Using the Electrochemical Etching as a Method for the Preparation of the Titanium Surface to Get Anodic Oxide Films

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***Abstract*—The polarization investigations of the anode behavior of titanium in mixed organic-&-aqueous fluoride-containing electrolytes have been carried out. The polarization curves constructed for electrode processes allow us to draw a conclusion that the simultaneous behavior of several processes is possible in the specified electrolytes and these processes include chemical etching of metal due to its interaction with solution components, electrochemical dissolution under polarization conditions and the formation of the oxide film due to the anode oxidation. The prevalence of one or other type of the process in this case is defined by the electrolyte composition and the electric electrolysis parameters. The obtained data serve as a basis for the development of the new method of combined etching that provides the homogenization of the titanium surface with simultaneous elimination of toxic reagents from the process or the reduction of their concentration.**

Keywords—passivation, polarization dependence, anodic behavior, etching, oxide film.

I. INTRODUCTION

Chemical resistance of titanium in ambient conditions depends on the availability of the thin surface oxide layer that forms the passivating layer of a barrier type on the metal surface [1]. The unavailability of this layer results in the rapid failure of titanium due to the interaction with corrosive components. A protection mechanism of the passive layer on the titanium surface is explained by the excellent insulating properties of the film that is characterized by a high value of specific electric resistance $\approx 10^{8}$–10^{12} Ohm·m), the absence of pores and a wonderful adhesion to the metal. Therefore, in spite of low thickness (of the order of several nanometers), it provides a deep titanium passivation in the oxidizing media. It is sufficient to note that the depth index of the corrosion rate of titanium in the earth atmosphere is equal to approximately 10–4 mm/year; it means that it will take about 10000 years for the destruction of the surface layer of 1 mm thick formed on the structure element made of titanium. In addition to a high passivating power the oxide films formed on the titanium surface have many other valuable properties. For example, these films possess photocatalytic properties [2] that offer the challenges for their use in the field of the development of the devices intended for the decontamination of harmful organic admixtures in different media [3]. The possibility of alloying with other oxides enables the use of such systems as a basis for the creation of the sensory-based gas analysis systems [4]. As for the electronic technology, the oxide films formed on titanium can be used for the creation of the thin electrical insulating layers of a barrier type [5]. Nevertheless, oxide films found the widest application in medicine for the implant surface modification [6]. Titanium dioxide formed due to the surface modification is characterized by a wonderful compatibility with human body tissues and it conditions a low probability of the inflammation processes after the implantation [7]. As a chemical substance, TiO_2 is absolutely harmless for human beings.

II. PROBLEM STATEMENT

To obtain oxide films on the titanium surface many methods were developed that include the oxidation in plasma or in the oxidizing medium, the diffusion saturation, pyrolytic spray, hydrolytic deposition and electrochemical oxidation. The last method is the most widely spread, because it allows us to obtain uniform films of a specified thickness on the items of a complicated shape using ordinary instrumentation [8].

In all the cases, the etching of the metal surface is used as one of the preliminary procedures carried out prior to the formation of oxide films. The etching consists in the treatment of titanium surface with the solutions that facilitate the removal of oxide films formed at the previous stages of the item life. Though, at first sight the removal of the oxide layer prior to the oxidation is believed to be senseless, nevertheless, the etching allows for the significant improvement of the quality of the obtained film. It is conditioned by the fact that the etching enables the removal of the external defective layer of metal and performs the homogenization of its surface. The etching effect is manifested in the form of the generation of uniform films with a good adhesion to the substrate and in the case of interference-colored layers it can be visualized in the form of the deeply colored homogeneous oxide layer. Titanium is usually etched using the chemical method that consists in the treatment of the surface with the mixture of nitric and hydrofluoric acids taken in the ratio of 3:1. The role of hydrofluoric acid consists in the activation of titanium due to the adsorption of fluoride ions on the oxide film and the breakdown of it [9]. Nitric acid is responsible for the redox reaction behavior in the solution. The drawback of the given method is that the solutions of corrosive acids are used whose contact with the skin results in the appearance of painful burns. In addition to the volatility of the solution itself, the etching results in the release of the great amount of toxic nitrogen dioxide. It is heated up and this heating-up can result in the over-etching of the items [11]. Proceeding from the above, the purpose of this paper was to develop the method of titanium etching free of specified drawbacks. To attain this goal we suggested a new combined method of the titanium etching that includes chemical and electrochemical approaches to the use of mixed organic-&-aqueous electrolytes with surface-active properties.

III. OBJECTIVE AND RESEARCH TASKS

The purpose is to investigate into the processes of the combined chemical and electrochemical etching of the titanium surface to provide a highly-developed surface intended for the electrochemical formation of oxide films.

The tasks:

– carrying out polarization investigations of the behavior of the VT1-0 titanium under anode polarization conditions in organically aqueous ethylene glycol-based fluoride-containing electrolytes;

– carrying out the gravimetrical survey of the specimens in mixed organically aqueous fluoride-containing electrolytes to establish the effect of the solution composition and the electric parameters of the electrolysis on the anodic dissolution current efficiency and the metal dissolution rate;

– establishing the opportunity for the formation of oxide films after the combined chemical and electrochemical etching procedure.

IV. METHODS OF EXPERIMENTAL INVESTIGATIONS

The anodic behavior of titanium was studied using the methods of the construction of polarization dependencies by means of the specimen polarization by the external power supply source with the potential sweep ranging from the steady state to the domain of positive values. The obtained anode polarization dependences enabled the estimation of the anode behavior of the specimens, the definition of the boundaries of the active and passive states of the specimens (if available), the repassivation, the oxygen release potential and the current density range to provide the modes for the active electrochemical metal etching or the modes for the electrochemical polishing. The potentiostat-galvanostat MTech PGP-550 M with the software provided by the developer was used for the performance of polarization measurements that enabled the potential sweep in the range of (–2.5) to (+2.5) V at the potential variation rate of 0.02 to 500 mV/s and the current measurement discreteness of 1 μA. The alloyed chrome-nickel steel of a Kh18N10T grade was used as an auxiliary electrode. The area ratio of the working and auxiliary electrodes S_w:S_a was 1:100. Working electrode potentials were measured relatively the saturated chloride-silver electrode; the obtained potential values were recalculated in the scale of the normal hydrogen electrode.

To carry out the investigations the titanium specimens of a VT1-0 grade were used in the form of the rods of 75 mm long and 3 mm thick. Prior to the measurements, the specimens were prepared using standard methods.

V. EXPERIMENTAL DATA

Fig. 1 and 2 give the results of polarization investigations of the anode behavior of the titanium electrode in ethylene glycol-&-water solutions with the addition of ammonium fluoride.

The obtained data show that the titanium behavior in mixed organically-aqueous solutions is characterized by the simultaneous conduct of several processes that include the chemical etching of titanium due to the surface activation with fluoride ions in the absence of the external anode polarization and the formation of passivating layers with a substantial biasing of the titanium potential to the domain of positive values [12].

The behavior of above processes is depicted on the obtained curves whose analysis allows us to draw several important conclusions. For example, Fig.1 shows the polarization dependences that were obtained in the conditions of the anode polarization of the specimens in the solutions with a different ethylene-to-glycol ratio. The dependence obtained for the ratio of $V(C_2H_4(OH)_2)$:$V(H_2O)$ = 50:50 (Fig. 1, *1*) has a shape peculiar for the polarization curve of the metal prone to the passivation under the anode polarization.

Three sections can be picked out on the curve that correspond to the domain of the active dissolution of titanium (ranging from the steady state potential through to the peak potential of E_p = –0.4 V that corresponds to the electrode passivation potential) and the domain that characterizes the passive metal state. In this domain, we observe the decay of current densities attaining the values of j_a = 0.8–1.4 mA/cm^2. It should be noted that after the onset of the passivation the current stabilization fails to occur for its steady-state value. The curve shows a smooth surge of current attaining a maximum value at the potential of approximately +0.75 V with its subsequent gradual decrease to 0.8 mA/cm^2. In addition, we observe no oxygen release during the anode polarization and it is indicative of the formation of the stable passive layer on the titanium surface; at the same time, the values of j_a in this passivation domain are rather substantial and it is conditioned by the chemical processes of the dissolution of the passive film in the electrolyte.

The latest observation allows us to draw a conclusion that the anode treatment of titanium in ethylene glycol solutions can be viewed as a method of the combined etching that consists in the electrochemical dissolution and passivation of titanium during the polarization and the chemical dissolution of metal in the absence of it. In this case, the use of electrochemical methods enables the control of the thickness of removed metal and the chemical dissolution enables the formation of the well-developed surface of the specimens.

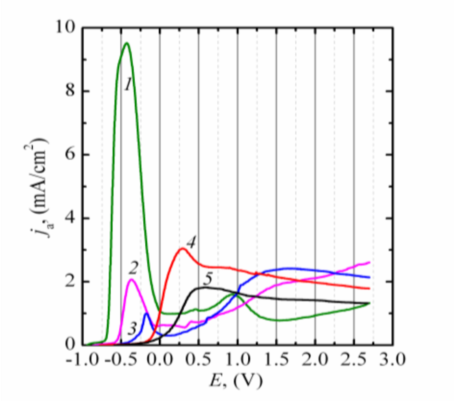

Fig. 1 Polarization dependences obtained under the conditions of anodic polarization of titanium in ethylene glycol-&-water electrolytes *c*(HF) = 3.36 g/dm^3; *c*(NH_4F) = 50 g/dm^3. *V*($C_2H_4(OH)_2$):*V*(H_2O), vol. %: *1* – 50:50; *2* – 60:40; *3* – 70:30; *4* – 80:20; *5* – 90:10

The Figure given herein shows that the increase in the portion of alcohol in the electrolyte from 50 to 70 vol. % conditions the current drop in the range of electrode potentials prior to the onset of the passivation. Apparently, ethylene glycol functions in this case as the inhibiting additive that inhibits the progress of electrochemical processes on the titanium surface. An interesting observation is that for the potentials that are more positive than (+0.88)–(+1.17) V, the current in the passive state domain is higher in these solutions in comparison to that observed for the ratio of *V*($C_2H_4(OH)_2$):*V*(H_2O) = 50:50, i.e. the inhibiting effect is disappeared. Possibly, it is relating to the ethylene- glycol adsorption and improved wetting power of the titanium surface with an increase in the alcohol content that contributes to the better delivery of the products of the anode reaction to the electrolyte volume. Starting from the ratio of *V*($C_2H_4(OH)_2$):*V*(H_2O) = 70:50 and on the curves show the biasing of the peak potential to the domain of positive values. In general, when the ratio varies in the range of 50:50 to 80:10, the passivation onset potential shifts from –0.430 to +0.288 V; and at the ratio of 90:10 the peak current is not observed.

Polarization dependences obtained for the titanium electrode in the electrolytes with a different concentration of ammonium fluoride (Fig. 2) are indicative of that the behavior of the specimens studied under polarization conditions is characterized by the availability of the domains that correspond to the active dissolution and the formation of surface films in the potential domains peculiar for each specific concentration of ammonium fluoride in the solution. Titanium polarization dependences are characterized by the availability of the peaks of a different shape whose maximum potential has different values; the same can be attributed to the range of the potentials that correspond to the peak domain outstretch. The studied data show that the increase in the concentration of ammonium fluoride in the solution from 1 to 5 g/dm^3 (Fig. 1, *1* and *2*) conditions an increase in current densities in the domain of potentials that corresponds to the active dissolution of titanium and in this case, a change in the specified parameter results in an abrupt change of the curve shape. If at *c*(NH_4F) = 1 g/dm^3 the curves show a gradual current build-up in the domain of the active dissolution with the electrode potential biasing to the domain of positive values, then at a five-fold increase in the salt concentration the active dissolution domain is characterized by an abrupt current build-up for the anodic potential sweep and it is indicative of an essential decrease in the value of the polarization resistance of the anode process. At the same time, the current density varies in the range of 5.68 to 6.55 mA/cm^2 with an increase in *c*(NH_4F) in the domain that corresponds to the formation of the passive layer on the electrode surface and it does not correspond to the effect of this parameter in the active dissolution domain.

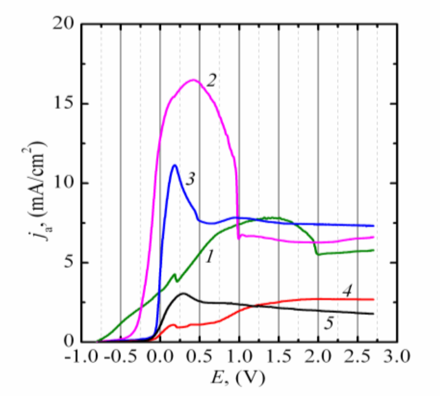

Fig. 2. Polarization dependences obtained under the conditions of the anode polarization of titanium in the ethylene glycol-&-water electrolytes. *V*($C_2H_4(OH)_2$):*V*(H_2O) = 80:20 vol. %; *c*(HF) = 3.36 g/dm^3. *c*(NH_4F), g/dm^3: *1* – 1; *2* – 5; *3* – 10; *4* – 25; *5* – 50

A further increase in the salt concentration results in the origination of new specific features in the trend of polarization curves. For example, at *c*(NH_4F) = 10 g/dm^3 the active dissolution domain is characterized by the rapid current buildup on attaining the potential of the electrolyte dissociation and it ends with the sharp peak at the potential of +0.188 V. At the same time, the deep passivation of the electrode fails to occur under these conditions and the density values of the current peak and those of the steady state (11.14 and 7.42 mA/cm^2, accordingly) are indicative of this fact. Evidently, this value does not correspond to the formation of the solid passivation film that should inhibit the electrode processes running under these conditions. It is of interest that an increase in the concentration of ammonium fluoride up to 25 g/dm^3 and higher results in the inhibition of electrode processes during the anode polarization of titanium (Fig. 2, *4* and *5*, accordingly). At *c*(NH_4F) = 25 g/dm^3 the current peak is actually unavailable in the active dissolution domain and it has the degenerated form. We can state on the whole that the anodic behavior of titanium is described in this case as the behavior that has no well-defined zones of active dissolution and passivation.

The polarization curve for the anodic potential sweep is characterized by the gradual current buildup with the formation of the two waves and insignificant bend at *E* = +0.161 V. In contrast to that, at *c*(NH_4F) = 50 g/dm^3 the domain is present on the curve that can be associated with the active dissolution domain and that ends with a well-defined maximum at *E* = +0.293 V. A further biasing of the anode potential conditions a gradual current drop and in this case, the current inversion is observed at the potential of *E* = +0.293 V for the solutions that contain 25 and 50 g/dm^3 ammonium fluoride. Apparently, a complicated character of polarization curves obtained for titanium during the anode polarization in ethylene glycol-&-aqueous fluoride-containing electrolytes is defined by the set of chemical and electrochemical processes that run on the titanium surface in this system. The results of gravimetric measurements made it possible to obtain the dependences of the anode current efficiency of metal dissolution on the composition of electrolytes (Fig. 3). The data obtained show that the values of the current efficiency in all cases exceed 100%, which indicates the occurrence of chemical etching of titanium during anodic polarization.In the absence of the external polarization, the titanium surface is exposed to the chemical etching due to the availability of fluoride-containing components, in particular fluoride acid and ammonia fluoride. The imposition of the anode polarization results in the run of the two competitive processes, i.e. the anodic digestion of titanium and the formation of the passive film adhering to the mechanism that corresponds to the electrochemical titanium oxidation. At the same time, we cannot exclude the possibility of the chemical dissolution of oxide due to the activating action of fluoride ions.

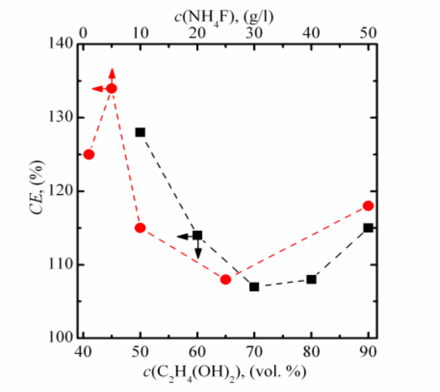

Fig. 3. Dependence of the anode current efficiency of titanium dissolution on the alcohol content and ammonium fluoride concentration in the electrolyte, $j_a = 1$ mA/cm^2

Nanosized barrier-type oxide films were obtained on the surface of titanium products treated by the method developed by us by the method of electrochemical oxidation (Fig. 4). They are characterized by uniformity, completely cover all cavities in the part and have excellent adhesion to the substrate. The data obtained are a prerequisite for the development of a technology for obtaining thin insulating films that contribute to the deep passivation of titanium in oxidizing environments.

VI. CONCLUSIONS

It was shown that the titanium behavior under the conditions of anode polarization in mixed organic-&-aqueous fluoride-containing electrolytes is conditioned by the solution composition. The polarization curves obtained for the changed volumetric ratio of organic and aqueous solvents in the solution are indicative of that an increase in the alcohol dose in the solution results in a decreased current density in the entire studied range of the potentials. The inhibition of the rate of electrode processes that occur on titanium is especially noticeable with the increase in the alcohol content from 50 to 70 vol. %.

A further increase in the alcohol doze reduces the effect. The curves obtained under the conditions of a change in the concentration of ammonium fluoride in the solution show that an increase in the NH_4F concentration from 1 to 3g/dm^3 results in an increase in the current densities due to the improved activating properties of the electrolyte; an increase in $c(NH_4F) > 25$ g/dm^3 results in the inhibition due to the salt passivation of the anode. On the whole, the obtained curves have in all the cases the shape peculiar for the metals prone to the anode passivation.

Gravimetric data allowed us to establish that titanium dissolution current efficiencies that were calculated on the assumption of only electrochemical dissolution exceed 100 % and it is indicative of the behavior of the processes of the chemical metal etching during the anode polarization.

Fig. 4 Photographs of titanium products subjected to combined etching after electrochemical oxidation in a solution of tartaric acid. Final voltage on the cell from 30 to 120 V

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