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IMPROVEMENT OF PERFORMANCE PROPERTIES OF TITANIUM ALLOYS BY APPLYING PEO COATINGS

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Abstract. Titanium and its alloys are widely used in various industries due to their unique properties - low density, high thermal stability and specific strength, high corrosion resistance, good biocompatibility. However, along with high physical and mechanical properties, titanium alloys have low wear resistance. In order to improve the properties of titanium and its alloys, plasma electrolytic oxidation (PEO) of their surface is considered as a reliable, simple and environmentally friendly method that allows to improve the performance characteristics of titanium and its alloys. The influence of the component composition of electrolytes and process modes, which affect the microstructure and formation of PEO films, was analyzed. It is shown that PEO coating is promising and can provide optimal tribological and corrosion properties of titanium and its alloys.

Key words: titanium and its alloys, PEO, electrolytes, coating, microhardness, corrosion behavior.

1. INTRODUCTION

Titanium and its alloys have such excellent properties as low density, high thermal stability and specific strength, high corrosion resistance, good biocompatibility. The main disadvantage of titanium and its alloys is unsatisfactory tribological properties. To improve the properties of titanium and its alloys, it is promising to apply protective coatings to their surface. By changing the phase and chemical composition, the structure of the surface of the material through chemical and thermal treatment, it is possible to significantly improve its operational properties, such as hardness, strength, wear resistance, heat resistance, corrosion resistance. To improve the surface properties of Ti and its alloys, anodization and plasma electrolytic oxidation (PEO) are most widely used.

In the case of conventional anodization, some of the disadvantages are the slow deposition rate, the need for pretreatment, and contaminating electrolytes.

Plasma electrolytic oxidation (PEO) as a reliable, simple and environmentally friendly coating method is more attractive and widely used to improve the properties of titanium and its alloys [1].

The PEO method can significantly increase the corrosion resistance and wear resistance of titanium and its alloys. The two-layer coatings formed by this method can significantly reduce the coefficient of friction and increase wear resistance [2, 3].

2. RESULTS AND DISCUSSION

We analyzed the PEO method, which allows forming oxide coatings with high performance characteristics. The main concept of the synthesis of wear-resistant and corrosion-resistant plasma-electrolytic layers on titanium alloys remains the development of such methods of surface treatment that allow adjusting the composition and structure of the coatings, providing the necessary operational

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characteristics with a minimum time for their formation. The development includes substantiation of the choice and study of the impact of electrolytes, as well as PEO process parameters on the composition and characteristics of PEO layers on titanium alloys to increase microhardness, wear resistance, corrosion characteristics and reduce their porosity. PEO is an electrochemical oxidation process by which a coating of ceramic oxide is formed on the surface of light alloys. The samples are anodically polarized to high voltages exceeding the dielectric breakdown voltage, creating discrete short-lived plasma microdischarges on the surface. Oxide layers, characterized by high hardness, adhesion and improved resistance to wear and corrosion.

Analysis of literature sources showed that there are several parameters that affect the microstructure and formation of PEO films. These are internal parameters: alloy composition, heat treatment, roughness, porosity of oxidized material and external parameters: component composition, concentration, pH and temperature of the electrolyte, PEO mode (polarity, frequency, amplitude and shape of voltage and current pulses, their ratio, processing time).

These factors determine the thickness of coatings, their composition, structure, density and porosity, microhardness, adhesion strength to the base, wear and corrosion resistance, electrical and thermal conductivity. The chemical composition of electrolytes, along with the material of the substrate, the mode and time of processing, is a determining factor of the PEO process, which significantly affects the composition, structure and properties of the resulting coatings [4].

Research results indicate that the coatings formed in the PEO mode have significantly higher corrosion resistance in both acidic and alkaline environments compared to those obtained by classical anodization, and the reduction of grain sizes and the formation of a microglobular structure of oxide systems contributes to the increase in resistance to abrasive wear. Note that the PEO technology has been well developed for aluminum alloys. As for titanium alloys, PEO technology contains many uncertainties and requires further research.

In order to improve the mechanical characteristics of titanium alloys, it is necessary to establish the regularity of the influence of the modes and composition of the electrolyte during the PEO process on the phase composition, microhardness and tribological characteristics of the coatings obtained by this method on titanium alloys. This will allow choosing the electrolyte and the PEO mode, which will ensure optimal tribological and corrosion properties of the coatings.

It was shown that for the formation of a technologically appropriate passive film, it is extremely important that it does not exhibit electronic conductivity, but rather ion conductivity. Only passivation and complex behavior with passive and transpassive regions are suitable for the formation of reaction layers suitable for PEO initiation [5]. The authors cite chemical reactions that occur during film growth.

	Anode	Cathode
$H_2O \leftrightarrow 2H^+ + O^{2-}$	$xMe^{n+} + yO^{2-} \rightarrow Me_xO_y$	$nH^+ + ne^- \rightarrow 0.5nH_2$
$Me \rightarrow Me^{n+} + ne^-$		
	$xMe^{n+} + y(OH)^- \rightarrow Me_x(OH)_y$	

$$xMe + yH_2O \rightarrow Me_xO_y + yH_2 \text{ (general reaction)}$$

The formation of an ion-conducting oxide layer leads to significant electrical resistance.

Maintaining the current flow requires an increase in potential until the electric field strength in said system reaches a critical value and a breakdown occurs. In addition, the formed film further increases the electrical resistance in the electrolyte/gas/oxide/electrode system.

The breakdown of the system is mainly influenced by the material of the substrate and the composition of the electrolyte, while it does not depend on the current density, temperature, surface roughness, and movement of the electrolyte [6, 7]. In the discharge channel, thermally activated ions originating from the substrate metal are ejected and away from the substrate by migration in the electric field, while oxygen ions move toward the substrate. Then, an oxide is formed because of the reaction of substrate ions and oxygen ions and settles in the boundary regions of the channel. The discharge channel is characterized by a local current of several kiloamperes per square centimeter under a strong electric field, which leads to a huge energy density. Thus, temperatures of several thousand Kelvin can be observed locally. The process involves many crystallizations and melting processes, as well as electrochemical oxidation at the micro discharge sites. Anions of the solution and cations of the substrate are attached to the discharge channel, react, and then settle on the wall of the discharge channel or the surface of the coating after cooling [9].

It is known that the PEO coating consists of two different films - an outer film with a significant number of cracks, porosity and other structural defects and a denser inner film. Pores and cracks in PEO coatings are formed due to the continuous high thermal stresses and spark discharges that occur during this process. The number and size of cracks and pores affect the surface characteristics [8].

In [10], the structure and properties of coatings on ПТ-3В and BT3-1 titanium alloys formed in different electrolytes were studied. The PEO process was carried out in an alkaline electrolyte with the addition of sodium aluminate ($NaAlO_2$), sodium hexametaphosphate $(NaPO_3)_6$ and liquid glass (Na_2SiO_3, $\rho = 1.4$ g/cm3). The current density varied within 20–100 A/dm^2, the duration of treatment was from 0.5 to 2 hours.

The analysis of the obtained results (tables 1, 2) showed that KOH increases the ability of the electrolyte to oxidize, ensures the alkalinity of the solution and reduces the hydrolysis of $NaAlO_2$. It was found that in the absence of KOH, the thickness of the coating does not exceed 10 ... 20 µm, and in the presence it is of ~ 100 µm. It is determined that $NaAlO_2$ supplies the material for the coating and Na_2SiO_3 provides the melting of the coating: without Na_2SiO_3 the coating is powdery.

Table 1. PEO coating on the BT3-1 alloy

Series	Electrolyte	Mode PEO		*h*, µm		Hardness, MPa
		τ, hours	ρ, A/dm^2	gener.	basic	
1	1 g/l KOH + 12 g/l $NaAlO_2$	1	40	110	70	5400
		2	20	90	60	5400
2	1.75 g/l KOH + 1 g/l Na_2SiO_3 + 2 g/l $NaAlO_2$	1	50	100	65	9000
		3	50	280	200	11000
3	2.5 g/l NaOH + 3 g/l $NaAlO_2$ + 3 g/l $(NaPO_3)_6$	1	25	50	20	4200
4	2.5 g/l NaOH + 6 g/l $NaAlO_2$ + 7 g/l $(NaPO_3)_6$	2	45	73	40	4000
5	2.5 g/l NaOH + 3 g/l $NaAlO_2$	2	25	73	60	6650

The authors noted that to form a coating with high hardness (HV > 7000 MPa) on titanium alloys (ПТ-3В and BT3-1 alloys) it is necessary to increase the content of sodium aluminate in the electrolyte.

Table 2. PEO coating on ПТ-3В alloy

Series	Electrolyte	Mode PEO		*h*, µm		Hardness, MPa
		τ, hours	ρ, A/dm^2	gener.	basic	
1	1 g/l KOH + 14 g/l $NaAlO_2$	2,5	50	210	160	7400
2	1 g/l KOH + 10 g/l $NaAlO_2$	2,5	40	180	150	5700
3	3 g/l KOH + 3 g/l $NaAlO_2$	0,5	100	160	90	4400
4	1.75 g/l KOH + 1 g/l Na_2SiO_3 + 2 g/l $NaAlO_2$	3	25	200	150	7500

It was established that the main phases of the coating are the phases TiO_2 – rutile, TiO_2 – anatase, as well as the compound Al_2TiO_5 – aluminum titanate. Depending on the thickness of the layer (duration of processing), the ratio between the main phases is different. Thus, under conditions of small thicknesses, the main phase is aluminum titanate (~ 90%). An increase in thickness (processing time) leads to an increase in the rutile content (~ 40%). In the studied coatings, the content of anatase did not exceed 10%, regardless of the processing time. Addition of liquid glass (Na_2SiO_3) to the electrolyte leads to the formation of mullite ($3Al_2O_3 \times 2SiO_2$), which leads to an increase in the hardness of the coating. Therefore, it is shown that in the electrolyte, which contains caustic potassium, sodium aluminate and liquid glass, coatings of heterophase composition (rutile, aluminum titanate and mullite) are formed, which provides greater hardness.

It is also shown that the PEO coating has a positive effect on the antifriction properties during friction in a pair with gray cast iron without lubrication. Thus, the use of PEO made it possible to reduce the coefficient of friction of the surface of titanium alloy BT3-1 in the process of dry friction by 5 times and reach the value f ∠ 0.1.

To date, several studies have been conducted on the influence of electrolyte composition and PEO modes on the surface morphology, corrosion resistance and wear properties of PEO coatings. Despite this, the mechanism of PEO is still not fully understood. In [11], the effect of electrolytes based on aluminate and carbonate on the properties of titanium oxide PEO coatings was investigated. It is shown that the coating formed in the sodium aluminate electrolyte has better corrosion behavior than the others because it also contains the $TiAl_2O_5$ phase in addition to the titanium oxide phases (rutile and anatase).

Analysis of the process in solutions based on phosphates, silicates and borates showed that PEO reduces the corrosion current density by an order of magnitude compared to uncoated samples in the following order: $I_{borates} > I_{silicates} > I_{phosphates}$. Note that the corrosion potential of the samples was positively shifted after PEO treatment. This caused a decrease in the thermodynamic tendency to corrosion; secondly, the anodic section of the curves was shifted toward lower current densities after PEO treatment. After PEO, greater chemical resistance of titanium was obtained.

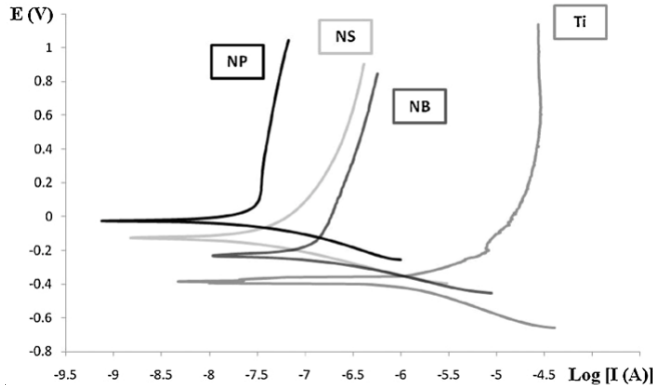

Figure 1. Tafel curves for untreated and PEO-coated samples in different electrolytes: NP-phosphates, NS – silicates, NB – borates [10].

The authors explain the better corrosion behavior of samples with a coating obtained in a phosphate electrolyte due to the formation of a thicker layer and a larger amount of rutile phase. Investigation of the phase composition of the coating obtained in the borate solution revealed a large amount of anatase and a small amount of rutile. A greater amount of rutile compared to the anatase phase was found in the coatings obtained in phosphate and silicate solutions. The rutile phase has a higher hardness compared to anatase, which improves the tribological characteristics of the coating. In addition, the rutile phase of titanium oxide in the coating provides good corrosion behavior.

The applied voltage, frequency, duty cycle and oxidation time are also important parameters of the PEO process. These parameters affect the spark voltage and, therefore, the spark energy. Note that changing the composition of the solution also leads to different spark voltages.

The energy of the spark affects the size of the micropores and the thickness of the coating, which determines the tribological and corrosion behavior of the coating. An increase in the spark voltage leads to an increase in the size of the pores and the inhomogeneity of their dispersion on the surface of the coating. Time also affects the thickness of the coating and on the properties of the coating.

In [11] the PEO process was carried out on titanium in the constant voltage mode using a pulsed power source. The thickness of coatings obtained in different electrolytes was investigated.

The coated sample obtained in silicate (NS) electrolyte had a thinner film than the coated sample obtained in phosphate (NP) electrolyte. This may be due to the lower spark voltage for this sample. The high spark voltage produces high-energy sparks that generate molten materials for form a thick ceramic film. Since the coated sample prepared in borate (HB) electrolyte did not show sparking, its coating thickness was smaller than other coatings (Fig. 2).

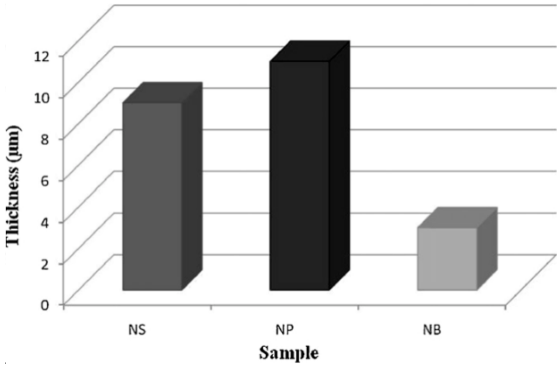

Fig. 2. Thickness of coatings obtained in different electrolytes: NP – phosphates, NS – silicates, NB – borates [11].

It is shown that at constant PEO parameters, a change in the composition of the solution leads to different spark voltages. An increase in the spark voltage leads to an increase in the size of the pores and the inhomogeneity of their dispersion on the surface of the coating.

In [12] it was investigated that one of the important parameters of the PEO process is the total current, which consists of the electronic current caused by spark formation and the ionic current caused by the diffusion of electrolyte ions into the oxide. The dominance of the electron current contribution at low current densities (30 and 40 mA/cm^2) was established. A large number of plasma discharges in this condition increases the porosity and roughness of the surface of the coating. These discharges provide sufficient energy to raise the temperature, promoting the formation of both stable rutile and stable anatase. The inclusion of the ion current increases with increasing the current density resulting in the formation of dense anatase coatings with high growth rates and lower roughness and porosity.

The effect of temperature on the PEO process of titanium alloy in an electrolyte containing 0.15 mol/l $K_2Al_2O_4$, 0.02 mol/l Na_3PO_4 and 0.015 mol/l NaOH was considered. It was established that less porous and more wear-resistant coatings are formed at lower temperatures [13].

The effect of voltage and frequency on the porosity of the coating obtained on titanium in an electrolyte containing 10 g/l $Na_3PO_4 \cdot 12H_2O$ was investigated in [14]. It was established that the pore size decreases with increasing frequency and the coatings obtained at a frequency of 500 Hz have the highest catalytic activity. It was shown [15] that the most important property of the coating, which is affected by process parameters, is its thickness. It increases linearly with the time of electrolysis.

3. CONCLUSIONS

It was established that the justified choice of electrolytes, as well as the parameters of the PEO process significantly affects the composition and characteristics of PEO layers on titanium and its alloys. The properties of PEO coatings depend on the microstructure of their surface. The morphology and composition of PEO coatings can be controlled over a wide range by controlling the PEO process. This creates prerequisites for the development of coating technology of a given morphology with increased operation resource and predictable characteristics.

It is shown that the technology of applying PEO protective coatings on titanium and its alloys provides for the creation of surface coatings that can provide high performance characteristics and expand the scope of practical use of titanium alloys.

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