Investigation of corrosion process in the alloy AA6060 containing anodic-oxide coatings of vanadium

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Electrochemical frequency modulation (EFM) was used to study the corrosion behavior of anodic-oxide coatings of aluminum alloy grade AA6060. Which was exposed to 0.03 M NaCl solution, as a non-destructive method of analysis [1, 2]. Investigated coatings were obtained during the anodizing process in sulfuric acid in the presence of vanadium oxoanions. Corrosion behavior of oxide films was evaluated based on the corrosion rates and corrosion currents obtained during the EFM analysis.

A comparison of the results shows that the addition of vanadium oxoanions to the anodizing electrolyte provides greater corrosion resistance of the coatings, compared to the oxide films obtained in a similar way in sulfuric acid.

Anodised aluminium is widely used for industrial purposes. Aluminum alloy grade AA6060 is used: for building structures, such as windows, facade structures. fences, handrails, heat-dissipating elements of electronic devices, including computers, flexible assembly systems, elements of machine-building equipment, truck body parts, domestic equipment of passenger cars, furniture and office equipment, sports equipment.

Due to wide industrial application, corrosion research of the given alloy and increase of its anticorrosive properties are actual problem [3].

1. Experimental

Composition AA6060 (Si - 0,20-0,60; Fe - to 0,5; Cu - to 0,10; Mn - 0.1; Mg - 0,45-0,90; Zn - 0.2 ; Ti - to 0,15; Al - rest) samples stamped plate diameter 40mm. Were previously subjected to grinding step by means of abrasive tape P180 - P280, followed by etching in a solution of sodium hydroxide. The final treatment consisted

in mechanical polishing, the components of the polishing paste were removed from the surface of the samples by means of ultrasonic treatment in a Stoddard solvent.

Anodic oxide films were prepared in a solution of sulfuric acid (150 g/dm³) with a different content of ammonium metavanadate (0.001 - 0.1 M). Solutions were prepared using chemical compounds of the class "chemically pure" and "pure, for analysis" and distilled water.

Anodizing process was carried out at 25 °C and anode current density of 1 A/dm² for one hour. Measurement of the parameters of the corrosion process was carried out in a 0.03M sodium chloride solution at a temperature of 25 °C in a three-electrode cell, and Ag/AgCl reference electrodes glassy carbon electrode were used as an auxiliary electrode.

The experiment was carried out using the potentiostat/galvanostat Autolab PGSTAT302N with the FRA 32N removal module by the controlled software Metrohm Autolab B.V. «Nova 2.1», EFM study data were collected at an open circuit potential during exposure to corrosive media for 8 hours.

2. Results and discussion

Corrosion behavior of samples of anodic oxide, on the AA6060 alloy, obtained during anodization in sulfuric acid in the presence of vanadium oxoanions, was studied in a 0.03M solution of NaCl. The results of the study are presented in the form of numerical values, parameters of the corrosion process obtained by electrochemical frequency modulation (EFM). Numerical values represent the average values obtained during 8 hours of continuous research in the working environment, each of the samples considered in this paper.

Vanadat ion (VO₃⁻) with high mobility characteristics was used as a modifying additive in a solution in the form of an ammonium metavanadate salt, to improve the corrosion resistance of the oxide film [4,5]. Ammonium metavanadate was added to the electrochemical oxidation solution in small amounts, gradually increasing the concentration from 0.001 M to 0.1 M.

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Fig. 1. The surface structure of the test sample: a - after mechanical treatment; b - after electrochemical oxidation.

During the formation of the anodic oxide film on the aluminum surface, as you can see in Fig. 1, significant change in the microrelief of the surface is noticeable. This is due to the different of the formation rate of the oxide film on the surface of the AA6060 alloy caused by the adsorption of vanadate anions having a high oxidizing ability.

2.1. Corrosion research

Considering the values of the corrosion rates shown in the figure 2, the cycling of the process of passivation/depassivation of the surface of the investigated alloy is noticeable.



Fig. 2. Graph of the change in corrosion rate from the time in a corrosive environment



Fig. 3. Graph of corrosion rate from concentration of ammonium metavanadate in anodizing electrolyte

Throughout the span of the corrosion observation, it is evident that the coatings obtained in the presence of 0.001 and 0.005 M metavanadate show the lowest rates and corrosion currents in the time interval under consideration and range from 1.84 to $2.9 \cdot 10^{-4}$ mm/year.

The introduction of vanadium axoanions into the anodizing electrolyte at a higher concentration leads to a slight increase in corrosion rates (Fig. 2.), the maximum of which is observed at a concentration of 0.01M. Further introduction of vanadium compounds in the electrolyte composition does not significantly affect the rate of corrosion damage of the anodic oxide coating [6].

Such behavior of the resulting coatings is due primarily to the anions included in the oxide film, which begin to oxidize the base metal during the course of the corrosion process. So low concentrations of metavanadate promote "healing" of the coating, that is, accelerate the progress of the passivation reaction. Coatings obtained at high concentrations of the modifying additive have an increased amount of VO_3^- -ions included in the anode oxide composition, which more actively oxidizes the surface of the test sample, increasing the average rate of corrosion process.

2.2. Mechanism.

The corrosive behavior of the AA6060 alloy with treatment in an anodizing electrolyte containing VO_3^- ions can be explained by the effect of vanadium

oxoanions at the metal/oxide interface during anodization. These anions act as passivators when adsorbed on active sites or defective areas of the surface. Adsorbed anions participate in the ongoing oxidation-reduction reactions and are include into the barrier layer of the anodic oxide. Ion VO_3^- has a high oxidizing ability, which promotes the healing and strengthening of the oxide film, hence, increasing corrosion resistance.

3. Conclusion

The corrosion resistance of AA6060 alloy samples anodized in sulfuric acid in the presence of vanadium oxoanions in a 0.03M NaCl solution using the EFM method is considered. The results show that the addition of vanadium compounds in an amount of 0.001-0.005 M to the electrolyte greatly reduces the rate of corrosion process. The corrosion rate, at given concentrations, varies in the range of 2.34 - 3.14 • 10^4 mm/year, for anodized without metavanadate of the alloy AA6060 it is 0.002307 mm/year. The further increase in the content of vanadium oxoanions in the anodizing electrolyte shifts the parameters of the corrosion process into the region of high corrosion rates, which is associated with a more active oxidation of the metal with VO_3^- ions.

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