

# Thin Calcium Phosphate Coating Deposited on NiTi and Ti<sup>1</sup>

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**Abstract – Calcium phosphate coatings with the thickness of up to 2.7 micron were deposited by rf-magnetron sputtering. Scanning electron microscopy, nanohardness technique, adhesion test, atomic absorption spectroscopy were used to study the properties of the coatings. The coatings thickness was determined by mechanical profilometry method. The nanohardness and Young's modulus of calcium phosphate coating are 10 and 110 GPa, respectively. The adhesion strength of the calcium phosphate coating to metallic substrates depended on the coating's thickness and decreased for a thickness more than 1.6  $\mu\text{m}$ . No difference was observed between NiTi and Ti substrates. Calcium-phosphate coating on the NiTi surface promoted a decrease in nickel release rate, which depended on the rf-power applied.**

## 1. Introduction

Release of such harmful elements as nickel, chromium and other implants can cause allergic reactions in human body. There are a few ways to overcome this problem. The first one is to use an implant made from materials harmful-free elements (e.g., titanium). The second way is to cover the surface of an implant with a thin biocompatible coating that is capable of reducing the release of toxic agents.

The modification of the surface of NiTi can facilitate some decrease in the nickel release rate. Under modification one understands a formation of an interface that would act like a barrier on the way of the nickel ions from the bulk. A thin biocompatible coating can be the best candidate that allows not only to prevent or decrease the leaching of nickel ions but to improve the surface properties of the metal. To deposit such a coating one should apply the technique that can give maximal efficiency, i.e., the coating must meet some requirements which are optimal for the long use of an implant (thickness, composition, adhesion strength and so on).

Rf-magnetron sputtering [1–6] is one of the best candidates to deposit thin calcium-phosphate coating because it allows to prepare a dense, pore-free with high adhesion strength coating to different metallic substrates such as  $\text{Ti}_6\text{Al}_4\text{V}$  [8, 9], NiTi [7] and titanium [7]. Hydroxyapatite (HA) is mostly used as a target material; therefore, the coating composition resembles calcium-phosphate. Hydroxyapatite,  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ ,

is an important geological calcium phosphate mineral and constitutes the inorganic component (biomineral) of human hard tissue, i.e., of teeth and bone [10, 11]. Due to its excellent biocompatibility, it is well established as coating for metallic implants in medicine, e.g., for hip endoprostheses and for tooth implants.

## 2. Materials and methods

Plates ( $10 \times 10 \times 0.5$  mm) of NiTi and Ti were used as substrates. Before sputtering, all samples were mechanically polished to the roughness class 10 ( $R_a = 0.1 \mu\text{m}$ ). An installation type Cathode 1M with a magnetron in the vacuum chamber was used to prepare a thin calcium phosphate coating. The following parameters were applied during the sputtering process: frequency of the rf-generator 13.56 MHz, working gas argon (0.5 Pa), incident power of the rf-generator 2 kW, reflected power 200 W, and distance between substrate and magnetron target 50 mm. The sputtering chamber was evacuated to less than  $5 \cdot 10^{-5}$  Pa and then argon was introduced as a sputter gas. By variation of the sputtering time from 10 to 320 min, the coating thickness was in the range 0.09–2.7  $\mu\text{m}$ . In the preliminary experiments, these parameters were found to be optimal for deposition of calcium phosphate coating.

We used a target made of microcrystalline synthetic hydroxyapatite prepared from a powder with a particle size of 80 nm by pressing at 70 MPa and subsequent sintering at 1000 °C in air for 1 h. The metallic substrate was heated to 500 °C by the plasma in experiments, and its temperature was controlled with a Pt/PtRh thermocouple. This set of parameters with a high value of the rf-power was fixed in the experiments because we aimed at a hydroxyapatite coating with high crystallinity [12].

The coating thickness was determined with a mechanical profilometer Talysurf 5 (Tyler–Hobson, England). The coating thickness was determined by shielding a part of the sample from the sputtering target, thereby preventing the coating formation on this part of the sample. The thickness of the coating was determined by measuring the profile of the resulting edge and determination of the step height. The profilometer vertical resolution was 10 nm and the horizontal resolution was 2  $\mu\text{m}$  (determined by the radius of scanning needle).

The mechanical parameters of the coating were determined by dynamic nanoindentation with a Vickers

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Nanohardness tester (CSEM Instruments). The immersion rate of the Vickers diamond pyramid with an angle between opposite faces of  $136^\circ$  was  $5 \text{ mN min}^{-1}$  and the time of a loading-unloading cycle was 2 min. Eight indentations were made on the coating surface of each sample and then an average value was calculated for each sample. The adhesion parameters were determined with a Micro Scratch Tester (CSEM Instruments) equipped with a Rockwell indenter with a tip radius of  $20 \mu\text{m}$ . The adhesion strength was measured in three ways: 1) acoustic emission data, 2) control of the friction coefficient, and 3) visual inspection of the coating failure area with an optical microscope after scratching. The parameters of the scratch test were chosen as follows: Indenter lateral motion speed  $7 \text{ mm min}^{-1}$ , loading rate  $2 \text{ N min}^{-1}$ , maximum applied load 2 N.

Atomic Absorption Spectroscopy (AAS) was chosen to measure the release of nickel from individual NiTi plates (surface area  $2.08 \text{ cm}^2$ ) with the sides coated by calcium phosphate. The immersion experiments were carried out for 42 days in ultra-pure water obtained with a Pure-lab Ultra Instrument (ELGA) and in saline solution 0.9% NaCl.

### 3. Results and discussion

All coatings to be used in medical practice require a sufficient mechanical strength, i.e., adhesion strength and cohesive resistance. In particular, the mechanical properties are very important with respect to the long-term stability of an implant.

Therefore, we determined Young's modulus  $E$ , nanohardness  $H$  and contact stiffness  $S$  of as-deposited coatings using nanoindentation, i.e., the penetration depth of a diamond indenter into the coating with continuously increasing load was measured.

Nanohardness  $H$  and Young's modulus  $E$  as a function of the coating thickness are shown in Fig. 1.

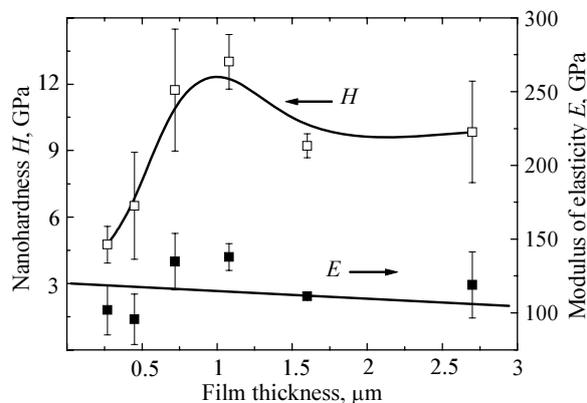


Fig. 1. Nanohardness  $H$  and Young's modulus  $E$  of calcium phosphate coating on titanium as a function of the coating thickness

The obtained data indicate that the titanium substrate influences the nanohardness of the calcium

phosphate coating only if its thickness is less than  $700 \text{ nm}$ . The nanohardness of a titanium substrate is about 4 GPa [13] and its Young's modulus is 110 GPa [14] are in good agreement with the values obtained in this study. The nanohardness of Ti is considerably lower than that of the thin calcium phosphate coating whereas Young's modulus is comparable (nanohardness about 10 GPa and Young's modulus about 110 GPa). For a NiTi substrate, very similar results were obtained with the exception that NiTi had a higher nanohardness [ $12.0 \pm 0.7 \text{ GPa}$ ] than titanium but a comparable Young's modulus [ $90 \pm 4 \text{ GPa}$ ]. This value depends on the phase composition of the NiTi but is in good accordance with the data known in literature (70 GPa) [15, 16].

We ascribe the scatter in the experimental results to the sensitivity of the nanohardness technique, i.e., the results obtained depend on the substrate surface roughness, the indenter state and other parameters. Although all substrates were carefully polished before sputtering, we assume that there are variations in the substrate surface morphology which caused the observed scatter.

The results (Fig. 1) indicated that the effect of substrate material vanished when the coating thickness becomes larger than  $700 \text{ nm}$ . We could confirm the excellent adhesion of the sputter-deposited calcium phosphate coating if its thickness does not exceed  $1.6 \mu\text{m}$ .

The typical view of the load-displacement curves obtained for the titanium substrate and for the calcium phosphate coating on titanium are shown in Fig. 2.

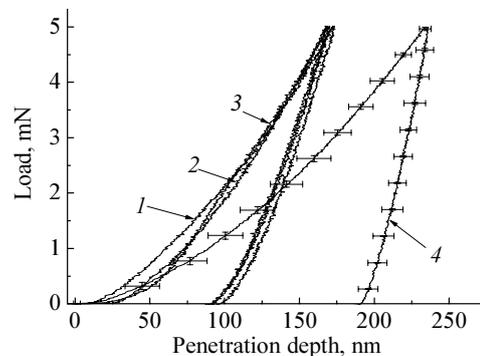


Fig. 2. Load-displacement curves from nanoindentation obtained for calcium phosphate coating of  $1.6 \mu\text{m}$  thickness on titanium (curves 1, 2, and 3) and a non-coated titanium substrate (curve 4)

The load-displacement curves showed that the deformation behavior of the coating as well as that of the titanium substrate was plastic with some elastic components, i.e., when the load was removed, a part of the deformation relaxed. Nanohardness and contact stiffness of the calcium phosphate coatings were larger than those of the titanium substrate. The substrate influenced  $H$ ,  $E$ , and  $S$  only if the coating thickness was lower than  $0.7 \mu\text{m}$ . We conclude that the nanohardness and the Young's modulus of the pure calcium phosphate coating itself are about 10 and 110 GPa,

respectively. We also found that the value of the nanohardness decreased when the indenter penetration depth increased, a phenomenon known as Indentation Size Effect [17, 18].

The adhesion strength between the calcium phosphate coating and the substrate was determined by the scratch test method. Calcium phosphate coatings deposited on Ti and NiTi substrates were studied. In the Figure 3 is shown that there are no signs of a coating failure near the scratch; the coating was not even damaged when a maximal chosen load of 2 N was reached.

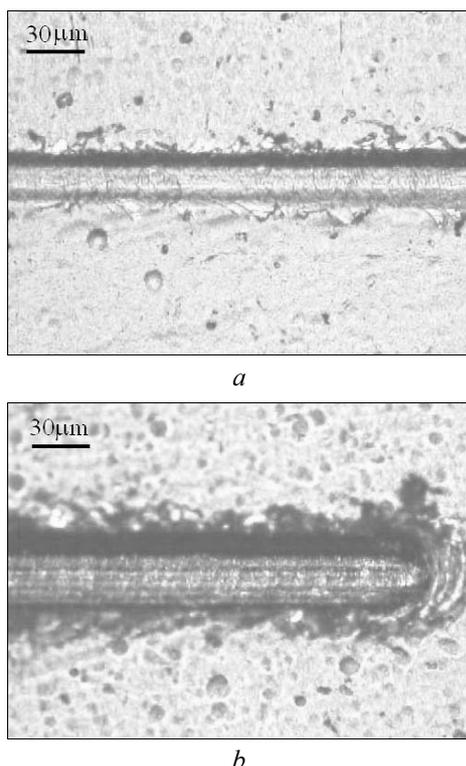


Fig. 3. At a film thickness of 1.6 μm, the calcium phosphate coating on titanium was not completely damaged during the scratch test experiment. There were some signs of the deformative wave ahead of scratching direction. The images (a) and (b) were taken at 0.87 and 2 N, respectively. Equivalent results were obtained for calcium phosphate on NiTi

When the indenter penetrated into the substrate, no tracks of coating bursting along a scratching direction were found. A similar behavior was observed when other samples (with the same or a smaller thickness) were investigated; these coatings were only impressed into the coating–metal interface and no signs of coating failure were seen at the edges of the scratch.

We conclude that all coatings with a thickness of less than 1.6 μm possess both a sufficient adhesion strength and cohesive resistance.

The high values of adhesion strength can be explained by the fact that during calcium phosphate coating growth, the ions ejected from the target form a chemisorbed state with the surface atoms of the substrate. For Ti and NiTi substrates, the surfaces are always covered with a very thin oxide layer. This

leads to a strong interaction (with a binding energy above 0.5 eV) between substrate and coating [19].

The mode of damaging of calcium phosphate coating with a thickness more than 1.6 μm differed from that of the thinner calcium phosphate coatings. The destruction of the coatings with a thickness less than 1.6 μm occurred only after its perforation, whereas thicker coatings collapsed by exfoliation, splits and chips along the scratching direction. With a thickness of 2.7 μm, cracking and detachment of the coating surface layers started at a loading force of 0.42 N. When the force reached 0.66 N, the coating burst, and at a force of 1 N, calcium phosphate coating was completely damaged. The acoustic emission signal at a force of 0.42 N also indicated the detachment of the coating from the substrate. This was observed for all forces up to 2 N.

To study an effect of the calcium phosphate coating on nickel release rate the following procedures were used. Rf-power was set at 290 and 30 W; argon, oxygen and a gaseous mixture of argon with oxygen (1%) were applied; all other parameters such as working gas pressure (0.1 Pa), the distance between magnetron and substrates (40 mm) were kept constant. All the samples were left unpolished to eliminate the difference in the surface roughness on the results of experiments. The release of nickel was measured for 42 days. The concentration of nickel in blind solutions as well as in all initial media used was always zero. The cumulated nickel release was shown in the Figure 4 and the calculated values for nickel release rate were summarized in Table 1.

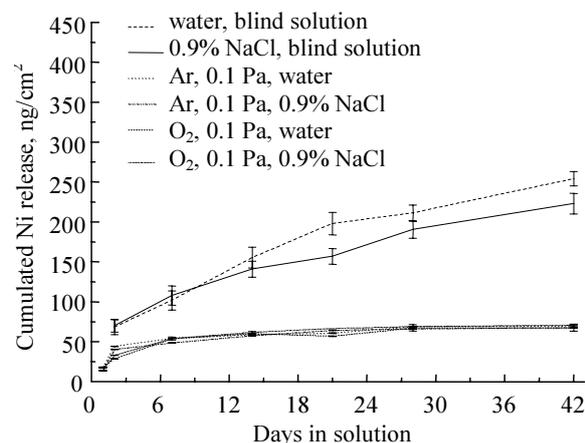


Fig. 4. The patterns of cumulated nickel release from uncovered NiTi substrates and substrates with a protective calcium-phosphate coating deposited at the rf-power of 290 W

Table 1. The nickel release rate

Rf-power, W	The rate of Ni release, ng/(cm <sup>2</sup> · day)	
	Pure water	Saline solution (0.9 % NaCl)
290	1.0 ± 0.4	1.1 ± 0.5
30	5.0 ± 2.8	5.5 ± 2.4

In case of un-coated NiTi samples the release of nickel was calculated to be  $5.0 \pm 2.4$  and  $4.5 \pm 2.2$  for water and saline solution, respectively.

There were found no coatings on the surface of NiTi that were deposited at rf-power of 30 W even after 1 day of exposure in both used solutions and the coatings had no favorable effect on nickel release rate.

We assume that the amorphous nature of calcium-phosphate coating deposited at low power is a main reason that explains a coating dissolution occurred. On the other hand, there were found some signs of the coatings delamination after exposure to the media when rf-power of 290 W was applied to prepare coatings. Moreover, the rate of nickel release was 5 times lower in compare to uncovered samples. We established no influence of the atmosphere during sputtering on the nickel release rate for the coating deposited at the power of 290 W. It is feasible to assume that calcium-phosphate coating on the NiTi surface promotes a decrease in nickel release rate, which depends on the rf-power applied. On the data obtained, we assume that the further decrease in nickel release rate can be achieved if a more crystalline coating is deposited.

#### 4. Conclusions

By rf-magnetron sputtering, it is possible to prepare thin, uniform and crystalline hydroxyapatite coating on titanium as a classical implant material and on nickel–titanium which is also applied as superelastic or shape-memory material for implants. The mechanical parameters of the coatings are optimal if they are thinner than 1.6  $\mu\text{m}$ . On the other hand, the effect of the substrate is only important if the film is thinner than about 1  $\mu\text{m}$ . There was established a positive effect of calcium-phosphate coating deposited by rf-magnetron sputtering on the nickel release rate. An average nickel release rate from the samples with a calcium-phosphate coating was 5 times lower in compare to uncoated ones and the coatings deposited at rf-power of 30 W. We established no influence of the solution composition (water or 0.9% NaCl) on the nickel release rate. The reasons explaining the release of nickel in case of the coatings deposited at 290 W can be as follows, dissolution of an amorphous part of the coating; residual stress in the coatings due to deposition process; not the whole surface can be concealed with a protective coating. Deposition of amorphous coatings (low rf-power) is unreasonable, for due to fast coating dissolution the effect of the coating on the nickel release is diminished. We suggest that

further decrease in nickel release can be achieved if more crystalline coatings are deposited, i.e., the coating crystallinity determines the dissolution rate.

We finally conclude that rf-magnetron sputtering is well suited to coat implant metals and alloys with a thin bioactive calcium phosphate layer.

#### References

- [1] E.M. Burke, J.D. Haman, J.J. Weimer, A.B. Cheney, J.M. Rigsbee, and L.C. Lucas, *J. Biomed. Mater. Res.* **41**, 57 (2001).
- [2] J.G.C. Wolke, J.P.C.M. van der Waerden, H.G. Schaeken, and J.A. Jansen, *Biomaterials* **24**, 2623 (2003).
- [3] V. Nelea, C. Morosanu, M. Iliescu, and I.N. Mihailescu, *Surface Coatings Technol.* **173**, 315 (2003).
- [4] S. Xu, J. Long, L. Sim, C.H. Diong, and K. Ostrikov, *Plasma Proc. Polym.* **2**, 373 (2005).
- [5] Y.T. Zhao, Z. Zhang, Q.X. Dai, D.Y. Lin, and S.M. Li, *Surface Coatings Technol.* **200**, 5354 (2006).
- [6] J. Long, L. Sim, S. Xu, and K. Ostrikov, *Chem. Vapor. Deposition* **13**, 299 (2007).
- [7] H. Monma, O. Nemoto, S. Takahashi, and H. Kobayashi, *J. Electroceramics* **4**, 135 (S1) (1999).
- [8] S. Rößler, A. Sewing, M. Stölzel, R. Born, D. Scharnweber, M. Dard, and H. Worch, *J. Biomed. Mater. Res. A* **64**, 655 (2003).
- [9] H. Urch, S. Franzka, D. Dahlhaus, N. Hartmann, E. Hasselbrink, and M. Epple, *J. Mater. Chem.* **16**, 1798 (2006).
- [10] S. Weiner and H.D. Wagner, *Annu. Rev. Mater. Sci.* **28**, 271 (1998).
- [11] S.V. Dorozhkin and M. Epple, *Angew. Chem. Int. Ed.* **41**, 3130 (2002).
- [12] V. Nelea, C. Morosanu, M. Iliescu, and I.N. Mihailescu, *Appl. Surf. Sci.* **228**, 346 (2004).
- [13] G.B. de Souza, C.E. Foerster, S.L.R. da Silva, F.C. Serbena, C.M. Lepiński, and C.A. dos Santos, *Surf. Coatings Technol.* **191**, 76 (2005).
- [14] W.D. Callister, *Materials Science and Engineering*, New York, John Wiley and Sons, 2000.
- [15] G.Q. Song and Q.P. Sun, *Smart Mater. Struct.* **9**, 693 (2000).
- [16] I. Mihalcz, *Periodica Polytechnica Ser. Mech. Eng.* **45**, 75 (2001).
- [17] D. Tabor, *The Hardness of Metals*, Oxford, Clarendon Press, 1951.
- [18] M. Atkinson, *J. Mater. Sci.* **30**, 1728 (1995).
- [19] A. von Keudell, *J. Plasma Sources Sci. Technol.* **9**, 445 (2000).