The effect of current frequency on the structure, composition and properties of oxide layers formed by plasma electrolytic oxidation on aluminum-silicon alloy

A V Polunin, E D Borgardt, P V Ivashin, A Ya Tverdokhlebov and M M Krishtal

Research division #4, Federal Government budgetary institution of higher education «Togliatti State University», 445667, Togliatti, Russia

E-mail: anpol86@gmail.com

Abstract. Oxide layers formed by plasma electrolytic oxidation (PEO) on pre-eutectic aluminum-silicon alloy 361.0 (9.8 wt.% Si) at various current pulse frequencies (50, 500, and 1000 Hz) were investigated. Scanning electron microscopy (SEM), energy dispersive X-ray microanalysis (EDXMA), x-ray diffraction analysis (XRD) were applied for the investigation of the oxide layers. Thickness, roughness, microhardness, wear resistance and thermal conductivity of the obtained oxide layers were measured. It was found that at a forming current frequency of 500 Hz, the best productivity of forming of the oxide layer is achieved, and the layer has the best hardness and wear resistance, and the smallest roughness.

Plasma-electrolytic oxidation (PEO) is a modern and fast developing method of the electrochemical modification of non-ferrous alloys (aluminum, magnesium, titanium, etc.) [1], that allows to form a wear-resistant and corrosion-resistant oxide layer on their surface. Properties of the obtained oxide layers depends on the processed material and its structure, electrolyte composition, as well as on the electrical parameters of the process. A lot of work has been devoted to variation of electrical parameters of PEO process. Particularly a lot of attention is paid to the frequency of current pulses (F, Hz) during PEO. For example, the influence of the frequency and duration of a current pulse during PEO was studied in [2–5]. However, major studies of the current frequency during PEO were done on aluminum alloys of Al-Mg, Al-Mg-Zn-Cu systems, and other silicon-free alloys. We were not able to find investigations of influence of the current frequency on the productivity of formation and properties of oxide layers on Al-Si alloys (silumins), which are the significant part of industrial non-ferrous foundry alloys in the world.

The aim of this work is to determine the effect of the frequency of current pulses on the productivity of formation, structure, composition, and properties of oxide layers obtained by PEO on silumin.

The samples were heat treated according to the T6(8) mode [6] and polished to Ra 1.25...2.5 μm before PEO. PEO process was carried out for 150 min in an electrolyte based on a water solution of potassium hydroxide KOH (3 g/l), sodium phosphate 12-aqueous Na2HPO4·12H2O (7 g/l) and sodium metasilicate Na2SiO3·9H2O (14 g/l) at a constant current density 20 A/dm². We varied frequency of pulses of forming current F (50, 500 and 1000 Hz). The duty cycle D, % was kept constant and equal to 60%. The ratio of current densities in the cathodic and anodic half-periods was kept constant and
equal to 1±0.05. The average thickness of the oxide layers was measured on transverse sections during SEM investigations. Structure and chemical composition of the oxide layers were studied on transverse sections using a Carl Zeiss Sigma scanning electron microscope with an EDAX TEAM EDX energy dispersive X-ray microanalysis unit (EDXMA). X-ray diffraction analysis (XRD) of the oxide layers was carried out using a Shimadzu Maxima XRD-7000 diffractometer (Bragg-Brentano geometry) with filtered CuKα radiation at a radiation power of 1600 W (current of tube 40 mA, accelerating voltage 40 kV). Speed of scanning was set at 0.2° min⁻¹ and scan step was 0.02° at 2θ angle. Phases of the oxide layers were identified using the Shimadzu PDF2 database. Profile analysis of XRD patterns was carried out by Le Bail method in the Jana 2006 program. The crystallites size of the oxide layers was calculated according to Scherrer equation and the magnitude of residual microstresses was calculated according to Stokes-Wilson equation. Microhardness HV0.2 was determined according to ISO 14577-1: 2002 on transverse sections of the oxide layers on Beijing Time Group HVS-1000 hardness tester (10 measurements). Roughness Ra, μm of the oxide layers was measured using an Olympus LEXT OLS4000 confocal laser scanning microscope (10 measurements) in accordance with ISO 25178. Wear resistance of the oxide layers was determined on a Nanovea TRB 50N universal tribometer according ASTM G133-99 (type A): dry friction; reciprocating motion; counterbody – steel ball O 6.35 mm with hardness HRC 62...65 and roughness Ra 0.01...0.02 μm; load – 25 N; the amplitude of the counterbody movement – 10 mm, the friction path – 50 m. Four tests were carried out for each sample. The upper 30–40% of the thickness of the oxide layer was grinded to a roughness Ra ≤ 1 μm before tests. The average mass wear of the oxide layer (mg per test) was taken as a measure of wear. Mass wear was estimated using a Sartorius ED-224S analytical balance with an accuracy of 0.1 mg. Thermal conductivity was measured according to the method described in [7].

Structure of oxide layers obtained at different frequencies of current impulses is shown on figure 1 and varies significantly. The oxide layer obtained at F = 500 Hz has the least amount of impurities and greatest thickness. In addition, it is the only sample without transverse cracks. The oxide layers obtained at frequencies of 50 and 1000 Hz have a smaller thickness and a significantly more numbers of defects in comparison with the layer obtained at a frequency of 500 Hz. Most of defects for all samples are concentrated in the loose upper part of the oxide layer. The inner sublayer of all samples is relatively homogeneous and practically has no defects.

![Figure 1](image1.png)  
**Figure 1.** Macrostructure of oxide layers formed by PEO on silumin 361.0 at a current frequency of 50 Hz (a), 500 Hz (b) and 1000 Hz (c).

EDXMA (figure 2) shows that aluminum and oxygen are distributed relatively homogeneously over the entire thickness of the oxide layers, while silicon is distributed gradiently: major part of silicon is concentrated in the upper and loose area of the oxide layer. Silicon is practically not presented in the inner zone of the oxide layer. The exception is specific areas of inheritance of the initial silumin structure [8]. The oxide layer obtained at a frequency of F = 1000 Hz is characterized by the presence of particles of primary (unmelted) silicon in the structure, inherited from the substrate. The results of quantitative chemical (elemental) analysis of the oxide layers are practically independent of the
frequency; the average concentration in the oxide layers: Si – 8–10% wt., Al – 45–48% wt., O – the rest.

Figure 2. Distribution maps of aluminum, silicon and oxygen in the oxide layers: (a), (b), (c) – 50 Hz; (d), (e), (f) – 500 Hz; (g), (h), (i) – 1000 Hz.

Increase in the frequency of current pulses from 50 Hz to 500 Hz and up to 1000 Hz did not lead to qualitative changes in the phase composition of the oxide layers (figure 3). The main phase of all samples is mullite. Gamma-alumina and corundum are presented in oxide layers in a smaller amount. Besides, samples formed at frequencies of 500 Hz and 1000 Hz have clear pronounced amorphous halo. Increase of the frequency can lead to a duration decrease of microarc discharges and increase their number. But it also can cause a decrease of molten volume around the channels of breakdown and increase of its cooling speed, which should help to form amorphous phase according to the mechanism of rapid cooling from the melt to a solid state.

Furthermore, the oxide layer formed at a current frequency of 500 Hz has the finest dispersed structure: the average mullite crystallite size (dominant phase) is 33 ± 4 nm against 44 ± 7 nm and 39 ± 9 nm for samples obtained at 50 Hz and 1000 Hz (± σ is given as an error). Residual deformations (microstresses) of mullite crystallites of the layer, obtained at a current frequency of 500 Hz are 0.44 ± 0.1% and are the largest comparing to samples obtained at frequencies of 50 Hz and 1000 Hz and having residual deformation (microstresses) of 0.38 ± 0.1% and 0.32 ± 0.03% respectively. The largest amount of corundum in the layer was revealed for the sample formed at a current frequency of 500 Hz.
Figure 3. XRD patterns of oxide layers obtained by PEO on silumin 361.0 at various frequencies.

There is an extremum (maximum) of thickness, hardness, roughness, and wear resistance of oxide layers, achieved by treatment of silumin 361.0 with a pulse frequency of 500 Hz in comparison with other samples (table 1).

| Parameters                      | Frequency, Hz | 50             | 500            | 1000            |
|---------------------------------|---------------|----------------|----------------|-----------------|
| Thickness of layer T, μm        |               | 81 ± 3.66      | 127 ± 6.4      | 112 ± 3.66      |
| Mass wear W, mg                 |               | 2.3 ± 0.4      | 1.5 ± 0.34     | 1.6 ± 0.85      |
| Microhardness HV0.2, MPa        |               | 490 ± 83       | 690 ± 170      | 525 ± 217       |
| Roughness Ra, μm                |               | 10.82 ± 1.49   | 9.87 ± 1.13    | 19.06 ± 2.80    |
| Thermal conductivity λ, W/(m×K) |               | 2.2 ± 0.04     | 1.7 ± 0.03     | 1.6 ± 0.04      |

*± 2σ is given as an error

The revealed hardness is obviously due to the minimum porosity of the layer, the highest content of corundum, and the highest internal values of mullite microstresses in the sample obtained at a pulse frequency of 500 Hz.

The best wear resistance is also can be attributed to the greatest hardness and homogeneity of the structure. Decrease of average size of mullite crystallites from 44 nm to 33 nm and 39 nm with an increase in the frequency of current pulses from 50 Hz to 500 Hz and 1000 Hz respectively, together with an increase in the fraction of the amorphous phase, probably leads to decrease of thermal conductivity of the oxide layers [9].
As a result of studies, it was found that it is possible to control effectively productivity of formation and properties of oxide layers on silumin by varying of the frequency of current pulses during PEO. It was revealed that the optimum frequency of the current is about 500 Hz (in the range of 50–1000 Hz). It is perspective to carry out further studies optimizing the shape of the current pulse, as well as selecting the optimal component composition of the electrolyte for high-frequency PEO processing of silumins. It is also necessary to study the dynamics of the layers formation depending on the duration of oxidation at different current frequencies. Obtained results allow to improve the properties of the oxide layers formed by PEO on silumin and to bring the technology closer to wide industrial use.

Acknowledgement
The research work was carried out at the expense of a grant from the Education and Science Ministry of the Russian Federation (project code 11. 3937.2017 / PCh)

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