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INVESTIGATION OF THROUGH POROSITY OF OXIDE CERAMIC COATINGS FORMED BY PLASMA ELECTROLYTIC OXIDATION

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Abstract: The article presents the results of investigation of through porosity of oxide ceramic coatings obtained by plasma electrolytic oxidation (PEO) on the aluminum parts surfaces, restored by soldering. The optimal modes and electrolyte composition for plasma electrolytic treatment of the restored surfaces are recommended to obtain oxide ceramic coatings with minimum through porosity and high coating and corrosive resistance.

Key words: *plasma electrolytic oxidation, micro arc discharges, current density, electrolyte, coating, through porosity, corrosive resistance, high temperature soldering, flux*

INTRODUCTION

Development of the environmentally friendly technologies of high capacity coatings application for parts hardening to increase their corrosive wear resistance is one of the most vital tasks of the modern science and technique [1-6].

Among new methods of creation multifunctional ceramic similar modified coatings with wide property complex, plasma electrolytic oxidation (PEO) is of special interest. The key point of plasma electrolytic oxidation (PEO) is in the formation of the thin layer wear resistant oxide ceramic coating consisting mainly of solid phase aluminum oxides [6-9] on the part surface under the conditions of influence of micro plasma discharges. Plasma electrolytic oxidation (PEO) allows formation of the coatings with 0,3 mm thickness on the complex profiled articles, internal surfaces and hidden cavities, with adhesion comparable with strength of base material [10-12].

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It is known that the mechanical properties of ceramics essentially depend on its porosity. At porosity equal to 5%, tension capacity decreases by 20-40% in comparison with non-porous material [9]. The ceramic coatings anticorrosion properties also depend on the number of through pores in a coating.

Mechanism of oxide ceramic coatings formation by the PEO method determines the presence of through and closed pores in them [9,12]. To a great extent, coatings porosity is influenced by two main factors: capacity of micro arc (micro plasma) discharges, provided by current density and electrolyte composition. Porosity also can be caused by inherent stresses, taking place at crystallization as the result of the difference of thermal coefficient of linear expansion of a base and a coating. At that, most probable is the presence of open porosity than the closed one. [12-13]. Pores reduce the cross sectional area and act as stress concentrators that at exploitation result in more intensive wear of a coating and decrease of its anticorrosion properties. The majority of scientists stress that the oxide ceramic coatings being formed by PEO on the aluminum alloys have porosity from 2% to 14% [4,5,12]. The information about porosity of coatings obtained by PEO on the parts restored by soldering is not presented in the literature.

At plasma electrolytic treatment of parts the weakly alkaline electrolytes on the KOH base with liquid glass additives Na_2SiO_3 are most advanced. The analysis of the phase composition of coatings obtained in the electrolyte of type «KOH- Na_2SiO_3 » shows that the higher the electrolyte content the more silicon compounds are observed in the hardened layer [5,9,10]. It is known that the silicon compounds have considerably lower temperature of melting and evaporation than aluminum oxide. Thus, varying the PEO modes and concentration Na_2SiO_3 in electrolyte, it is possible to a great degree influence on the porosity of the being formed oxide ceramic coatings. Obviously that the less porous coatings will be formed at low current densities and maximum liquid glass concentration (Na_2SiO_3), for the sake of filling cavities between crystals of aluminum oxide with silicon oxide.

The results of the investigation of the through porosity of the oxide ceramic coatings obtained by PEO at different modes and electrolyte composition, on the parts surfaces formed by high temperature soldering are presented below.

MATERIAL AND METHODS

The cylindrical samples (Fig. 1) made of aluminum alloy AK9h (AK9ч) (GK-AISi10Mgwa) are used for investigations. The material chose is based on the fact that the mentioned alloy is applied for production of great variety of part nomenclature of agricultural machinery and engines cooling system. To form the surfaces on the samples by soldering, aluminum solder of brand SA-12 (IIA-12) (TU 48-17228138/OPP-020-2003) (TY 48-17228138/OIII-020-2003), that is used for soldering the parts operating in corrosion severe conditions and also flux FA=40 (ΦA-40) (TU - 4817228138/OPP-019-2003) (TY-4817228138/OIII-019-2003) were used. The content of principal elements in the aluminum alloy and solder is presented in Table 1.

High temperature flame soldering was done on hydrogen-oxygen installation «Energia 1,5». The thickness of the soldered metal layer was 2...3 mm.

Before plasma electrolytic treatment the samples were subjected to grinding. Plasma electrolytic treatment of the coatings obtained by the soldering were done in electrolyte

of type «KOH-Na₂SiO₃» on installation PEO, operating in the anode-cathode mode (Fig. 2). Concentration C of liquid glass in the electrolyte was varied in the range of 3-15 g·l⁻¹ of distilled water. Current density D_c was changed from 10 to 30 A·Dm⁻².

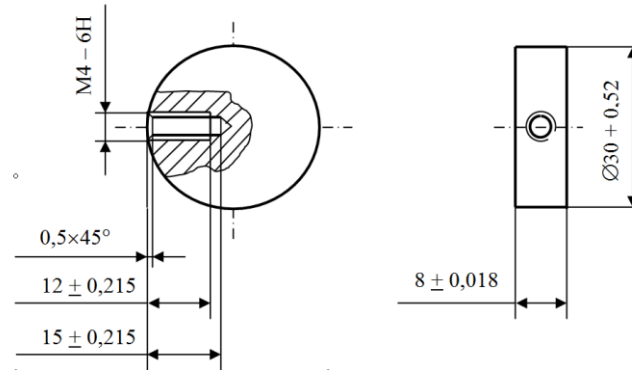


Figure 1. General view of the sample to study through porosity of coatings

Table 1. Content of principal elements (%) in the aluminum alloy and solder (base-aluminum)

Fe	Si	Mn	Ni	Al	Cu	Pb	Mg	Zn	Sn	Doping material
Aluminum alloy AK9h (GK-AlSi10Mgwa)										
to 1	8,0-10,5	0,2-0,5	to 1	86,94-91,63	to 0,3	to 0,05	0,17-0,3	to 0,3	to 0,01	total 1,6
Solder SA-12										
–	10-13	0,5	–		0,6	–	–	0,3	–	–



a.



b.

Figure 2. General view of installation for PEO
a. electrolytic bath; b. unit of power supply and control

Through porosity of the coatings was determined by the planimetry method [9]. After oxidation and removing the loose layer the samples were washed in distilled water, then they were plunged for 0,5 min into warm (35-40°C) solution NaOH (20 g·l⁻¹) and 1 min into clarification solution (nitrogen and fluorohydrogen acids, in the ratio 1:1). Prepared in such a way samples were placed for 5 min into the solution containing 20 g·l⁻¹ CuSO₄ and 20 ml·l⁻¹ HCl. The washed and dried samples with pink spots areas of

contacting released copper were examined under the microscope ($\times 20$). Through porosity of coatings was estimated in per cent of the measured length area.

RESULTS AND DISCUSSION

The preliminary investigations showed that concentration KOH in electrolyte at the rest constant parameters of PEO, does not sufficiently influence on the porosity of the coatings obtained on the soldered surfaces. That is why, to provide the maximum thickness of the hardened layer is necessary to consider the KOH content in electrolyte constant and equal to $3 \text{ g}\cdot\text{l}^{-1}$.

The change of concentration Na_2SiO_3 in electrolyte from 3 to $15 \text{ g}\cdot\text{l}^{-1}$, results in reduction of through porosity of the oxide ceramic coatings (Fig. 3, 4). The minimum porosity of coatings is provided at the concentration of liquid glass – $9\text{-}12 \text{ g}\cdot\text{l}^{-1}$ of solution. When concentration Na_2SiO_3 in electrolyte is more than $12 \text{ g}\cdot\text{l}^{-1}$, the increase of coatings porosity is observed. Obviously, it is connected with the changes of quality parameters of the process: micro arc discharges are changed by more powerful arc discharges, resulting in gradual destruction of the coating being formed. Such a feature is typical for the coatings of the majority of aluminum alloys, oxidized in electrolyte of type «KOH- Na_2SiO_3 » [4-10, 12, 14].

The current density at PEO also influences on the through porosity of the formed oxide ceramic coatings (Fig. 3). The least porous coatings are formed at low current densities. It is obvious from Fig. 3 that for oxidation of aluminum samples with the layers soldered in electrolyte of type «KOH- Na_2SiO_3 », the area of the maximum rational current densities is in the range $15\text{-}22 \text{ A}\cdot\text{Dm}^{-2}$. Oxidation of the samples less than $15 \text{ A}\cdot\text{Dm}^{-2}$ is irrational, because of low efficiency of the process and considerable increase of duration of PEO. The current density increase of more than $22 \text{ A}\cdot\text{Dm}^{-2}$ at the first stage of PEO results in the process intensification. But later powerful spasmodic micro arc discharges that result in the coatings destruction are observed.

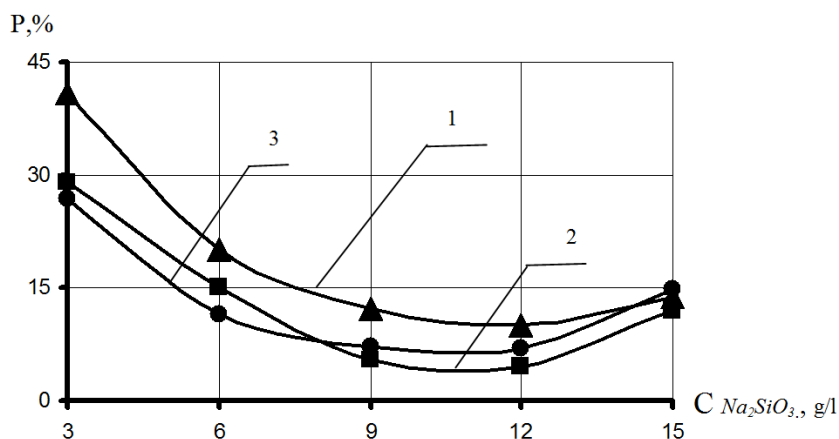


Figure 3. Influence of concentration Na_2SiO_3 and current density on coatings porosity, obtained by PEO in different cutting modes during 120 min:
1. $D_c = 10 \text{ A}\cdot\text{Dm}^{-2}$, 2. $D_c = 20 \text{ A}\cdot\text{Dm}^{-2}$, 3. $D_c = 30 \text{ A}\cdot\text{Dm}^{-2}$

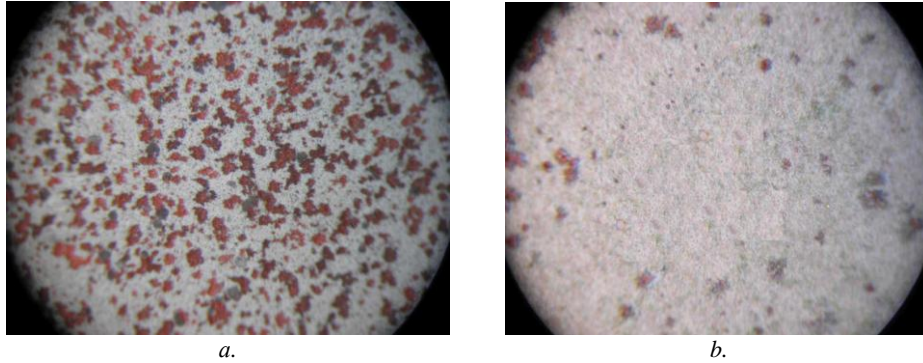


Figure 4. General view of the coatings of the samples with typical areas of released copper at different modes of PEO:

- a. $D_c = 20 \text{ A}\cdot\text{Dm}^2$; $t=20^\circ\text{C}$; $T=120 \text{ min}$; $C_{\text{KOH}}=3 \text{ g}\cdot\text{l}^{-1}$; $C_{\text{Na}_2\text{SiO}_3}=3 \text{ g}\cdot\text{l}^{-1}$,
 b. $D_c = 20 \text{ A}\cdot\text{Dm}^2$; $t=20^\circ\text{C}$; $T=120 \text{ min}$; $C_{\text{KOH}} = 3 \text{ g}\cdot\text{l}^{-1}$; $C_{\text{Na}_2\text{SiO}_3}=10 \text{ g}\cdot\text{l}^{-1}$

Investigating the influence that is produced by the duration of PEO and at the rest constant parameters of the process, it is possible to stress that the least porous oxide ceramic coatings are being formed during 1,5-2,0 hours (Fig. 5). For the specified period the formation of the sound coatings are practically completed. The excess of the specified time range results in appearance of more powerful micro arc discharges, increasing the porosity of the hardened layer and also increase of energy consumption.

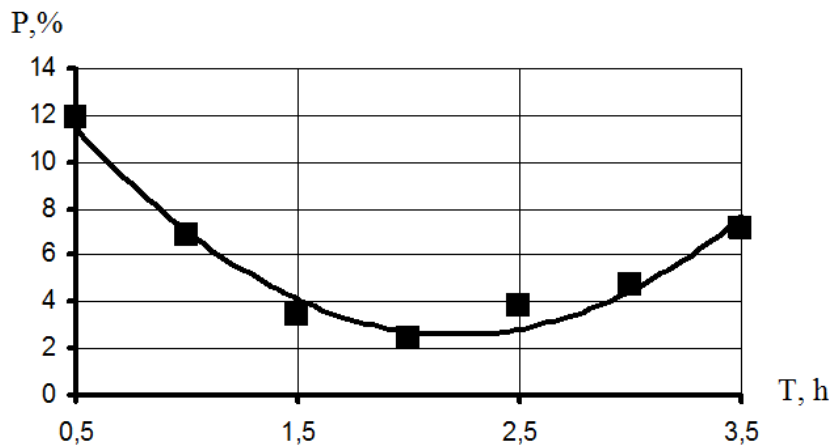


Figure 5. PEO duration influence on through porosity of the coatings:
 $D_c = 20 \text{ A}\cdot\text{Dm}^2$; $C_{\text{KOH}} = 3 \text{ g}\cdot\text{l}^{-1}$; $C_{\text{Na}_2\text{SiO}_3}=10 \text{ g}\cdot\text{l}^{-1}$

It was proved in the research that with the electrolyte temperature increase t at the rest constant parameters of PEO, through porosity of the coatings increases (Fig. 6). It is connected with the fact that with the electrolyte temperature increase the dissolution rate of metal base and the formed coating in dielectric weak points. For electrolyte of type «KOH- Na_2SiO_3 » the optimal temperature to obtain semi porous coatings is about 18-

25°C. Oxidation of coatings in electrolyte with the temperature less than 18°C is irrational, because the powerful cooling system of electrochemical bath is required.

The example of practical usage of oxide ceramic coatings obtained by PEO on the worn parts surfaces, preliminary being restored by soldering is presented in Fig. 7.

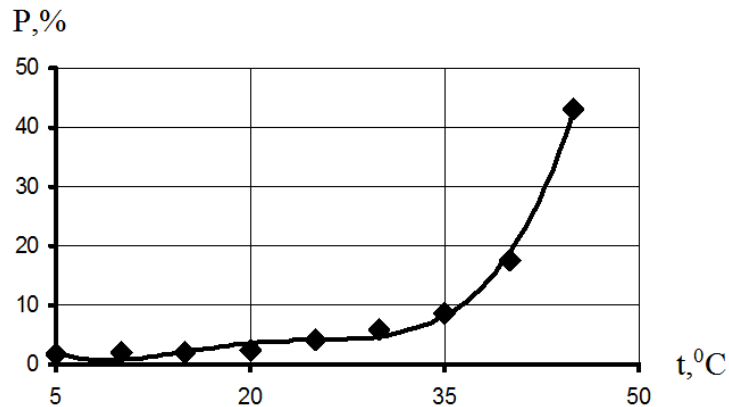
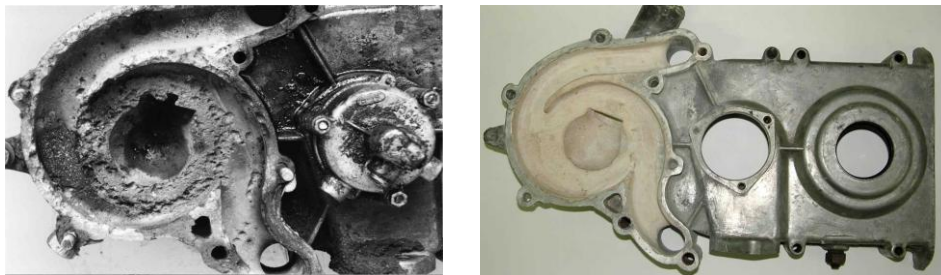


Figure 6. Influence of electrolyte temperature on through porosity of coatings:
 $D_c = 20 A \cdot Dm^{-2}$; $T = 2h$; $C_{KOH} = 3 g \cdot l^{-1}$; $C_{Na_2SiO_3} = 10 g \cdot l^{-1}$



a.

b.

Figure 7. Cover of engine timing gears ZMZ-53:

a. with the worn surface underneath water pump vane,

b. with surface underneath water pump vane, being restored by soldering and being hardened by PEO

CONCLUSIONS

Based on the research results and to form oxide ceramic coatings with minimal through porosity on the surfaces, obtained on aluminum alloys by high temperature soldering, the following modes of plasma electrolytic oxidation were recommended: current density - $15-22 A \cdot Dm^{-2}$, process duration - not less than 120 min. As an electrolyte for PEO, the solution of the following composition is recommended to apply ($g \cdot l^{-1}$ distilled water): KOH - 3; Na_2SiO_3 - 9-12. Operation temperature of electrolyte at oxidation must be kept in the range of 18-25°C. In the abovementioned modes the

thickness of the hardened oxide ceramic layer is not less than 120-150 μm , and its through porosity – not less than 4-6%.

The similar technology of formation of corrosive wear resistant coatings, can be applied at restoration and hardening of worn parts produced from aluminum and its alloys, operating in the conditions of different corrosive environment.

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ISPITIVANJE POROZNOSTI OKSIDNIH KERAMIČKIH PREVLAKA NANETIH PLAZMA ELEKTROLITIČKOM OKSIDACIJOM

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Sažetak: U ovom radu su predstavljeni rezultati ispitivanja unutrašnje poroznosti oksidno keramičkih prevlaka nanetih plazma elektrolitičkom oksidacijom (PEO) na površine aluminijumskih delova, restauriranih lemljenjem. Za optimalne elektrolitičke sastave za plazma elektrolitički tretman restauriranih površina preporučene su oksidne keramičke prevlake sa minimalnom unutrašnjom poroznošću, visokom pokrivenošću i otpornošću prema koroziji.

Ključne reči: plazma elektrolitička oksidacija, mikro lučna pražnjenja, gustina struje, elektrolit, prevlaka, unutrašnja poroznost, otpor prema koroziji, visokotemperaturno lemljenje, fluks

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