Influence of nanoparticle additions to the electrolyte on the structure, composition and corrosion resistance of oxide layers formed by PEO on cast Mg alloy

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Abstract. The effect of various nanoparticles (NPs) added to the electrolyte on the composition, structure, and properties of oxide layers formed by plasma electrolytic oxidation (PEO) on a cast magnesium alloy AZ81A was studied in this work. The oxide layers were obtained by alternating adding silicon dioxide SiO\(_2\), silicon nitride Si\(_3\)N\(_4\), yttrium oxide Y\(_2\)O\(_3\), tungsten carbide WC, and titanium carbide TiC NPs to the electrolyte. The obtained oxide layers were studied by scanning electron microscopy (SEM), energy dispersive X-ray microanalysis (EDXMA), X-ray diffraction analysis (XRD), instrumental indentation and potentiodynamic polarization (PDP). The thickness, roughness, microhardness, adhesion and corrosion resistance of the oxide layers were determined. The greatest increase in the oxide layer thickness, in its hardness and corrosion resistance was observed for TiC and WC NPs added to the electrolyte during PEO. The addition of Si\(_3\)N\(_4\) NPs leads to a decrease in the oxide layer thickness and its hardness, while the corrosion resistance is comparable to the one of the uncoated magnesium alloy.

1. Introduction
Magnesium alloys are widely used in the aviation and automotive industries due to the unique combination of high specific strength, good ductility and machinability. But they have significant disadvantages – low resistance to corrosion and wear [1]. Plasma-electrolytic (micro-arc) oxidation (PEO) is a promising technology for the protection of magnesium alloys, which allows the formation of multifunctional corrosion and wear-resistant oxide layers with unique properties on the surface of the material [2, 3]. However, traditional regimes and electrolytes for PEO of magnesium alloys do not always make it possible to obtain oxide layers with the required set of properties. Perforating pores and microcracks are formed in the oxide layers due to the sharp cooling of the oxide layer near the breakdown zone after quenching of the microarc discharge (MAD) [2, 3]. They provide electrolyte access to the barrier layer and appearance of a new microarc discharge. In addition, through them, nanoparticles enter the MAD zone and are embedded in the oxide layer. At the same time, after the formation of the layer at the stage of operation, the corrosive medium through perforating pores and microcracks can penetrate to the material [2, 4].

The quality and characteristics of oxide layers on magnesium alloys can be improved by forming the required structure and phase composition as a result of the use of electrolytes with additives of
The experience of using NPs Al₂O₃, SiO₂, CeO₂, SiC and other substances as additives to the electrolyte during PEO is known [8]. However, NPs of refractory carbides, for example, tungsten carbide WC, titanium carbide TiC, tantalum carbide TaC, and others, are used relatively rarely as additives to the electrolyte. These substances have high strength, chemical and thermal stability, wear resistance, and a number of other attractive properties that can be useful in the modification of oxide layers. In addition, most of the studies performed on the effect of additives in the electrolyte of various NPs were carried out under incomparable conditions – alloys, electrolytes, and PEO modes differ. Therefore, it is not possible to generalize the available results and select nanosized substances that have the strongest positive effect in the PEO of magnesium alloys.

The aim of this work is to identify and analyze the effect on the rate of formation, composition, structure, and properties of oxide layers obtained on a magnesium alloy under the same conditions of the PEO process, of various nanosized additives of a close average size, in equal concentrations, with different physical properties in a wide range of melting temperatures (Tₘ), elastic moduli, etc. (SiO₂, Si₃N₄, Y₂O₃, WC, TiC).

2. Experimental

The oxide layers were obtained on flat specimens (20 × 60 × 6 mm) from a cast magnesium alloy AZ81A. The chemical composition of the alloy was determined on a Thermo Fisher Scientific ARL 4460 OES optical emission spectrometer (wt%): 7.6 Al; 0.4 Zn; 0.21 Mn; 0.002 Si; <0.001 Fe; <0.001 Cu; <0.001 Be; the rest is Mg. Before carrying out PEO, the samples were sanded to Ra 1.25...2.5 μm and degreased with a petroleum solvent and acetone.

PEO was carried out in an electrolyte based on distilled water containing alkali NaOH (2 g/L), disubstituted sodium phosphate 12-hydrate Na₂HPO₄⋅12H₂O (5 g/L) and sodium fluoride (2 g/L) (base electrolyte) for 30 minutes. Various nanoparticles at a concentration of 1 g/L, selected from the literature data [9], were added to the base electrolyte. Silicon dioxide SiO₂ (X-ray amorphous powder, APS 100 nm, Tₘ ≈ 1700 °C), silicon nitride Si₃N₄ (X-ray amorphous powder, APS 80 nm, Tₘ ≈ 1900 °C), yttrium oxide Y₂O₃ (Cubic, Ia-3, APS 50 nm, Tₘ ≈ 2410 °C), tungsten carbide WC (Hexagonal, P-6m2, APS 55 nm, Tₘ ≈ 2870 °C), and titanium carbide TiC (cubic, Fm-3m, APS 82 nm, Tₘ ≈ 3200 °C) were used as additives to the electrolyte. The pulse frequency (50 Hz), the anodic amplitude forming voltage U₀ (500 V), the ratio of the effective currents of the cathodic and anodic half-periods K / A (0.5 ± 0.02), and the electrolyte temperature (288 ± 1 K) were set and kept constant during PEO.

The average thickness (T, μm), structure and elemental composition of the oxide layers were studied on transverse thin sections using a Carl Zeiss Sigma scanning electron microscope with an EDAX TEAM EDX energy dispersive X-ray microanalysis (EDXMA) unit and an Olympus LEXT OLS 4000 confocal laser scanning microscope. X-ray diffraction analysis (XRD) of the oxide layers was performed on a Shimadzu Maxima XRD-7000 X-ray diffractometer (CuKα radiation) in the glancing beam mode (GIXRD, glancing angle 2.5°) at a radiation power of 1600 W, a scanning speed of 0.1 ° min⁻¹ and step of 0.01°. The Shimadzu PDF2 database was used to identify the phase components of the layers. The microhardness of the oxide layers, HV, was determined in accordance with ISO 14577-1: 2002 on transverse thin sections using a Shimadzu DUH-211S microhardness tester at a load of 19.6 mN and holding for 10 seconds. The roughness, Sa, of the oxide layers was measured on an Olympus LEXT OLS4000 confocal laser microscope (10 measurements). The adhesion strength of the layers was carried out according to ASTM C1624-05 (reapproved 2010) on a Nanovea Mechanical Tester PB1000 scratch tester in a progressive load mode (from 0.1 to 25 N) with a scratch rate of 10 mm/min. The load on the indenter at the moment of failure, F, was determined as the characteristics of adhesion. The tests were performed at least 4 times for each sample. To take into account the thickness difference of the oxide layers as a characteristic of the adhesion strength, the specific failure load of the layer, Fₛₐₙ, was calculated as the ratio of the failure load F to the thickness of the oxide layer T. The study of the corrosion resistance of oxide layers was carried out using an IPC-Pro MF (1A) potentiostat according to ASTM G102–89 by the method of potentiodynamic...
polarization (PDP) in a 3 % NaCl solution with the determination of the corrosion potential, \( E_{\text{cor}} \), and the corrosion current density, \( j_{\text{cor}} \), according to Tafel's curves, as well as polarization resistance (\( R_p \)). The tests were carried out at least 3 times for each sample at a temperature of 293 ± 1 K in a three-electrode electrochemical cell with a Luggin capillary, Pt counter electrode (99.99 wt% Pt), and a silver/silver chloride (Ag/AgCl) reference electrode. A test sample with a wetting area of about 1 cm\(^2\) was used as a working electrode. Before polarization, the samples were kept in a corrosive environment until the open circuit voltage (OCP) stabilized (30–60 min). Polarization curves were recorded from the cathode to the anode region with a potential sweep rate of 1 mV/s until the anodic current density \( j_A = 100 \text{ mA/cm}^2 \) was reached.

3. Results
All oxide layers contain numerous pores, especially noticeable near the outer surface of the layer (figure 1 (a)). All samples are characterized by numerous transverse and longitudinal cracks, which indicate the uneven cooling of the layer and substrate during PEO, as well as crack formation as the dominant mechanism of relaxation of internal stresses in the layer during its formation. The introduction of Si\(_3\)N\(_4\), Y\(_2\)O\(_3\), and WC NPs into the electrolyte leads to the appearance of deep burn-throughs of the substrate to a depth comparable to or sometimes 2–4 times greater than the thickness of the oxide layer with the filling of these deepenings with an oxide layer (figures 1 (b), (c)).

The main components of the oxide layers are magnesium (45…49 wt. %), oxygen (34–39 wt. %), aluminum (5–10 wt. %), phosphorus (2–5 wt. %) and substance of nanoparticles. The oxide layers formed with additions of NPs to the electrolyte contain elements that make up the NPs: silicon for SiO\(_2\) and Si\(_3\)N\(_4\) nanoparticles, yttrium for Y\(_2\)O\(_3\), tungsten for WC, titanium for TiC. This indicates the introduction of NPs into the oxide layer (Table 1). The highest concentrations of the particle material in the oxide layer were recorded for the additions of SiO\(_2\) and Si\(_3\)N\(_4\), and the lowest for Y\(_2\)O\(_3\). Yttrium is present in the oxide layer in very small amounts, i.e. Y\(_2\)O\(_3\) NPs practically did not penetrate into the oxide layer (table 1).

![Figure 1](image-url)

**Figure 1.** Structure of oxide layers (transverse thin sections) formed by PEO on casting magnesium alloy AZ81A in a basic electrolyte (a) and with NPs additives Y\(_2\)O\(_3\) (b), WC (c).
The main phases of all oxide layers are magnesium oxide MgO (Cubic, Fm-3m) and an amorphous phosphorus-containing phase, which is similar to the data in [10]. The introduction of SiO₂ and Si₃N₄ into the electrolyte leads to formation of the magnesium silicate phase Mg₂SiO₄ (forsterite, Orthorhombic, Pmnb) in the oxide layer. This indicates the participation of NPs in chemical reactions during the formation of the oxide layer. Nanoparticles of WC and TiC, as well as any phases containing elements of these NPs, were not detected in the oxide layers by XRD in the selected exposure. The results of EDX analysis suggest a chemically inert interaction of these particles with the oxide layer (Table 1).

Table 1. Content of NPs elements (wt. %) in the oxide layer.

| Additive | SiO₂ | Si₃N₄ | Y₂O₃ | WC | TiC |
|----------|------|-------|------|----|-----|
| Element  | 1.618 Si | 1.425 Si | 0.0004 Y | 0.040 W | 0.794 Ti |

The determined characteristics of the oxide layers are presented in Table 2.

Table 2. Properties of the oxide layers.

| Parameter | Specimen | Thickness T, μm | Roughness Ra, μm | Hardness HV, MPa | Adhesion F_{SL}, N/μm |
|-----------|----------|----------------|-----------------|-----------------|----------------------|
| PEO-base  | 5.1 ± 1.1 | 2.41 ± 0.03   | 355 ± 109       | 3.2 ± 0.8       |
| PEO + n-SiO₂ | 5.6 ± 0.9 | 2.49 ± 0.03   | 292 ± 118       | 3.1 ± 0.6       |
| PEO + n-Si₃N₄ | 2.5 ± 0.6 | 12.23 ± 2.42  | 198 ± 30        | 3.5 ± 0.9       |
| PEO + n-Y₂O₃ | 5.2 ± 0.9 | 2.26 ± 0.04   | 314 ± 70        | 3.3 ± 0.6       |
| PEO + n-WC  | 8.5 ± 0.9 | 2.91 ± 0.02   | 439 ± 122       | 2.1 ± 0.4       |
| PEO + n-TiC | 12.0 ± 2.4 | 2.99 ± 0.04   | 603 ± 83        | 1.4 ± 0.5       |

$a ± 2\sigma$ is given as an error

When WC and TiC NPs were added to the base electrolyte during PEO, the average thickness of the formed oxide layers increased by ~ 1.5 and ~ 2.5 times, respectively (Table 2), and the average hardness increased by ~1.2 and ~1.7 times, respectively. This is probably due to the promoting effect of WC and TiC NPs on MAD, which can be assumed as follows. Electric-field-accelerated NPs, accelerating in vapor-gas bubbles, the formation of which in pore channels precedes a micro-arc discharge [3], can penetrate deeply into the oxide layer as a result of impact. The next MAD should cover larger volumes of matter as a result of branching on particles with electrical conductivity close to the level of conductors. This probably contributes to the oxidation of a larger volume of material and, accordingly, a greater increase in thickness. This hypothesis is confirmed by the appearance of deep burn-throughs in the substrate (figure 1 (c)). The obtained values of the hardness of the oxide layers are comparable with the results of other studies [11, 12]. It should be noted that none of the additives used improved the roughness and adhesion of the oxide layers, and the addition of TiC more than halved the average specific adhesive strength (Table 2).

An increase in the corrosion resistance of oxide layers obtained by PEO in an electrolyte with additions of SiO₂, Y₂O₃, WC and TiC NPs was revealed. The additions of WC, TiC and Y₂O₃ had a significant positive effect – the density of corrosion currents decreased by 2 orders of magnitude in comparison with the base oxide layer. In the case of SiO₂ addition, the corrosion current density decreases by one order of magnitude and the polarization resistance of the oxide layer, R_p, increases. The highest values of R_p were achieved with the additions of WC, TiC, and Y₂O₃ – R_p increased by two orders of magnitude compared to the base oxide layer (Table 3), which indicates an increase in the
insulating properties of the barrier layer and the oxide layer as a whole. It should be noted that the oxide layer obtained by adding Si₃N₄ to the electrolyte does not completely cover the Mg substrate; therefore, in fact, the corrosion process occurs on the uncoated regions of the alloy, which explains the almost identical \( j_{\text{cor}}, E_{\text{cor}}, \) and \( R_p \) values for the oxide layer modified with the nanoparticles Si₃N₄ and the uncoated alloy.

The introduction of new phases such as magnesium silicate Mg₂SiO₄ in the oxide layer composition does not lead to an improvement in its properties: the hardness and adhesion of the oxide layer obtained with the addition of SiO₂ practically did not change in comparison with the initial variant, and the addition of Si₃N₄ to the electrolyte leads to a significant (~ 1.8 times) decrease in hardness (table 2). It should be noted that the highest concentration of NPs in the layer is observed for SiO₂ and Si₃N₄ particles, while the material of WC and TiC particles in the layer is present in a significantly smaller amount, while the properties of the layers with the participation of WC and TiC NPs change significantly. With an equal initial concentration, this can be explained by the partial evaporation of WC and TiC particles as a result of their strong heating in MAD due to their high electrical conductivity.

![Figure 2](image_url). Tafel curves for samples of the uncoated AZ81A alloy, with a base oxide layer (PEO) and after modification with various nanoscale (n) substances.

| Specimen     | \( E_{\text{cor}}, \) mV | \( j_{\text{cor}}, \) mA/cm² | \( b_a, \) mV/dec | \( b_c, \) mV/dec | \( R_p, \) Ohm·cm² |
|--------------|--------------------------|-------------------------------|-----------------|-----------------|-----------------|
| uncoated alloy | -1508 ± 17               | (8.0 ± 1.0)\times10^{-3}     | 46 ± 13         | 185 ± 31        | (7.8 ± 0.8)\times10¹ |
| PEO-base     | -1495 ± 14               | (3.2 ± 1.4)\times10^{-3}     | 191 ± 19        | 309 ± 93        | (9.6 ± 1.8)\times10¹ |
| PEO + n-SiO₂ | -1443 ± 66               | (7.3 ± 3.9)\times10^{-4}     | 173 ± 23        | 353 ± 133       | (9.9 ± 4.2)\times10² |
| PEO + n-Si₃N₄ | -1514 ± 11               | (8.0 ± 2.5)\times10^{-3}     | 74 ± 10         | 274 ± 26        | (6.6 ± 1.8)\times10¹ |
| PEO + n-Y₂O₃ | -1426 ± 78               | (4.3 ± 2.6)\times10^{-3}     | 130 ± 3         | 274 ± 68        | (12.7 ± 7.9)\times10³ |
| PEO + n-WC   | -1342 ± 75               | (4.1 ± 1.9)\times10^{-3}     | 172 ± 9         | 257 ± 34        | (15.6 ± 8.8)\times10³ |
| PEO + n-TiC  | -1445 ± 32               | (7.5 ± 5.5)\times10^{-3}     | 82 ± 19         | 276 ± 4         | (12.5 ± 9.1)\times10³ |

\( a \) Results of PDP tests of the oxide layers.
±σ is given as an error; \( E_{\text{cor}} \) – stationary potential; \( j_{\text{cor}} \) – the corrosion current density; \( b_a \) and \( b_c \) – Tafel slopes of the anode and cathode branches, respectively; \( R_p \) – the polarization resistance of the sample.

At the same time, an increase in the continuity of the oxide layer with minimal incorporation of the nanoparticles into the oxide layer significantly improves its hardness and corrosion resistance. In this case, the layer thickness is also not decisive for the corrosion resistance - the sample obtained with the addition of TiC demonstrates the corrosion resistance comparable to the sample modified with WC NPs despite the greater thickness of \( \sim 1.5 \) times. That is, the key factor for the corrosion resistance is to ensure the minimum through porosity of the oxide layers providing minimum penetration of the electrolyte to the barrier layer separating the Mg substrate and the oxide layer. It should be noted that the addition of WC and TiC to the electrolyte leads to a significant increase in the hardness of the oxide layers - by \( \sim 1.24 \) and \( \sim 1.7 \) times, respectively (table 1). However, at the same time, for these additives, embrittlement of the oxide layer and a decrease in the adhesion strength of \( F_{\text{SL}} \) by \( \sim 1.5 \) and \( \sim 2.3 \) times, respectively, are also observed.

4. Conclusions

Thus, as a result of the studies, it was found that refractory NPs have the greatest positive effect on the properties of oxide layers on a magnesium alloy, probably as a result of their promoting effect on MAD. Apparently, the duration of the MAD burning increases, which leads to stronger heating of more extended sections around the breakdown channels, as well as to burn-throughs. Therefore, upon further cooling, cracking is not so intense. The burn-throughs would have to reduce the hardness, but at the same time, the porosity decreases, resulting in an increase of the effective hardness as well as corrosion resistance.

To develop and test a multivariate model describing the formation patterns of oxide layers and predicting their properties further research is needed.

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