

Formation of Solution-derived Hydroxyapatite Coatings on Titanium Alloy in the Presence of Magnetron-sputtered Alumina Bond Coats

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Abstract: Hydroxyapatite $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ (HAp) and calcium phosphate ceramic materials and coatings are widely used in medicine and dentistry because of their ability to enhance the tissue response to implant surfaces and promote bone ingrowth and osseointegration processes. The deposition conditions have a great influence on the structure and biofunctionality of calcium phosphate coatings. Corrosion processes and poor adhesion to substrate material reduce the lifetime of implants with calcium phosphate coatings. The research has focused on the development of advanced methods to deposit double-layered ceramic oxide/calcium phosphate coatings by a hybrid technique of magnetron sputtering and thermal methods. The thermal method can promote the crystallization and the formation of HAp coatings on titanium alloy Ti6Al4V substrates at low temperature, based on the principle that the solubility of HAp in aqueous solutions decreases with increasing substrate temperature. By this method, hydroxyapatite directly coated the substrate without precipitation in the initial solution. Using a thermal substrate method, calcium phosphate coatings were prepared at substrate temperatures of 100-105 °C. The coated metallic implant surfaces with ceramic bond coats and calcium phosphate layers combine the excellent mechanical properties of metals with the chemical stability of ceramic materials. The corrosion test results show that the ceramic oxide (alumina) coatings and the double-layered alumina-calcium phosphate coatings improve the corrosion resistance compared with uncoated Ti6Al4V and single-layered Ti6Al4V/calcium phosphate substrates. In addition, the double-layered alumina/hydroxyapatite coatings demonstrate the best biocompatibility during *in vitro* tests.

Keywords: Alumina, biocompatibility, hydroxyapatite, magnetron sputtering, thermal method, potentiodynamic testing.

INTRODUCTION

In recent years, there was a huge development in biomaterials for repair and reconstruction of different defects of human bone. Metal prostheses with coatings deposited by various physical and chemical methods are widely used in medicine. Most promising are coatings with bioactive properties that have the tendency to be gradually resorbed in the human body and substituted by bone tissue. Calcium phosphate, in particular hydroxyapatite (HAp) films and coatings are of special interest due to their superior osseointegration. Hydroxyapatite-coated components of modern prosthetic implants show a great potential for application in orthopedic and dental areas [1, 2]. A variety of techniques were developed to deposit calcium phosphate coatings on metal substrates, including thermal spraying

[3-5], electrophoretic deposition [6, 7], magnetron sputtering [8], sol-gel deposition [9], and biomimetic methods [10]. The main research effort is focusing on developing low cost and low temperature processes. Some effective methods such as magnetron sputtering, dip coating, and electrophoretic deposition form dense and adherent but amorphous or low crystalline coatings. Among other techniques, plasma spraying is most popular due to its high deposition rate and productivity. Another popular method to deposit HAp coatings with fine crystalline structure, uniform coating composition, and thickness is synthesis from aqueous solutions at elevated temperature ('thermal' method) [11-14].

The major factors affecting the implant fixation and its long-term stability are coating biodegradation and bone ingrowth processes. Deposited coatings as usual present a mixture of crystalline stoichiometric hydroxyapatite and additional phases, such as oxyhydroxyapatite, calcium-deficient hydroxyapatite, calcium oxide, α - and β -tricalcium phosphate, and tetracalcium phosphate. All these additional

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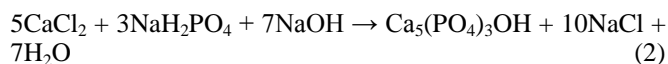
The experimental set-up (Fig. 2) was previously described in detail in Ref. [34].

Fig. (2). The experimental setup used for producing calcium phosphate coatings by the thermal deposition method [34].

The HAp coatings were deposited on Ti6Al4V and Ti6Al4V/Al₂O₃ substrates by the thermal method from aqueous solution.

The substrates were fixed by copper electrodes and immersed in 6 mmol/l NaH₂PO₄ and 10 mmol/l CaCl₂ solutions with a molar ratio Ca/P = 1.67. The tested samples were heated to set-point temperature interval (100-105°C) by variation of current values near 10 A. A copper-constantan thermoelectric couple controlled the substrate temperature. A magnetic stirrer was used to maintain a uniform temperature distribution in the primary solution volume. The substrate temperature was around 100-105 °C and deposition lasted for 2 hours according to previous results of X-ray diffraction and X-ray microanalysis of uniform base phase formation with Ca/P ratio close to that of hydroxyapatite [12]. The pH = 6.5 of the reactant solution was adjusted by adding sodium hydroxide.

The chemical reaction for HAp coatings formation is:



The surface morphology of coatings produced by magnetron sputtering surface pretreatment were examined by scanning electron microscopy (SEM). These investigations were carried out in combination with X-ray emission spectroscopy using the REMMA-102 device (SELMI, Ukraine). The surface chemical composition was determined with an energy-dispersive X-ray (JSC SELMI) Si(Li) detector equipped with a beryllium window. The power resolution of the energy-dispersive spectrometer (EDS) used was 200eV, the probe current was about 3 nA, and the accelerating voltage of the electronic probe was 20 kV. The spectrum acquisition time at each point was about 200 seconds. The analytical signal of the characteristic X-ray emission was integrated by scanning a 50 x 50 μm² area of the samples. SEM acquired micrographs of surfaces with single- and double-layered coatings with different magnifications in conjunction with EDS.

The adhesion, hardness and Young's elastic moduli of the coatings were measured by standard methods using a Revetest (CSM Instruments) with a Rockwell indenter with a tip radius 200 μm, within the load range of 200N[31]. Coating thicknesses were measured with a Calotest Calowear tester (CSM Instruments).

The corrosion parameters of single- and double-layered coatings were determined using a potentiostat Parstat 2263 (Ametek, USA). Anodic polarization was measured by a potentiodynamic method in the potential range between -1.0V and +2.0V with a scanning rate of 1mV/s in SBF solution. The composition of the SBF in g/l was NaCl 8.035, NaHCO₃ 0.355, KCl 0.225, K₂HPO₄·3H₂O 0.231, MgCl₂·6H₂O 0.311, CaCl₂ 0.292, Na₂SO₄ 0.072, at pH=7.4. and 37 °C. The samples were immersed in the electrolyte and the potential was monitored as a function of time until it reached a stable value. Corrosion in the form of anodic dissolution occurs in case of the substrate as dissolution-like uniform removal process and in case of the ceramic coating as corrosive electrolyte pore penetration process.

Cell viability and cytotoxicity were estimated *in vitro* tests by standard protocols. The cell cytology, morphology, and vital activity were determined by optical microscopy on cultivated substrates after 24 h, and 3 and 5 days cultivation. Rat hypodermic cellular tissue was extracted to obtain an initial fibroblast culture. The suspension of extracted cells was centrifuged at 750 r.p.m. for 15min. The cell density was 3x10⁵ cells/ml. The seeded area was 0.5 cm². The fibroblasts were cultivated as a monolayer in 3 ml of Dulbecco Modified Eagle's Medium (DMEM, Sigma) at thermostat condition (37°C) for 5 days. The cells were stained by hematoxylin and eosin for further characterization of structural organization of cultured cells on coated and uncoated substrates. Cell structure and morphology were analyzed by optical microscopy (Micros-50). The experiments were run in triplicate. Cell viability was tested on Ti6Al4V, Ti6Al4V/Al₂O₃, Ti6Al4V/HAp and Ti6Al4V/Al₂O₃/HAp substrates.

Qualitative and quantitative analyses were made. The number of detached cells was determined by quantitative assessment. Statistical processing of experimental results using the software package with a preliminary estimation of the normal distribution was conducted. Statistically significant differences were determined at a significance level P < 0.05.

RESULTS AND DISCUSSION

Photoelectron spectroscopy and X-ray diffraction analyses of the structure and composition of Al₂O₃ oxide coatings deposited by ion source-activated magnetron sputtering were previously reported [35]. The coatings have a dense and uniform amorphous structure with strong stoichiometric oxide composition. SEM and EDS analyses of alumina coatings deposited on Ti6Al4V substrates are shown in Fig. (3).

Fig. (4) shows SEM micrographs of calcium phosphate coatings deposited by the thermal method on Ti6Al4V substrates. Fig. (5) presents EDS analysis data that

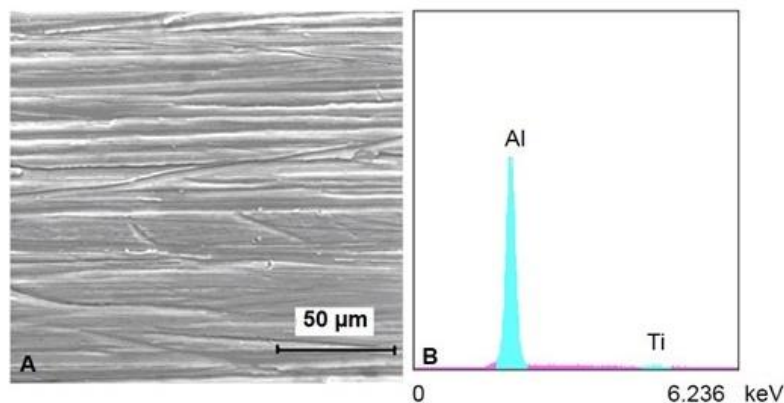


Fig. (3). (A) SEM micrograph of surface morphology of Al_2O_3 coatings deposited on a Ti6Al4V substrate by magnetron sputtering. (B) EDS analysis results.

demonstrate the formation of calcium phosphate compounds. The results of the elemental analyses of selected points are shown in Table 1. The EDS data show a low Ca/P ratio, which is result of calcium-deficient surface. An explanation of the deviation of the Ca/P ratio from the stoichiometric value of hydroxyapatite may be found in the fact that formation of octacalcium phosphate (OCP) with a Ca/P ratio of 1.33 often occurs as a transient precursor/intermediate during precipitation of thermodynamically more stable HAp and biological apatites, as OCP nucleates and grows more easily than HAp. In addition, the surface layer may have a composition different from that of the bulk material. A difference in the surface and bulk stoichiometric ratios was also observed in Refs. [36, 37].

Table 1. Results of EDS elemental analysis of calcium phosphate crystals on a Ti6Al4V substrate at selected points shown in Fig. (5).

Point	Ca	P	Ca/P ratio, at. %
1	21.07	11.62	1.41
2	20.01	11.07	1.40
3	20.96	12.57	1.29

The results of the EDS analyses of calcium phosphate coatings deposited by the thermal method on Ti6Al4V/ Al_2O_3 substrates are shown in Fig. (6) indicating the formation of calcium phosphate structures. An SEM micrograph with specific points selected for elemental microanalysis is shown in Fig. (6), center panel. The results of elemental analysis of the selected points are presented in Table 2.

Table 2. Results of EDS elemental analysis of HAp crystals on a Ti6Al4V/ Al_2O_3 substrate at selected points shown in Fig.6.

Point	Al	Ca	P	Ca/P ratio, at. %
1	1.97	68.12	29.91	1.77
2	2.31	66.16	31.53	1.62
3	2.73	65.58	31.69	1.60
4	2.34	66.68	30.98	1.67

The EDS data show Ca/P ratios close to those of stoichiometric hydroxyapatite. The calcium phosphate coatings deposited on Ti6Al4V substrates demonstrate a higher titanium content (Fig. 5) in comparison with HAp coatings on Ti6Al4V/ Al_2O_3 substrates (Fig. 6).

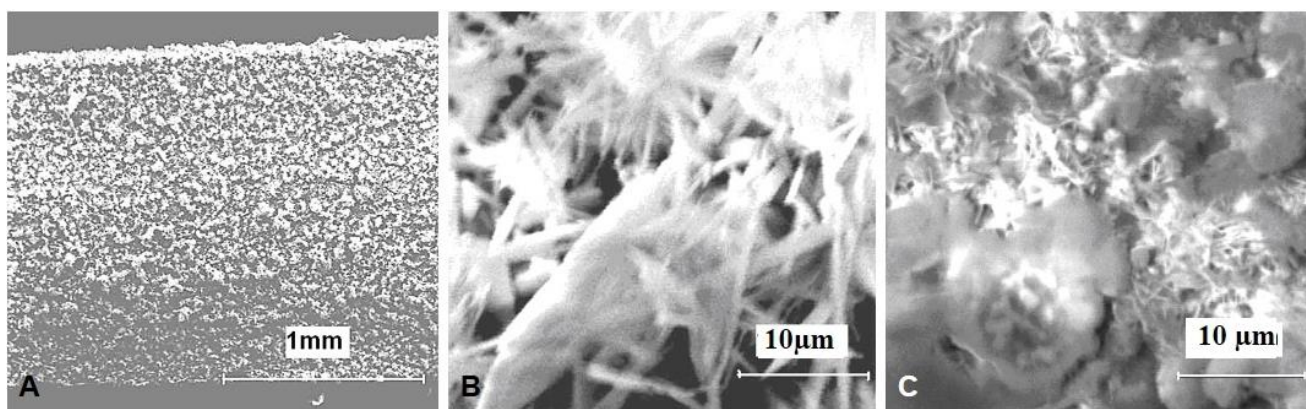


Fig. (4). SEM micrographs of calcium phosphate coatings deposited by the thermal method on a Ti6Al4V substrate at different magnifications.

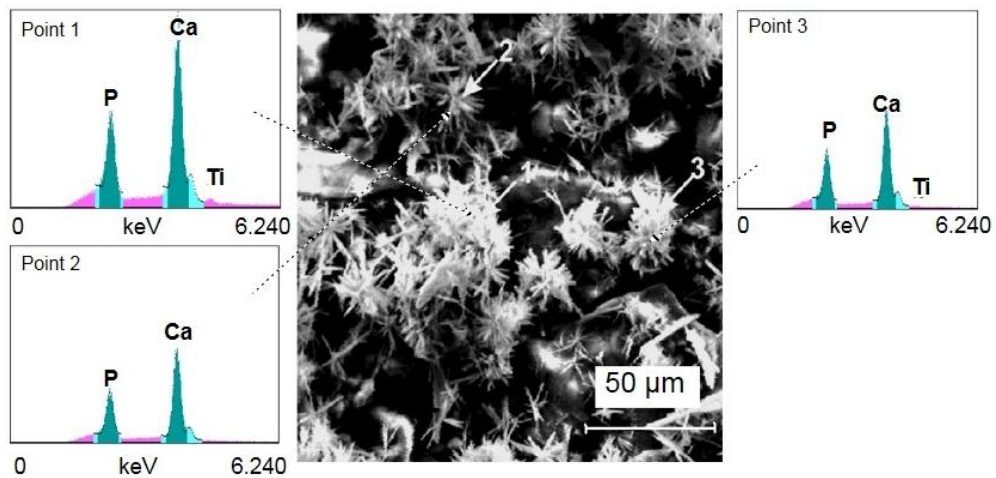


Fig. (5). EDS analyses data and SEM micrograph of the morphology of a calcium phosphate coating deposited by the thermal method on a Ti6Al4V substrate. Left and right panels: EDS analyses of selected points. Center panel: SEM micrograph with selected points indicated.

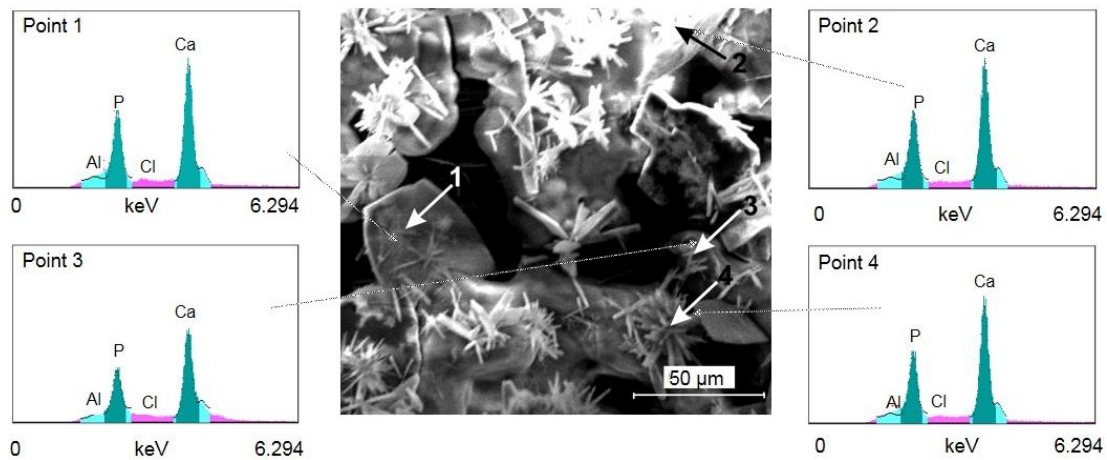


Fig. (6). EDS analysis data and SEM micrograph of the morphology of calcium phosphate coating deposited by the thermal method on a Ti6Al4V/Al₂O₃ substrate. Left and right panels: EDS analyses of selected points. Center panel: SEM micrograph with selected points indicated.

Fig. (7) presents the corrosion tests of Ti6Al4V, Ti6Al4V/Al₂O₃, Ti6Al4V/HAp and Ti6Al4V/Al₂O₃/HAp substrates in SBF solution. The ceramic oxide and the double-layered oxide-hydroxyapatite coatings demonstrate the highest corrosion potential compared with uncoated Ti6Al4V and single-layered Ti6Al4V/HAp substrates. The corrosion test results show that the oxide coating has significantly improved the corrosion resistance.

The mechanical characteristics of single-layer HAp

coatings and double-layered ceramic aluminum oxide/hydroxyapatite coatings deposited on Ti6Al4V substrates are presented in Table 3. The results demonstrate that corrosion resistance and mechanical parameters increase in the case of double-layered aluminum oxide /hydroxyapatite ceramic coatings.

The aluminum oxide-coated substrates show improved corrosion resistance compared to uncoated substrates. The surfaces with single-layer alumina and double-layered

Table 3. Mechanical characteristics of single-layer HAp coatings and double-layered alumina/hydroxyapatite coatings deposited on Ti6Al4V substrates.

Material/ coating types	Thickness [μm]	Adhesion strength [N]	Young's modulus [GPa]	Vickers hardness, HV [kgf/mm ²]
Ti6Al4V			110±10	415±20
Ti6Al4V /Al ₂ O ₃	2.1±0.2	39.8±2	172±15	953±30
Ti6Al4V/HAp	30.3±0.5	12.7±2	102±10	422±20
Ti6Al4V /Al ₂ O ₃ /HAp	1.9±0.2/28.4±0.5	35.2±2/8.9±2	151±10	831±30

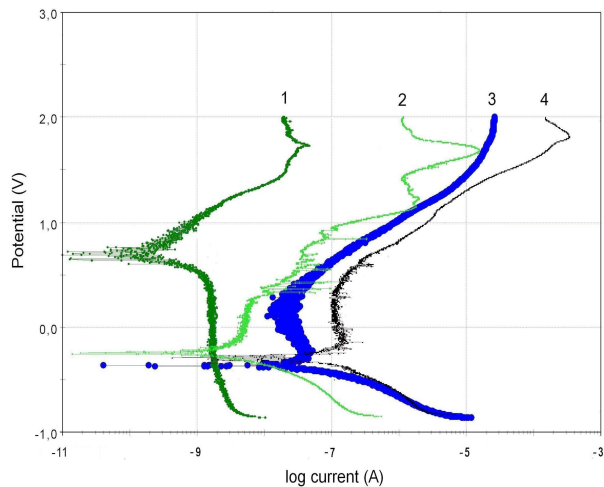


Fig. (7). Anodic polarization curves: 1- Ti6Al4V/Al₂O₃, 2- Ti6Al4V/Al₂O₃/HAp, 3- Ti6Al4V, 4- Ti6Al4V/HAp samples in SBF solution.

alumina/hydroxyapatite coatings have a strong capacitive response due to their electrically inert properties. The Vickers indentation hardness reaches maximum values up to 10 GPa in the case of Ti6Al4V/Al₂O₃ and Ti6Al4V/Al₂O₃/HAp coatings. The adhesion strength of HAp layers of comparable thickness was higher in the case of uncoated substrates (Table 3).

Cell cytotoxicity was estimated by *in vitro* tests. After 3 days immersion in DMEM culture medium fibroblast cells were well spread on all substrates. The cell structural organization corresponded to that of the initial fibroblast. After 5 days cultivation the density of cell increased for all samples. The majority of cells were ripe fibroblasts with strongly expressed phenotype, but meaningful differences in cell viability on substrate surfaces were not observed. However, a maximum number of detached cells were observed on uncoated titanium substrates after cultivation for 3 and 5 days (Fig. 8).

Cell morphology was observed by optical microscopy (Fig. 9). The cell profiles are well defined, with a great cytoplasm volume, large basophilic nuclei, hypochromic chromatin. Many cells are in different mitosis stages:

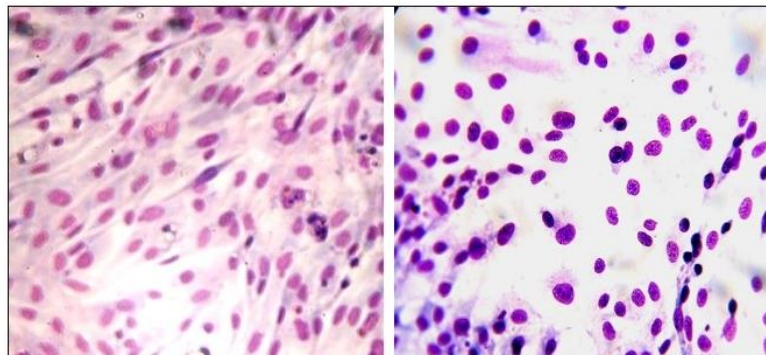


Fig. (9). Micrographs of fibroblastic cells on the surface after 5 days cultivation during *in vitro* tests. Left: double-layered alumina/calcium-phosphate coating on a Ti6Al4V substrate. Right: area with separated cells and naked-nuclear cells on an uncoated Ti6Al4V substrate. Staining with hematoxylin and eosin, magnification $\times 400$.

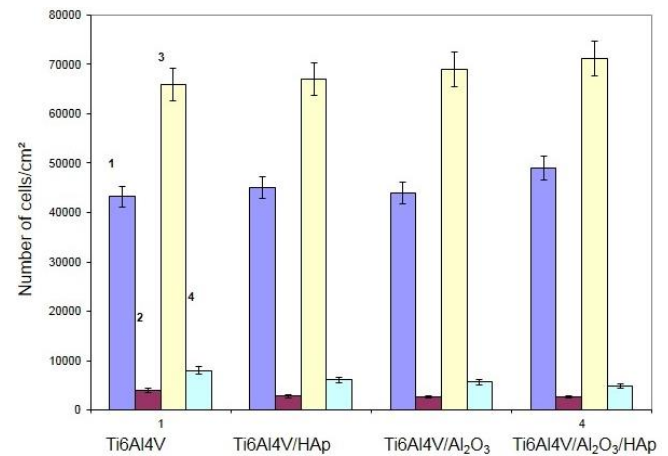


Fig. (8). Number of cells/cm² on the surface of Ti6Al4V substrates with single- and double-layered coatings: total cell number (1) and detached cell number (2) after 3 days cultivation, total cell number (3) and detached cell number (4) after 5 days cultivation; statistically significant differences were determined at a significance level $P < 0.05$.

prophase, metaphase, anaphase and telophase. Significant morphological differences in the cell structure, mitosis and destruction functions for samples Ti6Al4V/Al₂O₃, Ti6Al4V/HAp and Ti6Al4V/Al₂O₃/HAp in comparison with control ones were not observed. The distinction in the morphological structure of cell on the Ti6Al4V substrates was the formation of clusters of naked-nuclear cells. The presence of these cell types may be a signal of negative response of cell culture on the tested materials. The best biological response parameters (total cell number, viability and cell morphology) were obtained in the case of Ti6Al4V/Al₂O₃ and Ti6Al4V/Al₂O₃/HAp substrates in comparison with uncoated Ti6Al4V substrates. The Ti6Al4V surfaces coated with a double-layered aluminum oxide/hydroxyapatite coating demonstrate the best biocompatibility during *in vitro* tests.

CONCLUSION

A method was developed to deposit double-layered aluminum oxide/hydroxyapatite coatings by a hybrid technique involving magnetron sputtering and thermal deposition. The microhardness of aluminum oxide single-

and double-layered coatings deposited on Ti6Al4V substrates increased significantly. The aluminum oxide-coated substrates demonstrated improved corrosion resistance compared to uncoated titanium substrates. The best corrosion resistance in SBF solutions was found for single-layered alumina-coated Ti6Al4V/Al₂O₃ and Ti6Al4V/Al₂O₃/HAp double layer-coated materials. In conclusion, double-layered coatings with a calcium phosphate top layer over a protective aluminum oxide inner layer preventing ion diffusion were found to improve the mechanical properties as well as the biocompatibility during *in vitro* tests. Searching for new methods of surface modification and sputtering of inner layers with various chemical compositions should improve homogeneity and density of a calcium phosphate top layer formed by the thermal method.

CONFLICT OF INTEREST

The authors confirm that this article content has no conflict of interest.

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Declared none.

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