

Investigation of the structure of Al – Ca – Mn alloy sheets coated by micro-arc oxidation method

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The article investigates the structure of sheets made from the Al – Ca – Mn aluminum alloy system, coated using the micro-arc oxidation (MAO) method. The alloy sheets with a composition of Al – 2.5%Ca – 1.5%Mn – 0.4%Fe – 0.2%Si – 0.2%Cu – 0.8%Zn were produced through hot rolling and subsequently treated in a low-alkaline alkaline-silicate electrolyte. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) methods were employed to assess the microstructure and phase composition during the study. The results revealed a high dispersion of the alloy structure with various phases present, such as Al₄Ca and Al₆(Mn, Fe). The sizes of the dispersed eutectic precipitates ranged from 1.5 to 5 micrometers. The thickness of the obtained MAO coatings was between 20 and 30 micrometers. The coating structure in the middle of the samples was uniform, without through porosity, although some isolated pores and cracks were observed. X-ray phase analysis indicated the presence of aluminum oxides in the coating, such as α-Al₂O₃ and η-Al₂O₃. Additionally, other alloying elements like calcium, potassium, and sodium were noted. An important aspect was that the structure of the alloy near the coating remained stable, indicating good adhesion between the aluminum matrix and the coating. The authors emphasize the need for further research to optimize processes for producing strong and wear-resistant coatings, especially for applications in Arctic conditions. This work lays the groundwork for developing new structural materials with multifunctional coatings that could be beneficial in various industries, including automotive and shipbuilding.

Key words: aluminum, calcium, manganese, MAO, coatings, α-Al₂O₃, η-Al₂O₃.

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In recent years, many studies [1–7] have shown the possibility of using calcium as the main alloying element in foundry and deformable aluminum alloys. Its advantage over silicon, for example, as well as cerium or lanthanum is obvious. First of all, it is low density (1.55 g/cm³) in combination with the same minimum solubility in solid solution on the basis of aluminum. In addition, calcium is not expensive, due to its availability and distribution in the Earth’s crust.

It follows from literature data that calcium, as well as silicon, forms a eutectic type diagram with aluminum [8]. The eutectic concentration of calcium in the dual system is 7.4–7.6 wt.%, and the corresponding eutectic temperature is 613–617 °C. The most important advantage of using calcium is that alloys based on double eutectic (Al) + Al₄Ca have high casting properties [9].

Further studies by the authors [5, 10–12] have shown that the Al – Ca – Mn – Fe system is one of the most promising for research and development of new alloys.

It is known that iron, for example, is an inevitable and, as a rule, the most harmful impurity in aluminum alloys [13]. This element is practically insoluble in aluminum solid solution, and the morphology of phases containing iron largely determines the plasticity of castings and deformed semi-finished products. Manganese during crystallization is able to dissolve in the aluminum solid solution and to be released during annealing in the form of secondary manganese aluminides (e.g., Al₆Mn).

The works [5, 10–12, 14] show that in alloys of Al – Ca – Mn – Fe system in equilibrium with aluminum solid solution the following phases can be present: Al₄Ca, Al₉CaMn₃, Al₃Fe, Al₆(Fe, Mn), Al₁₀CaFe₂.

The most advanced solution among the alloys of this system is the work [15]. It proposes an alloy that can be used for the production of both shaped castings and deformed semi-finished products. It can be used to produce parts of automobile engines, parts of shipbuilding and water intake fittings, heating radiators and others. Such

alloy contains (wt.%): calcium 2.0-3.0, manganese 1.2–2.0, iron 0.2–0.4, silicon 0.1–0.3, copper 0.05–0.3, zinc 0.1–1.0, aluminum – the rest.

It follows from the work [15] that calcium in the alloy performs the role of the main eutectic-forming element, providing high casting properties. Iron and silicon – perform the function of modifiers of aluminum-calcium eutectic. Manganese, zinc and copper – provide the necessary level of strength by alloying the aluminum matrix and calcium-containing phase. It should be noted that manganese, zinc and copper are unavoidable impurities when using secondary raw materials.

However, taking into account its possible use in Arctic conditions, the authors suggest using additional corrosion- and wear-resistant coatings, for example, MAO-coatings.

According to [16–18], MAO is a process of obtaining various coatings in electrolytes mainly on the surface of valve metals and their alloys (aluminum, magnesium, titanium, zinc, etc.) due to the realization of microdischarges formed at various phase interfaces: metal-coating, metal-gas, coating-electrolyte. Depending on the composition of the electrolyte and electrical mode, the coating is formed to a different extent due to oxidation of the base metal and phases of alloying elements of the alloy, as well as due to the incorporation of components of the electrolyte. The most common electrolyte for MAO is alkali-silicate. When carrying out MAO in the soft mode, when the ratio of cathodic current density to anodic current density is greater than some critical value, when a certain coating thickness is reached, the realization of micro-arc discharges at the “metal-gas” boundary stops, and the coating formation occurs mainly at the “metal-coating” boundary due to the realization of internal micro-arc discharges [19]. The coatings obtained in the soft mode have higher functional properties.

The so-called working layer formed during MAO on Al-alloys consists mainly of two types of aluminum oxide: α - Al_2O_3 stable modification (corundum, type D5.1, hardness up to 2000 HV) and γ - Al_2O_3 [20–22]. Depending on the functional purpose, the thickness of the outer process layer can be varied by conducting the process in different electrolyte compositions and applying special electrical modes, as a result of which the composition of the oxide working layer will also vary. The coating may also contain other phases obtained by mixing powders into the electrolyte composition [23, 24].

At the same time, the authors have to state that the current data on the application of protective coatings by the MAO method on the surface of aluminum alloys containing calcium are very limited [25–27]. In these works, the very possibility of applying oxide coatings on the surface was shown and corrosion resistance was evaluated. The presence of eutectic Al + Al_4Ca colonies did not affect the growth kinetics of the coating

compared to pure aluminum. In addition, the work shows that α - Al_2O_3 phase is formed on the surface, which contributed to the high microhardness values (up to 1180 HV). It was found that MAO coatings significantly increase the corrosion resistance of alloys.

As a result, the analysis of the literature allowed the authors to formulate the following objective of the present work: to conduct a comprehensive study of the structure of alloy sheets Al – 2.5%Ca – 1.5%Mn – 0.4%Fe – 0.2%Si – 0.2%Cu – 0.8%Zn with MAO-coatings; to assess the very possibility of applying such coatings and to create an experimental basis for the subsequent development of modes of obtaining integral, durable and wear-resistant coatings on products made of this alloy.

Methodology

Obtaining ingots and sheet for research

The object of the study was sheets from the alloy Al – 2.5%Ca – 1.5%Mn – 0.4%Fe – 0.2%Si – 0.2%Cu – 0.8%Zn (hereinafter – AlCa2.5Mn1.5) [15]. The chemical composition of ingots is presented in **Table 1**. The ingots, 20×140×180 mm in size, were produced at the Aluminum Alloys Plant (Podolsk).

The initial charge consisted of the following components: aluminum grade A5 (GOST 11069–2019), calcium (99% purity) (TU 083.5.314–94), ligature AlMn80 in the form of tablets with manganese content of 75–85% (GOST R 53777–2010), ligature AlFe10 (A) (GOST R 53777–2010), alloy CAM4-1 (GOST 19424–97), silicon grade KR00 (GOST 2169–69).

The melt was prepared in a smelting gas furnace, in a graphite-chamotte crucible, the total mass of one melting was 1 kg. Initially melted aluminum at a furnace temperature of 850 °C, then removed slag and introduced ligatures, periodically stirring the melt to avoid precipitation. After dissolution of ligatures, under the mirror of the melt, silicon, calcium and alloy CAM4-1, wrapped in aluminum foil, were sequentially introduced in pure form. After complete melting of all components, the melt was thoroughly mixed and refined with argon (TU 6-21-12–94). After that it was kept for 10 minutes and poured into a graphite mold of a given size at room temperature.

The alloy ingots were subjected to hot rolling on the mill DUO-250, which resulted in sheets with a thickness of 2 mm. Before rolling, the alloy ingots were placed in a furnace at a temperature of 350 °C and kept at this temperature for 1 hour. The heated ingots were rolled with a draft of no more than 25% per pass, after which the deformed semi-finished product was again placed in the furnace for heating.

Table 1
Results of the chemical composition of the alloy

Elemental content (wt.%)	Ca	Mn	Fe	Si	Cu	Zn	Al
	2.5	1.5	0.4	0.2	0.2	0.8	Rest

Methodology of micro-arc oxidation (hereinafter – MAO)

To study the effect of the chemical and phase composition of AlCa_{2.5}Mn_{1.5} alloy on the structure of MAO coatings, sheet samples were treated in alkaline-silicate electrolyte. P70-ZAS MAO: current densities of 20 A/dm², in a low alkaline electrolyte. The cathodic current density is higher than the anodic current density. Process is 30 min [25–27].

Methodology for the study of microstructure, phase composition and hardness of AlCa_{2.5}Mn_{1.5} alloy and MAO coating

The structure of the cross-slits consisting of metal base and MAO coating was analyzed by scanning electron microscope (JSM-7100F) (SEM). Surveying was carried out in the central part (Down) and near the edge of the sample (Up). In this case – closer to the sample axis (Center) and near the coating (Edge) (**Fig. 1, a**).

Electron images were accumulated using a semiconductor back-reflected electron detector (BSE/BED) at an accelerating voltage of 10 kV.

Elemental analysis was performed by probe energy dispersive analysis using Oxford Instruments X-Max 50 detector at an accelerating voltage of 20 kV and a beam current of 1.5 nA. The results were processed in Aztec software package with normalization to 100%.

X-ray phase analysis of MAO coating was performed using Bruker D2 Phaser X-ray diffractometer equipped with Lynxeye XE-T detector. The imaging was performed with CuK α source at 2 θ angles from 10° to 80° with a step of 0.02° and integration time of 0.5 s. The diffractograms were corrected for the position of the 35.129° corundum reflex. The imaging areas are indicated in the image (**Fig. 1, b**).

The hardness of the MAO coating was determined on the Vickers scale on a DUROLINE MH-6 hardness tester

(Metkon, Turkey) with 50 g load and 10 s dwell time. The measurements were carried out on polished samples. The indenter was pressed into the end face of the coating to eliminate the influence of the substrate. The analysis was carried out in the “Down” zone (**Fig. 1, a**).

Study of microstructure and phase composition of AlCa_{2.5}Mn_{1.5} alloy away from MAO coating

The studies have shown high dispersibility and uniformity of the alloy structure, which is determined by the dispersed eutectic structure formed in the ingot and during subsequent deformation processing alternated by intermediate heat treatment. As a result, a detailed study of the coating microstructure, evaluation of its qualitative and quantitative parameters using light microscopy proved to be difficult.

Therefore, the authors focused on the study of the alloy structure using electron scanning microscopy and X-ray analysis.

These studies showed that the alloy structure recorded in the back-reflected electrons (**Fig. 2**) consists of aluminum solid solution (hereinafter – (Al)), on the background of which dispersed, lighter-colored selections are clearly visible. At most, the size of some of these separations reached 3–5 μ m in length and 1.5–2 in cross-section. At the same time, the majority of secretions are much more dispersed (see **Fig. 2, c, d**).

The phases and structural components presented in **Fig. 2** were identified using micro-X-ray spectra, the results of which are presented in **Fig. 3** and **Table 1**. It can be seen that the dark regions in the back-reflected electron images unambiguously represent (Al) regions, in which the presence of manganese can be observed (see **Fig. 3, a** (spectra 58–60), **c, e** and see **Table 1** for the content of components in spectrum 58). Most likely, manganese, in this case, is present on the background (Al) in the form of dispersed particles of Al₆Mn phase, released during

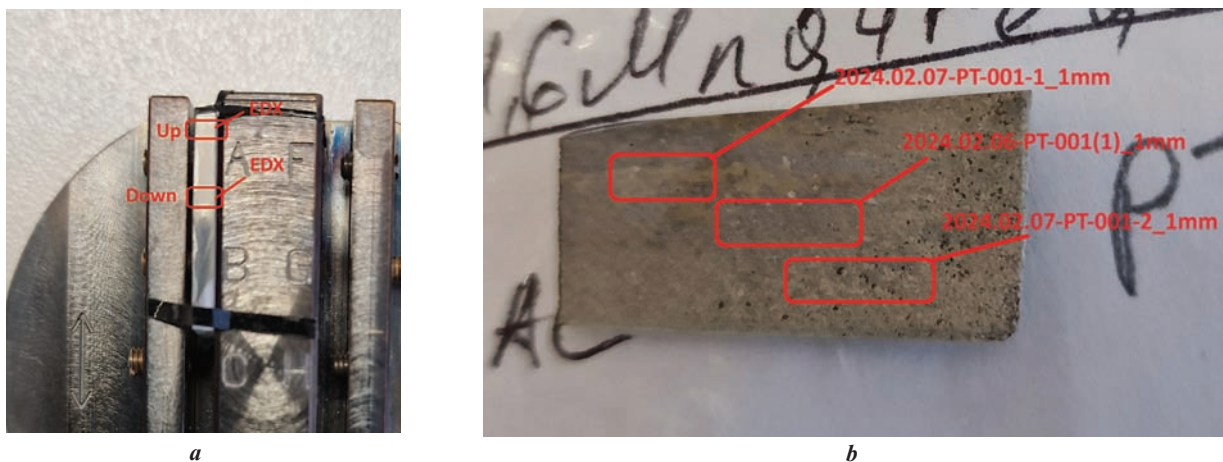


Fig. 1. Areas of structural studies of the specimen: *a* – cross section for SEM studies (“Down” – central part of the specimen; “Up” – area of the specimen closer to the edge; “Center” – study area closer to the axis of the specimen; “Edge” – near the coating); *b* – areas of X-ray phase analysis of the coating

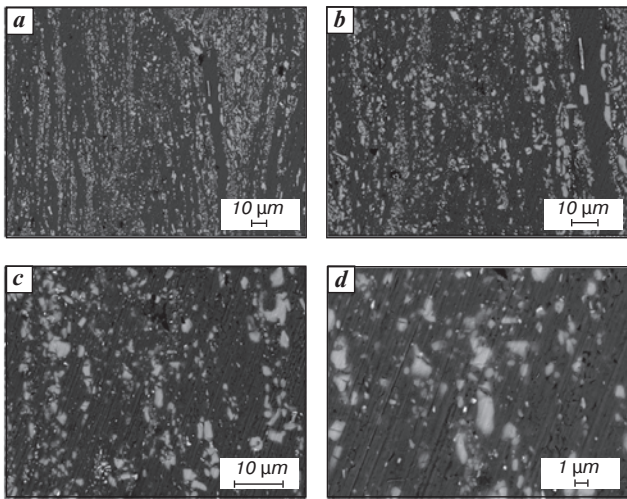


Fig. 2. Structure of the leaf in the “Down – Center” zone. Back-reflected electrons

intermediate thermal treatments, from the aluminum solid solution supersaturated during casting.

The particles of the phase containing mainly aluminum and calcium (the volume fraction of this phase is at least 30%) can be observed in the structure.

From the literature data [4–7, 9–12, 14, 25–27] it follows that this is the Al_4Ca phase formed during casting as a result of the eutectic reaction ($Al + Al_4Ca$). Further, during rolling and heat treatment cycle, the dispersed twigs of this phase crush and coagulate, eventually forming a uniform alloy sheet structure. At the same time, zinc is present in close proximity, in the background of the Al_4Ca phase (see Fig. 3, *a* (spectrum 67–69), *c, d, e* and see Table 2 for the content of components in spectrum 67). In accordance with the works [7, 15], it can be assumed that zinc indeed contributes to the solid-solution strengthening of the aluminum matrix and also partially performs the role of a modifier for Al_4Ca phase.

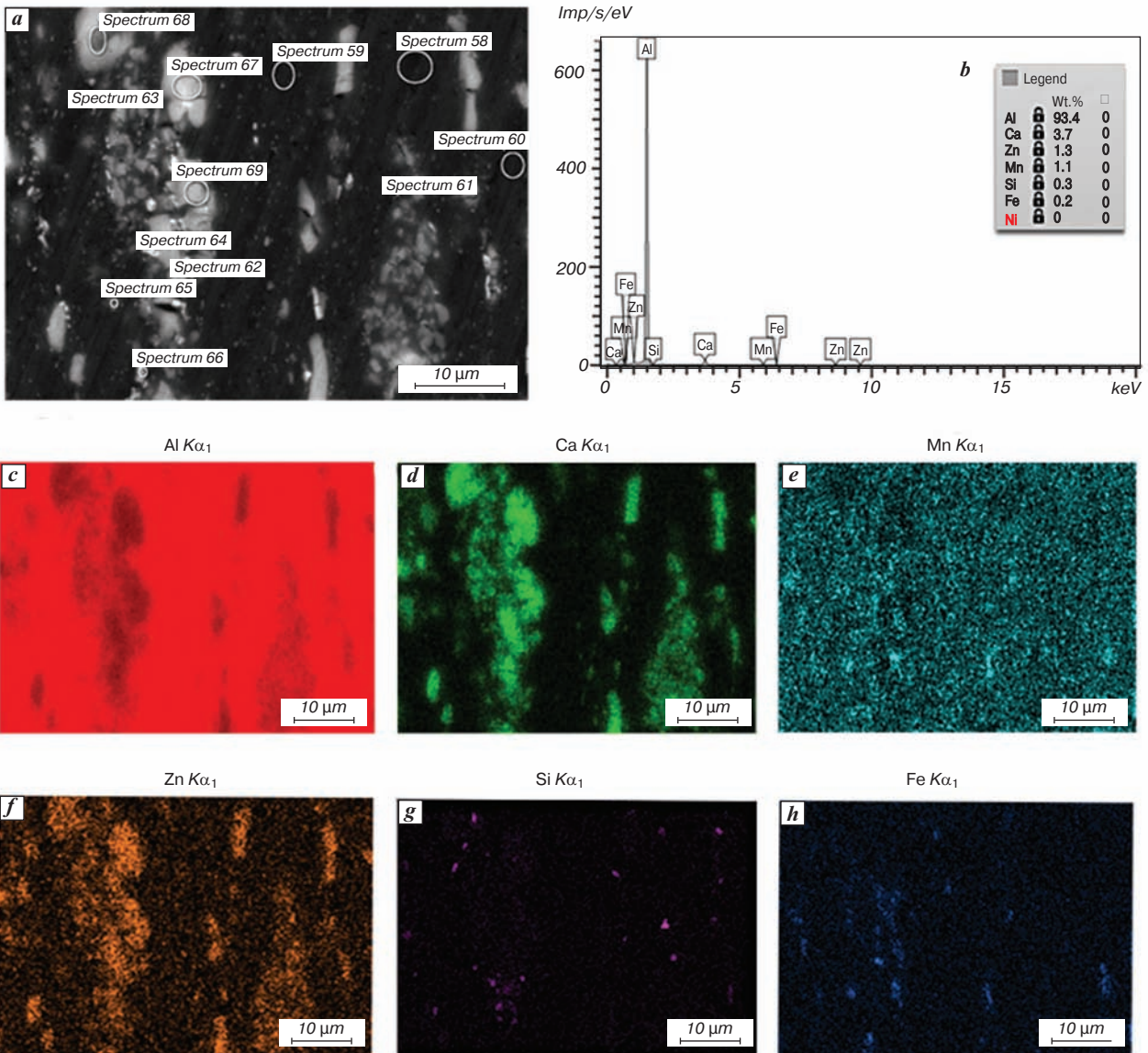


Fig. 3. Sheet structure in the “Down – Center” zone: *a* – back-reflected electrons; *b–h* – energy-dispersive analysis; *b* – summarized map taken from Fig. 3, *a*; *c–h* – images in $K\alpha$ – alloying elements

From Fig. 3 a, c, g, spectrum 61–63 it follows that in the structure there is a phase Al_2Si_2Ca , which can be illustrated by Table 2, which shows the simultaneous presence

of Al + Si + Ca in local places (see the composition in spectrum 61).

In addition, from Fig. 3, a, c, d and h (spectrum 64–66), as well as Table 2 (spectrum 65), it is evident that the structure contains individual compact selections containing Al, Mn and Fe, which can be identified with a high degree of probability as the $Al_6(Mn,Fe)$ phase.

The authors observed a similar structure, as shown in Figs. 2, 3, as well as in Table 2, in other zones of AlCa2.5Mn1.5 alloy samples.

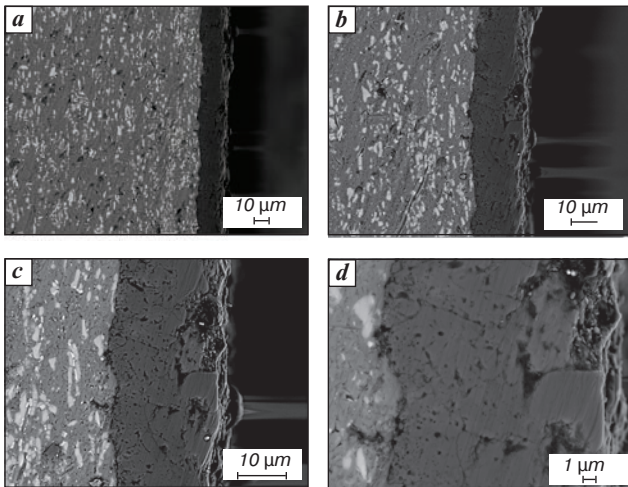


Fig. 4. Structure of the sheet with MAO coating in the “Down – Edge” zone. Back-reflected electrons

Table 2
Elemental composition according to Fig. 3, a of the “Down – Center” sample

Spectrum name	Content, wt. %					
	Al	Si	Ca	Mn	Fe	Zn
Spectrum 58	99.25	0.06	0.05	0.52	0.03	0.09
Spectrum 61	72.98	25.17	1.34	0.26	0.01	0.21
Spectrum 65	95.03	0.02	0.89	1.65	2.2	0,18
Spectrum 67	79.97	0.94	15.63	0.16	0.04	3.26

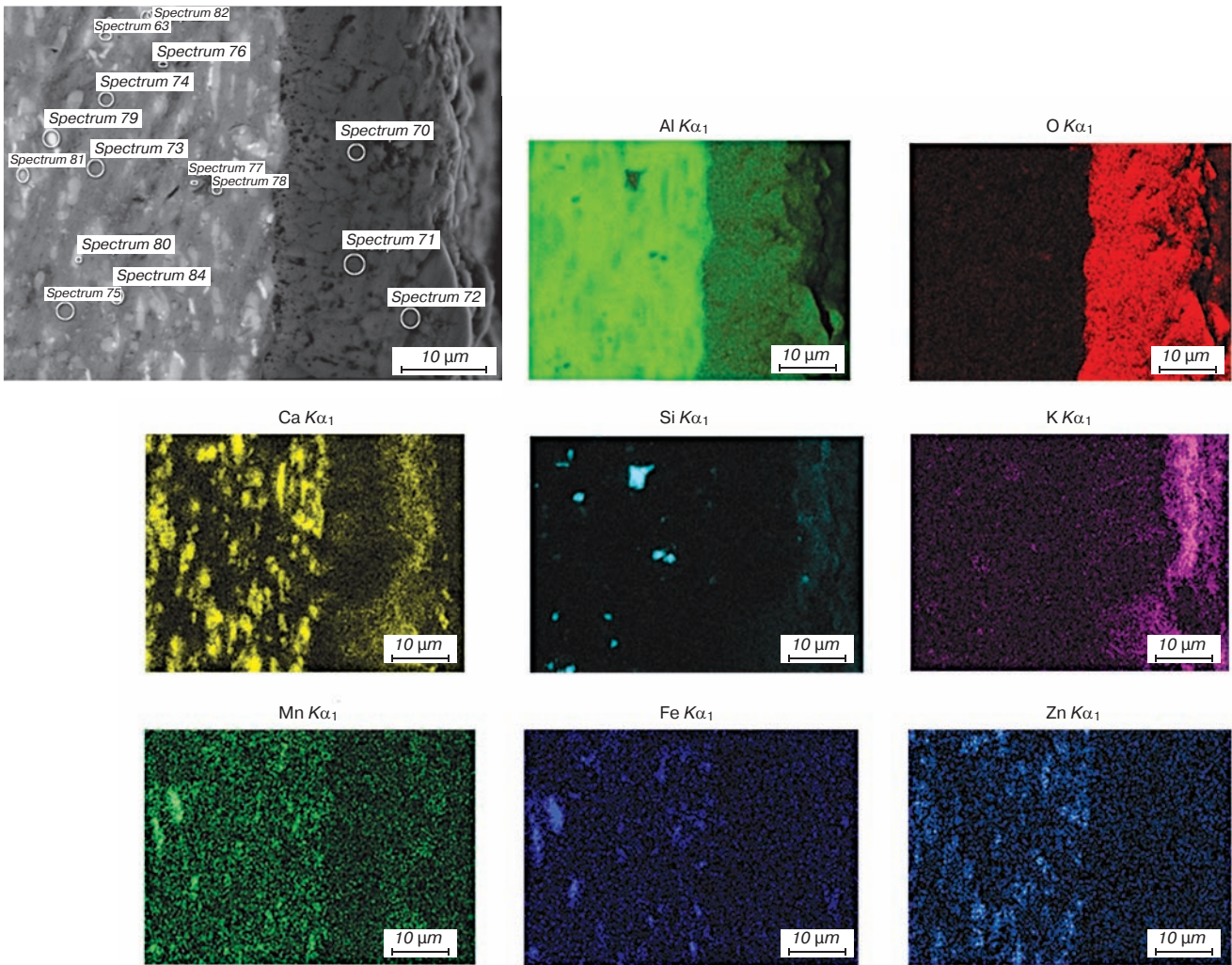


Fig. 5. Structure of MAO-coated sheet in the “Down – Edge” zone and images in $K\alpha$ – alloying elements

At the same time, it should be noted that the structure of the sheets of the studied alloy, the presence of structural components and phases in it, in general, turned out to be expected and consistent with the literature data.

Study of microstructure and phase composition of AlCa_{2.5}Mn_{1.5} alloy near the MAO-coating, at the interface “aluminum matrix-coating”, MAO-coating surface

A detailed analysis of the structure of the coated alloy showed that as we approach the interface, it practically does not change (see Figs. 4, 5). The novelty was observed only in the immediate vicinity of this interface, which, in turn, is quite smooth and not badly articulated with the metal matrix, except for separate and unconnected pores (see Figs. 4, 5). In general, the coating has a uniform structure, no multilayers are observed, and there is no through porosity.

The evaluation showed that the thickness of the coating varies between 20 and 30 micrometers, the outer layer is uniform. At the same time, a sufficient number of pores and cracks are observed in the coating itself (see Fig. 4), but there is no through porosity. Further investigations were focused on the study of the coating composition (Figs. 5–9, Table 2).

It is evident from the presented materials that the composition of the coating contains oxygen as well as potassium and sodium.

The concentration of potassium, sodium and silicon increases in the outer layer of the coating due to the incorporation of the main electrolyte components such as KOH, Na₂SiO₃, possibly B after transformation in microdischarges. It is possible that in through pores of the coating above phases Al₄Ca and Al₆(Mn,Fe), gas microdischarges are realized at the boundary “intermetallide-gas”, as a result of which the concentration of alloying elements of alloy Ca, Mn, Zn, Fe in the outer layer of the coating increases due to the plasma output on the outer surface of the coating.

It is important that aluminum in this case forms crystalline or amorphous oxides in which calcium, silicon, manganese, iron and zinc are also present (see Table 3, and Figs. 5, 6, 8, 9). The form of presence of these elements in the coating has yet to be revealed by the authors in subsequent studies.

Examination of the coating structure at the edge of the specimen revealed significant differences from that

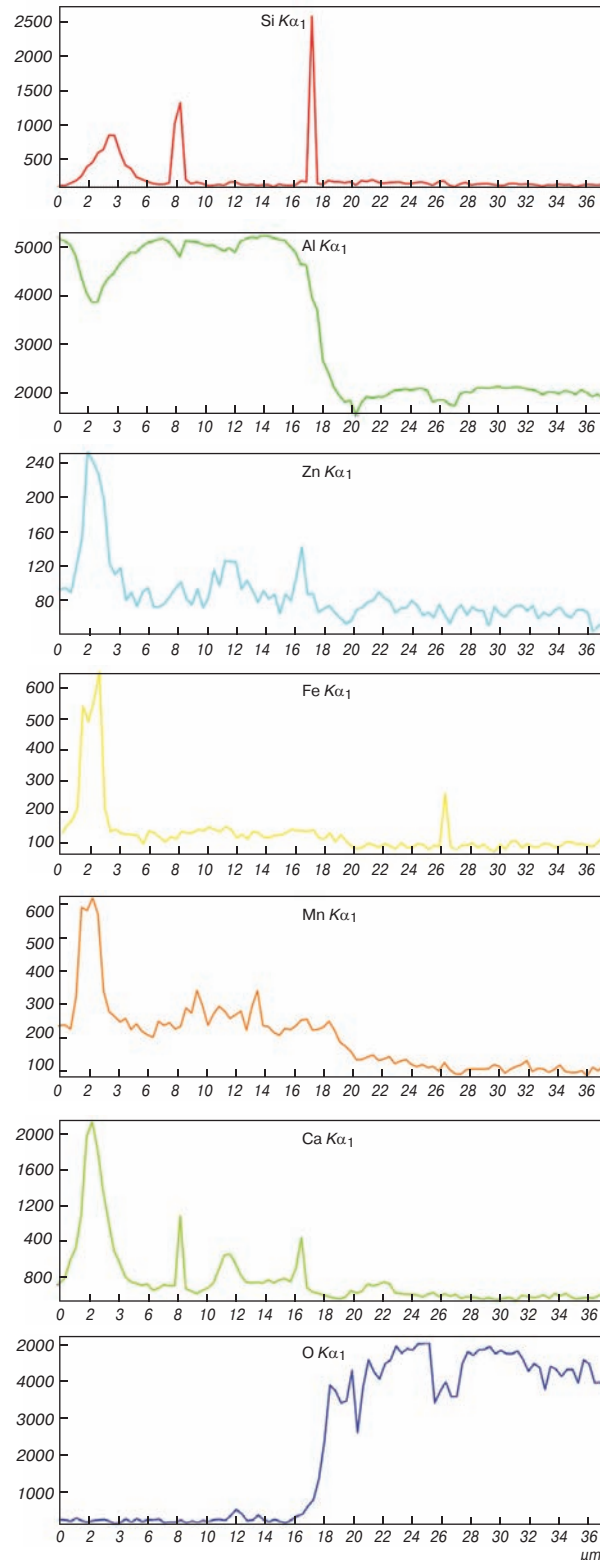
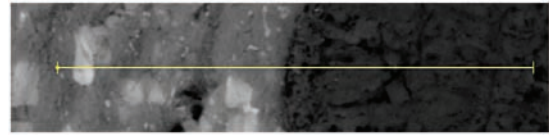


Fig. 6. Profile of the sheet with MAO coating in the “Down – Edge” zone. Micro-X-ray spectral analysis

Table 3
Elemental composition according to Fig. 5 of the “Down – Edge” sample

Spectrum name	Content, wt. %								
	O	Na	Al	Si	K	Ca	Mn	Fe	Zn
Spectrum 70	47.17	0.16	48.68	0.8	0.68	0.91	0.47	0.16	0.39
Spectrum 71	45.89	0.13	48.47	1.45	0.87	1.54	0.61	0.12	0.24
Spectrum 72	41.46	0.66	39.04	3.9	3.62	7.08	1.82	0.4	0.88

Fig. 7. Profile of the sheet with MAO coating in the “Up – Edge” zone. Micro-*X*-ray spectral analysis

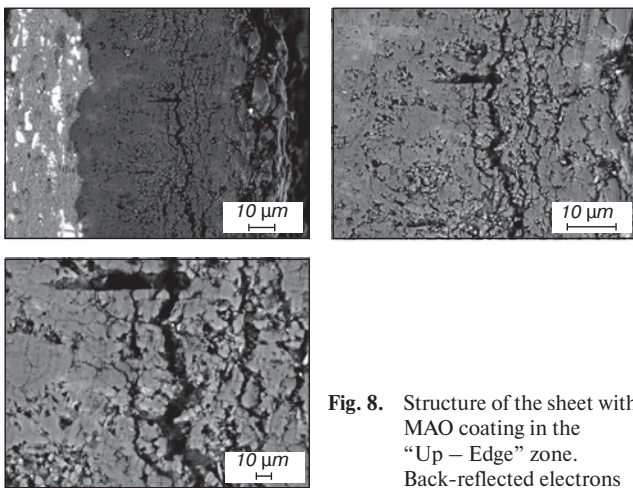
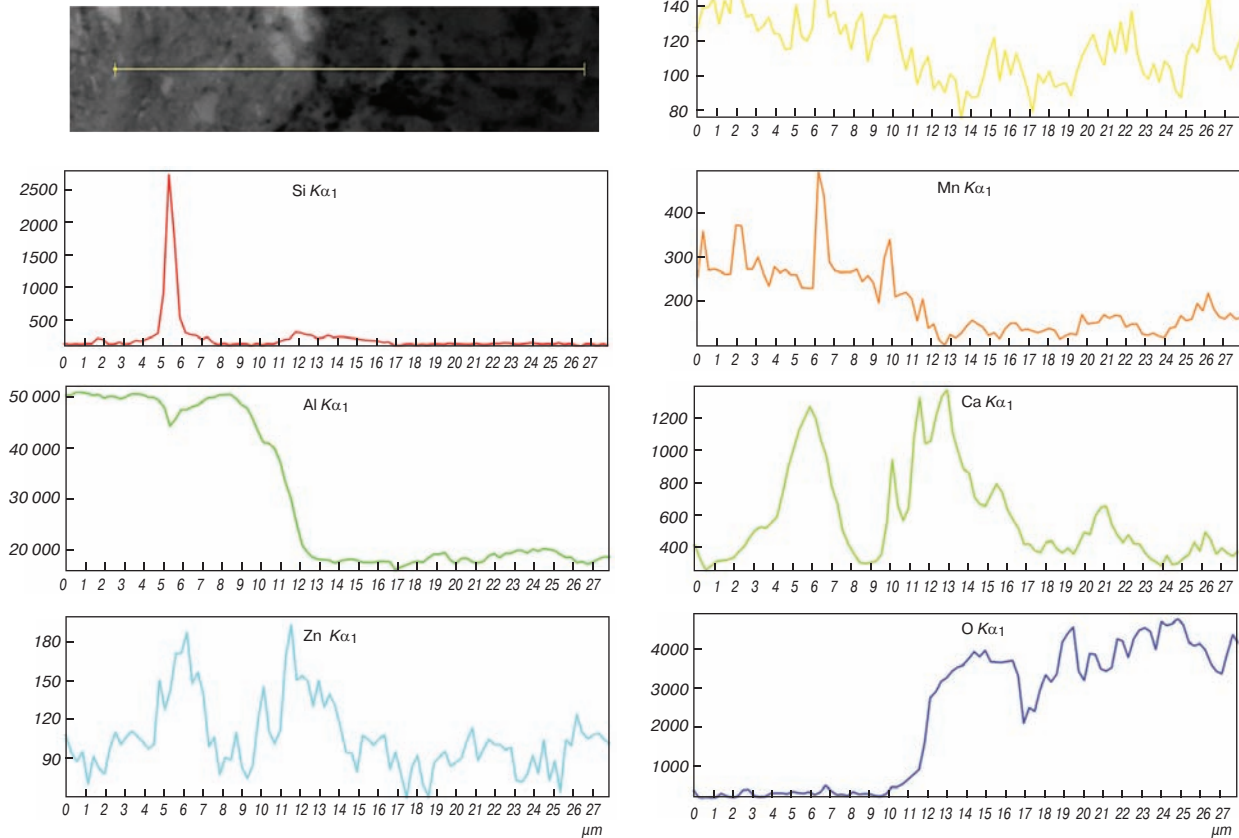


Fig. 8. Structure of the sheet with MAO coating in the “Up – Edge” zone. Back-reflected electrons

described earlier. The coating here looks much more porous, with cracks and non-flakes (see **Figs. 7, 8**), which is typical for similar coatings on aluminum alloys due to excessive stress at the edges [10].

At the same time, the elemental composition of the coatings practically did not differ from similar data in the “Down” zone (see **Fig. 9**).

The next stage of the work was the study of the surface of the MAO coating (**Figs. 10, 11**). The pictures obtained

in back-reflected electrons are characterized by a loose surface and contain surface cracks, which according to the literature can be called a “pancake” structure [16].

The evaluation of the phase composition of the coating by *X*-ray diffraction analysis showed the presence of the following phases (Al), α - Al_2O_3 and η - Al_2O_3 . The presence of aluminum solid solution on the *X*-ray diffraction patterns, in this case, indicates only the inevitable “back-lighting” of the aluminum-based matrix.

Fig. 12 shows the histogram of the distribution of measured hardness values for the MAO coating. The average value was 703 HV, with a standard deviation of 119. The hardness of the $\text{AlCa}2.5\text{Mn}1.5$ alloy after rolling was 69 ± 2 HV. It is evident that the most frequently occurring values are in the range of 700-900 HV. The recorded lower values can be attributed to the high porosity of the coating (see **Fig. 4**). These data are in good agreement with the results published in reference [27], although they are somewhat lower than the values for the alloy containing 3% calcium. The same study reported that the presence of certain chemical elements contributes to increased porosity of the coating and reduces its hardness by suppressing the formation of α - Al_2O_3 , particularly in the case of binary alloys. Some of these elements include zinc and manganese, which are present in the substrate alloy.

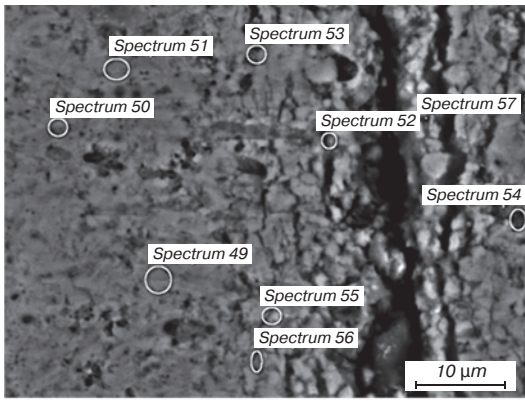


Fig. 9. Structure of MAO-coated sheet in the "Up - Edge" zone and images in $K\alpha$ - alloying elements

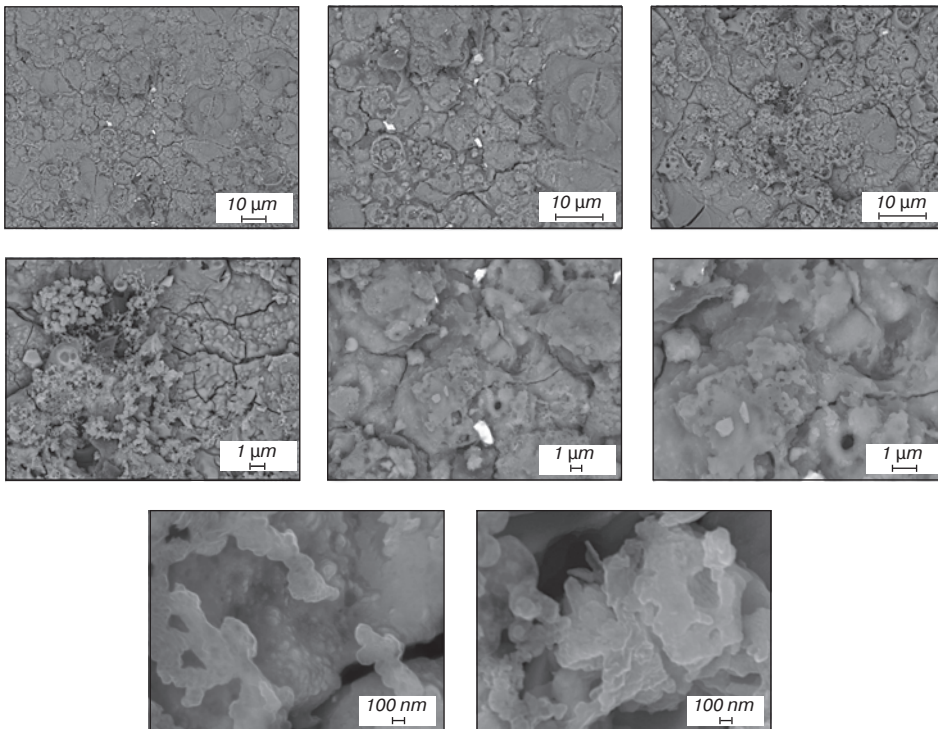
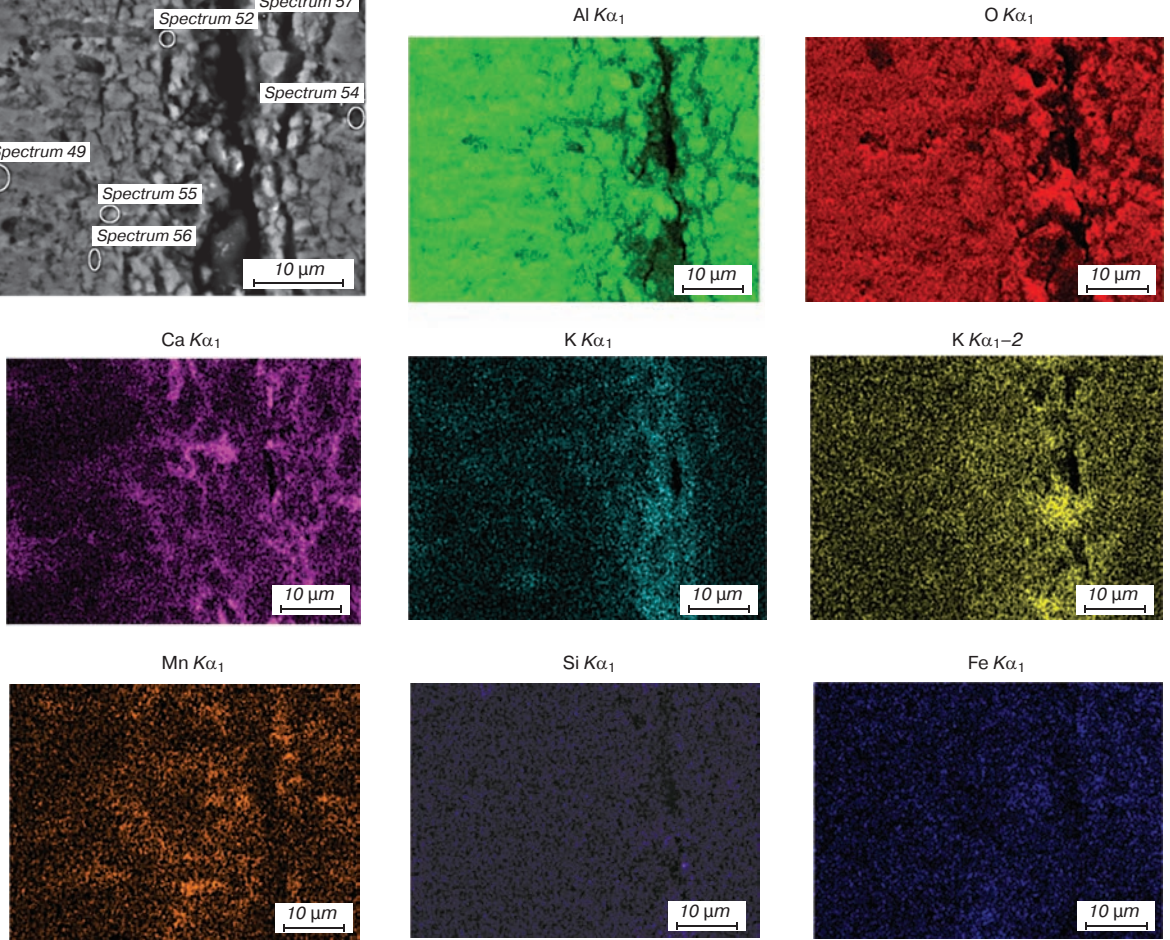


Fig. 10. Surface structure of MAO coatings. Back-reflected electrons

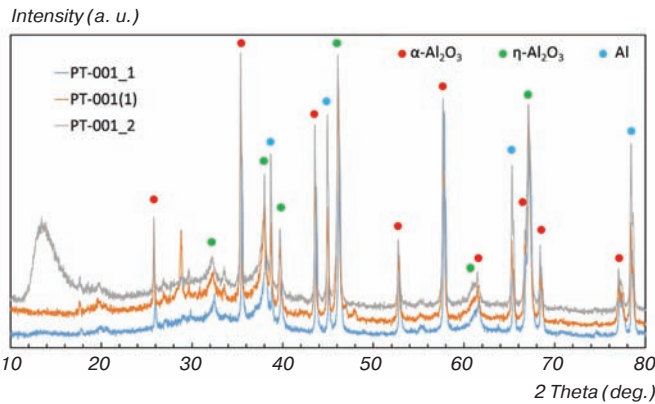


Fig. 11. Results of X-ray diffraction analysis of the surface of MAO coatings according to Fig. 1, b

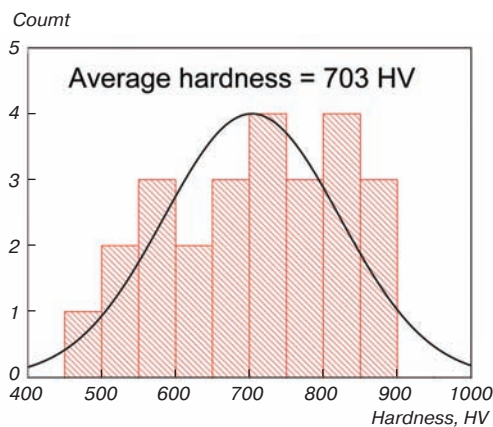


Fig. 12. Results of hardness measurements of the MAO coating in the "Down" zone

Thus, on the basis of structural studies and hardness measurements the possibility of obtaining relatively high-quality MAO coatings on the surface of AlCa2.5Mn1.5 alloy sheets (while maintaining the high quality of the metal base) has been demonstrated.

At the same time, further studies require experimental selection of MAO modes with inevitable adjustment of the alloy composition.

The studies will involve evaluation of the basic properties of the alloy with coatings, its corrosion and wear resistance, in-depth study of the structure and composition of the coatings themselves, transition zones and the metal-coating interface.

Conclusions

1. The study of the structure of Al – 2.5%Ca – 1.5%Mn – 0.4%Fe – 0.2%Si – 0.2%Cu – 0.8%Zn alloy sheets coated by micro arc oxidation.

2. The possibility of applying integral and durable oxide coatings has been confirmed, which creates a solid basis for the scientific basis for the development of the technology of applying MAO coatings on alloy products.

3. The structure and phase composition of the AlCa2.5Mn1.5 alloy sheets away from the MAO coating in general turned out to be expected and in accordance with

the literature data. At the same time, the technological process of coating had no significant effect on the internal structure of the sheet.

4. It is shown that the formation of α -Al₂O₃ and η -Al₂O₃ phases on the surface of the AlCa2.5Mn1.5 alloy sheet as a result of MAO, as revealed by X-ray diffraction analysis. At the same time, in the micro-pores of the coating due to the plasma output on the outer surface of the coating, there is an accumulation of calcium, manganese, zinc and iron in the outer layer of the coating.

5. The examination of the coating structure at the edge of the plate showed the presence of significant porosity, presence of cracks and non-continuities. In general, this is typical for similar coatings on aluminum alloys due to the realization of excessive stress at the edges. It is concluded that in the future the authors need to develop the modes of MAO coating application from the point of view of minimizing the negative edge effect.

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The structure study was performed using the scientific equipment of the Research Chemical and Analytical Center of SIC Kurchatov Institute.

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