The effect of tungsten carbide nanoparticles added to electrolyte on the composition and properties of oxide layers formed by plasma electrolytic oxidation on pre-eutectic silumin

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Abstract. The effect of a low concentration (500 mg/L) additive of tungsten carbide (WC) nanoparticles (NPs) with a dispersion of 50–80 nm in an electrolyte on the structure, composition, and properties of oxide layers formed by plasma electrolytic oxidation (PEO) on 357.0 aluminum-silicon alloy (7.5 wt.% Si) was investigated. The oxide layers were studied by scanning electron microscopy (SEM), energy dispersive X-ray spectral microanalysis (EDXMA), X-ray diffraction analysis (XRD), and instrumental indentation. The thickness, roughness, microhardness, and wear resistance of the oxide layers were determined. It was found that the addition of WC nanoparticles at a concentration of 500 mg/L into the base electrolyte leads to an increase in the average thickness of the layer from 73 μm to 92 μm. It was found that the average microhardness was increased from 882 MPa to 1307 MPa, and the average wear was decreased from 592·10^−9 g/(N·m) to 81·10^−9 g/(N·m).

Aluminum-silicon alloys (silumins), being the main group among all non-ferrous castings, have largely exhausted the possibilities of increasing mechanical properties. One of the promising methods of surface modification of non-ferrous alloys in order to increase hardness, wear resistance, and corrosion resistance is the technology of plasma electrolytic (microarc) oxidation (PEO). PEO allows to obtain the oxide layers with a unique set of properties on surfaces of almost any geometric shape [1]. However, the regimes of obtaining and traditional electrolytes for aluminum alloys during PEO do not allow obtaining the oxide layers with the adhesion, hardness, and wear resistance required for practical industrial applications on silumins [2, 3]. It is possible to improve significantly the quality and characteristics of the oxide layers on silumins by forming a certain distribution of silicon in silumin [2], as well as the use of electrolytes with additives of various insoluble nanoparticles (NPs), for example, silicon dioxide [3, 4].

The experience of using Al₂O₃ [5, 6], SiC [7], CeO₂ [8] NPs and other simple substances [9] as additives in the electrolyte in PEO is known. However, it is relatively rare to use refractory carbide NPs (with a melting point ≥ 2900 °C), for example, titanium carbide TiC, tantalum carbide TaC, tungsten carbide WC, and others, as additives to the electrolyte during PEO. These substances have high strength, chemical and thermal resistance, wear resistance and a number of other attractive properties that can be useful when modifying the oxide layers. It is promising, in our opinion, to use
tungsten carbide as a modifying additive in the electrolyte in the nanoscale form. In addition, we were not able to find out the known experience of adding WC NPs to the electrolyte in order to improve the quality and properties of oxide layers formed by PEO on silumin.

This paper is intended to analyze the effect of the addition of WC NPs in the electrolyte on the formation rate, structure, composition, and properties of oxide layers obtained by PEO on silumin.

The oxide layers were obtained on flat samples (20 × 60 × 6 mm) of 357.0 aluminum-silicon alloy (chemical composition in mass. %: 7.5 Si; 0.2 Fe; <0.010 Cu; 0.23 Mn; 0.29 Mg; <0.010 Cr; <0.010 Ni; 0.015 Zn; 0.008 Ti; <0.005 Be; <0.005 Pb; <0.005 Sn; <0.005 Zr; the rest is Al). The samples were heat treated according to the T6(8) [2] and grinded to Ra ≤ 1 μm before PEO. PEO was carried out in an electrolyte based on an aqueous solution of potassium hydroxide KOH (3 g/l), sodium pyrophosphate Na₃P₂O₇·10H₂O (7 g/l) and sodium metasilicate Na₂SiO₃·5H₂O (14 g/l) for 180 min (basic electrolyte). WC NPs (space group – P-6m2, further – n-WC) with a dispersion of 50–80 nm at a concentration of 500 mg/l were added to the electrolyte (modified electrolyte). The current density (30 A/dm²) and the ratio of current densities in the cathodic and anodic half-periods (0.97±0.02) were set and maintained constant during PEO. The average thickness T, μm of the oxide layers was measured using an EDAX TEAM EDX energy dispersive X-ray microanalysis unit (EDXMA). XRD analysis of the oxide layers was carried out using a Shimadzu Maxima XRD-7000 diffractometer (Bragg–Brentano geometry) with filtered CuKα radiation at radiation power of 1.6 kW. The scan speed was set at 0.1° min⁻¹ and the scan step was 0.015° at a 2θ angle. Phases 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 average crystallite size D, nm was calculated according to the Scherrer equation, taking the Scherrer constant K = 1. Residual microstresses in the crystallites were determined according to the Stokes-Wilson equation. The microhardness HV0.1, MPa of the oxide layers was determined according to ISO 14577-1: 2002 on transverse sections using a Shimadzu DUH-211S microhardness tester (at least 10 measurements). The roughness Ra, μm of the oxide layers was measured using an Olympus LEXT OLS4000 confocal laser microscope (10 measurements). The wear resistance of the oxide layers was determined on a Nanovea TRB 50N universal tribometer according to the recommendations of ASTM G133-99 (Type A): dry friction; reciprocating motion; counterbody – steel ball Ø6.35 mm, hardness HRC 62...65 and roughness Ra 0.01...0.02 μm; load 40 N; the amplitude of the counterbody movement – 10 mm; the friction path – 200 m. Five tests were performed for each sample. The upper 30–40% of the thickness of the oxide layer was grinded to a roughness Ra ≤ 1 μm before the tribological tests. The mass wear for each test was measured using a Sartorius ED-224S analytical balance with an accuracy of 0.1 mg. The average reduced mass wear of the oxide layer, g/(N·m), was taken as a measure of wear.

The oxide layer obtained in the electrolyte with the addition of n-WC (figure 1(a)) significantly differs from the oxide layer obtained in the base electrolyte (figure 1(b)). The introduction of n-WC into the electrolyte promotes the formation of the oxide layer with a more uniform and less defective structure. The addition of n-WC to the electrolyte leads to an increase in the thickness of the formed layer – from 73±9 μm in the base oxide layer to 92±18 μm in the modified n-WC oxide layer (+2σ is given as a measurement error).

EDXMA showed that the main components of the oxide layers are aluminum, oxygen, and silicon – their content in the oxide layer is 40–45 mass. %, 45–50 mass. % and 6–10 mass. %, respectively. In addition, tungsten is present in the oxide layer formed in the electrolyte with the addition of n-WC (figure 2) at a concentration of 0.8±0.35 mass. % (+2σ is given as a measurement error).

Nanoscale and submicron objects were identified that are distinguished by phase contrast during SEM (figure 3(a)) in the study of the oxide layer obtained in an electrolyte with n-WC. Most likely, these nanoscale objects are WC NPs embedded in the oxide layer. The size of the objects varies from 100–200 nm to 0.8–1 μm. EDXMA (figure 3(b)) showed that in the area of these objects the tungsten content increases to 6–9 mass. % (figure 3(c)).
Figure 1. Macrostructure of oxide layers, formed by PEO on silumin 357.0 in the base electrolyte (a) and in the electrolyte with addition of WC NPs (b).

Figure 2. Scanned area (a) of oxide layer, formed in the electrolyte with addition of WC NPs, and distribution of tungsten (EDXMA) in the oxide layer (b).

Figure 3. Objects (a), spectral areas (b) and elemental composition of areas (c) of the oxide layer formed in the electrolyte with n-WC additive (the spectrum of zone № 1 is presented as an example).
The base oxide layer consists of mullite, corundum, gamma alumina and theta alumina, and contains an amorphous component (figure 4). A change in the phase composition of the oxide layer takes place when n-WC were introduced into the electrolyte. WC NPs in the initial state (P-6m2) were found in the modified oxide layer. Consequently, a fully inert mechanism of behavior of nanoparticles during the formation of the oxide layer by PEO is observed [9]. Products of chemical reaction of WC NPs with alloy or electrolyte components in the oxide layer were not detected, i.e., there is no reaction mechanism for the behavior of WC NPs during PEO [9]. Taking into account the data of EDXMA (figure 3), we can conclude that the objects in the structure of the oxide layer (figure 3(a)) are n-WC embedded in the oxide layer during its formation by PEO. In addition, there is agglomeration of tungsten carbide nanoparticles in the electrolyte. WC NPs deposit into the oxide layer in agglomerated form, since the size of tungsten-containing objects in the structure of the modified oxide layer reaches a submicron level (0.8–1 μm). It is an order of magnitude larger than the size of the WC NPs (50–80 nm) added to the electrolyte. It should be noted that the introduction of n-WC into the electrolyte leads to a refinement of the microstructure of the oxide layer and an increase in the average residual deformations (microstresses) in the phases of the oxide layer by 1.1–1.25 times (table 1).

**Table 1. Phase composition and microstructure**

| Parameter       | Electrolyte | Base | With n-WC addition |
|-----------------|-------------|------|--------------------|
| Phase           | Al₆Si₂O₁₃   | α-Al₂O₃ | γ-Al₂O₃ | θ-Al₂O₃ | WC (P-6m2) |
| D, nm           | ε, %        | D, nm | ε, %    | D, nm | ε, % | D, nm | ε, % |
| **Base**        | 47.2 ± 0.31 | 50.9 ± 0.23 | 14.6 ± 0.09 | 15.9 ± 0.59 | 22.8 ± 0.5 | – | – |
| **With n-WC**   | 42.4 ± 0.35 | 44.5 ± 0.26 | 4.2 ± 0.08 | 16 ± 0.65 | 22.1 ± 0.62 | 33.8 ± 0.26 | 5.1 ± 0.05 |
| **addition**    | ±σ is given as a measurement error; D is the size of crystallites according to Scherrer, nm; ε - microstresses (residual strains) according to Stokes-Wilson, %. |

The addition of n-WC into the electrolyte leads to an increase of the average microhardness from 882 MPa in the base oxide layer to 1307 MPa in the modified n-WC oxide layer (≈ 1.5 times, table 2). In addition, a decrease in the mass reduced wear from 592 ng/(N·m) (base oxide layer) to 81 ng/(N·m) (modified n-WC oxide layer) was revealed (table 2) when n-WC was added into the electrolyte, i.e. wear resistance increases approximately 7.3 times.

**Table 2. Properties of the oxide layers**

| Parameter       | Electrolyte | Base | With n-WC addition |
|-----------------|-------------|------|--------------------|
| Thickness, T, μm| Roughness, Ra, μm | Hardness, HV0.1, MPa | Wear, W, ng/(N·m) |
| **Base**        | 73 ± 9 | 9.2 ± 1 | 882 ± 287 | 592 ± 292 |
| **With n-WC**   | 92 ± 18 | 9.9 ± 1.7 | 1307 ± 103 | 81 ± 22 |
| **addition**    | ±2σ is given as an error |

The increase in wear resistance is probably due to a significant increase in microhardness, an improvement in the structure, and a decrease in the porosity of the modified n-WC oxide layer (figure 1). The roughness of both oxide layers is almost the same; it does not depend on the addition of
n-WC to the electrolyte and is 9.2±1 μm and 9.9±1.7 μm for the base and modified n-WC oxide layers, respectively (table 2).

Thus, as a result of the studies, it was found that the addition of tungsten carbide nanoparticles into the electrolyte leads to refinement of the microstructure of the oxide layers, a significant increase in microhardness (1.5 times) and wear resistance (7 times), and also increases the productivity of the PEO process of silumin 357.0. It is advisable to carry out further studies in terms of optimizing the electrotechnical mode of the formation of the oxide layer by PEO on silumin in an electrolyte with the addition of WC NPs, as well as optimizing the concentration of WC NPs in the electrolyte. The obtained results make it possible to improve the properties of oxide layers formed by PEO on silumin and to bring the technology closer to industrial applications.

Figure 4. XRD patterns of oxide layers obtained by PEO on silumin 357.0 in base (1) and modified WC NPs (2) electrolytes.

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