Effects of different nanoparticles additions on composition and properties of oxide layers formed by plasma electrolytic oxidation on cast Al-Si alloy

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Abstract. The effect of additions to the electrolyte of SiO₂, Si₃N₄, Y₂O₃, WC and TiC nanoparticles (NPs) with a similar particle size on the structure, composition and properties of oxide layers formed by plasma electrolytic oxidation (PEO) on a cast Al-Si alloy 357.0 (7.5 wt % Si) was investigated. The oxide layers were studied by scanning electron and confocal laser microscopy (SEM and CLSM), energy dispersive X-ray microanalysis (EDXMA), X-ray diffraction analysis (XRD), and instrumental indentation. The thickness, roughness, microhardness and wear resistance of the oxide layers were determined. A complex positive effect of all types of particles added to the electrolyte on the hardness and wear resistance of the oxide layers has been established. The greatest positive effect was exerted by the addition of tungsten carbide NPs to the electrolyte – an increase in the average microhardness from 882 MPa in the base version to 1354 MPa and a decrease in the average reduced wear from 592 ng/(N*m) to 65 ng/(N*m), respectively.

1. Introduction

In the present aluminum-silicon alloys (silumins) occupy up to 90% of all aluminum casting products in the world [1] and their use is steadily growing [1, 2]. The possibilities of improving the surface properties of Al-Si alloys without the use of additional surface engineering technologies are practically exhausted. To operate in extreme friction conditions and under aggressive external corrosion, cavitation and erosion effects, Al-Si alloys require surface protection [1, 3]. One of the promising ways to improve the surface properties of aluminum alloys is the method of plasma electrolytic oxidation (PEO), which makes it possible to transform the surface of the alloy into a hard, wear-resistant and corrosion-resistant ceramic oxide layer. Distinctive features of the PEO method are high adhesion of the oxide layers, the ability to process samples of almost any geometric shape, as well as high environmental friendliness [3,4]. However, due to the presence of silicon in Al-Si alloys, which negatively affects the ignition, duration and distribution of micro-arc discharges (MAD) over the surface, the technological modes of PEO, traditional for wrought aluminum alloys, do not make it possible obtaining layers that are similar in hardness and wear resistance to layers formed on aluminum alloys with a low Si content [5–7]. A partial solution to this problem is to control the distribution of silicon in the silumin structure using heat treatment [5], but this solution cannot completely neutralize the negative effect of silicon. One of the promising solutions to further improve the quality of oxide layers on silumins is to modify the electrolyte by adding nanoparticles (NPs) of
various electrolyte-insoluble substances [4, 8, 9]. Unfortunately, most of PEO studies were carried out in non-reproducible and incomparable conditions, when the processed alloys, electrolyte compositions and PEO electrical modes were different. Therefore, it is not possible to derive regularities that allow predicting the effect of NPs introduced into the electrolyte on the characteristics of the oxide layers, as well as choosing substances that have the greatest positive effect. Also, it is not possible to identify the dominant mechanism of the behavior of nanoparticles during PEO, which can be either inert (with the introduction of NPs into the oxide layer in the initial state) or reactive (with the occurrence of a chemical reaction and the formation of new phases in the layer). In many cases, the behavior of particles and the nature of their chemical reactions with the oxide layer (homogeneous or heterogeneous) largely depend on their melting point.

This work is aimed to compare the effect of additions to the electrolyte of nanoparticles of various substances (SiO$_2$, Si$_3$N$_4, Y_2$O$_3$, WC, and TiC) with different physical properties, in a wide range of elastic moduli (70–700 GPa) and melting temperatures (1900–3600 K), on structure, composition and properties of oxide layers obtained under the same conditions of the PEO.

2. Experimental

The oxide layers were obtained on flat samples (20×60×6 mm) of 357.0 aluminum-silicon alloy (chemical composition in wt. %: 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). Before PEO, the samples were heat treated according to the T6 mode and polished to Ra ≤ 1 μm. PEO was carried out in an electrolyte based on an aqueous solution of potassium hydroxide KOH (3 g/L), sodium pyrophosphate Na$_3$P$_2$O$_7$·10H$_2$O (7 g/L), and sodium metasilicate Na$_2$SiO$_3$·9H$_2$O (14 g/L) for 180 min (base electrolyte). The electrolytes were alternatively doped with nanoparticles of SiO$_2$ (X-ray amorphous powder, size range (SR) – 60–190 nm, average particle size (APS) – 100 nm), Si$_3$N$_4$ (X-ray amorphous powder, SR – 20–100 nm, APS – 80 nm), Y$_2$O$_3$ (Cubic, Ia$3$-m, SR – 25–80 nm, APS – 50 nm), WC (Hexagonal, P-6m2, SR – 50–80 nm, APS – 55 nm), and TiC (Cubic, Fm-3m, SR – 50–200 nm, APS 82 nm) at a concentration of 400 mg/L (0.4 g/l). The choice of concentration was made on the basis of literature data [10]. All nanoparticles were of high chemical purity. Frequency (50 Hz), current density (30 ± 1 A/dm$^2$), current density ratio (0.97 ± 0.02) in half periods, and electrolyte temperature (293±1 K) were kept constant throughout the PEO process. The average thickness, T (μm), structure and chemical composition of the oxide layers were investigated on cross-sections using a Carl Zeiss Sigma scanning electron microscope with an EDAX TEAM EDX unit for energy dispersive X-ray spectral microanalysis (EDXMA). The X-ray diffraction analysis (XRD) of the oxide layers was performed on a Shimadzu Maxima XRD-7000 diffractometer (CuKα radiation) according to Bragg-Brentano with a radiation power of 1600 W (tube current – 40 mA, accelerating voltage – 40 kV), with a scanning rate of 0.1 ° min$^{-1}$ and a scanning step of 0.015 ° in an angle of 2θ. The phase components were identified using the Shimadzu PDF2 database. Profile analysis was performed according to Le Bail in the Jana 2006 program. The average crystallite size, D (nm), was calculated using the Scherrer equation, taking the Scherrer constant K = 1. Residual micro-stresses in the crystallites were determined using the Stokes-Wilson equation. The microhardness of the oxide layers, HV (MPa), was determined according to ISO 14577-1:2002 on cross-sections using a Shimadzu DUH-211S microhardness tester (at least 10 measurements). The roughness, Ra, of the oxide layers was measured on an Olympus LEXT OLS4000 confocal laser microscope (10 measurements). The wear resistance of the oxide layers was investigated using a Nanovea TRB 50N tribometer according to the recommendations of ASTM G133-99 (Type A) and according to the method described in [9].

3. Results

All obtained oxide layers are characterized by a two-layer porous structure (figure 1). Large (up to 10 μm) pores are located mainly in the upper part of the oxide layer. The oxide layers with the additions of Si$_3$N$_4$ and WC NPs (figure 1 (c), (e)) are characterized by an almost complete absence of cracks and pores in the middle and inner parts. The other layers are characterized by the presence of
longitudinal and transverse cracks, as well as submicron and micron pores. For most samples, the main «working» component of the layers is only 30–50 % of their thickness. Characteristic silicon (white) inclusions protrude near the alloy/oxide layer interface, as earlier described in [5].

![Microstructure of PEO layers obtained using the base electrolyte (a) and the electrolyte with the NPs additions of SiO₂ (b), Si₃N₄ (c), Y₂O₃ (d), WC (e) and TiC (f).](image)

**Figure 1.** Microstructure of PEO layers obtained using the base electrolyte (a) and the electrolyte with the NPs additions of SiO₂ (b), Si₃N₄ (c), Y₂O₃ (d), WC (e) and TiC (f).

Analysis of the elemental composition of the oxide layers by EDXMA showed a typical elemental composition for all PEO layers on silumins: the main components are aluminum, oxygen and silicon (table 1). The oxide layers formed with the addition of nanoparticles to the electrolyte contain additional elements that make up the nanoparticles (nitrogen for Si₃N₄, yttrium for Y₂O₃, tungsten for WC, titanium for TiC), which indicates the incorporation of nanoparticles into the oxide layer. It should be noted that the highest intensity of the incorporation of the particle substance into the layer was demonstrated by Si₃N₄ particles, while heavier substances showed less incorporation (table 1). For
SiO₂ particles, it is not possible to unambiguously determine their incorporation due to the impossibility of distinguishing the Si and O elements of the base oxide layer and NPs.

Table 1. Chemical (elemental) compositions* of the PEO layers, wt. %.

| Electrolyte | Al    | O    | Si    | Σ(P, Na, K) | N  | Y  | W  | Ti  |
|-------------|-------|------|-------|-------------|----|----|----|-----|
| Basic (B)   | 43.1 ± 0.3 | 46.1 ± 0.7 | 8.2 ± 3.8 | 2.5 ± 2.0 | -  | -  | -  | -   |
| B+SiO₂      | 47.5 ± 0.5 | 44.6 ± 0.2 | 6.2 ± 0.7 | 1.7 ± 1.2 | -  | -  | -  | -   |
| B+Si₃N₄     | 42.5 ± 1.8 | 46.2 ± 0.5 | 7.8 ± 1.4 | 2.3 ± 1.0 | 1.2 ± 0.2 | -  | -  | -   |
| B+Y₂O₃      | 44.4 ± 2.4 | 46.1 ± 1.0 | 6.6 ± 1.7 | 2.0 ± 1.2 | -  | 0.7 ± 0.06 | -  | -   |
| B+WC        | 43.7 ± 2.7 | 46.9 ± 0.5 | 6.14 ± 2.0 | 2.5 ± 1.7 | -  | -  | 0.78 ± 0.15 | -   |
| B+TiC       | 42.7 ± 2.0 | 45.3 ± 0.9 | 8.5 ± 1.9 | 2.6 ± 1.9 | -  | -  | -  | 0.81 ± 0.4 |

*±σ is given as an error

The XRD analysis of PEO layers showed that, for all samples, the main phases are mullite Al₆Si₂O₁₃ (Orthorhombic, Pbam), corundum α-Al₂O₃ (Rhombohedral, R-3c), γ-Al₂O₃ (Cubic, Fd-3m), and θ-Al₂O₃ (Monoclinic, C2/m). The introduction of SiO₂ NPs into the electrolyte does not change the qualitative phase composition. Apparently, SiO₂ NPs are introduced into the oxide layer with the subsequent formation of additional mullite under the action of MAD. Particles Si₃N₄ apparently, enter into a chemical reaction with the formation of aluminum nitride AlN (Cubic, Fm-3m). The profile analysis of the PEO layers obtained with adding of Y₂O₃ NPs showed yttrium silicates, Y₃SiO₅ and Y₃Si₃O₇, which may indicate the interaction of the introduced NPs with the silicate ions SiO₄²⁻ in the electrolyte. Titanium and tungsten carbides, TiC and WC, were found in the oxide layers in the initial state, which indicates their inert introduction into the oxide layer. All samples are characterized by the size of crystallites in the range of 10...70 nm and residual deformations in the range (2...6)·10⁻³. In this case, residual deformations are uniform along the reflection planes for all phases.

The use of nanoparticles as an additive in the electrolyte has a relatively weak effect on the thickness of the PEO layers, with the exception of the Si₃N₄, which had the greatest effect: the increase in thickness in this case was about 30 μm (from 83.9 μm for the base electrolyte to 113.7 μm for the PEO layer with nanoparticles) (table 2). The introduction of all types of NPs into the electrolyte reduces the uniformity of the oxide layer thickness, which can be seen from the values ± σ.

The surface roughness, Sa, of the PEO layers did not change with the introduction of NPs and for all layers it is about 9–10 μm.

The introduction of all types of NPs into the electrolyte led to an increase in the microhardness HV 0.1 of the PEO layers (table 2). The greatest increase in the microhardness, as well as its homogeneity, is achieved with WC NPs: HV increases from 882 MPa for the base electrolyte to 1354 MPa (by ~1.5 times). For the layer obtained by adding Y₂O₃ NPs, the microhardness turned out to be close to the base sample (table 2). It should be noted that the introduction of WC and TiC NPs...
into the electrolyte led to the higher homogeneity of the oxide layers: the variation of the hardness of these samples is 13.9 % and 17.3 %, respectively, which is more than 2 times lower than that of the base sample (32.5 %).

The wear resistance of the oxide layers increases with the introduction of any type of the NPs into the electrolyte (table 2), however, WC NPs had the greatest positive effect: the average reduced wear decreased 9 times – from 592 g/(N*m) for the base sample to 65 g/(N*m) for a sample modified with WC NPs. The introduction of other nanoparticles into the electrolyte also led to a decrease in wear by a factor of 3.6–4.9, as well as to an increase in the uniformity of wear resistance – the variation of the reduced wear of the NPs-modified specimens are 17.2–24.6 % versus 49.3 % for the basic sample.

Table 2. The properties of the PEO oxide layers.

| Electrolyte | Thickness, T, μm | Roughness, Ra, μm | Hardness, HV0.1, MPa | Wear, W, ng/(N*m)|
|-------------|----------------|------------------|---------------------|----------------|
| Basic (B)   | 82.9 ± 9.4     | 9.2 ± 0.5        | 882 ± 287           | 592 ± 292      |
| B+SiO₂      | 93.1 ± 21.8    | 9.3 ± 0.8        | 1233.9 ± 229.0      | 163 ± 28       |
| B+Si₃N₄    | 113.7 ± 14     | 10.9 ± 1.1       | 1125.1 ± 265.5      | 120 ± 6        |
| B+Y₂O₃     | 87.4 ± 19.7    | 9.5 ± 0.9        | 913.7 ± 228.9       | 151 ± 34       |
| B+WC       | 92.4 ± 18.6    | 8.9 ± 0.9        | 1354.6 ± 188.6      | 65 ± 16        |
| B+TiC      | 83.6 ± 15.1    | 8.2 ± 0.8        | 1206.8 ± 208.6      | 157 ± 31       |

*±σ is given as an error

The revealed improvement in the properties of the oxide layers is probably due to an increase in the density of the structure and a decrease in porosity under the influence of NPs introduced into the electrolyte. The most homogeneous structure (figure 2 (d)), and, accordingly, the highest hardness and wear resistance are observed for the sample obtained by adding tungsten carbide NPs, which have the largest elastic modulus among the used NPs (650–700 GPa) and one of the highest melting temperatures (3150 K). This suggests a possible correlation between the characteristics of the nanoparticle substance and the properties of the obtained PEO layer. However, for other substances, the correlations are not so obvious. Thus, using the chemically active Si₃N₄ NPs addition (when AlN phase appears in the oxide layer) results in a homogeneous PEO layer (figure 1 (c)), with a good hardness and wear resistance. This shows that the chemically active mechanism of particle incorporation can be very effective for obtaining optimal mechanical properties of the oxide layer. It was revealed by XRD analysis that Y₂O₃ NPs react, presumably, with the melted SiO₂ formed as a result of the silicon oxidation of the silumin under the action of MAD, with the formation of the mY₂O₃+nSiO₂ compounds in the oxide layer. Taking into account that the melting temperature of SiO₂ is about 2000 K, it can be assumed that the temperature reached in the reaction zone is ~2000 K or higher, and, as a result, the Y₂O₃ particles also melted and reacted with the molten silicon oxide. It is noteworthy that in the PEO layers obtained with WC and TiC NPs, there are no products of their chemical reactions with alloy or electrolyte components. This can be explained by the fact that the temperature of the melt in the breakdown zone of a MAD which was determined to be in the range of 2116–2643 K [11] is lower than the melting temperatures of WC (~3100 K) and TiC (~3600 K).

4. Conclusions
It can be concluded that prediction of the oxide layer properties depending on the properties of NPs introduced into the electrolyte is a multifactorial problem, and there is no simple connection between the PEO layer properties and the melting point of nanoparticles. Further detailed studies of all the key parameters of nanoparticles that affect the final properties of PEO coatings are required, which will
make it possible to predict and modify the properties of PEO layers in the future. To solve this problem, it is necessary to construct multivariate models, taking into account the thermal conductivity and melting temperature of NPs and substrate elements, the concentration and size distribution of NPs introduced into the electrolyte, electrical, temporal and other parameters of the PEO process, etc. The studies carried out made it possible to establish certain trends in the effect of the added NPs with very different melting points and elastic moduli, on which, however, other multidirectional factors are superimposed and which can significantly change the result of PEO process.

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References
[1] Zolotorevsky V S, Belov N A and Glazoff M V 2007 Casting Aluminum Alloys (Elsevier Ltd)
[2] Lumley R N 2018 Fundamentals of Aluminium Metallurgy (Elsevier)
[3] Suminov I V 2011 Plasma-electrolytic modification of the surface of metals and alloys (Moscow: Technosphera)
[4] Kaseem M, Fatimah S, Nashrah N, Gun Ko Y and Ko Y G 2020 Prog. Mater. Sci. 100735
[5] Krishtal M M 2004 Met. Sci. Heat Treat. 46 377–84
[6] He J, Cai Q Z, Luo H H, Yu L and Wei B K 2009 J. Alloys Compd. 471 395–9
[7] Xu F, Xia Y and Li G 2009 Appl. Surf. Sci. 255 9531–8
[8] Lu X, Mohedano M, Blawert C, Matykina E, Arrabal R, Kainer K U and Zheludkevich M L 2016 Surf. Coatings Technol. 307 1165–82
[9] Polunin A V., Borgardt E D, Shafeev M R and Krishtal M M 2019 Journal of Physics: Conference Series 1396 012032
[10] Stojadinović S, Tadić N, Radić N, Grbić B and Vasilić R 2018 Surf. Coatings Technol. 344 528–33
[11] Lee K M, Lee B U, Yoon S Il, Lee E S, Yoo B and Shin D H 2012 Electrochim. Acta 67 6–11