

## PHASE COMPOSITION AND PROPERTIES OF MAO COATINGS ON ZINC-ALLOYED ALUMINUM ALLOYS

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**Abstract** - The work is devoted to the study of the phase composition and properties of coatings formed by micro-arc oxidation (MAO) on zinc-alloyed aluminum. The relevance of this study is determined by the need to improve the durability and performance characteristics of machine components through the formation of wear-resistant and corrosion-resistant surface layers. MAO is a promising method for producing ceramic-like coatings on valve metals, particularly aluminum alloys, providing high physical and mechanical properties. The object of the study was aluminum samples containing 1 to 10% Zn, treated in an alkaline silicate electrolyte under an anodic-cathodic regime. It was established that, under identical processing conditions, coatings with a thickness of 100–110  $\mu\text{m}$  and a characteristic layered structure are formed. The phase composition of the coatings is represented by polymorphic modifications of aluminum oxide,  $\gamma\text{-Al}_2\text{O}_3$  and  $\alpha\text{-Al}_2\text{O}_3$ , as well as an aluminosilicate phase - mullite ( $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ). It is shown that alloying aluminum with zinc significantly affects phase formation in the coatings. In particular, an increase in the lattice parameter of  $\gamma\text{-Al}_2\text{O}_3$  with increasing Zn content was observed, indicating the incorporation of  $\text{Zn}^{2+}$  ions into its structure. An extreme dependence of the content of the stable  $\alpha\text{-Al}_2\text{O}_3$  phase and the microhardness of the coatings on zinc concentration has been revealed, with maximum values achieved at a Zn content of about 2%. It was established that coating formation proceeds via a staged mechanism: at the initial stage, a metastable  $\gamma\text{-Al}_2\text{O}_3$  phase is formed, which, under conditions of locally high temperatures in microdischarge channels, transforms into the stable  $\alpha\text{-Al}_2\text{O}_3$  phase. Simultaneously, mullite formation occurs due to the interaction of aluminum oxide with electrolyte components. The obtained results can be used for purposeful control of the structure and properties of MAO coatings.

**Keywords:** Micro-arc oxidation, Aluminum, zinc alloying, Phase composition,  $\gamma\text{-Al}_2\text{O}_3$ ,  $\alpha\text{-Al}_2\text{O}_3$ , mullite, Microhardness.

### 1. Introduction

Enhancing the durability of components in many engineering solutions is based on the application of various surface strengthening methods [1, 2]. Recently, the method of micro-arc oxidation (MAO) of valve metals and their alloys (Al, Ti, Mg, Ta, Nb, Zr) has been increasingly used for these purposes. The most widespread applications involve MAO treatment of aluminum, titanium, and magnesium alloys [3].

The MAO method makes it possible to form ceramic-like coatings characterized by high hardness, wear resistance, as well as dielectric and corrosion-resistant properties.

Ceramic coatings based on aluminum, depending on processing conditions, may consist of different

phases that significantly differ in their physical and mechanical properties. In particular, coatings obtained in an alkaline silicate electrolyte are mainly composed of the metastable  $\gamma\text{-Al}_2\text{O}_3$  phase, the high-temperature stable  $\alpha\text{-Al}_2\text{O}_3$  phase, and mullite ( $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ) [4-5].

Since the oxidation process sequentially proceeds through spark, micro-arc, and arc stages, the direct contact of the metal with the breakdown region suggests a significant influence of the chemical composition of the aluminum alloy on the properties of the formed coatings.

Microdischarges play a decisive role in the formation of the final characteristics of the modified surface. The thermal effect of microdischarges on the formed oxide layer leads to thermolysis of chemical compounds, melting and remelting of the coating

material, diffusion and redistribution of the elemental composition, phase formation, polymorphic phase transformations, and other processes. The conditions governing the phase transitions from the low-temperature  $\gamma\text{-Al}_2\text{O}_3$  modification to the high-temperature  $\alpha\text{-Al}_2\text{O}_3$  phase, as well as mullite formation and the quantitative phase ratios in the coatings, remain insufficiently defined. Data from different literature sources are contradictory. The content of  $\alpha\text{-Al}_2\text{O}_3$  in coatings can vary widely - from 5% to 80% and largely depends on processing conditions, making its prediction difficult [5-6].

It should be noted that coatings with a higher content of the  $\alpha\text{-Al}_2\text{O}_3$  phase are characterized by high hardness ( $\text{HV} > 15 \text{ GPa}$ ) and wear resistance, making them promising for use in friction units of various machines and mechanisms [7-8].

At the same time, a number of processes occurring during coating formation - such as cation adsorption on the coating surface, their redistribution during layer growth, crystallization and melting processes remain insufficiently studied.

Changes in phase composition and control of polymorphic transformations of aluminum oxide can be achieved not only by varying electrolysis conditions but also by optimizing the composition of the base material on which the coatings are formed. Studies show that the phase composition of coatings formed on different grades of aluminum alloys can differ significantly. This is likely due to the incomplete transformation of the low-temperature  $\gamma\text{-Al}_2\text{O}_3$  modification into the stable  $\alpha\text{-Al}_2\text{O}_3$  phase [9-10].

Published data do not provide a complete understanding of the influence of the chemical composition of aluminum alloys on the mechanism and rate of the  $\gamma \rightarrow \alpha$  phase transformation. The first paragraph after a title or sub-title needs to have a zero indentation [11].

## 2. Objective

The aim of this work is to investigate the effect of zinc alloying of aluminum on the phase formation processes in coatings formed in an alkaline silicate electrolyte under an anodic-cathodic regime.

## 3. Results and Discussion

The samples of zinc-alloyed aluminum (1-10% Zn) were subjected to micro-arc oxidation. It should be noted that zinc is one of the main alloying elements in aluminum alloys.

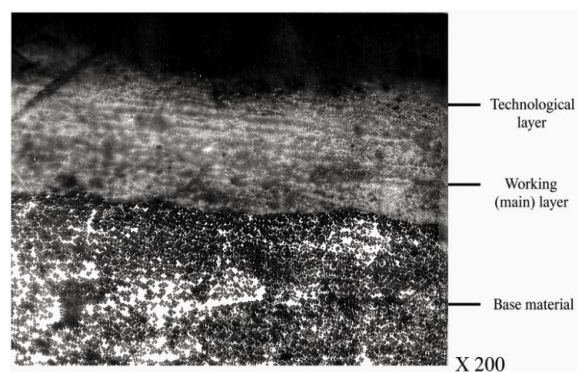
The treatment was carried out in an alkaline electrolyte with the addition of liquid glass. The electrolyte composition was 1 g/l KOH + 6 g/l

$\text{Na}_2\text{SiO}_3$ , which is universal for implementing the anodic-cathodic process in the micro-arc discharge regime.

MAO treatment was carried out in a 20 l stainless steel bath, with electrolyte bubbling and cooling provided. The bath body served as the counter-electrode. A capacitor-type power supply with a capacity of 10 kW was used. Oxidation was performed in an anodic-cathodic regime at a current density of 20-25 A/dm<sup>2</sup>. The treatment duration was 1 hour. All samples were processed under identical electrolysis conditions.

Thickness measurements showed that a coating layer of 100-110  $\mu\text{m}$  is formed within one hour of treatment. No influence of the chemical composition of the samples on the oxide layer growth rate was observed.

A microstructural feature of the coatings on the investigated samples is their layered structure, with the technological and working (main) layers distinguished, *Figure 1*.



*Figure 1: Microstructure of the cross-section of the coating on the Al + 5% Zn alloy*

The technological layer of the coating is characterized by increased porosity, low wear resistance, and can be easily removed by mechanical cleaning using abrasive paper. Its fraction is approximately 50% of the total coating thickness. In further analysis, only the characteristics of the base layer were considered, with a thickness of about 50  $\mu\text{m}$ .

It is well known that the performance properties of MAO coatings are largely determined by their phase composition and the ratio of crystalline modifications of aluminum oxide. To determine the structural and phase state of the formed coatings, X-ray diffraction (XRD) analysis was carried out.

The analysis of the obtained results made it possible to reveal the effect of zinc alloying of aluminum on the phase composition of MAO coatings (*Table 1*). Particular attention was paid to the identification of characteristic diffraction peaks corresponding to different polymorphic modifications of aluminum oxide.

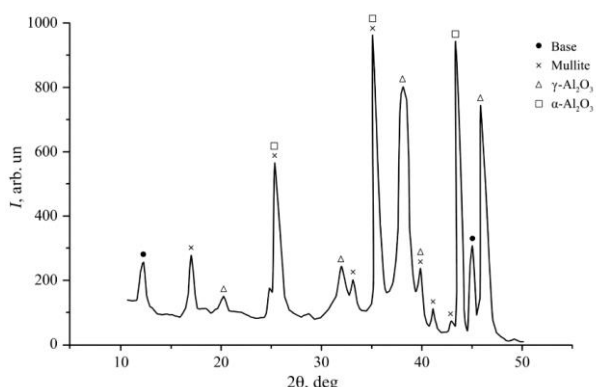
For a more detailed analysis of the phase composition and evaluation of the intensity of

diffraction peaks corresponding to the  $\gamma$ - $\text{Al}_2\text{O}_3$  and  $\alpha$ - $\text{Al}_2\text{O}_3$  phases, typical diffraction patterns of the obtained coatings are shown on *Figure 2*. It is known that the appearance and increase in the intensity of  $\alpha$ - $\text{Al}_2\text{O}_3$  diffraction peaks indicate the occurrence of high-temperature phase transformations in the microdischarge channels formed during the micro-arc oxidation process. This is associated with local temperature rise and rapid melting and crystallization processes in the coating material within the microdischarge zones.

*Table 1. Phase composition and microhardness of the investigated coatings*

№	Zinc content %	Phases, %			HV, GPa
	Zn	$\alpha$ - $\text{Al}_2\text{O}_3$	$\gamma$ - $\text{Al}_2\text{O}_3$	Mullite ( $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ )	
1	-	14	61	25	12,2
2	1	38	43	19	13,5
3	2	44	32	24	14,2
4	3.5	28	50	22	15,8
5	4	19	48	33	14,7
6	5	13	50	37	13,5
7	6	14	52	34	13,0
8	7	12	5.5	33	12,3
9	10	15	55	30	10,3

The analysis of the X-ray diffraction results allows the following conclusions to be drawn. The strengthened layer on all investigated samples has a crystalline structure. The relative intensities of the diffraction lines of the identified phases are close to standard reference values, indicating the absence of texture and suggesting a predominantly random orientation of crystals in the strengthened layer.



*Figure 2: X-ray diffraction pattern of the MAO coating (electrolyte: 1 g/l KOH + 6 g/l  $\text{Na}_2\text{SiO}_3$ )*

The main phases are polymorphic modifications of aluminum oxide:  $\gamma$ - $\text{Al}_2\text{O}_3$ ,  $\alpha$ - $\text{Al}_2\text{O}_3$ , as well as mullite. At the same time, the quantitative ratio of these

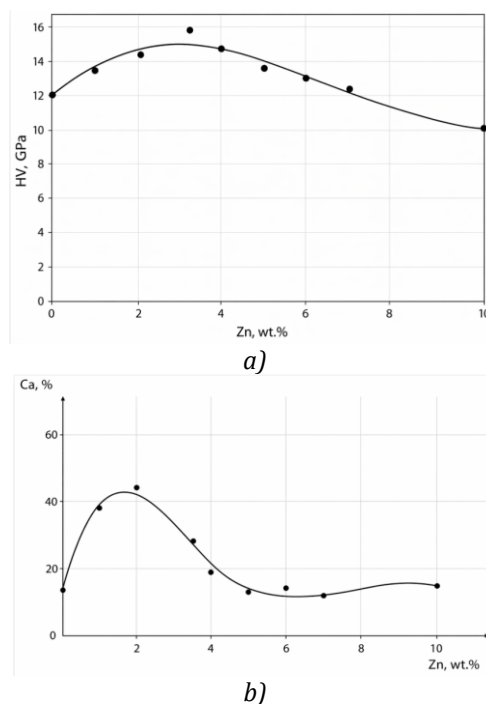
phases strongly depends on the degree of zinc alloying of aluminum.

With increasing content of the alloying element, changes in the intensity of diffraction peaks of the corresponding phases are observed, which may indicate the influence of the substrate's chemical composition on phase formation conditions during micro-arc oxidation. This is likely associated with changes in the thermal and electrophysical characteristics of the process in microdischarge channels, which affect the course of polymorphic transformations of aluminum oxide.

The analysis of the obtained results reveals a clear relationship between the phase composition of MAO coatings and their microhardness. The maximum hardness values are observed at a zinc content of about 2–3%, which corresponds to the highest fraction of the high-hardness  $\alpha$ - $\text{Al}_2\text{O}_3$  phase in the coating. This indicates that the formation of  $\alpha$ - $\text{Al}_2\text{O}_3$  during the micro-arc oxidation process is the key factor in strengthening the coatings.

A further increase in zinc concentration leads to a decrease in the fraction of  $\alpha$ - $\text{Al}_2\text{O}_3$  and a corresponding reduction in microhardness, which may be associated with changes in phase formation conditions within microdischarge channels and an increased proportion of less hard phases.

The corresponding dependences of coating microhardness on alloy composition are shown on *Figure 3*. The analysis demonstrates that both the phase composition of the coatings and their microhardness vary non-monotonically with increasing zinc alloying of aluminum.



*a – microhardness; b – concentration*  
*Figure 3: Concentration dependence of the  $\alpha$ - $\text{Al}_2\text{O}_3$  phase content and hardness*

High-precision X-ray diffraction studies have shown that the lattice parameter of the  $\gamma$ - $\text{Al}_2\text{O}_3$  phase varies depending on the degree of aluminum alloying, Figure 4. For the coating formed on commercially pure aluminum, the lattice parameter is 0.790 nm, which corresponds to the standard reference value. With increasing zinc content, a linear increase in the lattice parameter is observed.

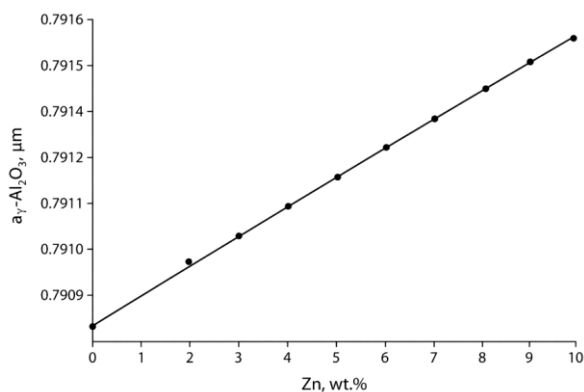


Figure 4: Effect of zinc alloying of aluminum on the lattice parameter of  $\gamma$ - $\text{Al}_2\text{O}_3$  during MAO treatment (electrolyte: 1 g/l KOH + 6 g/l  $\text{Na}_2\text{SiO}_3$ )

The obtained results indicate that during the formation of MAO coatings, the  $\gamma$ - $\text{Al}_2\text{O}_3$  phase becomes alloyed with components of the base material. The change in the lattice parameter in this case is обусловлена, on the one hand, by the difference in ionic radii of  $\text{Al}^{3+}$  ( $r = 0.67 \text{ \AA}$ ) and  $\text{Zn}^{2+}$  ( $r = 0.86 \text{ \AA}$ ), and on the other hand, by differences in their valence and the concentration of the dissolved element.

Considering that  $\gamma$ - $\text{Al}_2\text{O}_3$  has a defective spinel structure characterized by the presence of vacancies in the cation sublattice, partial substitution of  $\text{Al}^{3+}$  ions by  $\text{Zn}^{2+}$  ions or their localization in interstitial positions is possible. Due to the larger ionic radius of  $\text{Zn}^{2+}$ , an expansion of the crystal lattice occurs, which is reflected in the increase of its parameter with increasing alloying degree.

In addition, the incorporation of  $\text{Zn}^{2+}$  cations into the crystal structure of  $\gamma$ - $\text{Al}_2\text{O}_3$  may affect the stability of polymorphic modifications of aluminum oxide and the conditions of phase transformations during micro-arc oxidation. This is consistent with the experimental data shown in Fig. 5, where it is demonstrated that changes in the chemical composition of the alloy significantly influence the phase composition of the formed coatings. At the same time, the phase composition of the coatings on the investigated alloys differs both qualitatively and quantitatively (see Table 1, Figure 5).

The analysis of the obtained results shows that the mechanism of phase composition formation in MAO coatings is largely governed by the processes of stabilization and destabilization of the metastable  $\gamma$ - $\text{Al}_2\text{O}_3$  phase. The study results indicate that  $\text{Zn}^{2+}$

cations can contribute to the stabilization of this phase at zinc contents above 3%, which is manifested by an increase in its fraction in the coating structure.

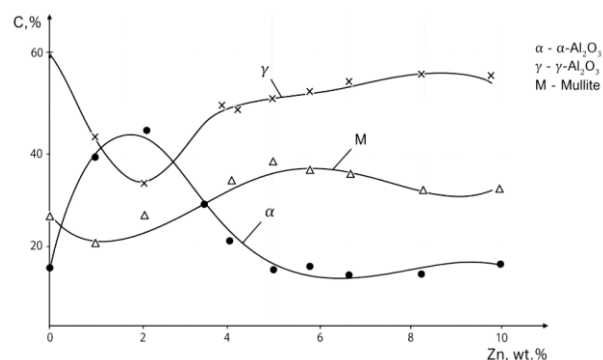


Figure 5: Quantitative ratio of the main oxide phases in the coating on the Al-Zn alloy

It is likely that adsorption of impurity cations on the surface of aluminum oxide particles plays an important role in the mechanism by which alloying additions affect the transformation of  $\gamma$ - $\text{Al}_2\text{O}_3$  into the thermodynamically stable  $\alpha$ - $\text{Al}_2\text{O}_3$  phase. Adsorbed ions are capable of changing the surface energy state of the particles and thus influencing the nucleation rate and crystal growth kinetics of new phases. As a result, the conditions governing polymorphic transformations of aluminum oxide during micro-arc oxidation are altered.

Ensuring high hardness and wear resistance of MAO coatings on aluminum alloys is directly associated with an increased content of the high-hardness  $\alpha$ - $\text{Al}_2\text{O}_3$  phase (corundum). The obtained results show that, when aluminum is alloyed with zinc, an extreme dependence of the  $\alpha$ - $\text{Al}_2\text{O}_3$  phase content on Zn concentration is observed. The maximum fraction of this phase is achieved at a concentration of about 2% Zn, which is consistent with the maximum microhardness of the coatings established in this work. A further increase in zinc concentration leads to an increase in the fraction of  $\gamma$ - $\text{Al}_2\text{O}_3$  and a corresponding decrease in the content of  $\alpha$ - $\text{Al}_2\text{O}_3$ , which may be associated with the stabilizing effect of  $\text{Zn}^{2+}$  ions on the metastable phase.

Taking into account the features of the micro-arc oxidation process, a two-stage mechanism of coating phase composition formation can be assumed. At the initial stage of oxidation, the metastable  $\gamma$ - $\text{Al}_2\text{O}_3$  phase is formed predominantly, its formation occurring by a topochemical mechanism on the metal surface. At the next stage, as a result of a local temperature rise in the microdischarge channels, a solid-state polymorphic transformation of  $\gamma$ - $\text{Al}_2\text{O}_3$  into the more stable  $\alpha$ - $\text{Al}_2\text{O}_3$  phase takes place.

In addition, when silicate electrolytes are used, silicon oxide is formed in the microdischarge zone, which, upon interaction with  $\text{Al}_2\text{O}_3$  at high

temperatures, can form aluminosilicate phases. In the coatings under study, this phase is mullite ( $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ).

Thus, the influence of alloying additions on phase transformations during the formation of MAO coatings is determined by a complex of physicochemical processes, including adsorption of impurity cations, changes in the nucleation conditions of new phases, and the specific features of thermal processes in the microdischarge channels.

Summarizing the obtained results, it can be concluded that zinc alloying of aluminum significantly affects the structural and phase state of MAO coatings. This is manifested in changes in the lattice parameter of the  $\gamma\text{-Al}_2\text{O}_3$  phase, redistribution of polymorphic modifications of aluminum oxide, and changes in the ratio of the main phases in the coating structure. The most favorable combination of phase composition is formed at a zinc content of about 2%, which is accompanied by the maximum content of the  $\alpha\text{-Al}_2\text{O}_3$  phase and a corresponding increase in coating microhardness. A further increase in Zn concentration leads to stabilization of the metastable  $\gamma\text{-Al}_2\text{O}_3$  phase and a decrease in the fraction of the corundum phase, resulting in reduced hardness. Thus, an extreme dependence of the phase composition and mechanical properties of MAO coatings on the degree of zinc alloying of aluminum has been established, opening up possibilities for controlling the structure and properties of the coatings through optimization of alloy composition.

#### 4. Conclusions

It has been established that micro-arc oxidation of zinc-alloyed aluminum in an alkaline silicate electrolyte leads to the formation of ceramic-like coatings, the phase composition of which is represented by polymorphic modifications of aluminum oxide,  $\gamma\text{-Al}_2\text{O}_3$  and  $\alpha\text{-Al}_2\text{O}_3$ , as well as mullite ( $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ). Zinc alloying affects the ratio of the  $\alpha\text{-Al}_2\text{O}_3$  and  $\gamma\text{-Al}_2\text{O}_3$  phases.

X-ray diffraction analysis showed that the lattice parameter of the  $\gamma\text{-Al}_2\text{O}_3$  phase increases with increasing zinc content, indicating alloying of this phase by  $\text{Zn}^{2+}$  ions and their incorporation into the defective spinel structure of  $\gamma\text{-Al}_2\text{O}_3$ .

An extreme dependence of the  $\alpha\text{-Al}_2\text{O}_3$  phase content and the microhardness of the coatings on the degree of zinc alloying of aluminum has been established. The maximum fraction of the corundum phase and the highest hardness of the coatings are observed at a Zn content of about 2%.

It has been shown that the formation of the phase composition of MAO coatings proceeds via a staged mechanism: at the initial stage, the metastable  $\gamma\text{-Al}_2\text{O}_3$  phase is formed by a topochemical mechanism,

while at the subsequent stage, under conditions of locally high temperatures in microdischarge channels, a solid-state polymorphic transformation of  $\gamma\text{-Al}_2\text{O}_3$  into the thermodynamically stable  $\alpha\text{-Al}_2\text{O}_3$  phase occurs, along with the formation of mullite.

It has been established that in the presence of silicates in the electrolyte, the formation of an aluminosilicate phase - mullite ( $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ) is possible, which is обусловлено the interaction of aluminum oxide with silica from the electrolyte at high temperatures.

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