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COMPARISON OF THE PHYSICOCHEMICAL PROPERTIES OF Al_2O_3 LAYERS APPLIED TO THE SURFACES OF cpTi AND THE Ti6Al7Nb ALLOY USING THE ALD METHOD

PRIMERJAVA FIZIKALNO-KEMIJSKIH LASTNOSTI Al_2O_3 PLASTI, NANEŠENIH NA cpTi POVRŠINE IN ZLITINO Ti6Al7Nb Z UPORABO ALD METODE

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Literature data show that atomic-layer deposition (ALD) is a very important method for depositing layers due to the mechanical and physicochemical properties of the surface. In the literature, little space is devoted to layers of Al_2O_3, which could also have a major impact on improving the physicochemical properties of metallic biomaterials. Therefore, the aim of this research was to determine the influence of the Al_2O_3 layer formed by the ALD method on the physicochemical properties of metallic biomaterials. Based on the results, a beneficial effect on the pitting and crevice-corrosion resistance of the applied Al_2O_3 layer was determined, compared to the initial state, devoid of the layer, regardless of the substrate used. On the other hand, the performed surface-wettability tests showed no influence of the ALD temperature on the obtained angle values. Proposing appropriate conditions for the surface treatment using the ALD method has some promise and will contribute to the development of a technological process with defined parameters for oxide-layer manufacture for implants used in bone surgery.

Keywords: cpTi (Grade 4), Ti6Al7Nb alloy, Al_2O_3 layer, adhesion, corrosion resistance

Podatki iz literature kažejo, da je depozicija atomskih plasti (ALD) zelo pomembna metoda za nanašanje plasti zaradi mehanskih in fizikalno-kemijskih lastnosti površine. V literaturi so plasti Al_2O_3 sicer le malo omenjene pa vendar imajo lahko velik vpliv na izboljšanje fizikalno-kemijskih lastnosti kovinskih biomaterialov. Cilj raziskave je bil zato ugotoviti vpliv Al_2O_3 sloja, tvorjenega z metodo ALD, na fizikalno-kemijske lastnosti kovinskih biomaterialov. Na osnovi rezultatov smo določili ugoden učinek uporabljene Al_2O_3 plasti pri odpornosti na luknjičasto in špranjsko korozijo, v primerjavi z začetnim stanjem, ki je bila brez sloja, ne glede na uporabljeno podlago. Po drugi strani pa so izvedeni testi površinske vpojnosti pokazali, da temperatura ALD-metode ne vpliva na dobljene kotne vrednosti. Ustrezni pogoji, predlagani za površinsko obdelavo z uporabo ALD-metode, veliko obetajo in bodo prispevali k razvoju tehnološkega procesa z določenimi parametri za izdelavo vsadkov, ki se uporabljajo v kirurški medicini in pri operacijah kosti.

Ključne besede: cpTi (Grade 4), Ti6Al7Nb zlitina, Al_2O_3 plast, oprijem, odpornost proti koroziji

1 INTRODUCTION

Material implanted into human tissues and body fluids must have a bio-electronic compatibility, and so have the appropriate electric and magnetic properties, similar to those of the surrounding living matter, which has mostly a dielectric characteristic. In addition, the selected set of mechanical properties of such a material should provide good relations in the implant-tissues-body-fluids system that are essential to the realization of biophysical cooperation and flexible load transfer. The materials' physicochemical properties chosen this way will protect the implant against the damaging process of its destruction, and consequently, general and reactive responses will be minimized and so will be the process of metalosis.[1–4]

To prevent such negative phenomena surface treatment methods, e.g., coating, are used on implants. However, until now satisfactory results have not been achieved in that manner. Therefore, a continuous search for the best solutions relating to the methodology, the chemical composition and physicochemical properties of the layers produced is being conducted by many experts in the field.[5–8] An attempt to improve the physical and chemical properties of implants used in bone surgery was taken by J. Szewczenko,[9] who carried out the process of anodic oxidation on titanium alloys. Similar studies were conducted by W. Walke,[10,11] who deposed layers of TiO_2 and SiO_2 on 316 LVM steel using the sol-gel method.

Among the many techniques for applying layers, ALD (Atomic Layer Deposition) deserves special attention because it does not change the geometrical features of the implant and allows manufacturers to control the layer thickness. The method was created in Finland in the 1970s. The method is based on the CVD technique

(Chemical Vapour Deposition). Otherwise, it can be described as layer-by-layer coating deposition. It is characterized by: chemisorption, which is the formation of strong chemical bonds between the precursors, impregnation, which is important in achieving uniformity of the layer, sequencing, which is a key feature of this method consisting of the fact that the precursors are introduced into the chambers in turns.

Literature data show that ALD is a very important method of depositing layers due to the mechanical and physicochemical properties of the surface. For this reason, numerous studies are conducted on it. A. Purniawan et al.[7] performed a study that uses a low surface roughness and the uniformity of the TiO_2 deposited by ALD in the creation of biomedical sensors used in the diagnosis of leaks during the operation of anastomosis of the colon, pancreas, etc. In this experiment, a layer of TiO_2 was used as an evanescent waveguide. After a series of tests, it was found that the layer is suitable for use as a biomedical sensor, detecting dangerous effects in humans.[3] Another example might be the use of a SiO_2 layer applied by ALD in order to improve the corrosion resistance of stainless steel. Layers were applied with different thicknesses: 300 nm, 100 nm, 30 nm, 10 nm. A measurement of the material's hardness using the Vickers method and a test of the layer's adhesion to the substrate were conducted. As a result the corrosion resistance was determined. Studies have shown that the thicker the layer the greater the delamination after the hardness test, and so the adhesion to the substrate is poorer. The layers deposited by ALD also increased the corrosion resistance of steel by reducing the corrosion current, and increasing the passive areas.[12]

In the literature, little space is devoted to layers of Al_2O_3, which could also have a major impact on improving the physicochemical properties of metallic biomaterials. Therefore, the aim of the completed research was to determine the influence of an Al_2O_3 layer formed by the ALD method on the physicochemical properties of metallic biomaterials.

2 EXPERIMENTAL PART

The study was conducted on the Al_2O_3 layer applied by ALD on the two selected metal substrates, i.e., cpTi and Ti_6Al_7Nb (**Table 1**). Samples were provided in the form of discs with a diameter of 14 mm and a thickness of 3 mm. The samples were subjected to a preliminary surface modification consisting of vibration machining using suitable ceramic grinding particles required to obtain a constant roughness $R_a < 0.4$ µm. Then, the surface of the samples was subjected to electrochemical polishing in a solution based on chromic acid (E-395 made by POLIGRAT Gmbh Company), with a current density = 10÷30 A/cm^2. The treatment made it possible to obtain a surface roughness of $R_a = 0.1$ µm. The surface was then covered with an Al_2O_3 layer using ALD (PICOSUN). The process of applying the layer was carried out under recurrent conditions for both materials. To deposit an Al_2O_3 layer using ALD, trimethylaluminum (TMA) and water vapor are sequentially pulsed through the reaction chamber.[13] The number of cycles was 830, which made obtaining a layer thickness of about 120 nm possible. Layers of this thickness are commonly used in the surface modification of metallic biomaterials in contact with bone tissue. The variable parameter was the temperature of the process. The authors proposed the execution of the process at reduced temperature of $T = 150$ °C and at an elevated temperature of $T = 300$ °C. All the samples were subjected to examinations before the sterilization treatment in an autoclave ($T = 135$ °C, $p = 2{,}1$ bar, $t = 12$ min).

2.1 Potentiodynamic test

Tests of resistance to pitting corrosion were carried out for different variants of the surface treatment using the potentiodynamic method. The study used VoltaLab® potentiostat PGP 201 by Radiometer. The reference electrode was a saturated calomel electrode (SCE), while the counter electrode was platinum wire. The anode, on the other hand, was cpTi+Al_2O_3/Ti6Al7Nb+Al_2O_3. The test was performed in Ringer solution (250ml), supplied by Baxter, at a temperature of $T = 37$ °C and pH = 6.8±0.2. The study was initiated by indicating the open-circuit potential E_{OCP}. Then, recording of polarization curves started from the potential $E_{start} = E_{OCP} - 100$ mV. Samples were polarized with scan rate of 0.16mV/s. Tests were carried out for five samples of each kind of substrate. Additionally, the Stern method was used to determine to the value of the polarization resistance R_p.

Table 1: Chemical composition of analyzed materials

cpTi, mass concentration, in mass fractions (*w*/%)								
Element	N	C	H	Fe	O	Ti		
ISO 5832-2	max. 0.05	max. 0.1	max. 0.0125	max. 0.5	max. 0.4	bal.		
Certificate	0.03	0.05	0.005	0.4	0.4	bal.		
Ti6Al7Nb, mass concentration, in mass fractions (*w*/%)								
Element	C	H	N	O	Ta	Fe	Al	Nb	Ti
ISO 5832-11	max. 0.08	max. 0.009	max. 0.05	max. 0.20	max. 0.50	max. 0.25	6.50–5.50	7.50–6.50	bal.
Certificate	0.008	0.003	0.03	0.08	0.37	0.22	6.24	6.84	bal.

2.2 Potentiostatic test

Evaluation of the resistance to crevice corrosion made use of the potentiostatic method, recording changes in the current density at +800mV potential for 15 min.[14] The measurement system was identical to the one used for potentiodynamic tests. The tests were carried out in the Ringer solution (250 mL), supplied by Baxter, at T = 37±1 °C and pH = 6.8 ±0.2.

2.3 Adhesion test

Adhesion of the Al_2O_3 film to the cpTi and Ti6Al7Nb was evaluated with the use of a scratch test.[15] During the test a scratch was made with the use of Rockwell diamond cone with gradual growth of the indenter's normal load. The critical force, a measure of adhesion, is the minimum normal force causing the loss of adhesion of the coat to the base. Evaluation of the critical force L_c based on the record of changes in acoustic emission, friction force and friction coefficient as well as a microscopic inspection with a light microscope, integrated with the platform. Tests were performed at the loading force, increasing from F_c = 0.03 N to 30 N and at the following working parameters: loading rate v_s = 100 N/min; table travel rate v_t = 10 mm/min, scratch length l = 3 mm.

2.4 Wettability test

Surface wettability and surface energy (SEP) were evaluated with the use of the Owens-Wendt method. The wetting-angle measurements used two liquids: distilled water (θw) (by Poch S.A.) and diiodomethane (θd) (by Merck). A measurement with a drop of the liquid and diiodomethane, placed on the outer layer of the material, was performed at the temperature T = 23 °C at the test stand incorporating a goniometer SURFTENS UNIVERSAL by OEG and a computer with Surftens 4.5 software to analyse the recorded drop image. Five drops of distilled water and diodomethane were applied onto the surface of each sample, each with capacity of 1.5 µL. The measurement began 20 s after the application of the drops. The duration of a single measurement was 60 s, with the sampling rate of 1 Hz. Next, the determined values of the contact angles θ and the surface energy were presented as mean values with a standard deviation.

3 RESULTS AND DISCUSSION

3.1 Potentiodynamic test

Polarization curves recorded for the substrates alone and samples covered with an Al_2O_3 layer deposited at a temperature of T = 150 °C and T = 300 °C for cpTi and Ti6Al7Nb are shown in **Figures 1** and **2**. Based on the received curves the characteristic values describing the resistance to pitting corrosion were determined (**Table 2**). Regardless of the type of substrate, a positive influence – improving the corrosion resistance – of the Al_2O_3 layer was established, as compared to baseline. An increase of corrosion potential E_{corr} and polarization resistance R_p was found. An increase of the application process temperature from 150 °C to 300 °C significantly reduced the corrosion resistance of the Al_2O_3 layer (**Table 2**).

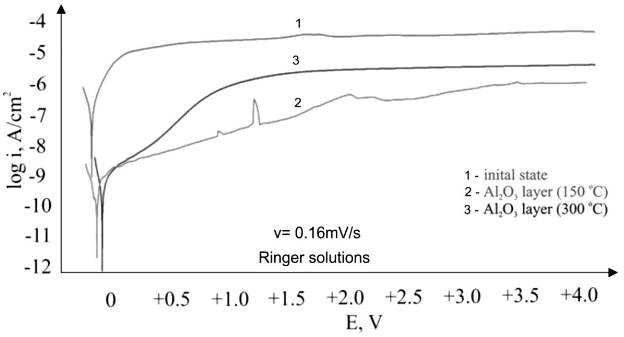

Figure 1: Polarization curves for the modified cpTi

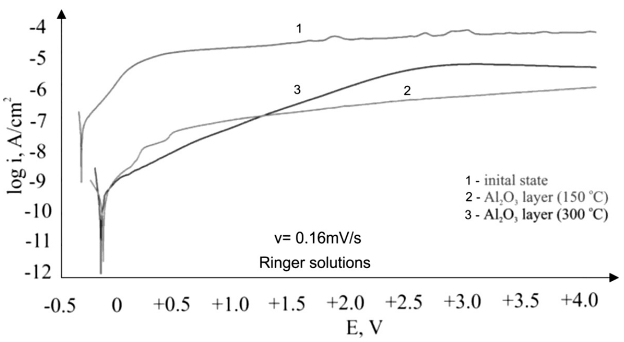

Figure 2: Polarization curves for the modified Ti6Al7Nb alloy

Table 2: The results of resistance to pitting corrosion test

Material	Temperature	E_{corr}, mV	R_p, MΩ cm²
cpTi	Initial state	-244	0.3
	150	-147	7.5
	300	-78	5.6
Ti6Al7Nb	Initial state	-309	0.1
	150	-155	5.1
	300	-126	4.0

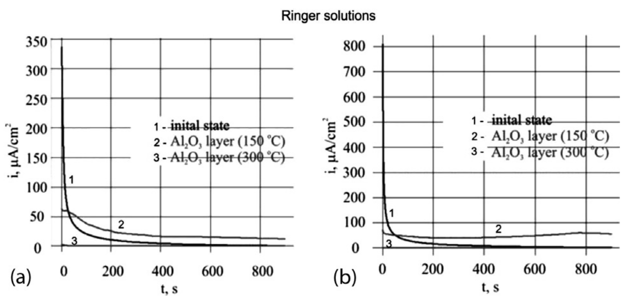

Figure 3: Examples of potentiostatic curves: a) cpTi in the initial state and with deposited Al_2O_3 layer, b) Ti6Al7Nb in the initial state and with deposited Al_2O_3 layer

3.2 Potentiostatic test

The test results of current density changes as a function of time in the test of resistance to crevice corrosion indicate that regardless of the type of the substrate (cpTi, Ti6Al7Nb), as well as the process temperature (150 °C, 300 °C) the Al_2O_3 layer is resistant to this type of corrosion (**Figures 3a** and **3b**). The results confirmed the formation of a compact Al_2O_3 oxide layer constituting a barrier separating the substrate from the corrosive environment in which the tests were performed.

3.3 Adhesion test

The results of the adhesion of the Al_2O_3 layer to the metallic substrate were shown in **Table 3** and **Figures 4** and **5**. The obtained results indicate the diverse adhesion of Al_2O_3 to the ground with both cpTi and Ti6Al7Nb. This is evidenced by the values of the individual parameters defined on the basis of the measurements. It was found that a sample with Al_2O_3 deposited on the Ti6Al7Nb surface shows better adhesion to the substrate (**Table 3**). Additionally, the influence of the process temperature on the adhesion of the analyzed layer, on both cpTi and Ti6Al7Nb, was found. Slightly better adhesion was observed in the case of the layer deposited using the ALD method at the temperature T = 300°C, regardless of the analyzed substrate material. During the test there was no acoustic emission signal, which indicates that the binding energy between the coating and the substrate was too low.

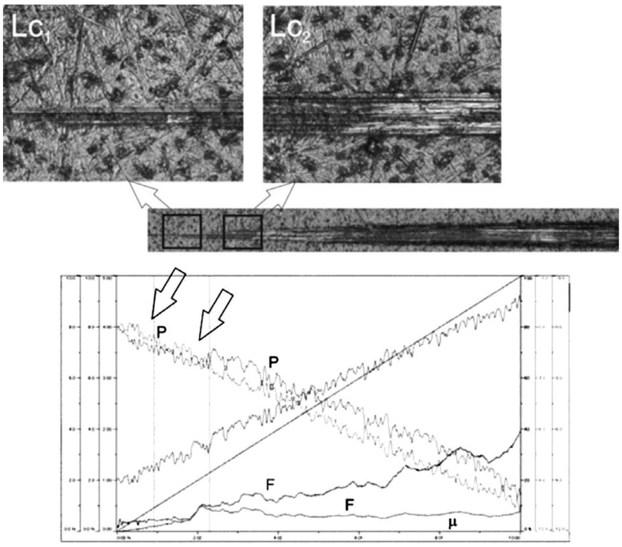

Figure 4: Examples of adhesion test results for the cpTi subjected to surface modification Al_2O_3 layer (T = 300 °C)

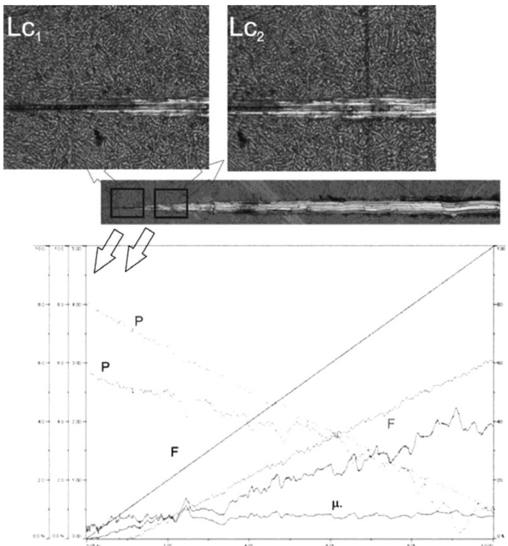

Figure 5: Examples of adhesion test results for the Ti6Al7Nb alloy subjected to surface modification Al_2O_3 layer (T = 300 °C)

Table 3: The results of scratch-test

Material	Temperature Al_2O_3 layer	Layer damages	Critical force F_n, N
cpTi	150 °C	Crack L_{c1}	0.33
		Delamination L_{c2}	1.02
	300 °C	Crack L_{c1}	0.55
		Delamination L_{c2}	1.14
Ti6Al7Nb	150 °C	Crack L_{c1}	1.32
		Delamination L_{c2}	2.42
	300 °C	Crack L_{c1}	1.20
		Delamination L_{c2}	2.89

3.4 Wettability test

The wettability test results were presented in **Table 4**. Based on the obtained results it was found that regardless of the substrate used, the Al_2O_3 layer showed hydrophobic properties. The average value of the contact angle for the Al_2O_3 layer, regardless of the temperature of the deposition process, was equal to θ_{avg} = 115°. On the other hand, the cpTi and Ti6Al7Nb substrates showed hydrophilic properties (θ_{avg} = 61°).

Table 4: Wettability test results

L_p	Ti			Ti6Al7Nb		
	Initial state (θ, °)	Al_2O_3 layer (T = 150 °C) (θ, °)	Al_2O_3 layer (T = 300 °C) (θ, °)	Initial state (θ, °)	Al_2O_3 layer (T = 150 °C) (θ, °)	Al_2O_3 layer (T = 300 °C) (θ, °)
1	56.9	118.2	116.8	68.2	117.8	112.5
2	58.1	109.7	124.3	65.3	114.0	107.2
3	57.8	111.8	121.8	66.9	119.7	117.0

4 CONCLUSIONS

In the ALD method, important parameters affecting the quality of the final layer are the number of cycles and the process temperature. Earlier works allowed the authors to specify the number of cycles for depositing layers with the best set of physicochemical properties.[11,16–17] On this basis, the application of a Al_2O_3 coating on a titanium substrate (cpTi and Ti6Al7Nb) at temperatures of T = 150 °C and 300 °C was proposed. The number of cycles used was L_c = 830. Based on the results, a beneficial effect on pitting and crevice corrosion resistance of applied Al_2O_3 layer was determined, compared to initial state, devoid of the layer, regardless of the substrate used. The dependence was not shown during the layer's adhesion to the substrate test and the wettability test. No significant influence of the deposition process temperature on the obtained results was found. Proposing the appropriate conditions for the surface treatment using ALD method has promise and will contribute to the development of technological process with defined parameters of oxide layers manufacturing on implants used in bone surgery.

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