 5 weeks of immersion about 40-50% of the coatings heat treated at 500 and 600°C was maintained. The coatings heat treated at 700°C showed no dissolution at all. On the other hand, as-coated and 300°C treated films were dissolved within 1 day. Scanning electron microscopy of the samples showed that directly after heat treatment no apparent cracks were present in the coatings. On the basis of these findings, we conclude that rapid heating with infrared radiation around 600°C is the best heat treatment for RF magnetron-sputtered coatings. © 1997 John Wiley & Sons, Inc. J Biomed Mater Res, 37, 60-67, 1997.

Key words: heat treatment; calcium phosphate; coating; sputter; implant

INTRODUCTION

Several shortcomings have been reported in the clinical use of plasma-sprayed calcium phosphate (Ca-P)-coated implants.1-5 To overcome these problems, use of thin film coating technologies for the deposition of thin and adherent ceramic films have been suggested. This has resulted in the introduction of a physical vapor deposition technique (PVD) for dental and medical applications. PVD is a generic term for vacuum evaporation, ion sputtering,6-8 ion plating,9 and ion beam dynamic mixing.10-11 RF magnetron sputtering is an improved ion-sputtering method and has been applied to deposit thin bioactive Ca-P films on titanium (Ti) oral implants.12-15 The deposited coatings were amorphous, which resulted in early dissolution after incubation in simulated body fluid (SBF). Heat treatment appeared to improve the dissolution properties.6,11,15 However, with conventional heat treatment in an electric furnace, the deposited films tended to degrade and crack easily.6,11 Therefore it was necessary to find a more suitable heat treatment procedure that controls the solubility of the Ca-P coatings without weakening their adhesion to the underlying Ti-substrate.

Recently, rapid heating with infrared radiation was introduced as a suitable heat treatment for thin Ca-P coatings.16,17 Consequently, this study is aimed at examining both dissolution properties and morphological changes produced in RF magneton sputtered Ca-P films after rapid heating with infrared radiation.

MATERIALS AND METHODS

Commercially pure wrought titanium (cp-Ti) disks (99.9 wt% Ti, 12 mm in diameter, 1 mm thick) and cylinders (2.8 mm in diameter, 12 mm in length) were used as the substrate material. The surfaces of the disks were ground down to 500-grit SiC paper, and the cylin-
INFRARED HEATING OF SPUTTERED CA-P COATINGS

Figure 1. Rapid heating method of cylindrical specimen with infrared radiation. One group of cylinders was heated perpendicularly (90 degrees) in one heating cycle (left); a second group was heated while inclined at 45 degrees with two heating cycles (one for each cylinder side, right).

Infrared radiation

Figure 2. Measuring areas of disk (left) and cylinder (right) for estimating the film thickness with electron probe micro-analysis. The measuring area was 60 \( \mu \text{m}^2 \) on the disks and 300 \( \mu \text{m}^2 \) on the cylinders.

RESULTS

X-ray diffraction

The X-ray diffraction spectra of the samples are shown in Figure 3. In the XRD spectrum of as-sputtered coatings were grit-blasted with Al\(_2\)O\(_3\) to a roughness of Ra = 6–7 \( \mu \text{m} \). Then all specimens were cleaned ultrasonically with propanol. RF magnetron sputter coating was performed using a commercially available unit (Edwards ESM 100). The substrates were mounted on a rotating substrate holder and were sputtered at 800W for 4 h at an argon pressure of \( 7 \times 10^{-4} \text{ Pa} \), resulting in a coating thickness of about 2.5 \( \mu \text{m} \). Plasma-sprayed hydroxyapatite disks were used as the target material.

After sputtering, the disks and cylindrical specimens were heat treated by infrared radiation to maximum temperatures of 300, 400, 500, 600, and 700°C. Infrared radiation was carried out under pure argon flow and using a technique that defocused the radiation. The time until maximum temperature of 300, 400, 500, 600, or 700°C was reached at approximately 4, 7, 11, 17, and 24 s, respectively. Temperature was measured with a Pt-PtRh thermocouple close to the specimen on the soft ceramic plate. Heat treatment of the cylindrical specimens was done in two ways (Fig. 1): one group of cylinders was heated perpendicularly (90 degrees) in one heating cycle; a second group was heated while inclined at 45 degrees with two heating cycles (one for each cylinder side).

The crystal structure of each specimen was determined by X-ray diffraction (XRD, θ-2θ diffractometer, Rigaku) utilizing CuKα-radiation, 35 kV, 20 mA. The XRD measurements were carried out directly after sputtering and after heat treatment with infrared radiation. In addition, infrared spectra of the coated films on the substrates were obtained by a reflection Fourier transform infrared spectrometer (FT-IR, Horiba).

Solubility in simulated body fluid was evaluated by estimating the film thickness. The as-coated and heat-treated specimens were immersed in simulated body fluid (SBF, Na\(^+\): 141.8, K\(^+\): 5.8, Mg\(^{2+}\): 1.9, Ca\(^{2+}\): 2.5, Cl\(^-\): 145.7, HPO\(_4^{2-}\): 0.9, SO\(_4^{2-}\): 0.8, HCO\(_3^-\): 4.2 mM) of 30 mL without organic species buffered to a pH of 7.3 with tris hydroxymethyl aminomethan and hydrochloric acid for 1 day, 1 week, and 5 weeks, at 37°C. The SBF medium was not renewed during the respective immersion periods. Immediately at the end of the immersion time, the specimens were washed with deionized water and dried with a gentle stream of dried air and stored in a desiccator. The solubility of coatings was evaluated by estimating the film thickness on the Ti substrate using electron probe micro-analysis (EPMA, Hitachi) for each specimen and each period. The X-ray intensity of Ca-Kα, P-Kα, and Ti-Kα was measured. Subsequently, the X-ray intensity ratio of (Ca + P)/Ti was calculated, and the film thickness was estimated according to a previously performed experiment. Although this technique generally is applied to smooth surfaces, we observed that it also can be applied to rough surfaces as used in this study. According to the Monte Carlo simulation, an accelerating voltage of 25 kV was considered to be suitable for estimation of the film thickness because the intensity ratio of (Ca + P)/Ti was almost 1.0 when the film thickness of HA onto Ti substrate was 1.0 \( \mu \text{m} \). Oxygen intensity was negligible because its intensity was much less than that of Ca or P at the accelerating voltage of 25 kV. Two areas were measured on the center of each disk, and on the upper and lower side of each cylinder (Fig. 2). The measuring areas on the cylinders always were located 2 mm from the upper and lower side. The measuring area was 60 \( \mu \text{m}^2 \) on the disks and 300 \( \mu \text{m}^2 \) on the cylinders.

To obtain information about the morphological changes in the coatings after heat treatment and SBF incubation, scanning electron microscopical (SEM) examinations were done.
film, an amorphous calcium phosphate structure between 2θ = about 25° and 34° and titanium peaks at 2θ = 35.04°, 35.38°, 40.10°, and 52.96° were observed. In the XRD pattern of films heat treated at 300 and 400°C, two peaks derived from CaO were observed in addition to an amorphous pattern. The films heat treated at 500 and 600°C showed a more crystalline structure. Some hydroxyapatite peaks were visible in these XRD patterns. In the XRD pattern of films heat treated at 700°C, peaks at 2θ = 25.83° (002), 31.80° (211), 45.72° (222), and 49.48° (213) could be assigned to peaks of hydroxyapatite (Fig. 3).

**FT-IR measurements**

FT-IR spectra (Fig. 4) for all the films showed two clusters of peaks at 900–1500 cm⁻¹ derived from P–O stretching modes, and at 550–600 cm⁻¹ from P-O bending modes. These peaks are attributed to the P–O bonds of calcium phosphate materials. The FT-IR spectrum of as-sputtered film showed broad peaks derived from P–O bonds of amorphous calcium phosphate. The FT-IR spectra of films heat treated at 300 and 400°C were similar to the spectrum of as-sputtered film. The
Dissolution in SBF

The change in coating thickness on the disks after immersion in SBF is shown in Figure 5. Films as-coated and heat treated at 300°C were almost dissolved within 1 day. Approximately 20 and 40% of the coating was maintained on the disks heat treated at 400 and 500°C, respectively. No apparent dissolution was recognized on the specimens heat treated at 600 and 700°C.

Change in coating thickness on the cylinders is shown in Figures 6 and 7. After 5 weeks of immersion, on the as-coated and 300 and 400°C heat treated 90 degrees specimens (upper side), only 20% of the coating was maintained. No apparent dissolution was recognized on the 90 degree specimens heat treated at 500–700°C. The change in film thickness, as measured on the low side of these specimens, was similar. For the 45 degree cylinders (upper side), the as-coated specimens showed almost complete coating loss after 5 weeks of immersion. Approximately 40–50% of the coating thickness remained on the specimens heat treated at 400 and 500°C. No apparent dissolution was recognized for the coatings heat treated at 300, 600, and 700°C. The change in film thickness, as measured for the lower side, was different. Only the as-coated cylinders showed a reduction in film thickness. All heat treatments resulted in maintenance of the coating in this measuring area.

SEM results of disks are shown in Figures 8–10. Before immersion, cracking of the coating was not observed on any of the heat treated disks (even if heat treated at 700°C). On the other hand, cracks were present in all the coatings after immersion. Furthermore, the coatings on the as-coated disks completely disappeared after a 1 week immersion. The coatings heat treated at 500°C showed partial dissolution after 1 week of immersion. At 5 weeks, a considerable amount of the coating was maintained. The coatings heat treated at 700°C showed no signs of dissolution. Finally, the formation of a precipitate was not observed on any of the specimens.

SEM of rapid-heated cylinders before and after 5 weeks of immersion in SBF is shown in Figure 11. No apparent cracks were seen in the coatings of any cylinders either before or after immersion in SBF. However, the coatings were very difficult to observe. They appeared to dissolve on the as-coated and the less than 500°C heat-treated cylinders. No precipitate formation was found on the maintained coatings.
Figure 8. Scanning electron micrograph of as-coated disks after immersion in SBF. Cracks were observed in the coatings on the disks after 1 day of immersion. The coatings disappeared after 1 week of immersion.

DISCUSSION

It is generally recognized that as-coated Ca-P films produced by the PVD method are amorphous and become crystalline when subjected to thermal energy if the stoichiometrical composition of the coatings is close to that of HA. The amount of thermal energy needed to induce this change is dependent on temperature and time. In this study, the rapid increase in heating temperature produced a more crystalline structure in the coated films. The XRD and FT-IR measurements revealed that the films heat treated at 300 and 400°C have amorphous structures and films heat treated at more than 500°C have crystalline structures. Van Dijk et al. observed CaO peaks in the XRD of films annealed at 800 and 1000°C. In this study, we observed CaO peaks in the XRD pattern of films heated at 300 and 400°C. Although the details of the mechanism are not clear, it must be noted that rapid heating by infrared radiation causes phase changes in Ca-P coatings at a lower temperature than does annealing by electric furnace. Furthermore, we saw the presence of another calcium phosphate in the XRD spectra, yet the main component of films heat treated at more than 500°C is hydroxyapatite. On the other hand, the intensity ratio of peaks of crystalline films in the XRD pattern is different from that of the JCPS powder pattern. Rapid heat

Figure 9. Scanning electron micrograph of rapid-heated disks at 500°C after immersion in SBF. After 1 week of immersion, coatings were partially dissolved. A considerable amount of the coating still was maintained after 5 weeks of immersion.
treatment of coated films is supposed to cause a recrystallization process of calcium phosphate in addition of phase changes. During this recrystallization process, it is possible that the growth of hydroxyapatite crystals is regulated by the titanium substrate. We hypothesize that the crystalline structure of hydroxyapatite in the deposited film is aligned in a certain direction, which causes the differences in relative intensities of the peaks. This hypothesis also explains the resolved peaks of P-O bonds of the crystalline structure in the FT-IR spectra.

Annealing by electric furnace causes some problems, e.g., cracking and detachment of the films from the substrate. Cracks are reported to appear in magnetron sputtered Ca-P coatings after annealing by electric furnace at a temperature higher than 400°C. The films showed a crystalline apatite structure after annealing at a temperature of 600°C or more. In this study, rapid heating with infrared radiation was applied to the sputtered films. The films were characterized by XRD and FT-IR measurements, and the solubility of the coatings was investigated in simulated body fluid. As a result, coatings revealed crystallinity after annealing at 500, 600, and 700°C for 11, 17, and 24 s, respectively. Neither apparent cracks nor detachment were observed in these coatings directly after infrared

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**Figure 10.** Scanning electron micrograph of rapid-heated disks at 700°C after immersion in SBF. No cracks were observed in the coatings before immersion. Cracks, but no sign of dissolution, were observed in the coatings after immersion.

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**Figure 11.** Scanning electron micrograph of rapid-heated cylinders before and after 5 weeks of immersion in SBF. No cracks were seen in the coatings on all cylinders. The coatings appear to have dissolved on the 300°C heat-treated cylinders.
heat treatment. The cracks observed after immersion
in SBF were due to the drying of the specimens before
SEM examination or hydration of coatings. The fact
that such cracks are not seen on the heat-treated cylin-
drical specimens can be explained by the difference in
surface microroughness between the disks and cylin-
ders. The higher surface roughness of the cylinders
results in an additional mechanical retention of the
coatings, which prevents cracking. Accordingly, the
surface roughness will play an important role in the
adhesion between the coating and the Ti substrate after
immersion in body fluid. The irregular structure on
the surface may not produce cracks at the boundaries
if a thin film coating is maintained uniformly along
the surface morphology.

These results indicate that high temperatures and
long duration such as heating in an electric furnace
are not necessary to obtain crystallinity in thin coatings.
Furthermore, heat treatments at low temperatures and
short times are able to reduce the oxidation of titanium
and the diffusion of elements that influence the bond
between the films and the titanium substrate. Conse-
quentially, a firm adhesion of coatings to the Ti substrate
can be expected.

In contrast to our previous studies,13 in this study
no deposit was observed on any sputter-coated sam-
ples even after an immersion period of 5 weeks. This
is due to the amount of SBF solution used in the
immersion experiment. In the previous study, the
fluid concentration per cm² was seven times higher,
with the result that a supersaturation condition was
obtained as required for Ca/P precipitation.18 This
also is dependent on Ca/P ratio, crystallinity, grain
size of Ca/P coatings, and the presence of impurities
in the coatings.

Finally, a remark has to be made about the inconsis-
tent result of the dissolution experiment with the
coated cylinders that were heat treated at an inclination
of 45 degrees. In this study, the 300°C treated speci-
mens appeared to dissolve less than the 400 and 500°C
treated cylinders. In addition, a difference was ob-
served in the reduction of coating thickness between
measurements on the lower and upper sides. It has to
be noted that all the 45 degree specimens were treated
twice. As a consequence, problems can occur in the
exact repositioning of the implants after the first heat-
ting cycle. Also, a part of the surface can be heat treated
twice because the second treatment can overlap the
first treatment. This will result in nonuniform coatings
in areas with a higher crystallinity, which, in turn, will
result in a different dissolution behavior.

In summary, we conclude that rapid heating
with infrared radiation around 600°C is the best heat
treatment for thin RF magnetron-sputtered Ca-P
coatings in order to obtain suitable dissolution proper-
ties without cracking and/or detachment of the
coatings.

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