Wearproof Composite Coatings on Ti

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Keywords: Coating Materials, Oxide Materials, Polymers, Composite Materials, Titanium

Abstract. In this work the formation of protective coatings on VT1-0 commercially pure titanium by plasma electrolytic oxidation (PEO) and subsequent fluoropolymer treatment is presented. The structure, morphology, corrosion, and mechanical properties of the formed composite coatings were studied. It was established that PEO coatings are an excellent basis for the formation of a solid composite layer with high adhesion to its surface. The presence of polytetrafluoroethylene in the composition of the coating reduces the corrosion current density by 4 orders of magnitude and increases the wear resistance by 2 orders of magnitude in comparison with the base PEO coating.

Introduction

Currently, titanium and its alloys are widely used in advanced industries from missilery to implant surgery. The use of titanium and its alloys is due to its several unique properties, such as high corrosion resistance and strength, low density, high heat capacity, etc. [1–5]. However, titanium and its alloys require additional surface treatment for improving the tribological and corrosion properties [4,6–8].

The formation of protective coatings is widely used to modify the surface properties of titanium alloys. In industries is more common thermal oxidation, the summary of which lies in the high thermal oxidation of metal [4]. As a result, a durable oxide coating is formed on the titanium surface. However, this method is labor- and energy-intensive, and has several technological limits.

Currently, many researchers have developed a method for the formation of protective coatings on titanium alloys by plasma electrolytic oxidation (PEO) [1,4–6,8,9]. After the analysis of previous studies, we have found that such surface layers are effective for protecting titanium from wear, prevent corrosion of metals in galvanic couple with titanium, and have a suitable surface structure for the formation of composite coatings (CC) by incorporating substances into the PEO layer for additional improving of the mechanical and electrochemical characteristics of the surface of treated material [5,10].

Previously, we have developed a method to forming CC by immersion samples with base PEO coating in a suspension of superdispersed polytetrafluoroethylene (PTFE). The possibility of using some commercial fluoroplastic suspensions is interest too. The use of such suspensions can significantly expand the range of materials used to create polymer-containing layers.

Materials and methods

As a material for the studied samples the VT1-0 commercially pure titanium (wt. %: 0.25 Fe; 0.12 Si; 0.07 C; 0.12 O; 0.04 N; 0.01 H; balance: Ti) was used. As a sample for the formation of coatings the rectangular plates (50×50×1 mm³) were used.

The formation of PEO coatings was carried out in a phosphate electrolyte, containing of 25 g L⁻¹ trisodium phosphate (Na₃PO₄) in a monopolar potentiodynamic mode. In the first stage, the voltage was increased from 50 to 300 V, the duration of process was 120 s. At the second stage, the voltage dropped to 240 V, the duration of process was 580 s.

For the formation of composite coatings, a commercial aqueous suspension of PTFE F4-D (Halopolymer, Russia) was used. The coatings were formed by immersion in a suspension (exposure time was 1 min). The dipping speed was 100 mm min⁻¹, the extraction speed was 10 mm min⁻¹. Then, the samples were dried in air and thermally treated in an L3/11 muffle furnace (Nabertherm, Germany) at 365°C for 20 min.

A scanning electron microscope (SEM) Merlin (Carl Zeiss, Germany) was used to study surface morphology of the coatings. SEM image was processed by the ImageJ software (National Institutes of Health, USA).

The electrochemical parameters of the coatings formed on VT1-0 commercially pure titanium under the study were obtained by potentiodynamic polarization method. The coatings were studied using a VersaSTAT MC electrochemical system (Princeton Applied Research, USA). The tests were carried out in the three-electrode cell at room temperature in an aqueous solution of 3.5 wt. % NaCl. A platinized niobium mesh was used as a counter electrode. The saturated calomel electrode (SCE) was used as a reference electrode. The samples area exposed to electrolyte was equal to 1 cm².

Potentiodynamic polarization test was carried out at a scan rate of 0.167 mV/s from $E_C - 0.15$ V to $E_C + 0.50$ V vs. OCP. The Levenberg-Marquardt [11] method was used to calculate the corrosion parameters of studied samples by fitting the experimental data (i.e. values of potential E , and current density I) to the following Equation (1):

$$I = I_C \left(10^{\frac{E-E_C}{\beta_a}} + 10^{-\frac{E-E_C}{\beta_c}} \right). \quad (1)$$

This method makes it possible to obtain the best fit values of corrosion potential E_C , corrosion current density I_C , the slope of the cathodic polarization curve β_c , and the slope of the anodic polarization curve β_a . The application of the Levenberg-Marquardt method ensured a high accuracy of the conducted calculations of the corrosion parameters. The polarization resistance R_p was determined in a separate experiment by linear polarization test at sweep rate of 0.167 mV s⁻¹ in the potential region $\Delta E = E_C \pm 20$ mV, in which the linear dependence $I = f(E)$ is observed [12,13]. The test was carried out after stabilization of the open circuit potential. Calculation of R_p values is carried out according to the Equation (2):

$$R_p = \frac{\Delta E}{\Delta I}, \quad (2)$$

The wear resistance of coatings was measured on a TRB-S-DE device (CSM Instruments, Switzerland). The tests were carried out in dry friction mode at a sliding speed of 50 mm s⁻¹ and a load of 25 N. The corundum ball (α -Al₂O₃) was used as a counter-body. The diameter of the ball was 3 mm, and the diameter of the wear track was 5 mm. To estimate the wear, the track profiles were recorded after the wear tests using a Surtronic 25 profilometer (Taylor Hobson Ltd, England). The wear was estimated using the profiles obtained from the wear track cross-section, and thus the wear rate, P (mm³ (N×m)⁻¹), was calculated using Equation (3):

$$P = \frac{\Delta V}{N F} \quad (3)$$

where ΔV is the worn volume (mm^3), N is the distance moved (mm), and F is the normal load (N). The wear volume was calculated using 2D profiles. In all the experiments carried out, the wear of the counter-body was not detected and was not considered at the calculation.

An adhesion characteristic of coatings was evaluated by Revetest Scratch Tester (CSM Instruments, Switzerland). The scratch length was 5 mm, the maximum applied load was 30 N. The rate of increase of the load was 30 N min^{-1} .

Results and discussion

Based on the analysis of SEM images (Fig. 1), it can be concluded that the fluoropolymer penetrates to the pores of the PEO coating and forms smooth thin film on the samples' surface (Fig. 1b). A significant number of pores of all sizes are equally sealed, and the surface becomes smooth and close to homogeneous. The polymer film in different areas has a different thickness, but whole thickness of the polymer film does not exceed $2 \mu\text{m}$. The porosity of the coatings over the surface (Fig. 1) with and without the fluoropolymer is 14.45% and 0%, respectively.

Fig. 1. SEM image of the PEO (a) and composite coatings (b)

Potentiodynamic polarization data indicate an improvement in the corrosion properties of the samples after formation of CC on their surface. Evaluation of the polarization curves (Fig. 2) presents an increase of the corrosion potential E_C for PEO coating in comparison with the bare material; however, due to the high porosity and the presence of microdefects in the coating, the corrosion current density decreases insignificantly. Treatment of a PEO coating with a fluoropolymer leads to a strong decrease of the corrosion current density (by four orders of magnitude in comparison with that for a PEO coating).

This effect is associated with the incorporation of polytetrafluoroethylene to the coating. Due to the high strength and uniformity of the polymer distribution over the surface of the CC, as well as the absence of pores and defects (in comparison with the PEO coating), the value of the corrosion current density decreases (Table 1).

Table 1. Electrochemical and mechanical properties for samples with different types of surface treatment.

Sample	E_c (V)	I_c (A cm ⁻²)	R_p (Ω cm ²)	L_{C3} (N)	P (mm ³ (N m) ⁻¹)
Ti	-0.38	$1.08 \cdot 10^{-7}$	$3.52 \cdot 10^5$	-	-
PEO	0.11	$3.06 \cdot 10^{-8}$	$9.15 \cdot 10^5$	14	$3.97 \cdot 10^{-4}$
CC	0.11	$1.02 \cdot 10^{-10}$	$7.16 \cdot 10^8$	23	$2.98 \cdot 10^{-6}$

Fig. 2. Polarization curves for sample with different types of surface treatment

Figure 3 shows optical images of the scratch on the PEO coating (Fig. 3a) and CC (Fig. 3b). Analysis of these images clearly shows that the value of the load L_{C3} , at which the coating peels off, is higher for the CC (Table 1), and is about 23 N (for PEO coating is about 14 N). These values indicate high adhesion of both the polymer film to the base PEO coating and the whole composite coating to metal.

Analysis of tribological test (Fig. 4) made it possible to establish that the wear resistance of composite coatings is more than 2 orders of magnitude higher in comparison with PEO coating

(Table 1). It is associated with the formation of a dense polymer film that forms a uniform smooth surface with a low coefficient of friction (about 0.01).

Fig. 3. Optical images of the scratch on a PEO coating (a) and CC (b)

Fig. 4. Dependence of the coefficient of friction μ on the number of cycles for samples with different types of surface treatment

Summary

Composite coatings were obtained on VT1-0 commercially pure titanium by plasma electrolytic oxidation with following processing in suspension of PTFE (F4-D, Halopolymer, Russia). This method of treatment significantly affects the morphology, structure, and properties of the surface

of the titanium, allowing its use in friction units and in the contact with another metals in corrosion environment.

Summarizing all the above, this enables one to conclude that processing of PEO coatings on VT1-0 titanium with PTFE suspension makes it possible to reduce the corrosion current density by 4 orders of magnitude, increase the adhesion of the coating to the metal surface and reduce surface wear by 2 orders of magnitude in comparison with PEO coatings.

Acknowledgements

This work was supported within the frames of the Grant of the Russian Science Foundation, project No. 20-13-00130. The electrochemical tests were carried out within the framework of the government assignments from Ministry of Science and Higher Education of the Russian Federation, project No. 0205-2021-0003.

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