The influence of SiO\textsubscript{2} nanoparticles addition into electrolyte on the wear resistance of oxide layers formed by PEO on aluminum-silicon alloy

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Abstract. Scanning electron microscopy, X-ray spectral microanalysis, X-ray diffraction analysis, and instrumental indentation were used for studying of oxide layers formed by plasma electrolytic oxidation (PEO) on the eutectic aluminum-silicone alloy A04130 in electrolyte with the addition of SiO\textsubscript{2} nanoparticles of different concentrations. The optimum concentration of SiO\textsubscript{2} nanoparticles in the electrolyte (3 g/l) was found, for achieving maximum microhardness and wear resistance of the oxide layer, exceeding the value obtained in the electrolyte without adding SiO\textsubscript{2} nanoparticles by 1.6 and 3.5 times, respectively.

Plasma-electrolytic (or microarc) oxidation – PEO – is a modern and dynamically developing method of modifying the surface of products of non-ferrous alloys (aluminum, magnesium, titanium, etc.) [1]. However, the method has a number of limitations, in particular, when processing aluminum-silicon alloys, which is due to the presence of silicon in the alloy structure [2–4]. Overcoming of the known [2, 3] restrictions is possible by optimizing the structure of the alloy [4], as well as by introducing micro and nanoparticles into electrolyte [5]. Previously, a positive effect of introduction of SiO\textsubscript{2} nanoparticles into the electrolyte on the microhardness and wear resistance of oxide layers was found [6, 7] with PEO of silumins. The minimum roughness, maximal microhardness and wear resistance of oxide layers were revealed with the addition of 3 g/l SiO\textsubscript{2} nanoparticles to the electrolyte with PEO of silumin 319.0 [6]. However, the reproducibility of the increasing in microhardness and wear resistance, achieved in work [6] on silumin 319.0, on other silumines has not been investigated. The purpose of this work is to verify the reproducibility of the effect of increasing of the microhardness and wear resistance of oxide layers on silumin with a high silicon content (up to 13 mass. %).

The oxide layers were obtained on flat samples (20×60×6 mm) of aluminum-silicon alloy of A04130 (chemical composition in % of mass: 12.2 % Si, 0.2 % Fe, 0.3 % Mn, 0.12 % Ti, 0.05 % Cu, 0.25 % Mg, 0.25 % Zn, and the balance Al). Before conducting the PEO, the samples were heat treated by the T6 (8) mode [4], ground to Ra 1.25...2.5 μm and then oxidized.

PEO was carried out for 120 minutes in anode-cathode mode with a current frequency of 50 Hz for a constant current density of 35 A/dm\textsuperscript{2} and a ratio of current densities in the cathodic and anodic half-periods of 1.0 ± 0.05. The electrolyte temperature during the PEO was set at 293 ± 1 K and was kept constant. PEO was carried out in an alkaline-phosphate-silicate electrolyte on the basis of an aqueous solution of sodium hydroxide NaOH (3 g/l), sodium pyrophosphate decahydrate Na\textsubscript{4}P\textsubscript{2}O\textsubscript{7}∙10H\textsubscript{2}O (10 g/l) and sodium liquid glass Na\textsubscript{2}O(SiO\textsubscript{2})\textsubscript{n} with density $\rho = 1.45\cdot10^3$ kg/m\textsuperscript{3} and silicate module
m = 3 (10 g/l) (base electrolyte). X-ray amorphous [8] SiO$_2$ nanoparticles (n-SiO$_2$) were added to the basic electrolyte with an average dispersion of about 20 nm at a concentration of 1 to 7 g/l (a range of concentrations of 1, 3, 5 and 7 g/l).

The macrostructure and the chemical composition of the oxide layers were examined on the metallographic polished cross-sections using scanning electron microscope Carl Zeiss Sigma with a block for the energy dispersive X-ray spectral analysis EDAX TEAM EDX.

X-ray diffraction analysis of the oxide layers was carried out using a Shimadzu Maxima XRD-7000 diffractometer with filtered CuKα radiation according to Bragg-Brentano method at a power of 2 K of indicative radiation with a scan rate of 0.1° min$^{-1}$ at angle of 2° and a scanning step of 0.02°. The phase components were identified by the Shimadzu PDF2 database. The profile analysis of the radiographs and calculation of the quantitative phase composition of the layers were carried out according to Rietveld method in the Jana 2006 software.

The Vickers hardness HV (microhardness) was determined according to GOST R ISO 6507-1-2007 on the metallographic polished cross-sections of oxide layers on the Beijing Time Group HVS-1000 hardness tester (10 measurements). The roughness of the oxide layers (Sa, μm) was measured with the Olympus LEXT OLS4000 confocal laser microscope (10 measurements) in accordance with the requirements of ISO 25178. The wear resistance of oxide layers was determined with Nanovea TRB 50N universal tribometer according to ASTM G133-99 (Type A): dry friction; reciprocating motion; counterbody – steel ball Ø6.35 mm with hardness HRC 62...65 and roughness Ra 0.01...0.02 μm; load 10 N; the amplitude of motion of the counterbody was 30 mm. 5 tests for each sample were performed. The upper 30-40% of the thickness of the oxide layer was ground to roughness Ra 1...1.5 μm before the tribo tests. The reduced mass wear of the oxide layer (W, μg/(N·m)) was determined [9].

As a result of the research, it was found that using of SiO$_2$ nanopowder as an additive in the electrolyte reduces the fracture and porosity of the oxide layer. Moreover, the thickness of the oxide layer was increased from 39 ± 12 μm to 135 ± 18 μm (figure 1).

**Figure 1.** Macrostructure of the layers formed in basic electrolyte (a); macrostructure of the layers formed in electrolyte with addition of SiO$_2$ nanoparticles 3 g/l (b).

It was found that the oxide layers formed in electrolytes with the addition of nanodispersed SiO$_2$ differs significantly from the base variant by the distribution of elements in the layer. In figure 2, as an example, a comparison was made by the distribution of silicon and aluminum for the oxide layers obtained in the base electrolyte and in the electrolyte with the addition of 3 g/l nanoparticles on A04130 alloy.

The increasing of silicon concentration was observed in outer and inner parts of the oxide layers with the addition of SiO$_2$ nanoparticles to the electrolyte (figure 2(a), (b)). Moreover, most silicon was deposited in the more porous outer zone of the oxide layer (about 24 mass %) (figure 2(b)). The decreasing of the aluminum content and uniformity of its distribution in the outer part of the oxide layer compared with the denser inner part was also noticed (figure 2(d)). The oxygen distribution was practically independent of the addition of nanoparticles to the electrolyte and identical in both cases of the electrolyte composition.

Oxide layers formed on A04130 alloy in base electrolyte consisted of mullite, gamma-alumina (γ-Al$_2$O$_3$) and in this case did not included corundum (α-Al$_2$O$_3$).

Introduction of SiO$_2$ nanoparticles in the electrolyte changes phase composition of the oxide layers in the direction of increasing the content of high-temperature phases in them, and also leads to the appearance of high pressure in the oxide layer of SiO$_2$ phases, namely, stishovite and coesite (figure 3). Stishovite is a polymorphous modification of super high pressure SiO$_2$, being formed at a pressure of
$p = 8 \text{ GPa} \left(8 \times 10^4 \text{ atm.}\right)$ at temperature of $720 \text{ K}$ and up to $p = 11 \text{ GPa} \left(11 \times 10^4 \text{ atm.}\right)$ at $T = 3000 \text{ K}$ [10]. Tridymite is a high-temperature phase of SiO$_2$, being formed at pressure of 0.1 MPa (1 atm.) in the temperature range from 1200 to 1950 [10]. Coesite is intermediate phase of SiO$_2$, which is formes at pressure from $p = 2 \text{ GPa} \left(2 \times 10^4 \text{ atm.}\right)$ at $T = 720 \text{ K}$ to $p = 11 \text{ GPa} \left(11 \times 10^4 \text{ atm.}\right)$ at $T = 2900 \text{ K}$ [10].

**Figure 2.** Distribution of silicon and aluminum in oxide layer formed in base electrolyte (a), (c); distribution of silicon and aluminum in oxide layer formed in electrolyte with the addition of 3 g/l nanoparticles SiO$_2$ (b), (d).

**Figure 3.** X-ray diffraction pattern of oxide layer on A04130 alloy (base electrolyte).
For all specimens of oxide layers, the maximum of stishovite content matched with the maximum of α-Al₂O₃ content and was revealed in electrolyte with concentration of SiO₂ 3 g/l.

The arithmetic mean (Sa, μm) of the height of the micro profile of the oxide layers surface was determined (figure 4). The roughness of the oxide layer has a minimum at a concentration of SiO₂ nanoparticles in the electrolyte of 3–5 g/l (figure 4), [10].

Microhardness and wear resistance of oxide layers reached its maximum when the SiO₂ nanoparticles were added to the electrolyte at a concentration of 3 g/l (figure 4). Compared with the basic version (0 g/l of SiO₂ nanoparticles), the maximum increasing of the microhardness of the oxide layer was by 1.6 times, and the wear resistance increasing was by 3.5 times (according to the adjusted wear), which is in good agreement with previous results for the 319.0 alloy [6]. The reproducibility of the previously revealed effect of the shift of the oxide layers phase composition to high-temperature stable phases and the improvement of the properties of the layers on silumin A04130 was observed under the influence of the addition of SiO₂ nanoparticles to the electrolyte.

![Figure 4](image)

**Figure 4.** Phase composition of the oxide layers on A04130 alloy (a); properties of the oxide layers on A04130 alloy (b).

The revealed increasing of wear resistance of the oxide layer and microhardness after modification of the electrolyte with nanosized SiO₂ is a consequence of the following factors:

− increase in the content of the high-strength α-phase of Al₂O₃ in the layer, and simultaneous decreasing of the content of metastable phases (figure 4);
− increasing of uniformity and continuity of the oxide layer (figure 1), which reduces abrasive component of the tribological tests.

Changes in phase composition, structure, microrelief, microhardness and wear resistance of the oxide layers formed in the electrolyte with addition of SiO₂ nanoparticles indicates changes in the oxidation process. Probably, a small addition in the electrolyte of SiO₂ nanoparticles affects the PEO process in two ways. First, the introduction of SiO₂ nanoparticles into the pores and cracks in the oxide layer could be the result of mass transfer from the electrolyte during its formation. This is evidenced by the oxide layer macrostructure improvement (figure 1) and saturation of the layer by silicon (Figure 2). Secondly, SiO₂ nanoparticles, decomposing in the plasma flow, are an additional source of charged particles, including ions, which promotes oxidation and being an additional supplier of oxygen. Accelerating in the plasma flow as a result of inelastic collisions, SiO₂ nanoparticles give their kinetic
energy. This increases the average temperature in the zone of oxidation reactions of the alloy and, in accordance with the Arrhenius law, promotes the process of oxidation of the processed alloy.

As a result of the research it was established that the use of the addition of nanodispersed SiO$_2$ in the electrolyte makes it possible to significantly increase the wear resistance of oxide layers. The reproducibility of the effect of the use of SiO$_2$ nanoparticles as an additive in the electrolyte with PEO of silumins with silicon content range of 5.5...13 wt. % was shown.

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