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Influence of discharge power level on the properties of hydroxyapatite films deposited on Ti6Al4V with RF magnetron sputtering

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The effects of discharge radiofrequency (RF) power and film thickness were studied on the characteristics of $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ (hydroxyapatite) thin films fabricated by RF magnetron sputtering. The structure and chemical composition were investigated with α -step (thickness), scanning electron microscopy (SEM), X-ray diffraction (XRD), Rutherford backscattering spectrometry (RBS), and infrared absorption spectrometry (FTIR). The films were analyzed as sputtered and after annealing at 550°C under argon flow. SEM showed that the film surfaces had no cracks or other defects. X-ray diffraction showed that the deposited films were amorphous with low-discharge RF power, and crys-

talline with high-discharge RF power. After annealing, all the films had the same crystalline structure as apatite. However, the RBS measurements revealed that all films had a higher calcium-phosphate ratio than standard synthetic hydroxyapatite. Furthermore, statistical testing of the RBS data revealed the existence of only a weak correlation between the Ca/P ratio and the discharge power level. Although all sputtered films showed phosphate bonds in the infrared spectrum, only after annealing did the OH bonds of hydroxyapatite become visible. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

During the last decade, a number of ceramic materials containing calcium and phosphorus have found increasing use for biomedical applications. This use is based on their biocompatibility and ability to form a chemical bond with bone. However, a disadvantage of ceramic materials is that they are brittle and can only function in unloaded situations. To eliminate this problem, it has been proposed to deposit calcium phosphate ceramics as thin coatings on metallic substrates.¹ There are various methods to prepare such coatings. Currently, plasma spraying is the most frequently used technique.²⁻⁵ In several studies, it has been demonstrated that such Ca/P coatings on titanium implants are very successful.⁶ However, despite this clinical success, it has also been recognized that the plasma-spray method has several disadvantages, such as the adherence of the coating to the substrate material, the thickness uniformity of the de-

posited layer, and the integrity of the structure and composition of the coating. Therefore, one of the goals of the research on Ca/P coatings is to further improve their characteristics. In addition, another goal is to develop other methods to produce more adherent and thinner coatings. For example, in our laboratory, all experimental efforts are directed at the further development of radio frequency (RF) magnetron sputtering as a method for the deposition of thin adherent calcium phosphate coatings on medical implant materials.⁷ The major goals of this research were to obtain Ca/P coatings with the physical and chemical structure of hydroxyapatite (HA), a high-adherence strength of the Ca/P coating to the substrate material, a uniform coating especially on complex implant materials, and the application of Ca/P coatings on heat-sensitive substrates such as polymers.

RF magnetron sputtering is a rather complex method, especially when used to sputter multicomponent compounds such as $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ (hydroxyapatite). There are many process parameters which

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can influence the physical and chemical properties of the coating. For instance, in a sputtering process the film composition depends not only on the target composition but also on sputtering parameters such as the ionized gas pressure⁸⁻¹⁰ and the substrate temperature.^{11,12} Furthermore, the energetic particle radiation (photons as well as particles) determines the growth of the layer.¹³ In an RF-discharge configuration, positive ions produced in the bulk plasma are accelerated across the plasma and may arrive at the substrate with significant impact energies. These energies have a distribution which is primarily determined by the excitation frequency of the discharge.¹³ This positive ion bombardment is the major part of the energetic particle bombardment occurring in RF discharges. It plays an important role during the film deposition in RF sputtering, because the temperature of the substrate may rise with increasing discharge power level.¹⁴ Different energetic and thermal circumstances may result in a different final quality and structure of the applied coating. The aim of this study was to determine the influence of discharge RF power level on the properties of the Ca/P films deposited on titanium substrates.

MATERIAL AND METHODS

RF magnetron sputter-coating was performed using a commercially available unit (Edwards ESM 100). This includes a radiofrequency generator operating at 13.56 MHz. Figure 1 shows a schematic drawing of the vacuum chamber with the position of the target and the substrate indicated.

The target materials were copper discs plasma-

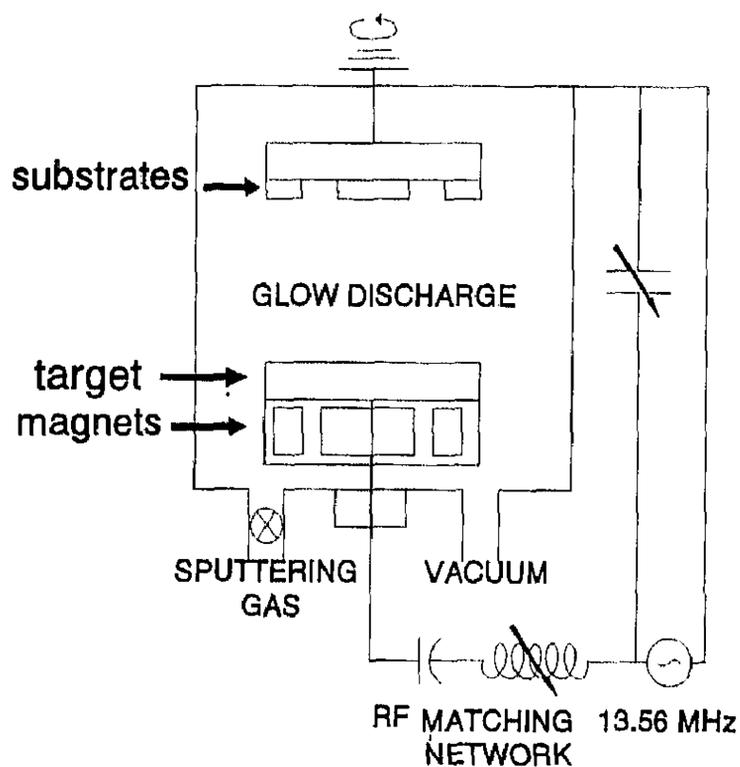


Figure 1. Schematic drawing of the sputter chamber with the position of the water-cooled target and substrate holder indicated.

spray-coated with HA. The targets were 60% crystalline hydroxyapatite. Figure 2 shows that compared to the infrared spectrum of pure (powder) HA, the infrared spectrum of the target material exhibits only limited OH bonding. The substrate materials used for our experiments were Ti6Al4V discs with a diameter of 12 mm. These discs were ground until 800 grit, after which they were polished with Buehler Masterpolish.TM The substrates were attached to a water-cooled specimen holder with silver paint. The specimen holder may be continuously rotated or may be indexed on a fixed position.

The substrates were sputtered at a discharge power of 200, 300, 400, 500, 600, 700, and 800 W. The sputter time varied from 1–4 h. This series of deposition was carried out on substrates mounted on indexed and rotating substrate holders. The pressure in the vacuum chamber was measured with pirani-penning heads, and the argon flow during sputtering was controlled with a gas controller (Vacuum General; Model 80-1). The argon pressure during each experiment was kept constant at 5.2×10^{-3} mbar. At the start of each run the background pressure was lower than 8.0×10^{-6} mbar. The temperature close to the substrate was measured directly after each run with a platinum–10% rhodium thermocouple.

The thickness of the deposited films was measured with an α -step instrument. The surface topology of the coatings was examined using scanning electron microscopy (SEM). The structure of each film was determined by X-ray diffraction (XRD) using a Philips θ -2 θ diffractometer utilizing $\text{CuK}\alpha$ -radiation. The XRD measurements were carried out directly after sputtering and after annealing of the samples under argon flow during 2 h at 550°C. The infrared spectra of the films on the substrates were obtained by a reflection Fourier transform infrared spectrometer (FTIR) (Perkin–Elmer). Standard $^4\text{He}^+$ Rutherford backscattering spectrometry (RBS) at 2.014 MeV was used to determine the calcium–phosphorus ratio of the films.

RESULTS

The α -step measurements showed that the deposition rate varied between 1.8 $\mu\text{m}/\text{h}$ at 800 W to 0.28 $\mu\text{m}/\text{h}$ at 200 W. The deposition rate with a rotating substrate appeared to be about two to three times as low. The temperature close to the substrate directly after sputtering varied from 100°C at 200 W (stabilized after 3 h) to 290°C at 800 W (after 3 h). In Table I the most relevant temperature and thickness measurements of the deposited films are listed for the various discharge power levels.

SEM pictures showed no difference between the

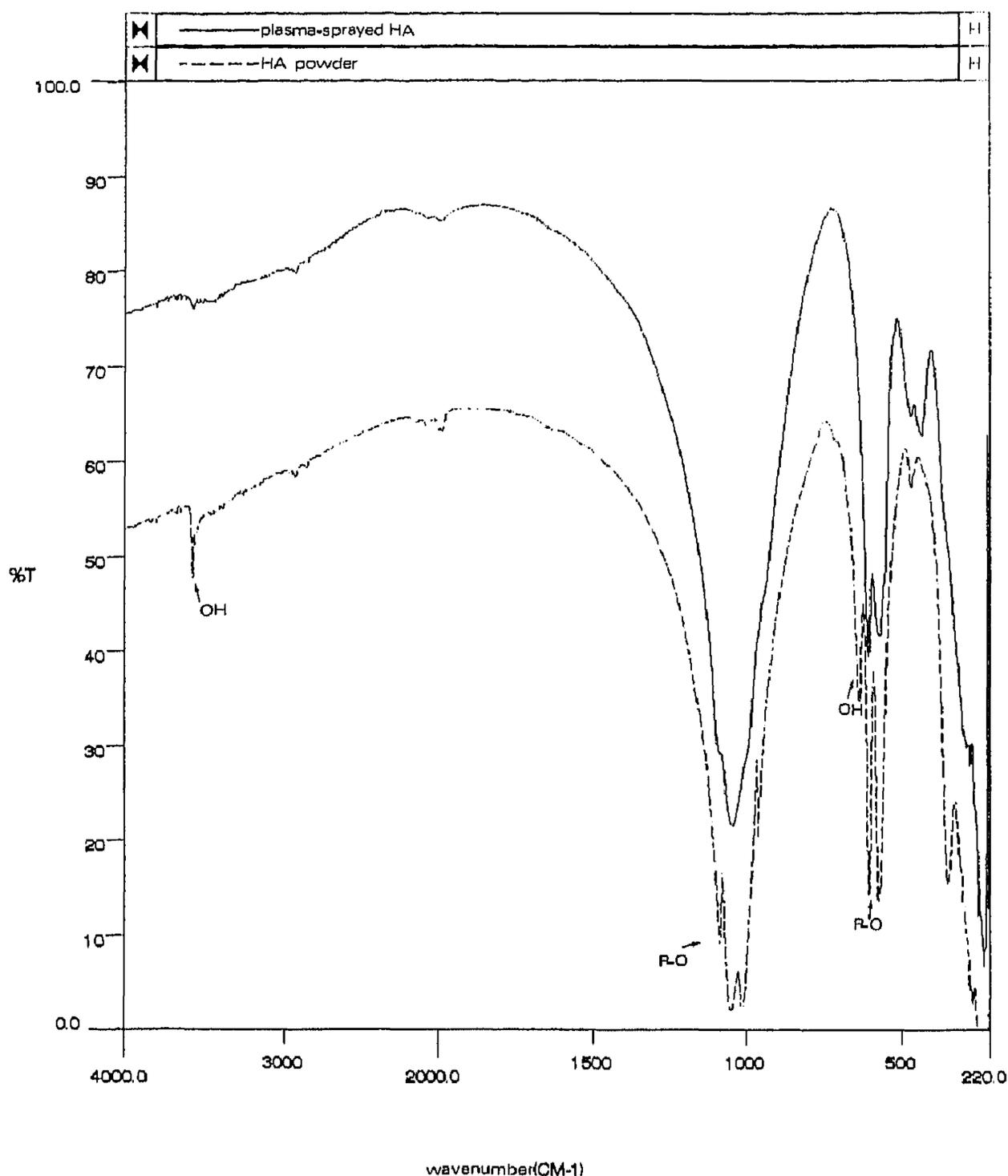


Figure 2. FTIR spectrum of (a) pure (powder) HA (---) and (b) plasma-sprayed HA target (—).

surface of the films sputtered at various discharge power levels or for various thicknesses of the films. All surfaces looked smooth and the surface of the apatite layer appeared to follow the surface of the underlying titanium substrate. No cracks or other defects were visible.

XRD measurements showed only a crystalline phase in the Ca/P films sputtered on an indexed substrate holder at 800 W for 2 h (Fig. 3). This XRD pattern showed a preferred (001) crystallographic orientation with the c-axis perpendicular to the substrate surface. Sharp (002), (102), and (211) peaks were visible at $2\theta = 25.88^\circ$, 28.1° , and 31.77° , respectively. This XRD pattern is similar to the XRD pattern of

apatite crystals in intact tooth enamel.⁷ The films sputtered with a lower discharge power level than 800 W and all films sputtered with rotating substrate holder appeared to have an amorphous structure (Fig. 3b). After annealing at 550°C under argon flow all these films became more crystalline (Fig. 3c). With the increase in crystallinity, randomly oriented apatite peaks appeared. The XRD pattern of the annealed sample was similar to that of the plasma-sprayed target. Besides these HA peaks most of the annealed films also showed $\text{Ca}_4\text{P}_2\text{O}_9$ (tetra-calciumphosphate) peaks at $2\theta = 29.35^\circ$, 29.95° , 31.25° , or 36.3° (Fig. 3).

Infrared measurements showed for all the films two clusters of peaks from 900–1150 and from 550–600

TABLE I
Temperature After 2h of Sputtering and Deposition Rate of Films Sputtered at Different Discharge Power Levels on Indexed Substrate Holder

| | 800 W | 700 W | 600 W | 500 W | 400 W | 300 W | 200 W |
|-------------------------------------|-------|-------|-------|-------|-------|-------|-------|
| Deposition rate ($\mu\text{m/h}$) | 1.75 | 1.4 | 1.15 | 0.9 | 0.75 | 0.48 | 0.29 |
| Temperature ($^\circ\text{C}$) | 290 | 280 | 260 | 210 | 180 | 150 | 100 |

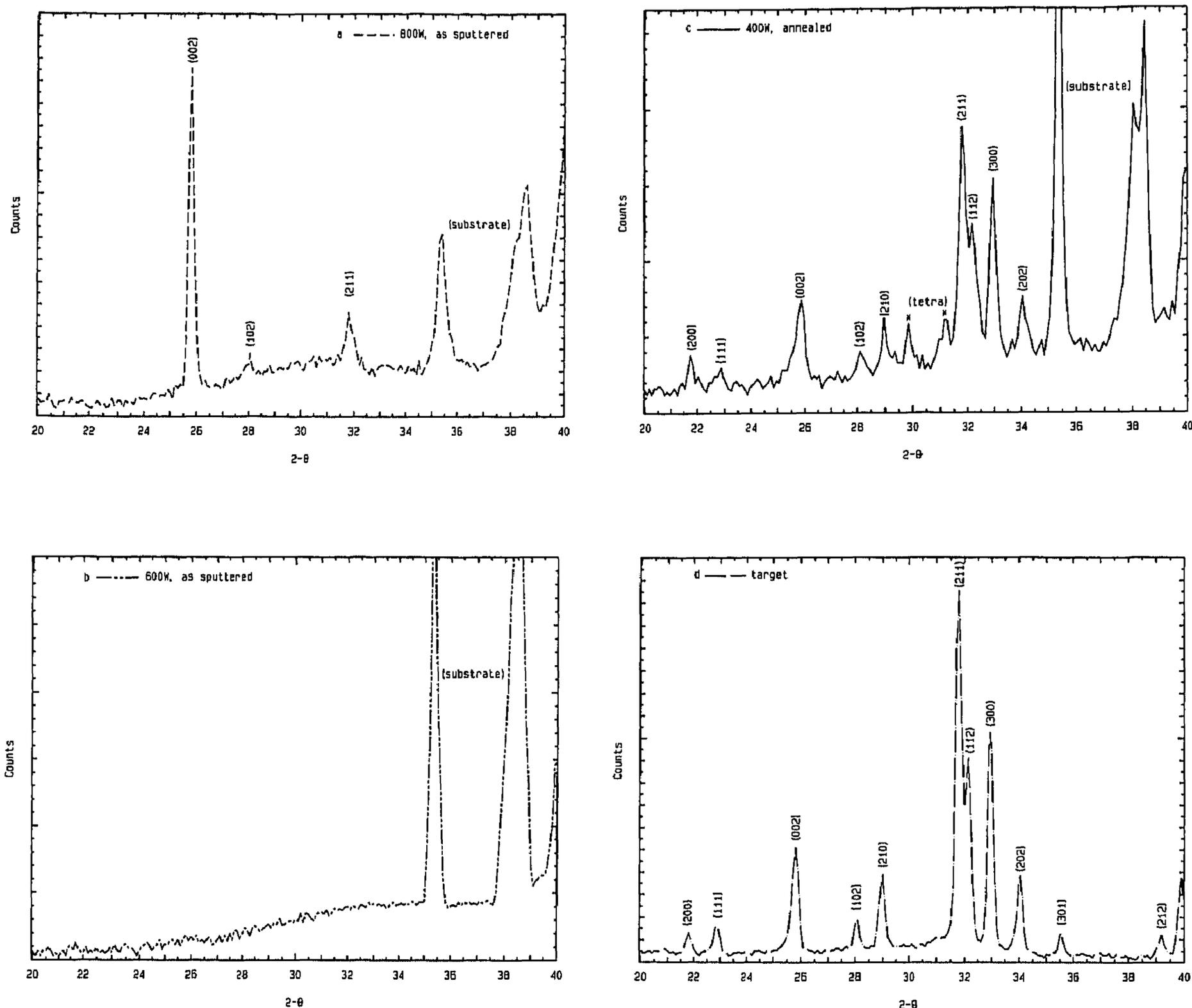


Figure 3. XRD pattern of (a) film sputtered at 800 W for 2 h (----), (b) amorphous sputtered film (-·-·-), (c) annealed film sputtered at 400 W (—), and (d) plasma-sprayed target (-·-·-).

cm^{-1} , which can be attributed to the major absorption modes associated with the presence of phosphate.¹⁵ For the thicker films ($>2 \mu\text{m}$) sputtered at higher discharge power level ($\geq 400 \text{ W}$) the broad peak in the region from $900\text{--}1150 \text{ cm}^{-1}$ split up into two peaks at 936 and 1124 cm^{-1} (Fig. 4). Furthermore, the peak in the region of $550\text{--}600 \text{ cm}^{-1}$ became higher compared to the peak of the other region. However, all the films also showed a broad peak over the region from $2800\text{--}4000 \text{ cm}^{-1}$, which is due to water absorbed from the surface of the films.^{15,16} An increase of power level did not change the broad peak in the region of the water band.

Annealing of the samples resulted in the appearance of the hydroxyl peak at 3570 cm^{-1} , characteristic for hydroxyapatite, and in the appearance of the various P-O bonds at a wavelength of $558, 597, 630, 945, 963, 1018, 1083,$ and 1124 cm^{-1} (Fig. 5). This was found for all films, only the intensity of the peaks varied for different films. For example, the intensity

of the 1018 peak was highest for the thinner films sputtered at low discharge power, while for the other films the intensity of the peaks in the region of $550\text{--}600 \text{ cm}^{-1}$ became higher.

Analysis of the RBS spectra, using the computer simulation program RUMP,¹⁸ provided information about the atomic concentration in the sputtered films. Measurements and calculations demonstrated that all deposited coatings had a higher Ca/P ratio than the theoretical value of 1.67 for $\text{Ca}_5(\text{PO}_4)_3\text{OH}$. For each sample the Ca/P ratio was constant over the whole surface. However, the Ca/P ratio between films sputtered in different runs varied considerably, i.e., from $1.9\text{--}2.5$ (Fig. 6). To examine the possible existence of a relationship between discharge power level and Ca/P ratio, a simple regression test was applied to the data shown in Figure 6. The statistical significance of the relationship between the two variables was determined by performing a t test. The computed correlation coefficient (r) for the data was 0.5 . This value

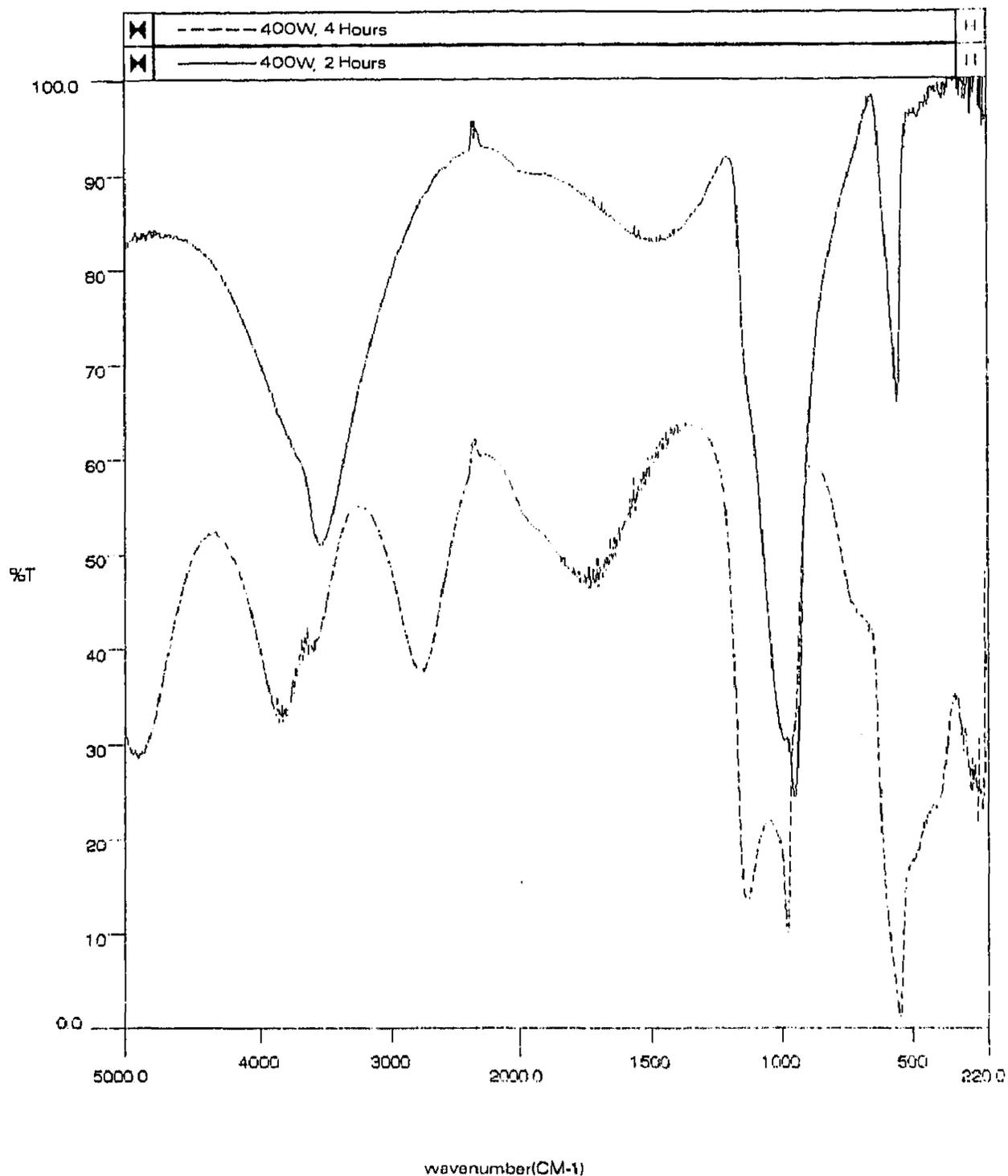


Figure 4. Reflection FTIR spectrum of (a) film sputtered at 400 W for 2 h (—) and (b) film sputtered at 400 W for 4 h (---).

reflected the existence of only a weak correlation between discharge power level and obtained Ca/P ratio. Further analysis of the data revealed that there was no systematic variation of the Ca/P concentration ratios and indexed or rotatory-sputtered films.

DISCUSSION AND CONCLUSION

Although RF magnetron sputtering is used widely for the deposition of nonconducting films, this technique is used only in our laboratory to apply Ca/P ceramic coatings on medical implants. We already provided some information about the characteristics of these coatings in previous publications.^{7,20,21} For example, we demonstrated that the *in vitro* dissolution in buffer solution appeared to be determined by the degree of crystallinity of the sputtered coatings. Furthermore, *in vitro* osteoblast cell culture experiments showed extracellular matrix formation on top of both amorphous and crystalline-sputtered coatings. In addition, under these conditions no severe

degradation of the coatings was observed. They even appeared to enhance bone formation. However, currently, the exact sputter parameters to produce these coatings on routine basis are not completely clear. Therefore, the purpose of this study was to investigate the influence of one of these parameters, i.e., the discharge power level, on the final film properties.

The results of the X-ray diffraction measurements showed that all deposited films in this experiment were amorphous, except the films sputtered at 800 W for 2 h (or more) on an indexed substrate holder. This is in accordance with the temperature measurements, because it can be assumed that when the temperature of the film is high enough, the lattice gets enough energy to crystallize. Considering the final crystallinity of the applied coatings, it is worth noting that the temperature of the substrate also depends on the angle between the substrate and the plasma sheath.¹⁹ Therefore, it is possible that under the same sputter conditions a film sputtered right above the target can be crystalline while a film mounted towards the edge of the substrate holder can be amorphous. The films that are crystalline after sputtering show 001 ori-

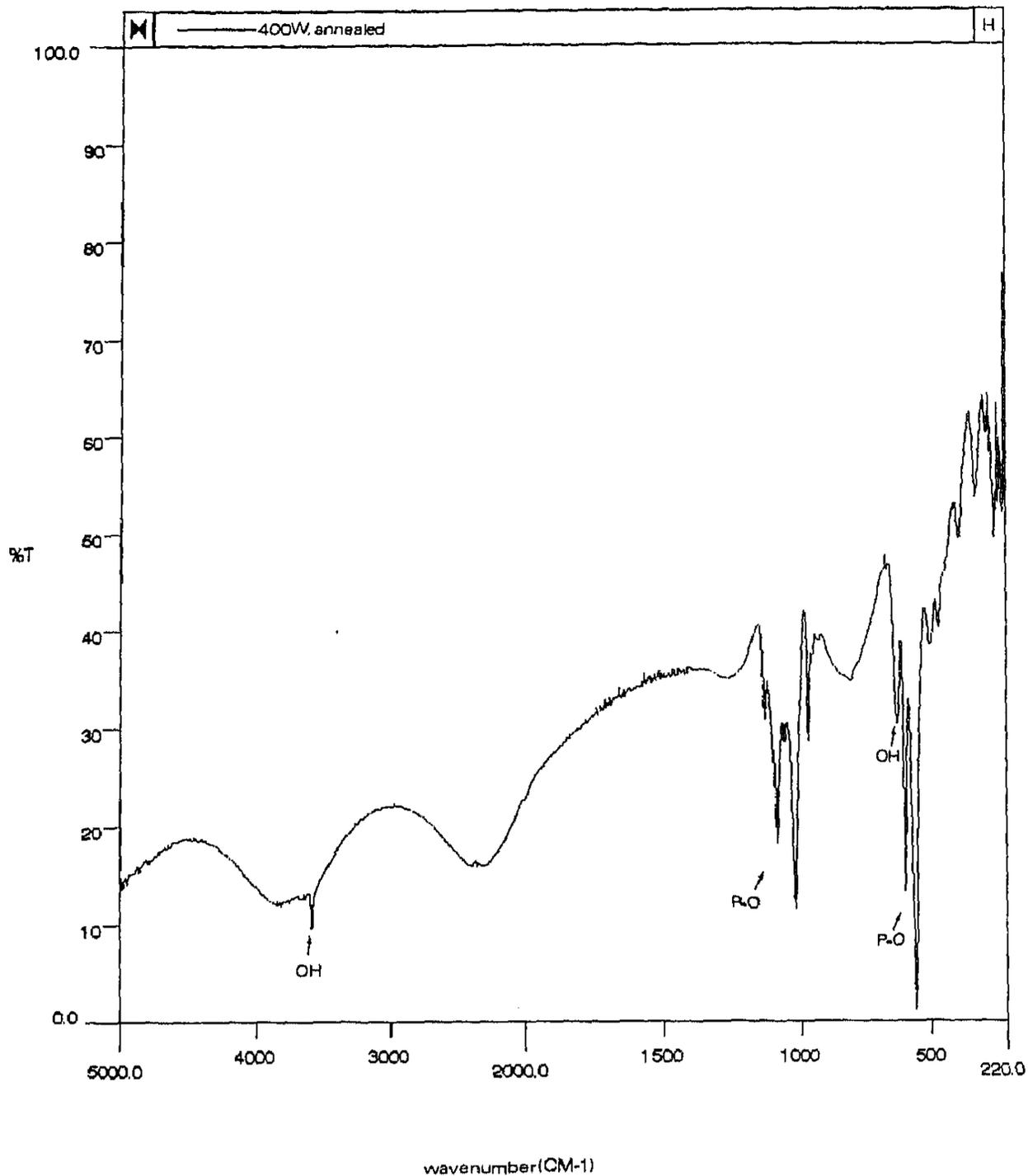


Figure 5. Reflection FTIR of a film sputtered at 400 W after annealing under argon at 550°.

entation with the *c*-axis perpendicular to the substrate surface.²⁰ The other films that were initially amorphous showed randomly oriented HA peaks with some tetrapeaks after annealing. According to Brown,²² the X-ray diffraction patterns of tetracalciumphosphate and hydroxyapatite are very comparable. Consequently, since the proportion of the

height of the HA peaks of the sputtered films are similar to those of the plasma-sprayed films, we suppose that the main component of our films is hydroxyapatite. Nevertheless, it has to be emphasized that the observed tetrapeaks indicate the presence of another phase than HA with a higher Ca/P ratio.

The presence of another phase with a higher Ca/P ratio is also confirmed with the RBS measurements. The analysis of these data indicated that most of the sputtered films had a Ca/P ratio of about 2.2. This cannot merely be explained by the presence of HA and tetra-calciumphosphate, as suggested by the X-ray measurements. The Ca/P ratio of HA is 1.67 and of tetra-calciumphosphate, 2. Therefore, this high Ca/P ratio suggests yet another phase. This could be CaO, although the infrared spectra do not show the CaO bonds at 1350 cm^{-1} or at 725 cm^{-1} .

On the other hand, this high Ca/P ratio can also be explained by taking into consideration the mass of Ca, P, and Ar atoms in relation to high energies involved in the sputter process.^{8,13} Since the mass of Ca is higher than both Ar and P, it can be assumed that the impulse of calcium is higher than that of phosphorus. Consequently, calcium arrives with a higher

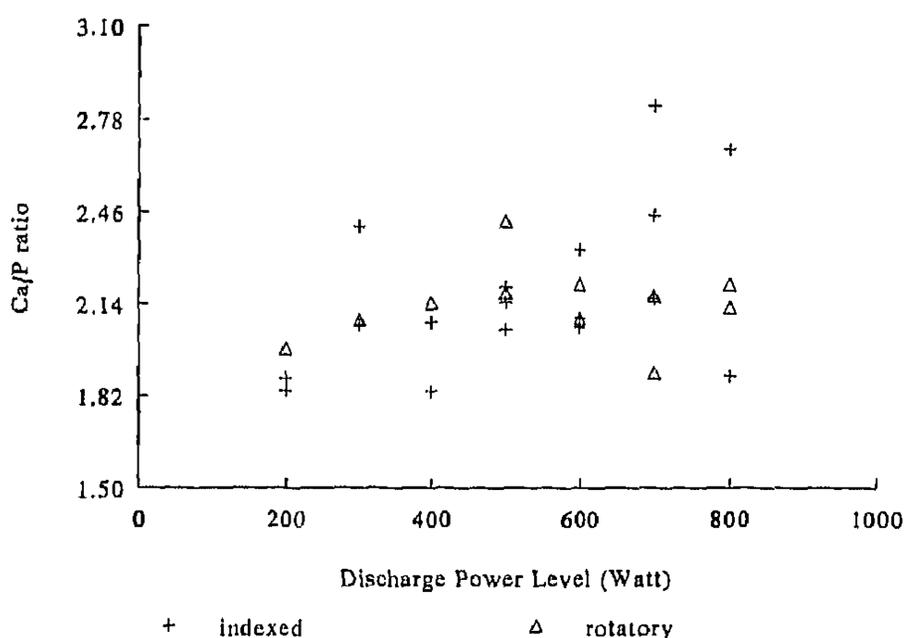


Figure 6. Ca/P ratio as a function of the discharge power level for rotatory or indexed sputtered films.

energy at the surface of the growing film than phosphorus. This could result in Ca implantation in the growing film or sputtering of phosphorus by calcium ions out of the growing film.²³ In this context, it has also to be noted that according to Han et al.,⁸ the ratio of atoms from a multicomponent target can be influenced by altering the argon pressure during sputtering. At a higher pressure the atoms with a lower mass should be more influenced by the scattering due to the plasma than atoms with higher atomic mass. Therefore, it is possible that the problem of the high Ca/P ratio can be solved by sputtering with a lower argon pressure.

Nevertheless, supported by the infrared measurements, we still think that the main component of our film is hydroxyapatite. As listed in Table II, the theoretical values²⁴ of the mean wavenumbers of the absorption due to phosphate bonds in HA are $\nu_1 = 962$, $\nu_2 = 473$, $\nu_3 = 1057$, and $\nu_4 = 580$. The vibrations of ν_3 and ν_4 can split in ν_{3a} at 1088 and ν_{3b} at 1042 cm^{-1} and ν_{4a} at 601 and ν_{4b} at 570 cm^{-1} . These values are also listed in Table II. For hydroxyapatite the OH peak can be found at 3571 cm^{-1} and the band due to the librational motion of the OH ion can be observed at 631 cm^{-1} . The sputtered films showed a broad peak in the region of the ν_1 and ν_3 wavenumbers and a broad peak in the ν_4 region. After the films were annealed under argon flow and became crystalline these broad peaks split up into the ν_1 , ν_{3a} , ν_{3b} , ν_{4a} , and ν_{4b} apatite peaks. Although the peaks at 1124 and 945 cm^{-1} also suggest the presence of another calcium-phosphate phase, the OH peak at 3571 cm^{-1} and at 630 cm^{-1} clearly proves that a part of our sputtered film is hydroxyapatite.

The RBS data showed that the Ca/P ratio varied considerably between various films. Because a weak correlation exists, this variation can only be partly related to discharge power level. Furthermore, it cannot be excluded that this diversity in Ca/P ratio is due to the used plasma-sprayed targets, since these targets are only about 60% crystalline apatite. The composition of the amorphous phase cannot be determined. There is, however, sufficient evidence to suppose that this phase consists of other calcium

phosphates.²⁵ The infrared measurement of the target compared with that of HA powder (Fig. 2) also shows that the target is not 100% hydroxyapatite. For example the plasma-sprayed target shows only few OH bonds. Therefore, it seems likely that the composition of the dislodged target particles by the bombardment of high energy ions can differ for each sputter run, resulting in wide variation in Ca/P ratios. Unfortunately, it is impossible to use dense sintered crystalline HA targets in the sputter experiments. Several pilot experiments, as performed in our laboratory, demonstrated that such targets break due to considerable heating during sputtering.

Besides, considering the performed temperature measurements with the thermocouple close to the substrate during sputtering, it has to be realized that they only give an indication of the real temperature of the substrate. The initial substrate temperature can be slightly lower than the observed temperature, because the substrate is mounted on a cooled substrate holder. Subsequently, when the film is growing, the bad thermal conduction properties of the ceramic Ca/P layer can result in an increase of the temperature. It is concluded that the temperature is higher when sputtered with an increasing discharge power level, but the exact temperature of the layer during deposition cannot be determined.

In summary, the most important finding of this study is that with RF magnetron sputtering, Ca/P films with an apatite structure can be deposited on titanium substrates as a thin layer. It has to be noted, however, that these films do not consist for 100% of HA. Therefore, further experiments are planned to improve the crystalline structure and to reduce the Ca/P ratio of the coatings.

These investigations are supported by the Netherlands Technology Foundation (STW). The authors thank Dr. J. Willemsse for helping with the FTIR measurements.

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TABLE II
Vibrations of Phosphate and Hydroxyl Ions
in Hydroxyapatite^{15,22}

| | Wavelength (cm^{-1}) | |
|-----------|------------------------------------|-----------------|
| P-O bonds | 962 ν_1 | |
| | 473 ν_2 | |
| | 1057 ν_3 | 1088 ν_{3a} |
| | | 1042 ν_{3b} |
| | 580 ν_4 | 601 ν_{4a} |
| | | 570 ν_{4b} |
| OH bonds | 3571 | |
| | 631 | |

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Received March 23, 1994

Accepted July 29, 1994