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OXIDATION RESISTANCE OF THE COATINGS OBTAINED BY PLASMA ELECTROLYTIC OXIDATION ON ALUMINIUM ALLOYS

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Abstract: Plasma electrolytic oxidation (PEO) is one of the new methods of obtaining thin layer oxide ceramic coatings on machine elements of different purpose of use; that allows considerably increase their durability.

This paper outlines the results of experimental studies on corrosion resistance of oxide ceramic coatings formed by PEO on various aluminum alloys using $KOH\text{-}H_3BO_3$ electrolyte.

Corrosion tests of the samples were performed using the following two methods:

1. According to ASTM G44 “Standard Practice for Exposure of Metals and Alloys by Alternate Immersion in Neutral 3.5% Sodium Chloride Solution”,
2. Polarization tests.

Both tests of corrosion resistance of aluminum alloys clearly demonstrate that plasma electrolytic oxidation significantly improves corrosion resistance: depending on an alloy, corrosion rates of PEO coated samples are by the factor of 2.5-80 lower as compared with non-coated samples.

Key words: *oxide-ceramic coating, plasma-electrolytic oxidation, electrolyte, aluminum alloy, corrosion medium, pole curve.*

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INTRODUCTION

Plasma electrolytic oxidation (PEO) implies formation of coatings on the surface of conducting material in electrolyte in a high voltage mode to ensure local microplasma discharges traveling along the surface when the material is anodically polarized [1,2].

PEO is a multifactor-controlled process. The quality of PEO coating can be controlled by compositions of electrolyte and alloy, temperature of electrolyte, treatment time and voltage, anodic current density, and the ratio of cathode to anodic current density, etc. [3]. High quality coatings can be formed by suitable selection of deposition parameters.

This process has a lot of advantages over conventional methods, such as anodic treatment, electrophoresis, plasma and flame spraying, etc.

Among the major advantages of plasma electrolytic oxidation are: formation of oxide ceramic coatings with good physical and mechanical properties (such as hardness, wear and corrosion resistance, adhesion to metal substrate, fatigue resistance); minimization of production space and shorter technological process because no thorough preparation of item and structure surfaces is needed; safe to the environment.

MATERIALS AND METHODS

Al5251, Al1035, and Al2024 aluminum alloy plates (3 x 30 x 100 *mm*) (chemical com- position is shown in Tab. 1.) with oxide ceramic coatings, as formed by PEO in electrolyte with the composition shown in Tab. 2, have been used as samples. Substrate plates were polished with #1200grit SiC abrasive paper before being coated by the PEO process. The oxidation was performed at the current density 10-30 $A\cdot dm^{-2}$ for 120 minutes on a home-made 40 *kVA* PEO station with a water-cooled bath made of stainless steel, which served as the counter electrode. General view of laboratory device for samples oxidation is presented in Fig. 1.

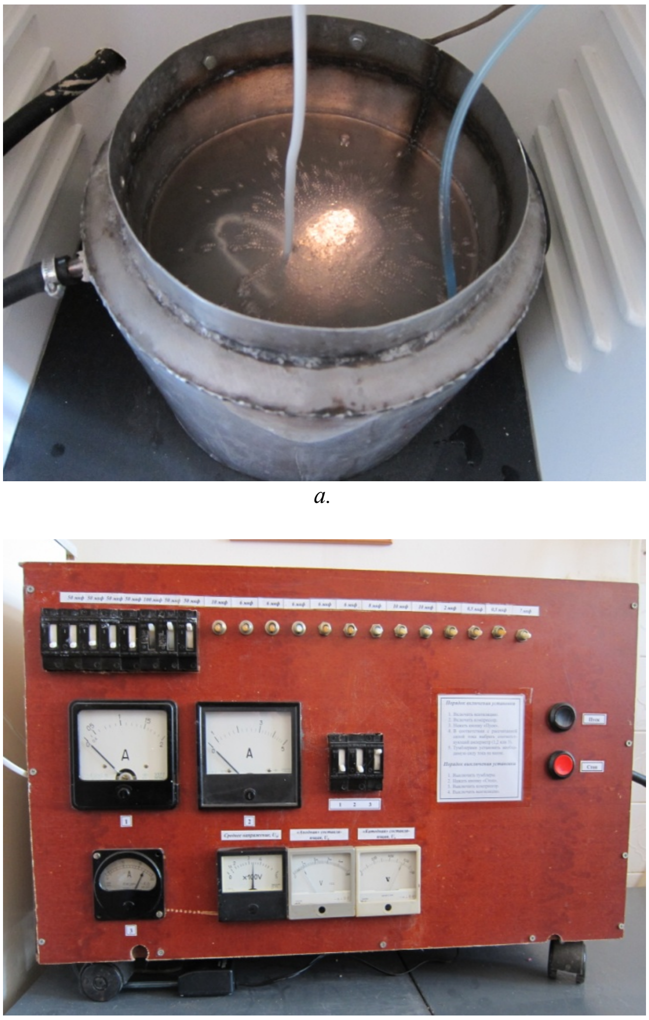
Table 1. Chemical Composition of Oxidized Alloys (% weight)

Alloys	*Fe*	*Si*	*Mn*	*Cr*	*Ti*	*Cu*	*Mg*	*Zn*
5251	*0.5*	*0.4*	*0.1 - 0.5*	*0.15*	*0.15*	*0.15*	*1.7 - 2.4*	*0.15*
1035	*∑0.7*		*0.05*	*-*	*0.03*	*0.10*	*0.05*	*0.10*
2024	*0.5*	*0.5*	*0.3-0.9*	*0.1*	*0.15*	*3.8-4.9*	*1.2-2.8*	*0.25*

Table 2. Electrolyte Composition for PEO Samples

Electrolyte Components	*Concentration* $[g\cdot l^{-1}]$
1. Sodium hydroxide, reagent grade, CAS 1310-73-2 (KOH)	*5*
2. Boric acid, reagent grade, CAS 10043-35-3 (H_3BO_3)	*20*

pH of the electrolytes was measured by a YK-2005WA pH/CD meter (ASTM D1125 -95 (2009) Standard Test Methods for Electrical Conductivity and Resistivity of Water).



a.

b.

Figure 1. General view of developed device for PEO
a. electrolytic bath, b. power supply and control unit

Corrosion tests of the samples were performed using the following two methods:

1. According to ASTM G44 “Standard Practice for Exposure of Metals and Alloys by Alternate Immersion in Neutral 3.5% Sodium Chloride Solution”. This method is based on accelerated, as compared to a standard salt spray test according to ASTM B117, corrosion by cycles of sample immersion into a special electrolyte solution and consequent air drying [4].

For the performing of corrosion tests, a special test station consisting of a bath and an engine responsible for cyclic immersion and lifting of samples according to ASTM G44, was designed and constructed. Test samples were fixed vertically.

The salt solutions were prepared by dissolving 3.5 ± 0.1 weight parts of NaCl (reagent grade, CAS 7647-14-5) in 96.5 parts of water (distilled or deionized water, reagent grade, ASTM 1193, type IV). The volume of the electrolyte solution in the bath was regulated in such a manner that at least 32 *ml* of the electrolyte were taken per 1 cm^2 of the total surface area of a sample.

Total duration of tests was 240 *hours*, with the electrolyte temperature of 18-20*°C*. Samples have been immersed in the solution for 10 minutes and then dried on air for 50 minutes.

On completion of tests, samples were rinsed by a jet of tap water and then by distilled water. Solid corrosion products were removed from the surface by mechanical and chemical means which were not affecting evaluation of test results as per ASTM G44.

Corrosion parameters were assessed in terms of mass loss per unit of surface area ($g \cdot m^{-2}$) according to Eq. 1.

$$\Delta m = \frac{m_0 - m_1}{S_{no}} \tag{1}$$

where:

Δm $[g \cdot m^{-2}]$ - mass loss per unit of surface area,
m_0 $[g]$ - mass of the sample before tests,
m_1 $[g]$ - mass of the sample after tests and removal of corrosion products,
S_{no} $[m^2]$ - sample surface area.

Corrosion rate was determined according to Eq. 2.

$$K_{cor} = \frac{\Delta m}{t_{cor}}, \tag{2}$$

where:

K_{cor} $[g \cdot m^{-2} \cdot year^{-1}]$ - corrosion rate,
t_{cor} $[years]$ - test duration.

Experimental device presented in Fig. 2 is used for carrying out corrosion tests.

Samples were weighed on ViBRA AF-220E analytical balance.

2. Potentiodynamic polarization tests were performed on Autolab PGSTAT12 Potentiostat – Galvanostat controlled by General Purpose Electrochemical System – GPES 4.9 software in a standard corrosion cell. Tests were performed according to ASTM G 59 Standard Test Method for Conducting Potentiodynamic Polarization Resistance.

The potentiodynamic polarization tests were carried out in 3.5 wt.% NaCl, and the solution was prepared using analytical grade reagents. A three-electrode cell with a specimen as a working electrode, saturated calomel electrode (SCE) as a reference electrode and stainless steel plate as a counter electrode was employed. Linear Sweep Voltammetry procedure was used for each specimen so that the sweeping rate was 1 mV/s and the scanning range was from about −250 *mV* to +250 *mV* vs. the open circuit potential. The tested area was 1 cm^2, with the remaining surface masked by a lacquer. The Tafel Extension Method was used to measure corrosion current densities, corrosion potential and corrosion rates.

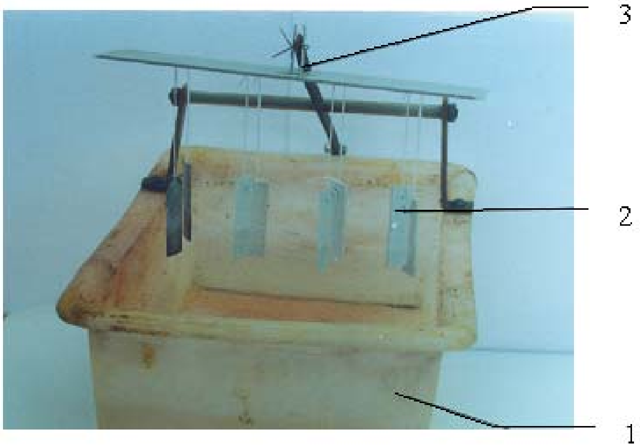


Figure 2. Experimental device for carrying out corrosion tests at intermittent immersion:
1. bath, 2. Samples, 3. balance

RESULTS AND DISCUSSION

Test results (Fig. 3, 4) confirm that corrosion parameters of micro-plasma treatment of aluminum alloys in KOH-H_3BO_3 electrolyte are directly depending on PEO mode and chemical composition of oxidized alloys. The higher current density, the higher is corrosion, which is attributed to higher porosity of coatings.

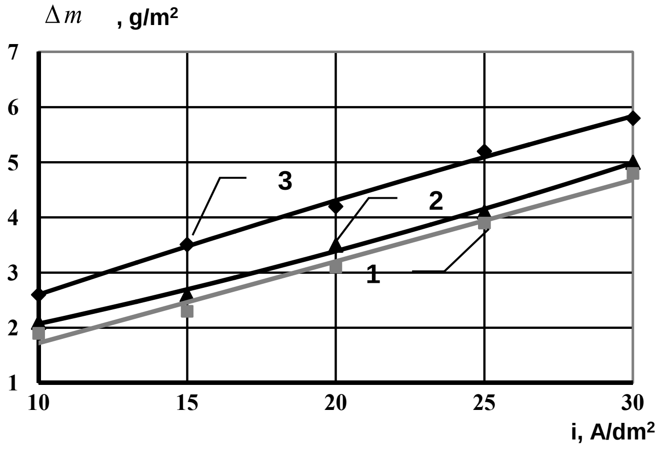


Figure 3. Mass loss Δm on current density i dependence
(t = 120 min; C_{KOH} = 5 g·l^{-1}; C_{H3BO3} = 25 g·l^{-1}) in 3.5% NaCl corrosive medium.
Line 1 for Al5251 alloy, 2 for Al1035 alloy, 3 for Al2024 alloy

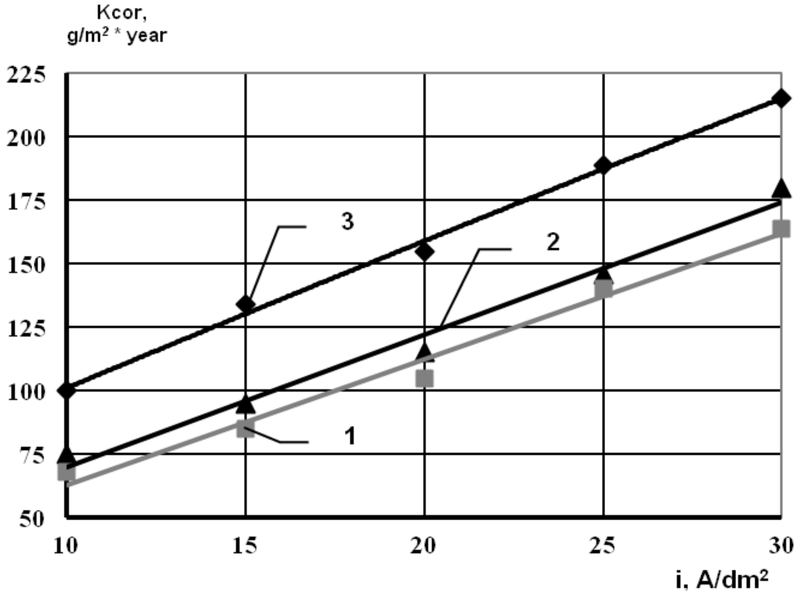


Figure 4. Corrosion rate K_{cor} vs. current density i dependence (t = 120 min; CKOH = 5 $g{\cdot}l^{-1}$; CH_3BO_3 = 25 $g{\cdot}l^{-1}$) in 3.5% NaCl corrosive medium. Line 1 for Al5251 alloy, 2 for Al1035 alloy, 3 for Al2024 alloy.

It deserves to be noted that pacing corrosion is observed for current densities of 10-20 $A{\cdot}dm^{-2}$, while only corrosion spots are observed for 20-30 $A{\cdot}dm^{-2}$. This should be attributed to corrosive medium penetrating through the pores to induce corrosion beneath the coating. Coatings are destroyed due to the presence of chlorine ions, since because of their small radius [5] they are capable of penetrating inside the coatings and destroy those. The interaction between the coating and corrosive medium results in adsorption of medium surfactants. Chlorine ions are capable of expelling oxygen out of crystalline Al_2O_3-containing coating, and the surface is therefore enriched with chlorine. Al2024 coatings are less corrosion resistant than those on Al5251 and Al1035. This is apparently due to the fact that the alloy contains copper which intensifies corrosion. Magnesium and silicon presence in oxidized alloys results in reduced number of through pores and reduced corrosion. This is attributed to formation of magnesium and silicon oxides with lower melting temperatures, as compared to aluminum oxide. Plasma electrolytic oxidation implies high temperatures, and magnesium and silicon oxides therefore more intensively melt and fill the pores, thereby improving protective properties.

Intensity of the study process can be judged by *pH* changes in the corrosive medium. Research results are shown in Fig. 5.

Sodium hydroxide is formed due to chemical interaction between the coating and corrosive medium, which results in higher *pH* of the medium.

Fig. 6 shows polarization curves of a non-coated sample and samples with ceramic coating of PEO.

The Tafel Extension Method was used to measure corrosion current densities, corrosion potential and corrosion speeds. Results are shown in Tab. 3 [6, 7].

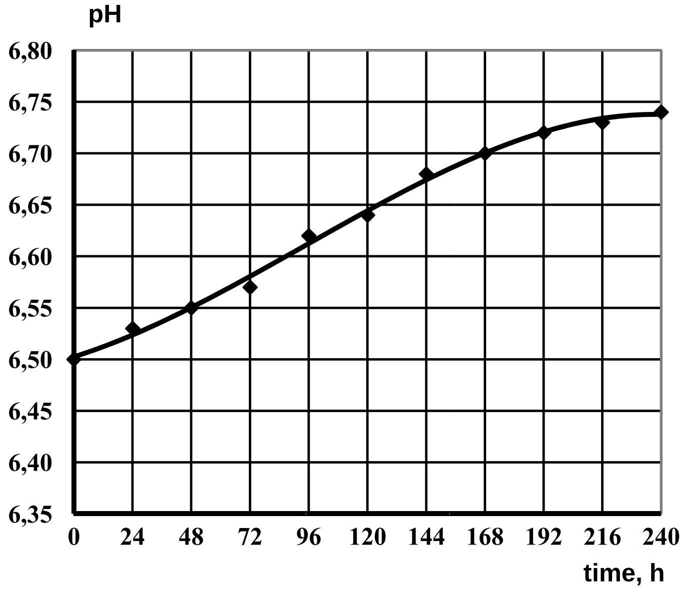


Figure 5. The change of pH in the course of corrosion tests

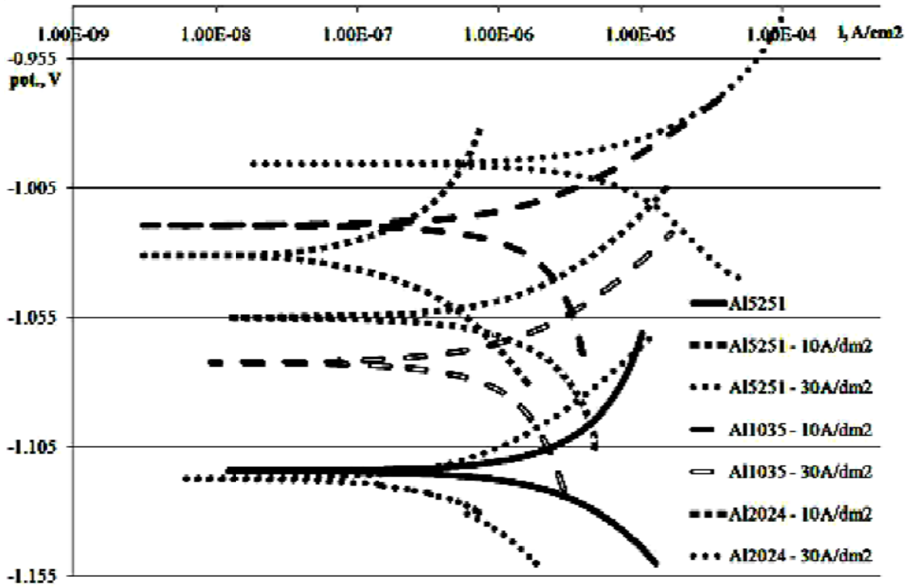


Figure 6. Polarization curves of a non-coated sample and samples with ceramic coating of PEO

Table 3. Corrosion measurement of alloys aluminum without and with PEO

	Unit	*Al5251 without PEO*	*Al1035*		*Al5251*		*Al2024*	
			$10A\cdot dm^{-2}$	$30A\cdot dm^{-2}$	$10A\cdot dm^{-2}$	$30A\cdot dm^{-2}$	$10A\cdot dm^{-2}$	$30A\cdot dm^{-2}$
Corrosion current densities	$[\mu A\cdot cm^{-2}]$	*15,99*	*2,66*	*1,68*	*0,93*	*0,98*	*3,77*	*4,30*
Corrosion potential	*[V]*	*- 1,126*	*-1,015*	*-1,072*	*-1,042*	*-1,118*	*-1,055*	*- 0,996*
Polarization resistance	*[kOhm]*	*0,145*	*2,059*	*0,355*	*0,4815*	*1,418*	*6,654*	*1,175*
Corrosion speed	*[μ/year]*	*230,0*	*2,9*	*3,0*	*9,5*	*14,8*	*48,5*	*89,1*

CONCLUSION

Both tests of corrosion resistance of aluminum alloys clearly demonstrate that plasma electrolytic oxidation significantly improves corrosion resistance: depending on an alloy, corrosion rates of PEO coated samples are by the factor of 2.5-80 lower as compared with non-coated samples.

The higher current density, the higher is the porosity and the number of corroding cracks in the coating. Corrosion rate is linearly dependent on oxidation current density for all alloys studied. With the increasing content of non-oxidizable alloying ingredients (like copper in Al2024), coating contains more and more porous oxides with no protective properties. This is also associated with much lower corrosion resistance, as compared to dilute alloys.

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OKSIDACIONI OTPOR PREMAZA NANETIH PLAZMA ELEKTROLITIČKOM OKSIDACIJOM NA LEGURAMA ALUMINIJUMA

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Sažetak: Plazma elektrolitička oksidacija (PEO) je jedan od novih metoda za dobijanje oksidno keramičkih premaza u tankim slojevima na elementima mašina različite namene, što značajno produžava njihov vek trajanja.

U ovom radu su izneti rezultati eksperimentalnih istraživanja otpora na koroziju oksidno keramičkih premaza nanetih pomoću PEO na različite aluminijumske legure upotrebom elektrolita KOH-H_3BO_3.

Testovi korozije na uzorcima su izvođeni upotrebom sledeće dve metode:

1. Prema ASTM G44 "Standardna praksa za izlaganje metala i legura alternativnim potapanjem u neutralni 3.5% rastvor natrijum hlorida",
2. Testovi polarizacije.

Oba testa otpornosti na koroziju aluminijumskih legura jasno su pokazala da plazma elektrolitička oksidacija značajno poboljšava otpornost na koroziju: zavisno od legure, stepeni korozije PEO zaštićenih uzoraka su 2.5-80 puta niži u poređenju sa uzorcima bez premaza.

Ključne reči: *oksido-keramički premaz, plazma elektrolitička oksidacija, elektrolit, legura aluminijuma, korozivno sredstvo, polna kriva.*

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