

Formation of the composite coatings as a method of restoration of titanium products after exploitation

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Today one of the most common methods of the coatings formation on titanium alloys is a thermal oxidation. Along with the merits, this method of surface modification has certain drawbacks: high energy and labor costs, lack of the possibility of restoration of the coatings after damage during exploitation, high probability of manufacturing defects formation. The importance of the above problems for the practice, as well as the increasing demands on the quality of the protective layers formed on metals and alloys indicates the relevance of the task of scientific search for alternative ways of formation and restoration the protective properties of coatings on products that have been in exploitation. This paper presents the results of investigation of plasma electrolytic oxidation modes of commercial pure titanium VT1-0 with an oxide layer on the surface, providing restoration of the protective performances of the coating, the integrity of which was destroyed during operation. The combination of plasma electrolytic oxidation and the subsequent application of a fluoropolymer material by dipping in the suspension of superdispersed polytetrafluoroethylene (SPTFE) and thermal treatment at 315 °C for 10 minutes allowed the formation of practically significant composite polymer-containing coating. Evaluation of the data obtained by the potentiodynamic polarization method indicates a decreasing the corrosion current density and an increasing the polarization resistance by more than three times for the formed composite coatings in comparison with the coating obtained using only plasma electrolytic oxidation treatment of samples with thermal oxide on the surface. Composite layers reliably protect products made of steel and copper-based alloys against galvanic corrosion at contact with titanium alloys in seawater. The technology of restoring the protective properties of the coating, the barrier layer of which was destroyed during the exploitation, was implemented in "Far East Shipyard "Zvezda" at the end of 2015.

Key words: titanium, thermal oxidation, protective coatings, plasma electrolytic oxidation, superdispersed polytetrafluoroethylene, composite coatings, corrosion.

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Introduction

Titanium and its alloys are now widely used in many industries due to the unique properties of this materials such as a combination of low density, high specific strength and corrosion resistance, ability to work at high temperatures without losing functional performances. However, the ability of titanium and its alloys to form galvanic couple with other metals and alloys in corrosive media leads to the necessity to find ways to protect the contacting materials. One of the most common modern methods

of protection is the thermal oxidation (TO). This method of surface treatment is one of the simplest and most effective ways of the treatment which improves the anticorrosive properties of titanium alloys. However, the TO has a number of significant drawbacks. The method is energy-consuming, long-lasting, and labor-intensive, and has a high percentage of the product defectiveness. This method not allows to repeat the process with purpose of re-oxidizing and restoring the coating on parts, which were in exploitation [1]. The drawbacks of the TO method, as well as the increasing demands on the quality of the formed protective layers, make it an

actual task to search for alternative ways of the coatings formation and restoration of its protective properties. A possible way of the solution of this problem is using of the plasma electrolytic oxidation (PEO) method [2–8] to restore barrier properties of the coatings on titanium alloys parts that have been previously in operation, with subsequent formation of a composite polymer-containing layer. As a polymer component, fluoropolymers are of particular interest due to their high chemical resistance and excellent electrical insulating properties [9]. Such coatings can have higher protective performances in comparison not only with the untreated alloys, but also with the base PEO-coating [10–12].

In this paper, the electrochemical properties of composite coatings (CC) obtained on a commercially pure titanium VT1-0 pretreated by thermal oxidation were described.

Materials and methods

The samples were titanium plates of the commercially pure titanium VT1-0 with dimensions 30×15×1 mm. Before coating process all samples have been mechanically treated with the grinding paper with a grain size reduction of down to 15 μm in order to standardize the surface. The samples have been then washed with distilled water and degreased with acetone using an ultrasonic bath.

In order to investigate the possibility of restoration of the protective properties of the surface layers, titanium samples have been previously subjected to thermal oxidation. The TO-coatings have been formed during low-temperature oxidation in the furnace at 800 °C for 1 h, followed by slow cooling of the samples in the furnace down to 300 °C and then outside the furnace down to the room temperature.

Plasma electrolytic oxidation of the samples have been carried out in a phosphate-containing electrolyte in a combined monopolar mode in two subsequent potentiodynamic stages. During the first one the voltage was sweep from 0 up to 500 V at a rate of 5.25 V/s to create a plasma microdischarges at the electrolyte / oxide film interface. The discharges are necessary to form the PEO-layer. Then the voltage was sweep down to 300 V at a rate of 0.22 V/s. A gradual decrease in voltage provided a moderate intensity of plasma microdischarges on the sample surface during second stage that promoted a uniform growth of the PEO-coating without defects.

The superdispersed polytetrafluoroethylene (SPTFE) powder (trademark Forum®) was used as an organofluorine material (component of the polymer-containing coating) [10]. In order to improve the processability of the composite layer application, a 1.1% suspension of SPTFE powder in deionized water with adding of surfactant was used. The organofluorine material has been applied by dip-coating method at experimental

parameters such as a slow immersion in an aqueous SPTFE suspension, exposure to a solution for 15 s, fast withdrawal. After that the sample was dried in air for 20 min at 25 °C, and then heat treated at 315 °C for 10 min in order to melt the organofluorine material and incorporate it into the pores of the base PEO-layer. The fluoropolymer-containing coating have been applied successively up to 3 times in order to study the effect of multiple treatment on the protective properties of coatings.

Electrochemical parameters of formed coatings have been investigated by potentiodynamic polarization method and electrochemical impedance spectroscopy with the use of electrochemical system VersaSTAT MC (Princeton Applied Research, USA). Measurements have been carried out in a three-electrode cell in a 3% NaCl solution at room temperature. The niobium grid covered by platinum and the saturated calomel electrode (SCE) were used as a counter electrode and reference electrode, respectively. The exposed area of samples was equal to 1 cm². Before beginning of electrochemical measurements for stabilization of the corrosion potential (E_C) the sample have been kept for 15 min in electrolyte. During the impedance measurements, the sinusoidal signal with amplitude of 10 mV (rms) has been used. A spectrum has been recorded at a stabilized

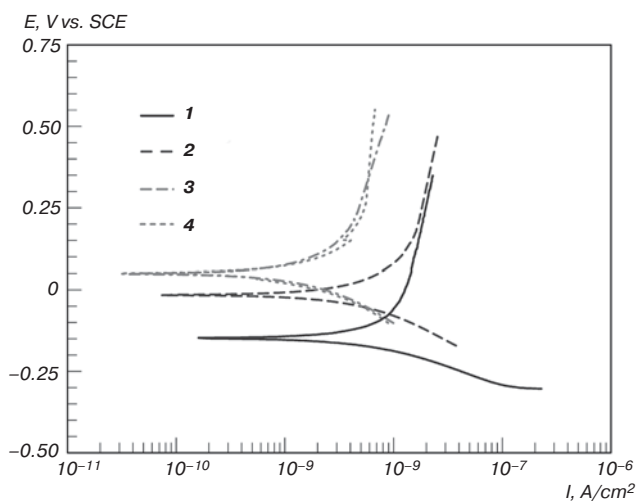


Fig. 1. Polarization curves of samples with PEO-coating (1) and composite coatings obtained by single (2), double (3) and triple (4) treatment of the PEO-layer with an aqueous suspension of SPTFE

Corrosion properties of investigated coatings

Type of coating	E_C , V vs. SCE	β_a , mV/decade	β_c , mV/decade	I_C , A/cm ²	R_p , Ω·cm ²
PEO-coating	-0.15	407	97	4.7·10 ⁻⁹	7.3·10 ⁶
CC-1x	-0.02	330	130	3.9·10 ⁻⁹	1.0·10 ⁷
CC-2x	0.05	366	163	1.5·10 ⁻⁹	3.3·10 ⁷
CC-3x	0.05	320	170	1.4·10 ⁻⁹	3.5·10 ⁷

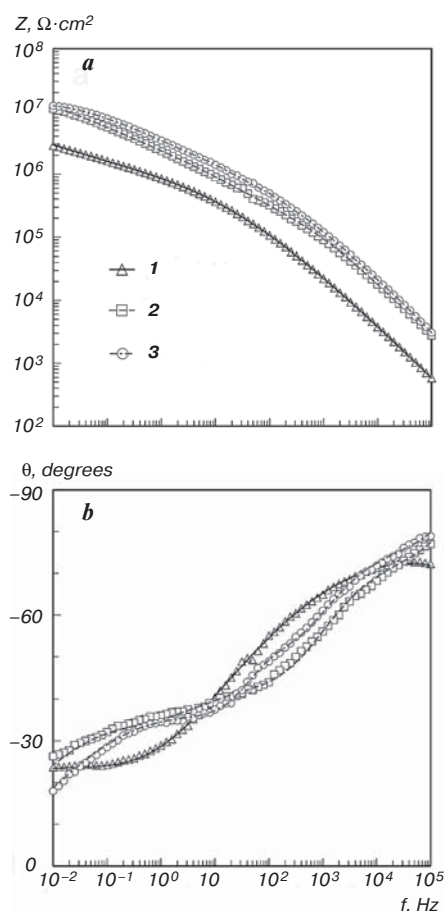


Fig. 2. Bode plots (dependence of impedance modulus $|Z|$ (a) and phase angle θ (b) on frequency f) for samples after single, double and triple application of SPTFE. The theoretical curves are indicated by lines, the experimental data by the symbols: 1 – CC-1x; 2 – CC-2x; 3 – CC-3x

potential E_C in the frequency range from 0.01 Hz to 0.1 MHz at logarithmic sweep at 10 points per decade. Potentiodynamic measurements have been carried out at sweep rate of 0.17 mV/s from $E_C - 0.15$ V to $E_C + 0.5$ V.

Results and discussion

The analysis of the polarization curves (Fig. 1) recorded for composite coatings indicates a significant effect of the multiplicity of the base PEO-layer polymer treatment on the protective performances of the coatings (Table). After single application of the fluoropolymer (CC-1x), the corrosion characteristics change insignificantly in comparison with the base PEO-layer, which is due to the small number of polymer-covered areas on the surface of the PEO-layer and, consequently, there are the unfilled pores presence in the coating. After double application (CC-2x) a significant decrease in the corrosion current density I_C and an increase in the polarization resistance R_p by more than three times in comparison with the untreated PEO-coating are observed. A further increase of the treatment multiplicity leads to a no significant increase in the protective performances. The observed

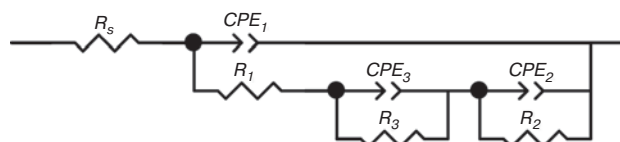


Fig. 3. Three-R-CPE-circuit equivalent electrical circuit used for fitting of the experimental impedance spectra

increase of the corrosion potential E_C up to 0.05 V is associated with improve of the protective properties of the composite coating after application of a polymer.

The protective characteristics of composite coatings are also higher than those of TO-coatings. Thus, for CC-3x the corrosion current density I_C is reduced by more than four times in comparison with TO-coating for which $I_C = 6.7 \cdot 10^{-9}$ A/cm².

Data obtained by electrochemical impedance spectroscopy are presented in the form of Bode plots (Fig. 2). The impedance spectra presented in Fig. 2 contain the experimental data (marked with symbols) and theoretical curves based on the calculated parameters of the equivalent electrical circuit (EEC) (Fig. 3) and describing with a high accuracy experimental results (the values of the parameter χ^2 are in the range $(1.0-1.5) \cdot 10^{-4}$).

Based on the interpretation of the obtained results, it can be concluded that all three dependences of the phase angle θ on the frequency f for composite coatings have three time constants, which are due to the structure of the composite layer. Each spectrum may be described using an equivalent electrical circuit with three R-CPE-chains (Fig. 3) [10]. It should be noted that the character of the presented dependences varies with the multiplicity of treatment of the base PEO-layer with the fluoropolymer material. For the CC obtained by single application of the SPTFE the first time constant is located on the dependence of the phase angle θ on frequency f (Fig. 2, b) in the high frequency region (10^3-10^5 Hz) with a minimum of the phase angle -73° . This time constant corresponds to the R_1 - CPE_1 -circuit (Fig. 3), which describes the geometric capacity of the coating [10]. The second bend of the curve is located in the middle and low frequency region ($10^{-1}-10^3$ Hz), practically merging with the first time constant; it corresponds to the R_2 - CPE_2 -circuit (Fig. 3), which characterizes the thin inner nonporous sublayer in the PEO-coating (Fig. 2, b). For CC-1x at the low frequency region of the Bode plot (Fig. 2, b) a third time constant is located, due to the presence of air space in the structure of the composite layer (between the polymer plug and the bottom of the pore). This time constant corresponds to the R_3 - CPE_3 -circuit in the EEC presented in Fig. 3.

Dependences of the phase angle θ on the frequency f for composite layers with double and triple application of SPTFE are similar to the dependence presented for CC-1x (Fig. 2, b); however, there are certain differences in the positions of time constants. For these polymer-

containing coatings, it could be also distinguish three time constants in the Bode plots: in the high frequency region with phase angle minima of -76° and -79° for CC-2x and CC-3x respectively, in the middle frequency region from 1 to 80 Hz for CC-2x and from 10 to $6 \cdot 10^2$ Hz for CC-3x, and also in the low frequency region of the spectrum (Fig. 2, b). The presence of these time constants is explained by the same reasons as for CC-1x. The similarity of the graphs of coatings CC-2x and CC-3x and their difference from the graph of CC-1x are due to the fact that when the polymer is applied twice, a pseudo-continuous polymer layer is formed, and triple application increases the thickness of the layer, thereby increasing the barrier properties.

Conclusion

A method of the anticorrosive composite coatings formation using the plasma electrolytic oxidation and subsequent application of the polymer from an aqueous suspension of superdispersed polytetrafluoroethylene has been developed. The obtained composite polymer-containing coatings decrease the corrosion current density by three times in comparison with the base PEO-coating. The technology of restoring the protective properties of the coating, the barrier layer of which was destroyed during the exploitation, was implemented in "Far East Shipyard "Zvezda" at the end of 2015.

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