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Evaluation of the surface characteristics of VT8 titanium alloy bio-functionalized through plasma electrolytic oxidation

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Abstract

Titanium and its alloys are considered promising materials in the medical field due to a number of mechanical and corrosion properties, as well as biocompatibility. In order to improve the operational properties of such alloys, their surface is modified by various methods, particularly plasma-electrolytic oxidation (PEO). The main feature of the PEO method is the wide possibility of controlling the physical and mechanical properties of coatings by changing the electrolyte composition and operating modes. These include hardness as one of the important functional properties of oxide-ceramic biocompatible coatings which can be changed in a wide range. The hardness should be controlled to avoid brittle fracture of coatings. In this work, a number of PEO regimes were developed by varying the electrolyte composition, the ratio of anodic to cathodic currents, and the treatment duration. Coatings with a hardness in the range of 1400–2500 MPa and a thickness of 3.4–12 μm were synthesized. An acceptable correlation between the hardness and thickness of the coating was revealed. It enables the assessment of coating thickness by measurements of hardness and can be used for non-destructive evaluation of coating thickness.

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Keywords: titanium alloy, plasma electrolyte oxidation, microhardness and thickness of coatings, diagnostics of functional properties

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1. Introduction

Titanium and its alloys are considered promising materials for medical applications due to their mechanical and corrosion properties and biocompatibility as well. In order to improve the functional properties of such alloys, their surface is modified by various methods, in particular, using plasma-electrolytic oxidation (PEO). The main feature of the PEO method is the wide possibility of controlling coatings' physical and mechanical properties by changing the electrolyte composition and the synthesis parameters. It enables obtaining coatings with the desired properties.

The PEO method is widely used for aluminium (Raj and Mubarak Ali (2009), Erfanifar et al. (2017), Imbirovych et al. (2021), Kovalchuk et al. (2023)), magnesium (Arrabal et al (2008), Nykyforchyn et al (2008), Guo et al (2009), Mori et al (2014), Oleshko et al. (2020)), zirconium (Pauporté et al (2005), Klapkiv et al (2006), Nykyforchyn et al (2008), Lee et al (2011), Cheng et al (2011)) and titanium (Klapkiv et al (2006), Diamanti et al (2007), Nykyforchyn et al (2008), Yao et al (2008), Galvis et al (2015), Imbirovich et al. (2015), Kyrylenko et al. (2023)) alloys. The authors indicate an enhancement of the physical and mechanical properties of the obtained oxide-ceramic coatings (OCC).

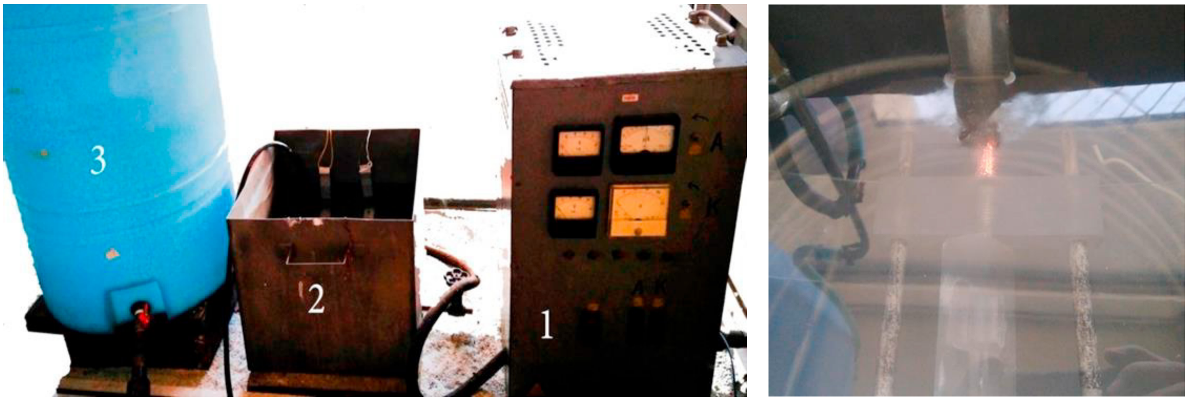
It is known that titanium alloys are very promising in implantology due to their biocompatibility with human tissue, as demonstrated by Geetha et al. (2009), Galvis et al. (2015), and others. Titanium alloys are suitable for generating highly biocompatible films on their surface. Other important properties of materials used for fabricating implants are mechanical and fatigue resistance properties, wear resistance, and corrosion resistance in the biological environment (Geetha et al. (2009), John et al. (2016), Yavari et al. (2016), Tkachuk et al. (2022), Kyrylenko et al. (2023), Imbirovych et al. (2023), Pohrelyuk et al. (2023)).

Osseointegration is important for implant materials and their coatings. Under operating conditions, the implant surface is affected by loads. As a result, this can lead to increased internal stresses and coating damage or fracture. Therefore, hardness is an important functional property of biocompatible oxide ceramic coatings synthesized on titanium alloys. It is very important to know the correlation between thickness and hardness to use oxide ceramic coatings on Ti alloys. The properties of the coatings obtained using the PEO method are significantly influenced by a change in electrolyte components, synthesis time, and current density. In this work, the effect of the composition of the electrolyte for the PEO of the VT8 titanium alloy and parameters of the synthesis on the surface characteristics, namely hardness and thickness of the formed OCC, has been investigated. The possibility of an evaluation of hardness by a non-destructive method is also analysed.

2. Methods of experimental research

The OCC formation by the PEO method and the coating's properties were investigated on titanium alloy VT 8 samples with a total surface area of 1 cm^2 used for the experiment.

The synthesis of OCC was performed using the IMPELOM-1 installation (Fig. 1, a); it includes a current control unit and a power source (1), a bath for electrolyte (2), and cooling units (3). A stainless steel bath is a cathode; it is filled with an electrolyte. Using measuring devices (voltmeter and ammeter), the values of the time dependence of the voltage of the anode and cathode currents were recorded. Distilled water was used for preparing electrolytes. They were constantly mixed during experiments by using air.



a b

Fig. 1. IMPELOM-1 equipment for the synthesis of OCC (a), and the process of OCC formation (b)

The process of synthesis of OCC takes place in three stages (Fig. 1, b). In the process of synthesis by the PEO method, plasma electrolytic reactions occur between the electrolyte components and the sample. This leads to the formation of an electric discharge on the sample surface. First of all, hydrogen is released. Next, a characteristic spark appears on the sample surface. The last stage is characterized by a uniform distribution of sparks over the entire surface of the tested sample, and the oxide is formed.

The main electrophysical parameters of the process are the anode voltage Ua, the cathode voltage Uc, the densities of the cathode and anode currents Ia/Ic, the duration of the pulses and their frequency, and the process duration τ. The parameters used for PEO are presented in Table 1.

Table 1. Modes of synthesis of titanium alloy VT8.

Mode of PEO	Duration τ (min)	Current density Ia/Ic (A/dm^2)	The composition of the electrolyte (g/l)				
			KOH	Liquid glass	$Ca(OH)_2$	$Na_4P_2O_7$	$Na_6P_6O_{18}$
1	20	8/8	0.5	0.5	0.5	0.5	0.5
2	60	10/10	0.5	0.5	0.5	0.5	0.5
3	25	66/46	0.5	0.5	0.5	-	-
4	25	160/67	0.5	0.5	0.5	-	-

The hardness of the coating was determined using a stationary Micro Vickers hardness tester NOVOTEST TC – MKB1. A pyramidal indenter and a load of 10 MPa was applied. Exposure time was 10 s.

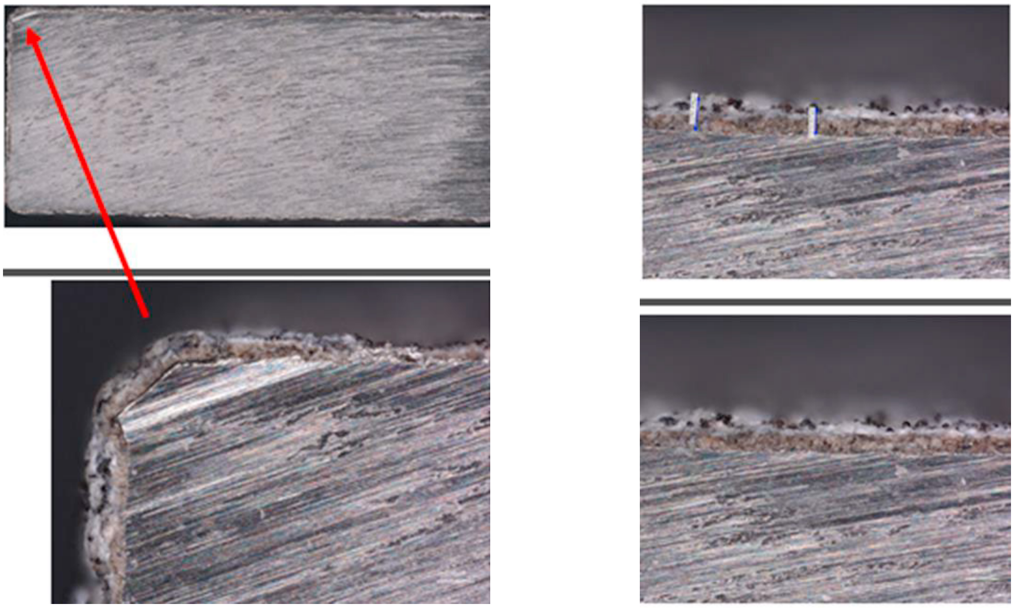
3. Results and discussion

Four modes of PEO were used (Table 1) for the synthesis of OCC on the VT 8 titanium alloy. The order of modes 1–4 is given according to the increase in the amperage characteristic of PEO, although the duration of treatment is also variable, within 20–60 min. The main components of the electrolyte are potassium hydroxide, liquid glass and calcium hydroxide. However, for modes 1 and 2, which were characterized by low energy intensity, the electrolyte was enriched with sodium pyrophosphate and polyphosphate. The introduction of additional components into the main electrolyte requires providing the system with more energy, which is supplied through discharges, necessary for the melting of particles (in this case, sodium pyrophosphate and polyphosphate) in the breakthrough channel for the further possibility of their entering into a reaction with the components of the electrolyte and the matrix. Thus, in the end, the system containing particles receives much less energy at the output, and therefore, it is obvious that the initial current density does not coincide with its initial value and is smaller.

Cross-section analysis of the coating showed good repeatability of the shape of the base metal (Fig. 2). In addition, these photos show that the coating is rough. It should be noted that these properties contribute to increasing the biocompatibility of the coating.

The results of hardness measurement are presented in Figure 3. It is evidence that parameters of synthesis influence the hardness of coatings. Using regimes 1–3 for the synthesis of OCC by PEO, high values of hardness *H*, in the range of ~ 2200–2500 MPa, are achieved. At the same time, the desired, relatively low value of hardness was received in mode 4, which is characterized by the highest level of PEO current density. From the presented results, this factor seems to be responsible for the obtained hardness.

It was established that the thickness t of the coatings also depends on the PEO regimes (Fig. 4). The smallest thicknesses were obtained for modes 1–3 (range 3.4–5.0 μm), while mode 4 stands out in this study with a high value of *t* = 12.0 μm. In the electrolyte of a higher concentration, a coating of a smaller thickness is formed due to the higher value of the energy spent for reserving the system for plasma-chemical reactions. Synthesis into an electrolyte consisting of KOH and $Ca(OH)_2$ requires a smaller energy reserve of the system, so, in this case, the coating is obtained with a greater thickness. Mode 4 is characterized by high amperage indicators of PEO, so it should be expected that the thickness of the coating increases with the increase in processing energy.



a b

Fig. 2. Cross-section images of the coating synthesised using the PEO mode 1: view on the corner of the sample (a); view on the flat surface of the sample (b) (x250).

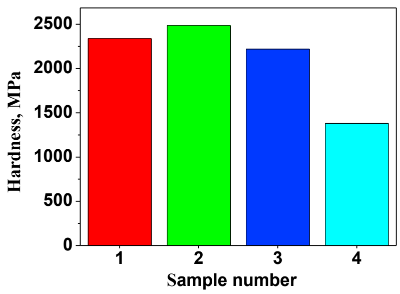


Fig. 3. Hardness of the coatings synthesized according to the PEO regimes given in Table 1.

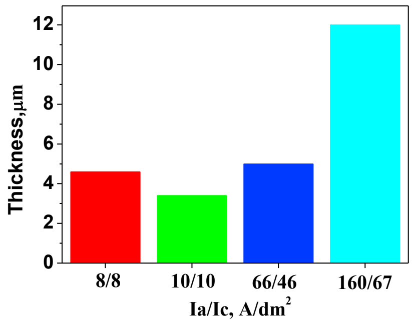


Fig. 4. Thickness of the coatings synthesized according to the PEO regimes given in Table 1.

Mann (2001) proves the relevance of using functional biomaterials, discussing chemical principles and concepts of biomineralization and their properties in detail. He singles out five main principles of influence on the mechanism of biomineralization, among which are chemical, spatial, structural, morphological and constructional. Therefore, control of the thickness of synthesized coatings is of particular importance.

The dependence between thickness and hardness for synthesized coatings is presented in Figure 3. An inverse linear dependence between hardness and coating thickness was revealed, which varied for the adopted PEO regimes in the 3.4–12.0 µm range. Using regression analysis, the dependence satisfies the following relation:

$$t = 22.7312 - 0.0078 \cdot H, \quad R = -0{,}998, \qquad (1)$$

where t and H are the thickness and hardness of the coatings synthesized in modes 1–4.

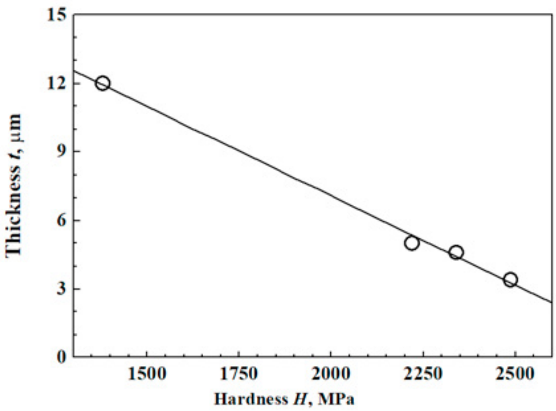


Fig. 5. Correlation dependence between the thickness and hardness of the OCC.

An acceptable correlation between the thickness t and the hardness H of the coatings synthesized in different modes (Fig. 5) was found, allowing us to estimate the thickness of the coating by measuring its hardness. Determining the hardness of the surface after PEO is simple, while the thickness is much more difficult. However, a correlation revealed between the thickness and the hardness of the coatings makes it possible to predict the value of thickness t based on the determined indicator hardness H.

4. Conclusions

For the PEO of the VT8 titanium alloy with a wide processing regime, certain regularities of the hardness formation of the coating were established, the range of which was ~ 1400–2500 MPa. The lowest value of hardness *H* was obtained when using the high ampere characteristics of the PEO.

The influence of the PEO modes on the thickness *t* of the coatings was investigated and the thickness range of 3.4–12.0 µm was obtained for the modes used. The general regularity confirmed that an increase in the amperage characteristics of PEO leads to an increase in the thickness of the coating.

An inverse linear relationship between hardness and coating thickness was revealed. The obtained correlation dependence is recommended to be used for an evaluation of the thickness of the coating based on the determined hardness.

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