Properties of magnetron hydroxyapatite coatings deposited on oxidized substrates

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Hydroxyapatite (HA) coating were formed on oxidized niobium surfaces by the high-frequency magnetron sputtering method using hydroxyapatite and tricalcium phosphate targets. The structure, substructure and mechanical properties of the Nb–Nb_2O_5–HA system were investigated by X-ray diffraction, atomic force microscopy and nanoindentation and the stress state was assessed. The synthesized hydroxyapatite film had the following characteristics: thermal expansion coefficient 10^{-5} K^{-1}; modulus of elasticity 120 GPa; adhesive strength not less than 0.45 kg/mm^2; density 2900 kg/m^3. The stress magnitude in the metal oxide substrate was from 11 to 14 MPa after hydroxyapatite film deposition.

Keywords: elasticity modulus, hydroxyapatite, magnetron sputtering, nanohardness, macrostresses, oxide

1. INTRODUCTION

Materials based on hydroxyapatite (HA), $Ca_{10}(PO_4)_6(OH)_2$, are widely used in medicine because their chemical and phase composition is similar to the mineral component of bone tissue [1]. A major obstacle to the use of HA as an independent structural material for the production of medical implants is its poor mechanical properties. The most efficient solution involves applying HA coatings on metal implants [2]. This allows, on the one hand, the ability to limit the contact of bone with metals that are generally more active in comparison with ceramics and, on the other hand, to achieve a more rapid and complete integration of the implant into the bone tissue after surgery.

Most methods for producing HA coatings have significant disadvantages [3, 4]: sol–gel, electrophoretic and electrolytic depositions do not provide sufficient reproducibility of homogeneity and elemental and phase composition. There is the problem of coating contamination by solution components as well as insufficient adhesion due to the contamination of substrates. To increase coating crystallinity, additional thermal treatment is required. Biomimetic methods provide good repeatability, but are extremely slow and do not solve the contamination problem for coating and substrate. Plasma spraying does not provide compositional homogeneity of the coating phase and significantly embrittles the substrate due to the high temperature stream. Maximum repeatability of the coating's composition and structure is reached by vacuum deposition methods: electron-beam sputtering, laser ablation, ion-beam sputtering or high-frequency magnetron spraying [5].

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The major technical difficulty of deposition of HA coatings on metal substrates is the low adhesion of hydroxyapatite to metal, in particular titanium [6]. To solve the problem, it has been proposed that a preliminary ultrasound treatment of the metal to grind off grain and increase hardness is followed by microarc oxidation of the titanium surface in combination with the deposition of HA microparticles [7]. In spite of the initial positive results from applying this method, the HA layer can be fully resorbed during continuous functioning of the implant. In this case, the electrochemical corrosion processes are activated with an intensity that depends upon the electrical conductivity of contacting layers [3] in the contact zone of the new osteoinductive bone with the metal implant. Because crystalline titanium oxide has significantly greater electric conductivity in comparison with amorphous oxide of even smaller thickness, the latter is more effective as a passivating coating before deposition of the HA layer.

The formation of an amorphous oxide on some metals (Ti, Zr, Nb, Ta) by the anodic oxidation method provides a softer surface in comparison with microarc oxidation and includes sequential potentiostatic and galvanostatic oxidation steps. The HA layer in this case can be deposited by vacuum methods.

To obtain durable compact HA coatings with high phase and structural homogeneity, the ion sputtering technique is most promising and provides more complete retention of the sputtering target chemical composition in the film. However, despite the considerable number of studies devoted to HA coating methods, there is no consistent set of data on the regularities of phase structure and substructure formation during coating

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deposition. Also, the problem connected with the adhesion strength of HA coatings on titanium surfaces has not yet been completely solved.

The aim of this paper is the study of the peculiarities of HA coating deposition by high-frequency magnetron sputtering on metal substrates with an amorphous oxide layer, as well as the study of the structure, morphology and mechanical properties of the coating.

2. MATERIALS AND METHODS

Niobium foil was annealed in vacuum at a pressure $P \sim 10^{-3}$ Pa and a temperature $T = 1600$ °C during $\tau = 1$ h in order to reduce mechanical tension and clean the surface of the substrates.

The technique of anodic oxidation was used [8]. As a result, niobium oxide Nb_2O_5 in an amorphous state was formed on the niobium surface. To confirm the oxide type, the oxide film was converted from an amorphous state to a crystalline one by photon annealing, after which the crystal oxide phase of Nb_2O_5 was confirmed by X-ray diffraction analysis on the niobium surface.

Production of calcium phosphate films was carried out by high-frequency magnetron sputtering [9]. The target had a stoicheiometric composition with a Ca/P ratio = 1.67. Deposition of films was carried out on metal (Nb) and metal oxide (Nb–Nb_2O_5) substrates. The distance between target and substrate was 50 mm and the growth rate of the films was about 0.2 nm/s. Calibration of the growth rate was via measurement of film thickness by scanning probe microscopy (SOLVER P47).

The X-ray determination of the phase structure used a DRON-2.0 diffractometer according to the Bragg–Brentano scheme θ-2θ. To eliminate reflexions from the K_β-radiation, a manganese filter was used. The survey was conducted pointwise with 0.1° steps and the exposure at each point was 10 s in the angular range 2θ = 15–120°.

The thickness *t* of the HA coatings was controlled by a Linnik interferometer, together with scanning electron micrographs of the sample lateral surfaces and X-ray fluorescence analysis using signal attenuation from the niobium substrate. The morphology of the surface was investigated using atomic force microscopy (AFM).

The standard method of the cylindrical butt joint was applied to determine heterostructure adhesive durability. A cylinder made of stainless steel (diameter 2 mm) was epoxy-glued to the prepared samples. The force applied to the surface was 3–5 kg/cm^2 and the exposure time was 24 h. A destructive test of the cylindrical samples was made with a 2038P-005 machine with a greatest maximum load of 500 N; the specimen under test was set in the holder of the machine and was monitored for effort and separation moment at stressing. After rupture the surface was examined under an optical microscope in the torn area enabling calculation of the mechanical tension that led to separation.

The tension in the metal–oxide substrate after HA film deposition was estimated using substrate bending [10]. The calculation can be made in two ways: by analysing the bending of the central part, or according to substrate end bending with the other end firmly fixed; the latter was used in the present work:

$$\sigma = \frac{16Ed^2y}{27tl^2}, \quad (1)$$

where *E* is the modulus of elasticity of the substrate; *d* the substrate thickness; *t* the film thickness; *y* the substrate end bending and *l* the substrate length. The values of the modulus of elasticity and the thermal expansion coefficient of the niobium substrate were determined using handbook information [11].

In addition, the modulus of elasticity and the thermal expansion coefficient of the HA layer was determined experimentally from the movement of the free sample ends during mechanical or thermal loading when the other end was firmly fixed.

3. RESULTS AND DISCUSSION

X-ray phase analysis showed that the calcium phosphate coatings deposited by high-frequency magnetron sputtering on a Nb–Nb_2O_5 metal–oxide substrate were generally single-phase and consisted of hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ (Fig. 1). It can be seen that there are two systems of diffraction lines—strong lines from the niobium substrate and weak lines from the HA film. The halo of the amorphous oxide film was essentially absent. The intensities of the niobium lines in the diffraction pattern are different from the literature data, namely the (200) line is strengthened. This can be explained by the presence of a rolling texture acquired during foil manufacture. Groups of less intense lines coincide with the reflexions of the HA phase. However, the ratios of line intensities also differ from reference data and indicate the presence of (001) texture.

From the broadening of the small angle (002) diffraction line, it is possible to estimate the size *L* of the coherent dispersion area from the Selyakov–Scherrer formula. The X-ray investigation used a tube with an iron anode (λ = 1.93728 Å); broadening of the (002) line was 0.34° and the line angle θ = 16.3°, whence the calculated *L* was 340.6 Å.

Figure 2 shows AFM scans of the niobium plate surface before oxidation, after deposition of Nb_2O_5 of 200 nm thickness, and after high-frequency magnetron

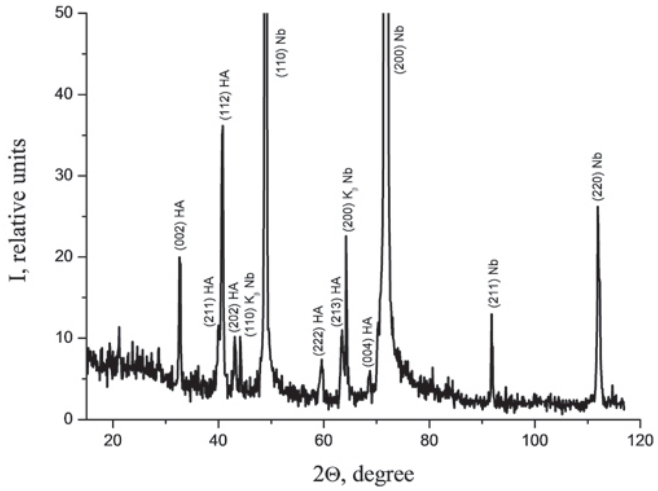

Figure 1. The XRD pattern of a niobium sample with oxide and hydroxyapatite coating.

deposition of HA (layer thickness ~ 1 μm). Table 1 gives the surface topography parameters calculated by the SOLVER P47 software. The topography of the initial niobium plate surface (Fig. 2a) is determined by a periodic band relief typical for metal surfaces after electrochemical polishing. The surface morphology is characterized by clear delineation of areas with lateral dimensions of 1–2 μm, indicating the blocky structure of the polycrystalline niobium plate. The low relief parts show the homogeneity and smoothness of the prepared surface.

The topography of the oxidized niobium plate surface (Fig. 2b) is determined by globular relief inhomogeneities with lateral dimensions in the range 0.1–0.3 μm. On forming the oxide layer with a thickness of about 100 nm on the niobium plate there is a development of surface relief—the formation of separate projections of height 100–160 nm. A smooth homogeneous surface topography is formed with an increase of integral oxide thickness to 200 nm.

For oxidized niobium plates with an HA layer (Fig. 2c) the surface topography indicates the formation of a particular relief peculiar to films of amorphous (nanocrystalline) hydroxyapatite. The lateral dimensions of relief inhomogeneities were 100–1000 nm, indicating the layered nature of film growth. A smoother and homogeneous HA film is formed on niobium substrates with oxide 200 nm thick.

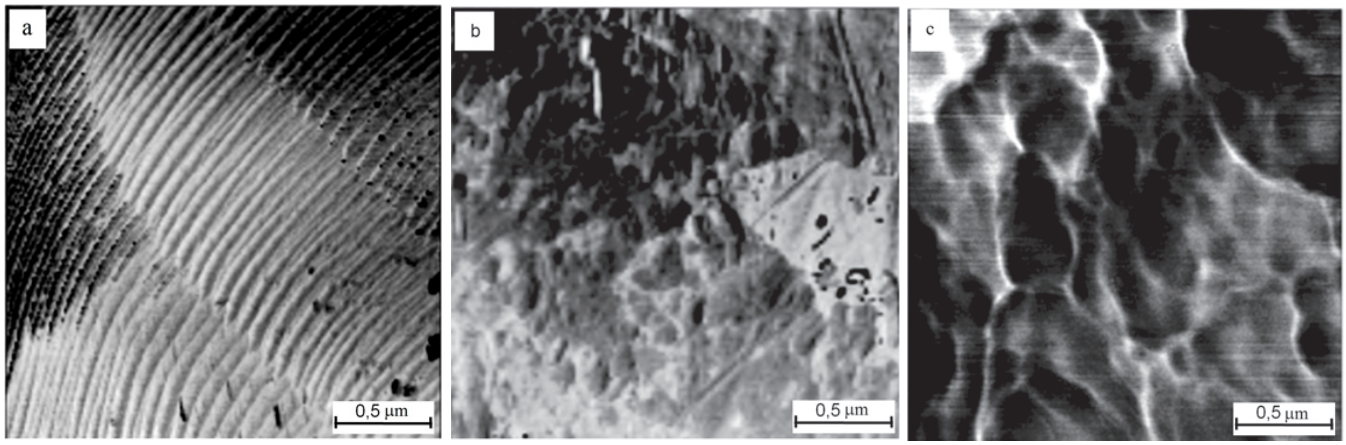

Figure 2. AFM surface scans. (a) Nb, (b) Nb–Nb_2O_5, (c) Nb–Nb_2O_5–HA.

Table 1. The parameters of the samples surface relief.

Sample characteristics	Roughness / nm	Average relief height / nm	Elevation / nm
Nb	11	29	60
Nb–Nb_2O_5 (100 nm)	32	62	160
Nb–Nb_2O_5 (200 nm)	8	33	65
Nb-HA	35	120	150
Nb–Nb_2O_5 (100 nm)–HA	46	280	450
Nb–Nb_2O_5 (200 nm)–HA	18	85	120

The HA film density ρ was found to be 2900 kg/m^3 by small-angle X-ray scattering, less than that of compact HA (3140–3210 kg/m^3).

Nanoindentation results of samples at various stages of coating deposition are given in Table 2. The experimentally obtained values of the modulus of elasticity and hardness of niobium are in good agreement with previously published data [12]. Anodic oxidation of niobium increases the hardness, which almost doubled, while the modulus of elasticity was not

changed significantly. The hydroxyapatite coating has a higher stiffness and a considerably higher hardness as compared with niobium in the initial state and after anodic oxidation.

Table 2. The modulus of elasticity E and the hardness H of various samples.

Sample	E/GPa	H/GPa
Nb	108.9	3.17
Nb–Nb_2O_5 (100 nm)	118.1	6.59
Nb–Nb_2O_5 (200 nm)	99.4	6.65
Nb–Nb_2O_5 (100 nm)–HA	164.5	12.36
Nb–Nb_2O_5 (200 nm)–HA	145.3	10.16

The hardness and elastic deformation upon indentation of the HA film increase with increasing load, which is associated with the particular morphology of the film surface. The hardness of the HA films on the surface of the heterostructure Nb–Nb_2O_5 does not depend on the load in the range 1.0–2.0 mN, which is the criterion for a compact structure.

Destruction for all Nb–Nb_2O_5–HA samples occurred at the HA-epoxy boundary when testing adhesive strength, which indicates a high adhesion of both the Nb–Nb_2O_5 and Nb_2O_5–HA interfaces. The adhesive strength of the HA–epoxy boundary was about 0.45 kg/mm^2. Hence, the adhesive strength of the HA coating on the Nb–Nb_2O_5 surface must be not less than that.

Because the metal–oxide substrate and the HA coating have different properties, there are mechanical stresses in the layers after high-frequency magnetron sputtering of HA and cooling. These stresses can reach a critical value and cause delamination of the HA coating. Therefore, monitoring of mechanical stress should be carried out both in the initial state and during thermal cycling. This will prevent possible destruction of the coating during implant sterilization (heating to 200° C in an aggressive sterilizing environment) and implant installation into the bone tissue.

The thickness of oxide film is not included in the calculation because it was substantially less than substrate thickness and hydroxyapatite coating thickness. The calculation was made according to the formula (1). Parameters of the samples and calculated values are given in Table 3.

Table 3. Parameters of samples and calculated stresses in HA.

Parameter	Sample № 1	Sample №2
Sample length / mm	51	45
Niobium substrate Thickness / μm	80	80
HA coating thickness / μm	1	1.66
Stress / MPa	11.2 ± 0.5	13.6 ± 0.5

An estimation was made of the HA coating modulus of elasticity using a system of Nb–Nb_2O_5–HA bending with one end fixed and an external mechanical load applied to the free end. Tests were performed for a system with an oxide layer thickness of 200 nm.

The thermal expansion coefficient α_{HA} was determined upon thermal loading of the system without external mechanical load. One sample end was fixed and heat was supplied to the other end. The bending depended on the difference of the thermal expansion coefficients of niobium and HA, because the amorphous oxide thickness was negligible in comparison with the substrate and HA film. Using literature data for niobium (E_{Nb} = 110 GPa, $\alpha_{Nb} = 7.3 \times 10^{-6}$ K^{-1}) [10] we obtained the following values for HA: E_{HA} = 120 GPa, $\alpha_{HA} = 10^{-5}$ K^{-1}. This value of the HA modulus of elasticity is 10–15% less than the value using nanoindentation, which may merely individual differences between samples.

We also investigated the changes of mechanical stress in the Nb–Nb_2O_5–HA system under isothermal (T = 400 °C) and isochoric (exposure time τ = 1 h) annealing. X-ray diffraction patterns taken after annealing were similar to those of the original sample (Fig. 1), indicating no change of phase composition during thermal treatment.

The results of thermal tests of the Nb–Nb_2O_5–HA system are shown in Fig. 3. In the initial state the tension is determined by both structural and thermal factors. Samples with different initial stress values end up with the same constant stress $\sigma \sim 5$ MPa. The magnitude of the residual stress according to Hooke's law is determined by the formula:

$$\varepsilon_{def} = \frac{\sigma}{E_{Nb}}. \quad (2)$$

Taking into account the niobium substrate modulus of elasticity E_{Nb} = 110 GPa, the relative deformation is $\varepsilon_{def} = 4.5 \times 10^{-5}$. Because the residual deformation is constant, it can be assumed that the deformation is caused by the difference of thermal expansion coefficients of contacting layers:

$$\varepsilon_{def} = (\alpha_{HA} - \alpha_{Nb}) \cdot \Delta T. \quad (3)$$

Using the magnitude of residual deformation, the HA thermal expansion coefficient was estimated from the formula:

$$\alpha_{HA} = \frac{\alpha_{Nb} \times \Delta T + \varepsilon_{def}}{\Delta T} \quad (4)$$

(it was assumed that the substrate was heated during deposition of the coating to $T \sim 400$ °C, and we know the niobium thermal expansion coefficient $\alpha_{Nb} = 7.3 \times 10^{-6}$ K^{-1}). The resulting HA thermal expansion coefficient is of the same order as the value calculated by the temperature effect of Nb–Nb_2O_5–HA bending.

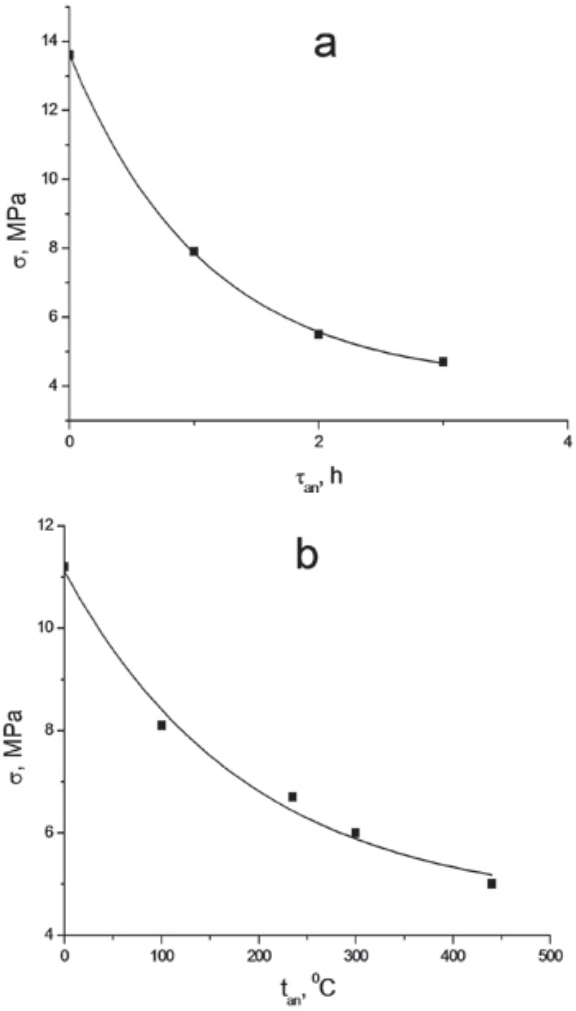

Figure 3. Dependence of mechanical stress in the system Nb–Nb_2O_5–HA on time (a) and temperature (b) annealing.

4. SUMMARIZING CONCLUSIONS

A comprehensive study of the structure, substructure and mechanical properties of the Nb–Nb_2O_5–HA system and its individual layers was carried out by X-ray diffraction, atomic force microscopy, nanoindentation and a complex of techniques for the estimation of the stress states of thin layers and systems based on them.

It was found that a single-phase $Ca_{10}(PO_4)_6(OH)_2$ coating is formed on oxidized niobium by magnetron sputtering of tricalcium phosphate and HA targets.

The obtained characteristics of the hydroxyapatite film deposited by high-frequency magnetron sputtering are: thermal expansion coefficient $\alpha_{HA} = 7.5 \times 10^{-6}$ K^{-1}; modulus of elasticity E_{HA} = 120 GPa; adhesive durability of hydroxyapatite coating on the Nb_2O_5 oxide $\not<$ 0.45 kg/mm^2; density = 2900 kg/m^3.

The magnitude of mechanical stresses in the metal substrate during HA film deposition is in the range 11–14 MPa. The relaxation of this stress in the Nb–Nb_2O_5–HA system was investigated as a function of both annealing temperature and annealing duration.

REFERENCES

1. Ben-Nissan, B. *Advances in Calcium Phosphate Biomaterials,* p. 547. Berlin: Springer (2014).
2. Leon, B. and Jansen, J.A. *Thin Calcium Phosphate Coatings for Medical Implants,* p. 326. New York: Springer (2009).
3. Yang, Y., Kim, K.H. and Ong, J.L. A review of calcium phosphate coatings produced using a sputtering process —an alternative to plasma spraying. *Biomaterials* **26** (2005) 327–337.
4. Nguyen, H.Q., Deporter, D.A., Pilliar, R.M., Valiquette, N. and Yakubovich, R. The effect of sol-gel-formed calcium phosphate coatings on bone ingrowth and osteoconductivity of porous-surfaced Ti alloy implants. *Biomaterials* **25** (2004) 865–876.
5. Hulshoff, J.E., van Dijk, K., van der Waerden, J.P., Wolke, J.G., Kalk, W. and Jansen, J.A. Evaluation of plasma-spray and magnetron-sputter Ca-P-coated implants: an *in vivo* experiment using rabbits. *J. Biomed. Mater. Res.* **31** (1996) 329–337.
6. Klimenov, V.A., Ivanov, Yu.F., Karlov, A.V., Solonenko, O.P., Trofimov, V.V., Semukhin, B.S. and Botaeva, L.B. Structure and phase composition of apatite coatings on implants in plasma spraying. *J. Adv. Mater.* **3** (1997) 402–408.
7. Klimenov, V.A., Ivanov, Yu.F., Karlov, A.V., Solonenko, O.P., Trofimov, V.V., Semukhin, B.S. and Botaeva, L.B. Structure and phase composition of apatite coatings on implants under plasma deposition. *J. Adv. Mater.* **3** (1997) 44–50.
8. Starikov, V.V., Starikova, S.L., Mamalis, A.G., Lavrynenko, S.N. and Ramsden, J.J. The application of niobium and tantalum oxides for implant surface passivation. *J. Biol. Phys. Chem.* **7** (2007) 141–145.
9. Mohammadi, S., Esposito, M., Hall, J., Emanuelsson, L., Krozer, A. and Thomsen, P. Long-term bone response to titanium implants coated with thin radiofrequency magnetron-sputtered hydroxyapatite in rabbits. *Intl J. Oral Maxillofacial Implants* **19** (2004) 498–509.
10. Singer, P. Film stress and how to measure it. *Semiconductor Intl* **10** (1992) 54–58.
11. Emsley, J. *The Elements,* p. 300. Oxford: University Press (1997).
12. Dub, S.N. and Starikov, V.V. Elasticity modulus and hardness of niobium and tantalum anode oxide. *Functional Mater.* **14** (2007) 347–350.