Increase of the α-Al$_2$O$_3$ phase content in MAO-coating by optimizing the composition of oxidated aluminum alloy

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By the method of microarc oxidation of technically pure aluminum and aluminum doped with copper, vanadium and zinc (in an alkali silicate electrolyte at a current density of ~ 20 A/dm^2), the resulting coating is about 100 µm thick. The nonmonotonic dependence of the phase composition and hardness on the doping level of aluminum (Al + Cu, Al + Zn, and Al + V systems) is revealed. It was established that the degree of influence of alloying elements on the transformation process of γ-Al$_2$O$_3$ → α-Al$_2$O is determined by their crystal-chemical characteristics (charge, ionic radius). Therefore, the mechanism of formation of the phase composition should be associated with the stabilization and destabilization of the γ-Al$_2$O phase. The results indicate that Cu^{2+} cations contribute to destabilization of the γ-Al$_2$O$_3$ phase, while Zn^{2+} and V^{5+} cations stabilize the γ-Al$_2$O$_3$ phase (with a Zn and V content of more than 3 wt.%). A model is proposed for explaining the results obtained, which is based on the formation of the γ-Al$_2$O phase in the initial period of time and the appearance of the γ-Al$_2$O$_3$ phase in subsequent periods (as a result of an increase in the power of microdischarges). It is shown that the highest hardness of coatings on aluminum alloys (about 16 GPa) is achieved with a copper content in the range of 3−4 wt.%.

Keywords: microarc oxidation, corundum, structural engineering, anode-cathode regime, coating thickness, phase composition, properties.

Методом микродугового оксидирования технически чистого алюминия и алюминия легированного медью, ванадием и цинком (в щелочно-силикатном электролите при плотности тока ~ 20 А/дм^2) получены покрытия толщиной около 100 мкм. Выявлена немонотонность зависимостей фазового состава и твердости от степени легирования алюминия (системы Al + Cu, Al + Zn и Al + V). Установлено, что степень влияния легирующих элементов на процесс преобразования γ-Al$_2$O$_3$ → α-Al$_2$O$_3$ определяется их кристалохимическими характеристиками (заряд, ионный радиус). Показано, что механизм формирования фазового состава следует связывать со стабилизацией и дестабилизацией фазы γ-Al$_2$O$_3$. Результаты работы свидетельствуют о том, что катионы Cu^{2+} способствуют дестабилизации фазы γ-Al$_2$O$_3$, а катионы Zn^{2+} и V^{5+} стабилизации γ-Al$_2$O$_3$ фазы (при содержании Zn и V более 3 %). Предложена модель для объяснения полученных результатов, которая базируется на формировании в начальный период времени в основном фазы γ-Al$_2$O$_3$ и появлении фазы α-Al$_2$O$_3$ в последующие периоды (как следствие увеличение мощности микроразрядов). Показано, что наибольшая твердость покрытий на алюминиевых сплавах (около 16 ГПа) достигается при содержании меди в интервале 3−4 масс.%.

Збільшення вмісту фази α-Al₂О в МДО-покритті шляхом оптимізації складу окси-дуємого алюмінієвого сплаву. *В.В.Суботіна, U.F.Al-Qawabeha, О.В.Соболь, В.В.Білозеров, В.В.Шнайдер, Т.А.Табаża, S.M.Al-Qawabar.*

Методом мікродугового оксидування технічно чистого алюмінію і алюмінію легованого міддю, ванадієм і цинком (у лужно-силікатному електроліті при щільності струму ~ 20 А/дм²) отримано покриття товщиною близько 100 мкм. Виявлено немонотонність залежностей фазового складу і твердості від ступеня легування алюмінію (системи Al + Cu, Al + Zn і Al + V). Встановлено, що ступінь впливу легуючих елементів на процес перетворення γ-Al₂O₃ → α-Al₂O₃ визначається їх кристалохімічними характеристиками (заряд, іонний радіус). Показаноб що механізм формування фазового складу слід пов'язувати зі стабілізацією і дестабілізацією фази γ-Al₂O₃. Результати роботи свідчать про те, що катіони Cu²⁺ сприяють дестабілізації фази γ-Al₂O₃, а катіони Zn²⁺ і V⁵⁺ -стабілізації γ-Al₂O₃ фази (при вмісті Zn і V більше 3 мас.%). Запропоновано модель для пояснення отриманих результатів, яка базується на формуванні у початковий період часу в основному фази γ-Al₂O₃ і появі фази α-Al₂O₃ у наступні періоди (як наслідок збільшення потужності мікророзрядів). Показано, що найбільша твердість покриттів на алюмінієвих сплавах (близько 16 ГПа) досягається при вмісті міді в інтервалі 3–4 мас.%.

1. Introduction

At present, structural engineering is the basic method for creating materials with high functional properties [1, 2]. This is determined by a significant expansion of the possibilities of managing the structural state in non-equilibrium conditions (which is characteristic of modern methods for obtaining materials) [3, 4]. At the same time, the highest functional properties were achieved by deposition of ion-plasma coatings of the injection phase [5]. In this case, the system "solid surface — plastic base material" was created. The use of such a composite allowed to achieve even higher functional properties in the formation of multiperiod structures on its basis [6, 7].

However, to obtain highly solid protective coatings on valve materials (Al, Ti, Mg, Ta, Nb, Zr), the use of the anodic spark discharge phenomenon (anodic spark electrolysis [8, 9]) has shown greater efficiency. This process is often referred to in articles as microarc oxidation (MAO) [10]).

Microarc oxidation is an electrochemical process that takes place at a high electric field intensity [11] and is accompanied by the formation of microplasma [12] and microregions with high pressure due to the resulting gases [13]. This leads to the occurrence of high-temperature chemical transformations [14], and the transport of matter in the arc [15].

Aluminum, titanium, and magnesium alloys are most frequently treated with MAOs [12, 16–18]. The MAO method allows forming ceramic-like coatings with high hardness, wear resistance, dielectric properties, corrosion-resistant. The oxidation process spontaneously undergoes successive stages of spark, microarc, and arc oxidation. The characteristic view of the MDO process is shown in Fig. 1.

Ceramic coatings based on aluminum oxide, depending on the conditions of the process, may consist of different phases having a significant difference in the physicomechanical properties.

If the MAO treatment was carried out in an alkali silicate electrolyte, the coatings on aluminum alloys mainly consist of the metastable γ-Al₂O₃ phase with inclusions of the high-temperature α-Al₂O₃ phase [17, 18]. Note that coatings containing a large amount of the α-Al₂O₃ phase have high hardness ($HV > 15$ GPa) and wear resistance. This makes them indispensable in the manufacture of various parts of the friction.

It should be noted that in the process of forming MAO coatings, the physicochemical effect of microdischarges has a decisive influence on the final characteristics of the modified surface [16, 17].

It is possible to change the phase composition and control polymorphic transformations based on aluminum oxide not only due to changes in the electrolysis conditions, but also by optimizing the composition used to produce coatings. The presence of direct contact of the metal and the breakdown area allows to expect a large influence of the chemical composition of the aluminum alloy on the properties of the coatings. Studies show that the phase composition of coatings on different grades of aluminum alloys is different, which is apparently due to the incompleteness of the transformation of low-temperature modification of aluminum oxide γ-Al₂O₃ to a stable α-AlO₃ modification.

Fig. 1. View of micro-arc oxidation process.

At the same time, the important processes that determine the formation of the coating are the adsorption of cations on the surface of the coating, their redistribution during the growth of the coating, the processes of crystallization and melting. However, these processes have so far been little studied.

The aim of this work is to study the effect of aluminum doping on the phase formation processes, structure and hardness of the coatings formed in an alkali silicate electrolyte during the anodic-cathodic mode of the microarc oxidation process.

2. Experimental

Micro-arc processing was subjected to technically pure aluminum and aluminum alloyed with copper (from 3 to 9 wt.%), with zinc (from 1 to 10 wt.%) and vanadium (from 1 to 5 wt.%). The composition of aluminum alloys is given in Table 1. Note that copper and zinc are the main components of wrought aluminum alloys, hardened by heat treatment. The treatment was carried out in an alkaline electrolyte with the addition of technical liquid glass (Na_2SiO_3). An electrolyte of composition 1 g/l KOH + 6 g/l Na_2SiO_3 was used, which is the most universal for the organization of the anodic-cathodic process in the mode of microarc discharges.

The MAO treatment was carried out in a 20 liter stainless steel bathroom, sparging and cooling of the electrolyte was provided. The body of the bath served as a counter-electrode. A 10 kW power supply was used. The oxidation was carried out in the anode-cathode mode at a current density of 20–25 A/dm^2, the processing time was 1 h. All samples were processed under identical electrolysis conditions.

Table 1. Chemical composition of aluminum alloys

No sample	Alloy	Chemical composition, wt. %		
		Cu	Zn	V
0	100 % Al			
1	Al + Zn		1	
1			2	
2			2	
3			3,5	
4			4	
5			5	
6			6	
7			7	
10			10	
13	Al + Cu	3		
14		4		
16		6		
19		9		
20	Al + V			1
21				2
22				3
23				4
24				5

Determination of the phase composition of MAO coatings was carried out according to the results of X-ray phase analysis in comparison with the data of the "Powder Diffraction Files" [19]. The studies were carried out on a DRON-3 installation (Burevesnik, Russia) in monochromatic $K_{\alpha\text{-}Cu}$ radiation. The survey was carried out in the pointwise mode with a step of $2\theta = 0.1°$.

For carrying out quantitative phase analysis, the method of reference mixtures was used [20].

The coating thickness was determined on the instrument (vortex thickness auge) VT-10 NC (Kontrolpribor, Russia). Measuring range of thickness 0–2 mm.

Microhardness was determined on the device PMT-3 (LOMO, Russia).

3. Results and discussion

The control of the coating thickness showed that a coating with a thickness of 100–110 μm is formed in one hour of processing. No significant effect of the chemical composition of the processed sample on the oxidizing ability was revealed.

The microstructural feature of the coating on the samples under study is a layered structure — the technological and main layers are clearly revealed (Fig. 2). The technological layer is porous, non-wear-resistant,
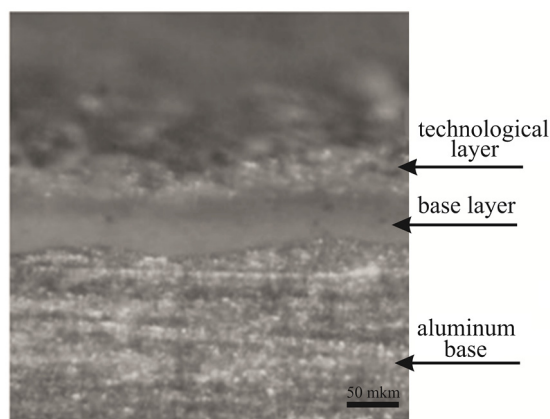
Fig. 2. The microstructure of the cross-section of the coating on the alloy Al + 9 wt.% Cu.

Fig. 3. X-ray diffraction patterns of materials after MAO treatment: 1 — aluminum, 2 — Al + 2 wt.% Zn, 3 — Al + 10 wt.% Zn.

easily removed by stripping on abrasive paper. The share of the technological layer is 30–40 % of the total coating thickness. The results given below will be related to the base layer, which thickness is ∼ 60–70 μm.

It is known that the properties of coatings (base layer), first of all, are determined by their phase composition. The X-ray phase analysis performed in this work made it possible to reveal the effect of doping on the phase composition of the coatings. Typical diffraction patterns of the coatings are shown in Fig. 3.

On the basis of the X-ray diffraction data obtained and their processing, patterns can be distinguished that are characteristic of all types of coatings. Such characteristic patterns include the fact that the hardened layer on all samples studied has a crystalline structure. The relative intensity of diffraction peaks for the identified phases is close to tabular, which indicates the absence of a pronounced texture, i.e. chaotic orientation of crystals of the hardened layer. The hardened layer has an identical phase composition, but the quantitative ratio is determined by the degree of aluminum doping.

The results of the phase analysis are summarized in Fig. 4.

The analysis of the XRD patterns (Fig. 3) and concentration dependences of the phase composition shown in Fig. 4 makes it possible to distinguish some regularities. Thus, it was found that the coatings formed in an alkali silicate electrolyte consist of α-Al_2O_3 (PDF 02-1373), γ-Al_2O_3 (PDF 02-1420), aluminum oxides and $3Al_2O_3 \cdot 2SiO_2$ mullite (PDF 15-0776). The greatest decrease in the percentage of mullite wi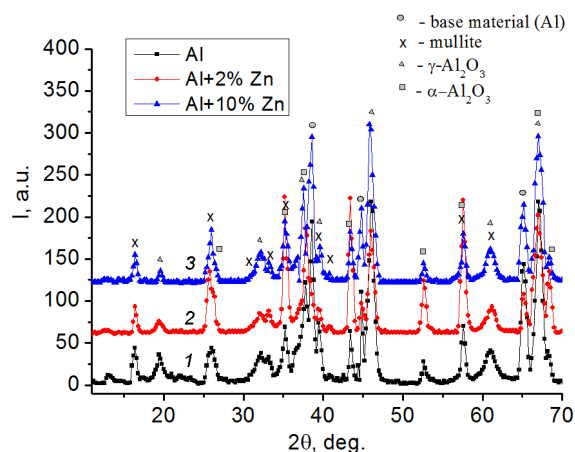th increasing content of the alloying element is observed in the Al + Cu system. The content of γ-Al_2O_3 phase at a concentration of alloying elements of about 4 wt.% goes to a stationary value (about 55 % for Al + Zn and about 40 % for Al + Cu and Al + V). The maximum content of α-Al_2O_3 (high hard corundum) corresponds to an alloying element content of about 2 wt.%, in Al + Zn and Al + V systems and about 4 wt.%, in Al + Cu systems. For the Al + Cu system, this corresponds to a maximum α-Al_2O_3 phase content of about 60 %.

As shown by precision studies, the lattice period of the α-Al_2O_3 phase varies depending on the doping level of pure aluminum (Fig. 5). For coating on pure aluminum, the lattice period is 0.790 nm, which corresponds to the table value. With an increase in the degree of doping, an increase in the lattice period is observed, both in the case of doping with copper and doping with zinc.

The obtained results indicate that the γ-Al_2O_3 phase is doped with the base components. The change in the lattice period in this case will be determined, on the one hand, by the difference in the ionic radius of Al^{3+} ($r = 0.067$ nm) and the ionic radii of Cu^{2+} ($r = 0.087$ nm) and Zn^{2+} ($r = 0.086$ nm), and on the other hand, by the difference in valence and dissolved element concentration. Comparing the ionic radius of Al with the ionic radius of the cations of the additive, it can be concluded that the Cu and Zn cations should lead to an increase in the lattice period of the γ-Al_2O_3 phase. The addition of V cations practically does not change the lattice period.
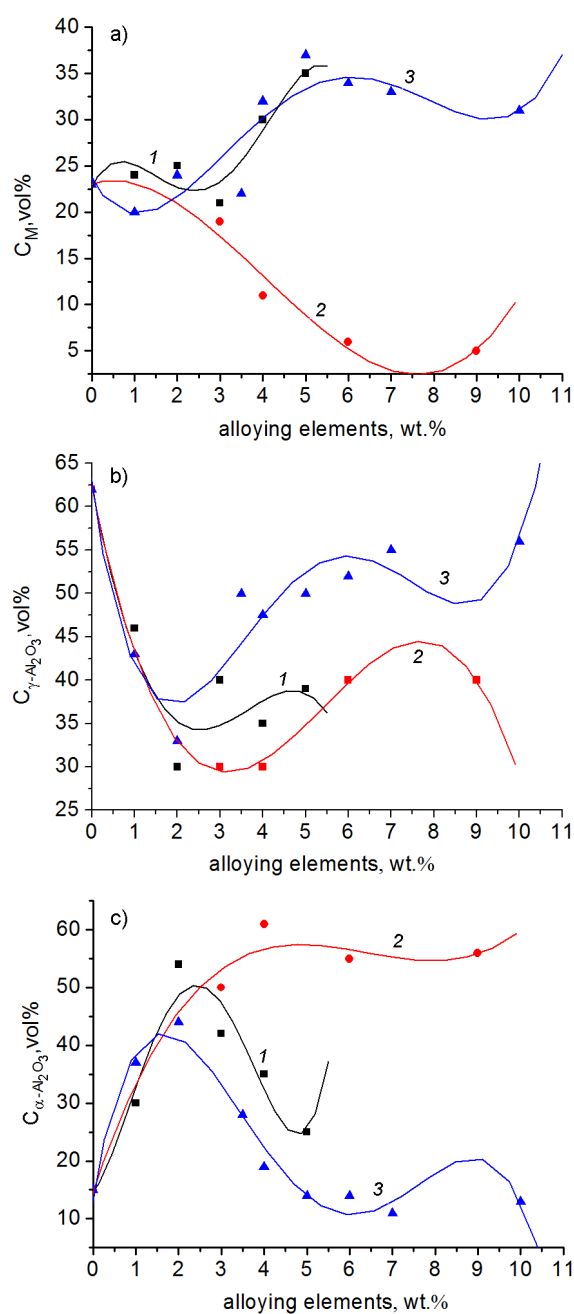
Fig. 4. Phase composition of MAO coatings: a — composition of mullite, b — composition of γ-Al₂O₃, c — composition of α-Al₂O₃. 1 — Al + V, 2 — Al + Cu, 3 — Al + Zn.

Fig. 5. Effect of aluminum doping on the γ-Al₂O₃ lattice period: 1 — Al + V, 2 — Al + Cu, 3 — Al + Zn.

Fig. 6. The concentration dependences of the hardness of the alloy after the MAO treatment: 1 — Al + V, 2 — Al + Cu, 3 — Al + Zn.

The most universal characteristic of physical and mechanical properties is hardness. Therefore, in the work, the identification of general patterns of structural engineering was based on a comparison of the revealed patterns of phase analysis with the hardness of the material. Corresponding dependences of hardness on the composition of alloys are shown in Fig. 6.
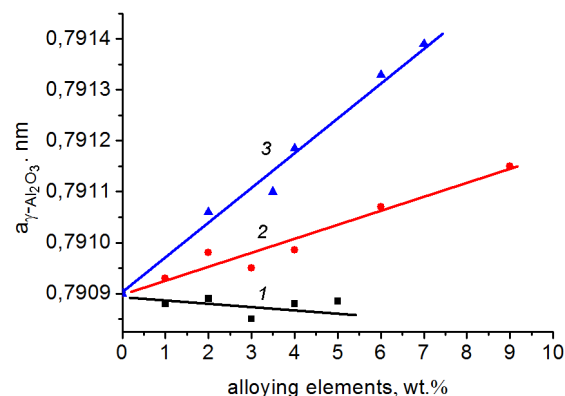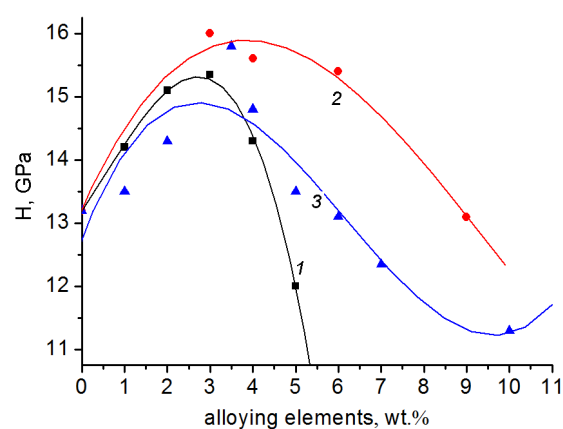
As can be seen from the data in Fig. 6, the maximum hardness in the case of Al + Cu alloy is ensured when the Cu content is in the range of 3–4 wt. %. In the case of Al + Zn and Al + V alloy, the maximum hardness is when the content of alloying elements is in the range of 2–3 wt.%.

The main effect of microdischarges (during the formation of the oxide layer) is thermal. This effect causes the thermolysis of chemical compounds, melting and remelting of the coating material, diffusion and redistribution of the elemental composition, phase formation, polymorphic phase transformations, etc. [21].

The conditions for the phase transitions of the low-temperature modification of γ-Al₂O₃ to high-temperature α-Al₂O₃ and the proportion of the phases in the resulting coatings are variable [17, 18]. The content of α-Al₂O₃

Table 2. Characteristics of added cations and properties of MAO coatings

Cations	Atomic radius	Ion radius	Concentration of additive, wt.%	Phase, %			Microhardness[*], GPa
				α	γ	m	
Al^{3+}	1.43	0.67	–	14	61	25	12.2
Cu^{2+}	1.28	0.87	3	50	30	20	16.0
			4	61	30	9	15.5
			6	55	40	5	15.4
			9	55	40	5	13.0
V^{5+}	1.34	0.68	1	30	47	23	14.2
			2	55	30	25	15.2
			3	40	40	20	15.4
			4	35	35	30	13.2
			5	25	40	35	12.0
Zn^{2+}	1.39	0.86	1	38	43	19	13.5
			2	44	32	24	14.2
			3.5	28	50	22	15.8
			4	19	48	33	14.7
			5	13	50	37	13.5
			6	14	52	34	13.0
			7	12	55	33	12.3
			10	15	55	30	10.3

[*]Hardness before MAO treatment did not exceed 0.3 GPa.

strongly depends on the conditions of the formation of coatings and cannot be predicted in advance.

Analysis of the results shows that the mechanism of formation of the phase composition should be associated with stabilization and destabilization of the γ-Al_2O_3 phase. The results indicate that Cu^{2+} cations contribute to destabilization of the γ-Al_2O_3 phase, while Zn^{2+} and V^{5+} cations stabilize the γ-Al_2O_3 phase (with a Zn and V content of more than 3 %).

Generalized data characteristics of added cations, phase composition and hardness of MAO coatings are shown in Table 2. Note that in the mechanism of the influence of additives on the formation of α-Al_2O_3 from γ-Al_2O_3, the adsorption of impurities on the surface of aluminum oxide particles significantly affects. At the same time, the determining factor is the regulation of the rates of nucleation and grain growth of new phases.

Ensuring high hardness and wear resistance of MAO coatings on aluminum alloys is associated with the need to ensure a high content of the α-Al_2O_3 phase (corundum). The results of this work indicate that doping with copper contributes to the formation of the α-Al_2O_3 phase in the coating. In the case of aluminum doping with zinc and

vanadium, an extreme dependence of the α-Al_2O_3 phase content on the concentration of zinc and vanadium is observed. The maximum content of the ,$E alpha-$Al_2O_3$ phase corresponds to 2 wt.% Zn and 2 wt.% V.

These results can be explained if we proceed from the fact that, at the initial stage of oxidation, the γ-Al_2O_3 phase is mainly formed, and the α-Al_2O_3 phase appears in subsequent periods (as a result, the power of microdischarges and temperature increases [21]). This defines two stages of the process. At the first stage, the formation of aluminum oxide occurs as a topochemical reaction, and at the second stage, as a solid-phase polymorphic transformation of γ-Al_2O_3 to α-Al_2O_3.

Naturally, if there are silicates in the electrolyte, then the silica formed from them can form aluminosilicates when heated with Al_2O_3 (in our case, mullite — $3Al_2O_3 \cdot 2SiO_2$).

4. Conclusions

The method of microarc oxidation of technically pure aluminum and aluminum doped with copper, vanadium and zinc (in an alkali silicate electrolyte at a current density of ~ 20 A/dm^2) was obtained coatings with a thickness of about 100 μm.

Data of X-ray structural analysis of the base layer (about $60-70$ μm thick) of the coatings indicate the crystalline structure of the coatings. The phase composition of the coatings includes aluminum oxides α-Al_2O_3 (corundum) and γ-Al_2O_3, as well as mullite ($3Al_2O_3 \cdot 2SiO_2$), which provide high hardness (HV > 10 GPa) of the surface layer.

The nonmonotonic dependence of the phase composition and hardness on the doping level of aluminum (Al + Cu, Al + Zn, and Al + V systems) was revealed.

It was established that the degree of influence of alloying elements on the transformation process of γ-$Al_2O_3 \rightarrow \alpha$-$Al_2O_3$ is determined by their crystal-chemical characteristics (charge, ionic radius).

An explanation of the phase formation processes of coatings during MAO — treatment in an alkaline — silicate electrolyte is proposed. For practical use, you should choose those alloying elements that affect the destabilization of γ-Al_2O_3, which ensures the formation of the α-Al_2O_3 phase (corundum).

In explaining the mechanism of the effect of additives on phase transformations occurring during the formation of MAO coatings, it was proposed to proceed from the topochemical mechanism of transformation associated with the formation of nuclei of new phases on the surface of particles caused by adsorption of impurities on the surface of aluminum oxide particles.

An explanation of the effects observed in the work based on two stages of the process has been proposed. At the first stage, the formation of aluminum oxide occurs as a topochemical reaction, and at the second stage, as a solid-phase polymorphic transformation of γ-Al_2O_3 to α-Al_2O_3.

It is shown that high hardness of coatings on aluminum alloys is provided with a copper content in the range of 3–4 wt.%, and zinc and vanadium in the range of 2 to 3 wt.%.

On the basis of the obtained results, it is shown that, in order to ensure maximum hardness of coatings, it is necessary for each type of aluminum alloys to conduct preliminary phase — structural studies (structural engineering), allowing to optimize the technological modes of microarc processing.

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