The following full text is a publisher's version.

For additional information about this publication click this link.
http://hdl.handle.net/2066/24920

Please be advised that this information was generated on 2019-05-01 and may be subject to change.
Stability of radiofrequency magnetron sputtered calcium phosphate coatings under cyclically loaded conditions

J. G. C. Wolke*†, J. P. C. M. van der Waerden*, K. de Groot† and J. A. Jansen*

*University of Nijmegen, Department of Oral Function and Prosthetic Dentistry, Laboratory of Biomaterials, Dental School, PO Box 9101, 6500 HB Nijmegen, The Netherlands; †University of Leiden, Department of Biomaterials, Prof. Bronckhorstlaan 10, 33723 MB Bilthoven, The Netherlands

The stability of radiofrequency (RF) magnetron sputtered calcium phosphate was studied under cyclically loaded conditions. The coatings were deposited on titanium bars and tested in either dry or wet conditions. X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray (EDX) analysis and Fourier transform infrared (FTIR) spectroscopy were used to characterize the as-sputtered and tested coatings. XRD demonstrated that the amorphous structure after annealing at 650°C changed into a crystalline apatite structure. The residual stresses were determined by the XRD cos²θ method. These residual film stresses were influenced by the coating conditions and the crystalline sputtered coating showed the presence of compressive stresses. SEM demonstrated that, after cyclic loading conditions in air, the crystalline sputter-coated Ti-6Al-4V bars showed a partial coating loss. Furthermore, in wet conditions (simulated body fluid) only the heat-treated sputter-coated bars appeared to be stable. On the other hand, the amorphous coating only showed signs of delamination in the more highly stressed regions, while in the less stressed regions a Ca-P precipitate was formed. On the basis of these results we conclude that calcium phosphate coatings subjected to cyclic loading conditions show an important difference in fatigue behaviour when tested in either dry or wet conditions. © 1997 Elsevier Science Limited. All rights reserved

Keywords: Coatings, magnetron sputtering, calcium phosphates, cyclic loading

Received 7 May 1996; accepted 22 September 1996

Previous work by our group investigated the use of radiofrequency (RF) magnetron sputter deposition as a method of applying thin adherent calcium phosphate coatings to titanium implants1-4. In these studies the physico-chemical as well as the biological properties of various amorphous and crystalline deposited coatings were investigated. The results showed that the deposited films had a uniform and dense structure, especially on complex implant materials, and excellent adhesiveness. The in vitro dissolution appeared to be determined by the degree of crystallinity of the sputtered coatings. In vitro osteoblast cell culture experiments showed extracellular matrix formation on both amorphous and crystalline sputtered coatings. Furthermore, under in vitro conditions the coatings appeared to induce apatite formation. In vivo animal studies revealed that the sputtered coatings showed the same process of bone healing as plasma-sprayed calcium phosphate coated implants5.

However, we also know that biological behaviour is not the only prerequisite for long-term safe application of Ca-P coated implants. For example, several reports have already been published about the degradation and resorption of plasma-sprayed hydroxyapatite (HA) coatings8,9. Since the occurrence of these phenomena is supposed to be related to the fatigue properties of these deposited coatings8,9,10, this last parameter always requires critical evaluation. In view of this, it is also important to note that previous research demonstrated that the finally observed fatigue properties of HA coatings depend on the experimental conditions used ('wet' or 'dry' testing)11,12 and the presence of the residual stress in the coated layer13-17.

Therefore, the aim of this study was to investigate the delamination and dissolution behaviour of Ca-P magnetron sputter coatings subjected to cyclic loading in different test conditions. Further, we determined whether this performance was influenced by the occurrence of residual stress in the sputtered film.

MATERIALS AND METHODS

Test specimen

For the experiments Ti-6Al-4V bars (190 x 23.5 x 3 mm³) were used (Figure 1). RF magnetron sputter coating was performed using an
Stability of cyclically loaded calcium phosphate coatings: J. G. C. Wolke et al.

Edwards High Vacuum ESM100 sputter system. The target material consisted of plasma-sprayed HA coated on top of a copper disc. The process pressure was 5 x 10^{-2} mbar using argon gas. The deposition rate of the ceramic was 200–250 nm min^{-1} (power level 700 W). The titanium bars used in this experiment were coated while fixed on a rotary or stationary indexed substrate holder.

The bars were provided with the following coatings:
1. Stationary sputtered coating, with a thickness of 3.5–4 μm.
2. Rotated sputtered coating, with a thickness of 3.5–4 μm.
3. Rotated sputtered coating, with a thickness of 3.5–4 μm, additionally heat-treated for 1 h at 650°C.

The crystal structure of each film was determined by X-ray diffraction (XRD) using a Philips diffractometer utilizing Cu Kα radiation. The infrared spectra of the films on the substrates were obtained by reflection Fourier transform infrared (FTIR) spectroscopy (Perkin-Elmer). The morphology of the coatings was examined with a Philips SEM 525 scanning electron microscope. An energy dispersive X-ray (EDX) detector (Tracor) was used to obtain information about the elemental composition of the coated specimens. Ca and P concentrations were measured by using calibration standards of known Ca/P content.

Stress measurement
The residual stress state in a material can be determined via XRD by measuring the d spacing of a given reflection along several different directions in the sample. If the unstressed lattice spacing d_c is known, then the measured lattice spacing can be converted to strain components ε in the film and the stress σ can be calculated. Furthermore, the Young’s modulus E and the Poisson ratio ν must be known. A modification of the sin^2 ψ method first presented by Haase^{18}, assuming a Poisson ratio of 1/3, gives the cos 2φ method:

\[ ε(φ) = -ε_1 \cos 2φ \]  

In practice, a straight line is fitted to the (d_{obs} - d_c)/d_c data points plotted as a function of ε(φ).

The stress in the films was determined by thin-film XRD using a Philips diffractometer with CuKα radiation, angle of incidence θ = 0.25° and a scan of 2θ = 20–70°. An internal standard of silicon powder was dispersed on the sputtered films to correct the observed diffraction angles for errors caused by small sample displacement.

Three-point bending tests
A four-station, three-point cyclic apparatus (Instron^{8}) was used. The test bars were supported at 108 mm from their end and loaded centrally with a hemispherical indenter at the side opposite to the coated side. Maximum interfacial stresses in bending of 280–300 MPa were utilized and the samples were tested at a frequency of 7 Hz until 10^6 cycles were reached. This corresponds to approximately 52 h per sample. The displacement at the maximum interfacial stresses was 2 mm. Tests were executed according to ASTM E 855 and the test environments were air and simulated body fluid (SBF) buffer with a pH of 7.2 at 25°C (see Table 1, Figure 1). After testing, the bars were inspected by scanning electron microscopy (SEM) using an EDX detector.

RESULTS

Macroscopic findings
Macroscopic evaluation of amorphous coated bars tested in wet conditions showed signs of delamination of the coating in the more highly stressed region (Figure 1). Macroscopically, the other bars did not reveal any sign of delamination.

X-ray diffraction
The XRD pattern of a stationary deposited sputter coating showed a crystalline structure (Figure 2) with a preferred (002) crystallographic orientation (reflections 002, 102, 112 and 202 respectively at 25.9, 28.1, 32.4 and 34.0° 20).

A rotated sputter coating showed an amorphous structure without specific reflection lines. Heat treatment for 1 h at 650°C changed the amorphous structure into a more random apatite structure (Figure 3), comparative with the XRD pattern of HA powder (JCPDS No. 9-0432).

Fourier transform infrared spectroscopy
For all the amorphous and crystalline films in air, FTIR measurements showed two clusters of peaks at 800–

---

Table 1 Composition of simulated body fluid (SBF)^{*}

<table>
<thead>
<tr>
<th>Ion</th>
<th>Concentration/mM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺</td>
<td>142.0</td>
</tr>
<tr>
<td>K⁺</td>
<td>5.0</td>
</tr>
<tr>
<td>Ca^{2+}</td>
<td>2.5</td>
</tr>
<tr>
<td>Mg^{2+}</td>
<td>1.5</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>147.9</td>
</tr>
<tr>
<td>(HCO₃)⁻</td>
<td>4.2</td>
</tr>
<tr>
<td>(HPO₄)²⁻</td>
<td>1.0</td>
</tr>
<tr>
<td>(SO₄)²⁻</td>
<td>0.5</td>
</tr>
</tbody>
</table>

*Buffered with tris(hydroxymethyl)aminomethane (50 mM); set at pH 7.2 with 1.0 M hydrochloric acid^{19}.

---

Figure 1 Photograph of the coated bars after cyclic loading in air and in simulated body fluid buffer: A, amorphous coating; B, crystalline coating; C, amorphous heat-treated coating; ●, tested in air.
had a uniform smooth coating, with a preferred (002) crystallographic orientation. The Si peaks are from the internal silicon standard.

1150 and 550–600 cm⁻¹ attributed to the major absorption modes associated with the presence of phosphate (Figure 4). Heat treatment resulted in the appearance of hydroxy peaks at 621 and 3571 cm⁻¹, characteristic of HA, and the appearance of various P–O bonds at wavelengths of 567, 587, 948, 965, 1009, 1083 and 1124 cm⁻¹ (Figure 5).

Residual stress measurement

Figures 6 and 7 show the results of the residual stress measurements; the fits of the reflection data demonstrated the presence of compressive stresses in the crystalline sputter coating. The data for the heat-treated amorphous coating indicated an almost stress-free film. Of course, the amorphous coating was stress free.

SEM and EDX analysis

SEM and EDX evaluation revealed that:

1. All deposited coatings had a uniform smooth surface appearance. The Ca/P ratio of the coatings varied between 1.8 and 2.2.
2. Crystalline sputter coating tested in air demonstrated partial coating loss (Figure 8).
3. Amorphous and amorphous heat-treated coated bars tested in air did not show any morphological changes (Figure 9).
4. Crystalline sputtered coatings tested in wet conditions disappeared totally from the titanium bars.
5. Amorphous coated bars tested in wet conditions only showed signs of delamination in the more highly stressed region and a crackle appearance of the maintained Ca–P sputter coating. This crackle appearance was due to a drying artefact. In addition, a reprecipitated amorphous layer was observed in areas where the coating was maintained.

Figure 2 The X-ray diffraction pattern of a stationary deposited sputter coating, showing a crystalline structure, with a preferred (002) crystallographic orientation. The Si peaks are from the internal silicon standard.

Figure 3 The X-ray diffraction pattern of a rotated sputter coating, heat treated for 1 h at 650°C, showing a random orientated crystalline structure. The Si peaks are from the internal silicon standard.

Figure 4 Fourier transform infrared spectrum of a film sputtered at 700 W.

Figure 5 Fourier transform infrared spectrum of a film sputtered at 700 W after annealing for 1 h at 650°C.

Figure 6 Plot of (d_020 – d_01)/d_0 as a function of ε(ϕ) for a stationary deposited sputter coating. The crystalline film is under compressive stress.
Stability of cyclically loaded calcium phosphate coatings: J. G. C. Wolke et al.

Figure 7 Plot of $(d_{\text{obs}} - d_{c})/d_{c}$ as a function of $E(\phi)$ for a rotated sputter coating, heat treated for 1 h at 650°C. The data for the heat-treated coating show a stress-free film.

Figure 8 Scanning electron micrograph of a crystalline coated bar after cyclic loading tested in air, showing partial coating loss.

Figure 9 Scanning electron micrograph of an amorphous heat-treated coated bar after cyclic loading tested in air, showing no morphological changes.

Figure 10 Scanning electron micrograph of an amorphous coated bar after cyclic loading tested in simulated body fluid buffer, showing a crackle appearance of the coating and the formation of Ca–P precipitate (arrow).

DISCUSSION AND CONCLUSIONS

Fatigue behaviour of materials is generally determined by the presence of surface defects like cracks. Therefore, to evaluate the fatigue life of materials mostly cross-sectional analysis of the fracture interface is performed. However, due to the very low thickness of sputtered calcium phosphate coatings such research could not be performed and we had to confine ourselves to surface analysis of the tested coatings. Nevertheless, we can conclude that calcium phosphate coatings subjected to cyclic loading conditions show an important difference in fatigue behaviour when tested in dry or wet conditions.
Furthermore, we observed that the coating conditions (rotary or stationary substrate holder) influenced the residual film stress. Crystalline sputtered coatings showed the presence of compressive stresses. These measured residual stresses are attributed to processes occurring during film growth. During the deposition of the arriving atoms, the substrate temperature increases and the grains grow, resulting in a columnar structure. Subsequently, when the film is growing, the poor thermal conductivity properties of the ceramic Ca-P layer cause an increase in temperature of this film. As a result, the grains get more energy and grow. In this way, the grain size distribution increases and may reflect a change in the film structure with depth. This phenomenon causes the stress to vary with depth. For example, Hoffman and Thornton\(^2^5\) showed a linear relationship between force per unit and film thickness for sputtered material. In their experiment they sputtered chromium films and observed that the very thin film adherence was in a state of tension, but this was not manifested in thicker deposits because of the addition of a constant amount of compressive force per increment of film thickness.

Post-heat treatment at 650°C of amorphous deposited coating results in a stress-free crystalline film. This shows that the annealing of the amorphous film gives a uniform crystal structure with depth.

For the cyclically loaded calcium phosphate coatings tested in air, only the crystalline sputtered-coated bars showed a loss of coating. This phenomenon can be explained by the compressive stresses present in the deposited film. All the other air-tested coatings show no sign of delamination or any loss of coating after cyclic loading. On the other hand, in wet conditions (SBF) the amorphous coatings also appeared to be less stable. However, it should be noted that the amorphous coating only showed signs of delamination in the highly stressed regions, while in the less stressed areas a Ca–P precipitate was formed. Only the heat-treated sputter coating appeared to be stable under the test conditions. This is probably due to the very low dissolution rate of this stress-free film. The applied stress, due to the cyclic loading, should be considered as an important factor for the coating dissolution. Therefore, it can be suggested that the amorphous phase in a Ca–P coating demonstrates different fatigue behaviour. The different composition of this phase might alter the behaviour of an apatite coating under stress\(^2^2,2^3\). This theory is confirmed by Clemens\(^1^1\), who found extensive microscopical changes of plasma-sprayed amorphous HA coatings after cyclic loading under wet conditions, while crystalline coatings did not show any changes. Apparently, in his plasma-sprayed coating the combination of stress and dissolution had a dramatic influence on the integrity of the amorphous or glassy phase of the HA coating.

Furthermore, SBF buffer in combination with cyclic loading influenced the morphology of the amorphous sputter coating. The Ca, P and Mg concentrations in SBF are almost equal to those of human blood plasma. After 52 h the ion concentration will be increased and as a result a precipitate will be formed. The start of this precipitation process can be attributed to local supersaturation of both Ca and P caused by the dissolution of these ions from the film\(^1^9\). The crystalline and annealed amorphous sputter coating did not change the ion concentration in the SBF and no precipitate could be observed. The Ca/P ratio of the precipitate varied from 1.44 to 1.78 and the crystallographic structure indicated an amorphous calcium phosphate (ACP). It has been reported that Mg ions can inhibit apatite maturation and growth. The most important parameters driving this phenomenon seem to be the temperature and the pH of the solution\(^2^4\). In slightly alkaline solutions ACP transforms in a few hours to HA or non-stoichiometric apatite. Another possible mechanism is that ACP (in the presence of Mg ions) first forms octacalcium phosphate (OCP). This suggests that the transformation proceeds via an OCP-like crystalline phase, followed by hydrolysis into apatite\(^2^5,2^6\). Furthermore, it should be pointed out that this apatite formation process will influence the final bone-bonding properties.

In summary, our findings show clearly that the integrity of calcium phosphate sputter coatings under cyclically loaded conditions demonstrated different behaviour when tested in dry or wet conditions. The heat-treated sputter coating appeared to be the only stable coating under the applied cyclic stress levels. However, it has to be emphasized that extrapolation of these in vitro results to in vivo behaviour is very complicated\(^6,7\).

ACKNOWLEDGEMENTS

This study was supported by the Netherlands Technology Foundation (STW). The authors thank Mr M. O'Driscoll, University of Dublin, Department of Mechanical Engineering, for his help with the three-point bending test.

REFERENCES

Stability of cyclically loaded calcium phosphate coatings: J. G. C. Wolke et al.


