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INFLUENCE OF COATING FORMATION CONDITIONS IN CHLORINE-CONTAINING MEDIA ON THE CORROSION PROPERTIES OF TITANIUM

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Abstract

Due to its high plasticity, the ability to absorb vibrational vibrations and impact energy, the possibility of cutting, and most importantly, the high specific strength, titanium and its alloys begin to be widely used for the manufacture of structures and parts in shipbuilding and mechanical engineering, aircraft and rocketry, as well as in the manufacture of consumer goods, in particular, cases of computers and mobile phones. At the same time, due to the insufficient resistance of the passive film, especially in environments containing chlorine ions, high thermodynamic activity, titanium, and often its alloys, have low corrosion resistance in various environments. In this regard, it is necessary to obtain anti-corrosion coatings on their surfaces. The paper considers the possibilities of increasing the corrosion resistance of titanium. It is shown that the relationship between the anticorrosive properties of PEO coatings and the stages of their growth can be of a general nature during PEO treatment of valve metals and alloys of different nature in electrolytes of different compositions. The effect of the duration of PEO-treatment on the time of pitting formation τ_p, thickness, contact angle and elemental composition of coatings, as well as on the dependence of the time of formation of pitting, referred to the unit of coating thickness τ_p/h has been established. In addition, the type of the surface of the coatings formed over different times and the dependence of the change in voltage on the electrodes on the time of formation of $U=f(t_f)$ of the coating were determined. The elucidation of the reasons for the increased anticorrosive resistance of coatings formed under galvanostatic conditions in the region of the transition from the sparking stage to the stage of more powerful microarc electric discharges requires further research.

Keywords: Plasma-electrolytic treatment, oxide coatings, anodizing methods, titan, electrophoresis, alumin.

Introduction

Obtained by various anodizing methods, oxide coatings on titanium and magnesium alloys are highly porous. They are used only as a sublayer for finishing coatings, in particular, paint and varnish and enamel, therefore, anodizing processes should be classified as intermediate, since they do not provide sufficient protection against corrosion of both cast and wrought alloys.

Plasma-electrolytic treatment (PEO) of titanium and its alloys is the most developed method of their protection against corrosion. A number of researchers call the method of plasma-electrolytic treatment microarc oxidation, other researchers - anodic spark oxidation or plasma-electrolytic oxidation. At the same time, the growth of coatings occurs both by the mechanism of oxidation of the metal base and by the mechanism of electrolysis and/or electrophoresis. According to the latter mechanism, the formation of the coating occurs from compounds formed from salts introduced into the composition of the electrolyte. Undoubtedly, it is correct to call this method plasma-electrolytic treatment, and not plasma-electrolytic oxidation. It was electrolysis that made it possible to obtain decorative coatings with 6 different colors on aluminum and titanium alloys, as well as wear-resistant coatings on titanium alloy VT6. The color of the coatings, as a rule, will depend on the alloying components of the alloys, and coatings containing corundum cannot be obtained on titanium alloys.

For the first time (1956–1966), this method was used to obtain complex oxide coatings on aluminum and magnesium alloys, consisting of electrolyte components that underwent oxidation of the metal base and plasma-electrolytic treatment. Thus, the name of the method - plasma-electrolytic treatment, is correct.

During the PEO processes of structural alloys, the formation of short-lived anode plasma microdischarges takes place , which, as it were, move along the surface of the sample or product immersed in the electrolyte. The power realized in plasma anode microdischarges is a function of the duration of the PEO processes, the shape of the current, and the compositions of alloys and electrolytes.

This method (PEO) has found wide application for modifying the surface of articles made of titanium and aluminum alloys in a given direction.

Significantly more than 3000 °C is the temperature in the core of plasma anode microdischarges during PEO of structural alloys in alkaline electrolytes. The latter provides significant advantages of this method in comparison with other methods designed to modify the surface of products made of alloys based on aluminum, titanium and magnesium. The main advantages of the PEO method are: 1) there is no need for careful surface treatment of alloys before its modification, which makes it possible to significantly reduce the area of production sites; 2) the creation of multifunctional coatings with desired properties: decorative, anticorrosive, wear-resistant, with high adhesion to the metal base and breakdown voltage, as well as with special coatings on products made of magnesium, aluminum and titanium alloys.

The properties of zirconium oxides are widely used in practice, in particular in catalysis, including high-temperature catalysis, in medicine, as part of protective layers and ceramics. Previously, it was shown that coatings formed on titanium by plasma electrolytic oxidation (PEO) in an electrolyte with zirconium sulfate $Zr(SO_4)_2$, consist of ZrO_2 and TiO_2 $_{\text{oxides}}$, their surface layer is enriched with zirconium, they have good protective properties in chlorine-containing environments. The resulting layers have a fairly regular distribution of relatively small pores, with a diameter of about or less than 1 μm, on the surface. The composition and structure of PEO layers depend both on the composition of the electrolyte and on the modes of formation. It is of scientific and practical interest to elucidate the influence of the conditions for the formation of coatings with ZrO_2 on titanium on their anti-corrosion properties in chlorine-containing media.

Methods and Materials

PEO coatings were formed on commercial titanium VT1-0 in the galvanostatic mode at an effective current density i = 0,08 A/sm² for 1...120 min. An aqueous solution of 34.9 g/L $Zr(SO_4)_2 \cdot 4H_2O$ was used. The anticorrosive properties of the coatings were evaluated using the assembled laboratory setup. The plus of the voltage source was connected to the bare metal of the sample through a milliammeter, and the minus was connected to the counter electrode . A drop of 3% NaCl solution , an analogue of sea water, was placed in the gap between the electrodes . A potential difference of 50 V was applied to the electrodes. A stopwatch was used to measure the time interval τp from the moment the drop of the coating solution touched to a sharp increase in the current through the sample. The contact angle of wetting of the coating surface was measured by the "sitting" drop method. The elemental composition of the coatings was determined using a microprobe analyzer JXA 8100 (Japan) with energy-dispersive attachment INCA (England), depth of analysis depending on sample composition from 2 to 5 μm. The coating thickness was determined using an eddy current thickness gauge VT-201 (Russia).

All methodology and research methods used in the work are similar to those used in.

Results and Discussion

The resulting dependence of the time of electrically stimulated pitting τ_p from the time of formation of coatings t_f is shown in fig. 1a. With an increase in t_f up to ~8 min, the value of τ_p gradually increases. At t_f 9 - 11 min there is a sharp increase in the time of formation of pitting. Then the value of τ_p at t_f >11 min also sharply decreases. That is, with an increase in the formation time, the behavior of the anticorrosion properties of coatings changes not monotonously, but abruptly, which was not previously noted in the literature.

Meanwhile, the coating thickness h , Fig.1b, the wetting angle of the coating with water θ , Fig.1c, and the elemental composition of the coatings, Fig. 1d, change monotonously with increasing time of galvanostatic formation t_f , no sharp changes in these characteristics of the coatings are observed.

On fig. 1e the calculated values of the formation time of the electrically stimulated pitting τ_p , referred to the thickness unit h of the formed coatings in the entire range of the studied t_f . According to Fig. 1e, three time intervals can be distinguished, which are characterized by an approximately constant value of τ_p / h . From the constancy of the values τ_p / h it follows that at each time interval the increase in time τ_p is proportional to the increase in thickness h , i.e. coatings grow with approximately the same internal structure. The most dense and resistant to the penetration of chloride ions coatings at the selected current density and salt concentration in the electrolyte were obtained at a formation time t_f 9 - 11 min.

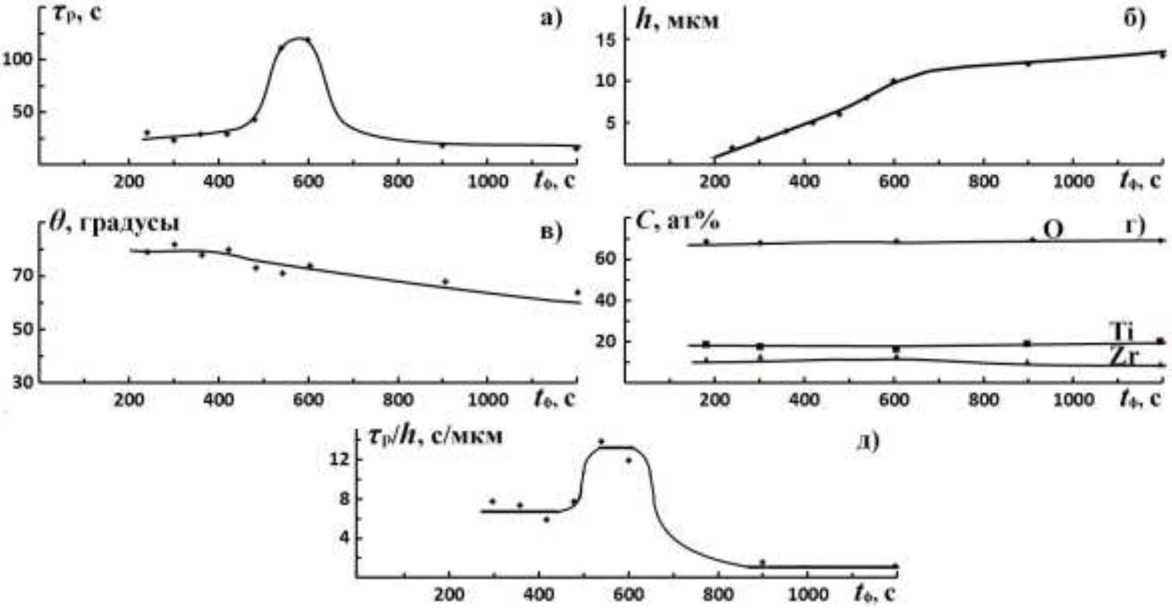

Fig.1. Influence of the duration of PEO treatment on the time of pitting formation τ_p (a), thickness (b), contact angle (c) and elemental composition (d) of the coatings, on the dependence of the time of pitting formation per unit thickness of the coating τ_p/ h (e)

It is known that in the case of galvanostatic PEO, with increasing t_f, the stages of coating growth change : prespark (I), spark (II), and microarc (III) [3]. Figure 2 shows the dependence of the change in the voltage on the electrodes on the formation time $U = f(t_f)$, observed in our experiments. On the basis of its analysis, characteristic stages of galvanostatic PEO are identified on it. Comparison of Figs. 1 and 2 shows that in the stage of formation of coatings by spark discharges $t_f \sim$ up to 5 min., the value of τ_p /h is much higher than in the stage of formation by more powerful microarc discharges, $t_f \geq 15$ min. Those. in the sparking stage, denser and less defective coatings are formed than in the microarc stage .

Similar data were obtained earlier when studying the corrosion properties of PEO coatings on a magnesium alloy formed in a silicate-alkaline electrolyte [5–10]. The most dense and most resistant to the formation of pitting in a chlorine-containing medium in the studied case, as in [11–15], are formed in the region where the microarc stage starts. Perhaps this is a common property of PEO coatings formed on valve metals of different nature and in electrolytes of different composition under galvanostatic conditions.

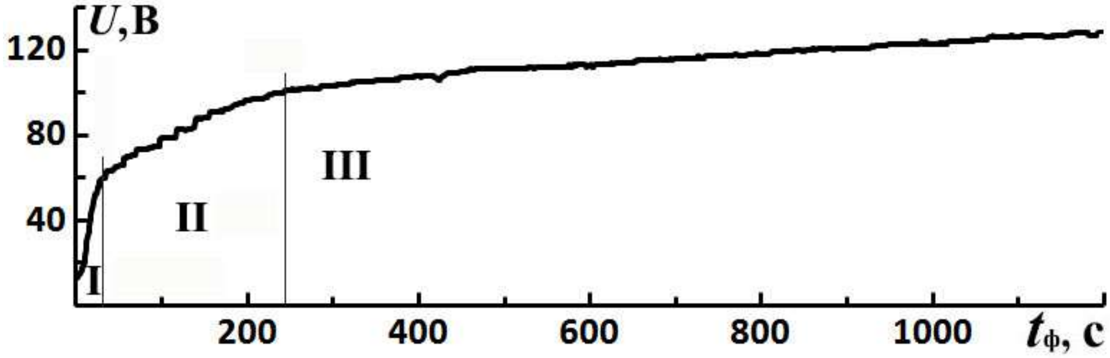

Fig.2. The dependence of the voltage changes on the electrodes U on the formation time t_f

It should be noted that in the region of the transition from the spark stage to the microarc, inflections are also observed on the dependences h = f (t_f), Fig. 1b, θ = f (t_f), Fig. 1c, which also indicates changes in the formation mechanism and structure coatings. Meanwhile, the elemental composition of the surface layer of coatings with a depth of ~2 μm, determined by the method of microprobe analysis, changes little during the transition from the spark to the microarc stage of formation, Fig. 1d.

Figure 3 shows micrographs of the surface of the coatings formed during 5, 10, and 20 min, i.e. , at the characteristic stages of formation. On the surface, pores alternate (dark rounded or oval areas in the photographs), uplifts around the pores, and depressions between uplifts. This surface structure is typical for coatings formed by the PEO method. The most characteristic diameters of pore mouths for the surface under study are up to ~0.3 μm, although individual pores up to 2 μm in diameter are observed. An analysis of images of coatings formed at different t_f shows that in the studied interval, the most characteristic pore diameters little depend on the stage of coating formation, but the density of pores per unit surface, as well as the proportion of the surface occupied by pores, decrease with the time of coating formation, table1.

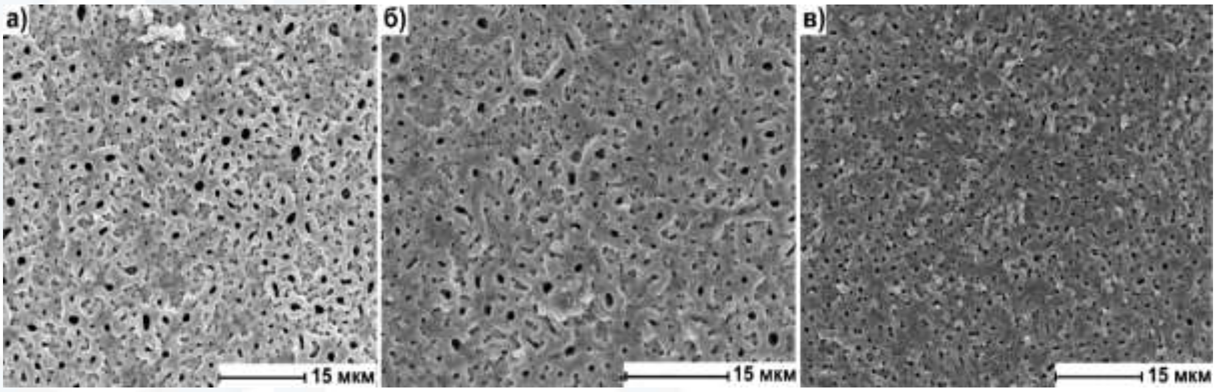

Fig.3. General view of the surface of coatings formed during 5 (a), 10 (b), and 20 min (c).

Complex dependence of the pitting formation time with a pronounced maximum at the formation time of 9–11 min, Fig. 1a, cannot be associated with a change in the thickness, composition, and porosity of the coatings. The change in the resistance of coatings formed at different durations can be associated with the behavior of such parameters as the structure and volume of pores in the cross section of the coatings, defectiveness and inhomogeneity of the composition and structure of the formed layers over the thickness. This is indirectly evidenced by the data in Fig. 1e, which show the formation of coatings with different resistance to pitting per unit thickness of the formed layers in the noted time intervals.

It was previously shown that in the time interval of formation of the coatings under study, about 10 min, along with spark and microarc electric discharges, propagating ones also act. They lead to the appearance of locally elevated areas above the common surface (areas of greater thickness). It is possible that at the beginning of the action, propagating discharges reduce the total number of pores on the surface of the coatings and their depth, increase the total average thickness of the coatings, which affects the structure of the coatings and, ultimately, their resistance to pitting in the formation time range of 9–11 min. Further, the action of propagating discharges, causing the spread of elevated areas over the entire surface area of the coatings, can lead to an increase in the defectiveness of their internal part. In addition, it has been shown that reduced titanium and zirconium are present on the walls and bottom of the pores [7–12]. It is possible that the behavior of pitting resistance is also associated with a change in the pore structure.

The influence of the coating formation time on the pore density was studied (Table 1).

Table 1. Effect of coating formation time on the pore density

No.	t_f, min	Pore density, cm $^{-2}$	Sn/S , %	Note
1	5	$1.56\ 10^{6}$	4.2	Uniform pore distribution
2	10	$1.51\ 10^{6}$	2.9	Uniform pore distribution
3	20	$1.45\ 10^{6}$	1.6	Uniform pore distribution

Thus, from the point of view of anticorrosion properties, coatings formed on titanium in an electrolyte with zirconium sulfate under galvanostatic conditions of the PEO process at $i = 0.08$ A/cm ^{2} for a treatment time of 9–11 min are of interest. There is a correlation between the stages of galvanostatic formation of coatings and their anticorrosion properties.

Conclusion

The results obtained, the relationship between the anticorrosion properties of PEO coatings and the stages of their growth can be of a general nature during PEO processing of valve metals and alloys of various nature in electrolytes of different compositions. Elucidation of the reasons for the increased anticorrosion resistance of coatings formed under galvanostatic conditions in the region of the transition from the stage of sparking to the stage of more powerful microarc electric discharges requires further research.

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