

New features of surface modification of magnesium alloys by microarc oxidation (MAO)

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The work investigates the features of forming MAO coatings on magnesium alloys. It is shown that due to the choice of electrolysis conditions (electrolyte composition, current density and oxidation time) the process of microarc oxidation in the microarc discharge mode is stably implemented. It has been established that as a result of MAO treatment, ceramic coatings containing phases of magnesium oxide MgO , spinel $MgAl_2O_4$, Mg_2SiO_4 and $Mg_3(PO_4)_2$ are formed. The phase composition of the coatings is determined by the composition of the electrolyte. The electrolysis conditions studied in this work provide high hardness of the coatings, reaching 7500 MPa, as well as high corrosion resistance. The obtained results allow us to recommend MAO coatings obtained on magnesium alloys both as an outer (functional) layer with high adhesion to the substrate and as a sublayer for the subsequent application of protective coatings (varnishes, polymers, in particular polytetrafluoroethylene).

Keywords: microarc oxidation, magnesium alloys, electrolytes, phase composition, hardness, adhesion, corrosion resistance.

Нові особливості модифікування поверхні магнієвих сплавів методом мікродугового оксидування (МДО), О.В. Субботін, В.В. Білозаров, В.В. Субботіна, С.А. Князєв, О.О. Волков, О. І. Лазорко

У статті досліджено особливості формування МДО-покриттів на магнієвих сплавах. Показано, що шляхом підбора умов електролізу (склад електроліту, щільність струму, час оксидування) стійко реалізується процес мікродугового оксидування в режимі мікродугових розрядів. Встановлено, що в результаті МДО-обробки формуються керамічні покриття, що містять такі фази, як оксид магнію MgO , шпінель $MgAl_2O_4$, сполуки Mg_2SiO_4 і $Mg_3(PO_4)_2$. Фазовий склад покриттів визначається складом електроліту. Досліджені в роботі умови електролізу забезпечують високу твердість покриттів, яка досягає до 7500 МПа, а також високу корозійну стійкість. Отримані результати дозволяють рекомендувати МДО-покриття, отримані на магнієвих сплавах, як у якості зовнішнього (функціонального) шару з високою адгезією з основою, так і в якості підшару для наступного нанесення захисних покриттів (лаків, полімерів, зокрема політетрафторетилену).

1. Introduction

Magnesium alloys are becoming more and more common in the national economy as a structural material. They are used due to their high strength ($\sigma_v = 25-30 \text{ kg/mm}^2$), good machinability and, especially, low density ($\rho = 1.7 \text{ g/cm}^3$). Magnesium alloys also have an important ability to dampen the energy of impact and vibrations. The main problem that

significantly limits the widespread use of magnesium-based alloys is their high chemical activity [1-6] and, as a result, low resistance to corrosion damage. The problem is solved by forming protective coatings on the surface of alloys using various methods, one of which is the microarc oxidation method [7, 8].

Studies [9, 10] have shown that micro-arc oxide coatings formed on magnesium alloys

consist mainly of magnesium oxide and hydroxide and have different thicknesses and significant porosity. The formation of dense coatings can be facilitated by additives to the electrolytes used in the microarc process. Therefore, numerous electrolytes used differ in composition, which makes it possible to increase the hardness of coatings, reduce their porosity and improve other properties [11-15].

It should be noted that today there are no uniform approaches and principles to the selection of the electrolyte composition and the oxidation regime. In each case, they are selected empirically. Therefore, a very important task is to study the kinetics and mechanism of formation of MAO coatings on Mg and its alloys, as well as the effect of the chemical composition and structure of the magnesium alloy on the structure and properties of MAO coatings for different types of electrolytes. This would increase the efficiency of MAO treatment and expand the range of alloys to be treated [16, 17].

2. Experimental

The study was carried out on samples of magnesium alloys AZ91 and MA60V, obtained by cold rolling, with dimensions of 70 x 30 x 5 mm. AZ91 alloy is a cast magnesium alloy that is widely used in aircraft engines and helicopter industries due to a set of valuable properties – low density $\rho = 1.8\text{--}1.9\text{ g/cm}^3$, high specific strength, and the ability to absorb impact energy and vibration oscillations. MA60V alloy is a wrought magnesium alloy used in aviation, rocketry, automotive and electronics industries. The chemical compositions of the alloys are shown in Table 1.

The surface modification of magnesium alloys was carried out as follows. Oxidation was carried out in the anode-cathode mode on equipment with capacitor-type power supply; the processing time was up to 60 minutes, the current density was 20-40 A/dm². Electrolytes based on aqueous alkali solutions (NaOH and KOH) and liquid glass Na₂SiO₃ were used; sodium aluminate (NaAlO₂), hydrogen peroxide H₂O₂, and sodium hexamethosphosphate (NaPO₃)₆ were used as additional reagents.

The presence of phases, their identification, and determination of the relative content of phases was carried out on an X-ray diffractometer DRON-3 with Bragg-Brentano focusing in K α -Cu radiation [18]; for qualitative phase analysis, the ASTM (American Society for Testing Materials) card index was used [19]. The phase content was determined by quantitative X-ray diffraction analysis using a previously constructed calibration curve based on the data of the standard mixtures.

The microhardness of the coatings was measured at room temperature using the PMT-3 device according to the standard method [20] using a diamond indenter in the form of a tetrahedral pyramid with angles at the apex between opposite faces of 136°. The thickness of the coatings was measured using a vortex thickness gauge VT-10NC; the metallographic method of measuring the thickness of the coating on transverse sections was also used. The protective properties of coatings were determined by the droplet method in salt fog in accordance with GOST 9.302-88 [21].

3. Results and discussion

As the main electrolyte, aqueous solutions of KOH (or NaOH) and liquid glass Na₂SiO₃ with a module of 3 were used, which do not contain harmful substances. This choice was based on repeated researches of magnesium alloys of various compositions during MAO treatment [13, 14]. In [13, 14], microarc oxidation was proposed to be carried out in silicate-alkaline electrolytes in the anode-cathode mode. The content of liquid glass (sodium silicate) and potassium hydroxide (KOH) in the electrolyte was varied. However, it was found that during such treatment, a sharp drop in anode voltage may occur, accompanied by attenuation of the microarc discharge and etching of the formed oxide layer. Thus, such modes become unsuitable for practical implementation.

We have found that treatment in an aqueous silicate solution (Na₂SiO₃ – liquid glass) transfers the MAO process immediately to the high-power arc discharge mode, which leads to surface melting and the formation of large craters. It was found that in an alkaline electrolyte (aqueous solution of KOH or NaOH) it is not possible to organize a microarc process on the surface of a magnesium alloy. This is due to the fact that a dielectric barrier layer is not formed on the treated surface due to the lack of interaction of magnesium with alkali [13]. The MDM process in the microarc discharge mode is implemented in multicomponent electrolytes containing alkali (KOH or NaOH), sodium silicate Na₂SiO₃, sodium aluminate NaAlO₂, and sodium hexametaphosphate (NaPO₃)₆.

Table 1 – Chemical composition of the researched alloys

Alloy	Main components, %			
	Mg	Al	Mn	Zn
AZ91	90	9.0	0.3	0.7
MA60B	93.6	6.0	0.4	-

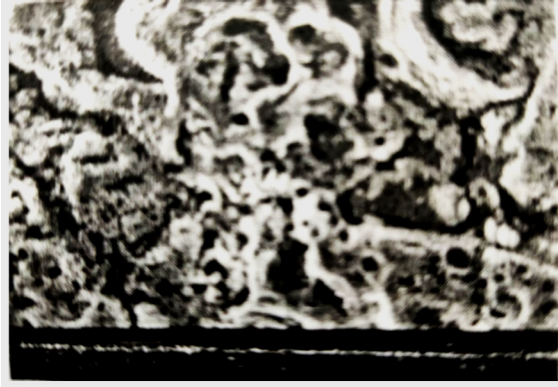


Fig. 1. SEM image of MAO surface as received (x 1000)

When choosing the composition of the electrolytes, preliminary studies were carried out on the initial process of ignition of the spark discharge, which largely depends on the composition of the electrolyte. Thus, at a concentration of 1 g/l of KOH without liquid glass in the electrolyte at a current density of 20 A/dm², small and weak discharges occur on the metal surface, and no coating is formed. When 1 g/l of liquid glass is added to the previous electrolyte composition, blue discharges are ignited on the metal surface, indicating intense emission of magnesium ions and OH radicals. After a certain time, green sparks appear in the discharges (emission of magnesium atoms and ions). In this case, the coating is formed unevenly and rough as a result of spark breakdowns and dissolution of the substrate metal and, ultimately, often peels off. At a concentration of liquid glass of 2 g/l and KOH of 2-3 g/l, i.e. when using an alkaline-silicate electrolyte of different composition, the discharge glow is bright and the microarc process lasts up to 5 hours. Thus, observ-

ing the color of discharges, their size and glow, the electrolyte compositions were selected.

In this work, it was found that the alkaline-silicate electrolyte forms a coating with high surface porosity (Fig. 1, scanning microscope image). Corrosion tests revealed crevice corrosion between the substrate and the MAO coating (Fig. 2). A reduction in porosity can be achieved by increasing the specific volume of the coating relative to the substrate.

Table 2 shows the compositions of electrolytes that can form coatings up to 300 μm thick in the microarc discharge mode at a current density of 20 A/dm².

Micro-arc oxidation made it possible to transform the surface layer of the products into ceramic coatings consisting of crystalline oxides and spinels. The X-ray phase analysis showed (Fig. 3) that the main phases of the coating are MgO, MgAl₂O₄, Mg₂SiO₄ and Mg₃(PO₄)₂; the quantitative ratio between the phases is determined by the composition of the electrolyte and the electrolysis parameters (processing time and current density).

It has been determined that in electrolytes (No.1, 2, 6, 7, 9) containing Na₂SiO₃, the phases MgO and Mg₂SiO₄ are found in the composition of coatings (Table 2). In electrolytes (No.1, 3, 4, 5, 8, 9) with sodium aluminate NaAlO₂, the coatings containing the MgO and MgAl₂O₄ phases are formed. The main phase is MgO. Addition of (NaPO₃)₆ in an amount of 3 g/l to the electrolyte leads to a three-phase state of the coatings (Table 2). Addition of the 4th component (NaF) to the 5th type of electrolyte leads to an increase in the relative content of MgAl₂O₄ and Mg₃(PO₄)₂.

The use of a high content of liquid glass in the 6th and 7th types of electrolytes is accompanied by the appearance of a halo-like compo-

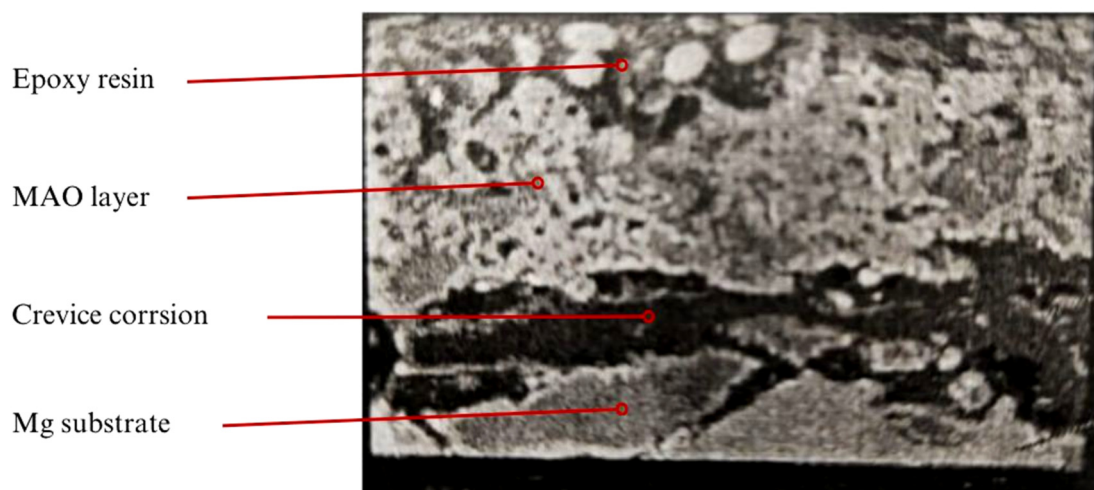


Fig. 2. Sem MAO cross-section (x 1000)

Table 2 – Phase composition of MAO coatings on magnesium alloys obtained in different electrolytes

No	Electrolyte	Phase composition of the coating
1	alkali-silicate 2 g/l KOH + 12 g/l Na ₂ SiO ₃	MgO + Mg ₂ SiO ₄
2	alkali-silicate g/l Na ₂ SiO ₃ + 2g/l H ₂ O ₂	MgO + Mg ₂ SiO ₄
3	alkaline-aluminate-phosphate 2,5 g/l NaOH + 3 g/l NaAlO ₂ + 1 g/l (NaPO ₃) ₆	MgO + MgAl ₂ O ₄
4	alkaline-aluminate-phosphate 2,5 g/l NaOH + 3 g/l NaAlO ₂ + 3 g/l (NaPO ₃) ₆	MgO + MgAl ₂ O ₄ + Mg ₃ (PPO ₄) ₂
5	alkaline-aluminate-phosphate + NaF 2,5 g/l NaOH + 3 g/l NaAlO ₂ + 3 g/l (NaPO ₃) ₆ + 1,5 g/l NaF	MgO + MgAl ₂ O ₄ + Mg ₃ (PO ₄) ₂
6	silicate + NaF 50 g/l Na ₂ SiO ₃ + 1,5 g/l NaF	Halo + MgO + Mg ₂ SiO ₄
7	silicate + NaF 110 g/l Na ₂ SiO ₃ + 1,5 g/l NaF	Halo + α-SiO ₂ + MgO + Mg ₂ SiO ₄
8	alkali-silicate– aluminate 6 g/l KOH + 5 g/l Na ₂ SiO ₃ + 3 g/l NaAlO ₂	MgO + MgAl ₂ O ₄ + Mg ₂ SiO ₄
9	alkaline-aluminate 2,5 g/l NaOH + 3 g/l NaAlO ₂	MgO + MgAl ₂ O ₄

ment in the diffraction spectra. This is due to the formation of a finely dispersed phase under the influence of silicon [13]. For these types of electrolytes, α-SiO₂ and Mg₂SiO₄ are found as accompanying phases.

The surface of the coatings is heterogeneous, with the presence of discontinuities. This type of surface is typical for magnesium alloy MAO coatings formed with all types of electrolytes used. When the thickness of the coatings is more than 50 μm, microcracks are found on their surface. The appearance of the microcracks can be caused by the presence of tensile stresses due to the fact that the specific volume of the coating is smaller than that of the substrate.

It should also be noted that the surface morphology of the coatings allows the use of MAO coatings as a sublayer for additional improvement of corrosion resistance by applying other protective coatings.

Thus, the developed surface and relatively high hardness (Table 3) make it possible to use MAO coatings both as an outer (functional) layer and as a sublayer for further improving corrosion resistance by applying other protective coatings (varnishes, paints, polymers, etc.), while ensuring good adhesion. Analyzing the results obtained, we can conclude that by se-

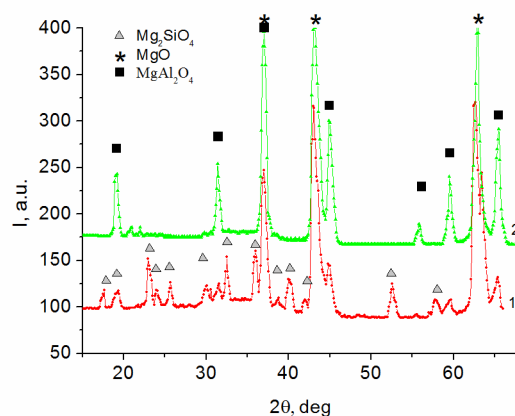


Fig. 3. Diffraction pattern fragments of MAO coatings (Kα-Cu radiation). 1 – electrolyte No.8 (6 g/l KOH + 5 g/l Na₂SiO₃ + 3 g/l NaAlO₂), 2 – electrolyte No.9 (2,5 g/l NaOH + 3 g/l NaAlO₂)

lecting the appropriate electrolyte composition, it is possible to increase the growth rate of MAO coatings on magnesium alloys from 25 μm/h to 190 μm/h, which makes it efficient to form coatings with a thickness of 200-300 μm.

The most universal method of testing the mechanical properties of a surface is to measure its hardness. The hardness of MAO coatings (obtained in different electrolytes) on magnesium alloys is shown in Table 3.

Table 3 Effect of oxidation parameters on the thickness and hardness of MAO coatings

No	Electrolyte	The duration of the process, τ , min	h, μm	Hardness HV, MPa
1	2 g/l KOH + 12 g/l Na_2SiO_3	30	55	1200
			60	1250
		60	90	1600
			95	1500
2	3 g/l Na_2SiO_3 + 2g/l H_2O_2	30	110	2700
			110	2500
		60	160	2950
			155	2900
3	2,5 g/l NaOH + 3 g/l NaAlO_2 + 1 g/l $(\text{NaPO}_3)_6$	30	40	2000
			45	2100
		60	60	2800
			65	2900
4	2,5 g/l NaOH + 3 g/l NaAlO_2 + 3 g/l $(\text{NaPO}_3)_6$	20	40	1700
			45	1800
		30	80	1650
			85	1600
		60	110	1800
			110	1850
5	2,5 g/l NaOH + 3 g/l NaAlO_2 + 3 g/l $(\text{NaPO}_3)_6$ + 1,5 g/l NaF	30	25	3400
			25	3500
		60	190	7400
			185	7500
6	50 g/l Na_2SiO_3 + 1,5 g/l NaF	30	60	2300
			55	2350
7	110 g/l Na_2SiO_3 + 1,5 g/l NaF	60	60	3000
			65	3400
8	6 g/l KOH + 5 g/l Na_2SiO_3 + 3 g/l NaAlO_2	60	65	3800
			60	4200
9	2,5 g/l NaOH + 3 g/l NaAlO_2	60	50	5500
			55	600

P.S.: numerator – coating on MA60V alloy, denominator – AZ91

As can be seen from the presented results, the coatings obtained in the 5th type of electrolytes (KOH + Na_2SiO_3) are characterized by a rather high growth rate, but the hardness of such coatings does not exceed 1600 MPa. The addition of H_2O_2 (electrolyte No.2) stimulates an increase in the content of Mg_2SiO_4 . This leads to an increase in hardness up to 2800 MPa. The hardness of the coating obtained in the 3rd type of electrolytes is approximately at the same level, although the phase composition in this case is different (MgO + MgAl_2O_4). For the coatings obtained in the 4th type of electrolytes, a significant increase in the build-up rate (Table 3) did not lead to higher hardness (the highest hardness is 1800 MPa).

The highest hardness was achieved in the coatings obtained in the 5th type of electrolytes. These coatings have a higher content of the MgAl_2O_4 phase and $\text{Mg}_3(\text{PO}_4)_2$ crystallites. It should be noted that the obtained hardness of the coatings (7500 MPa) is almost 13 times higher than the hardness of the alloy base material (600 MPa). The silicide components in the 6th and 7th types of electrolytes lead to a multiphase crystal composition (Table 2), and the hardness of such coatings does not exceed 3300 MPa.

Thus, MAO treatment of magnesium alloy ensures the formation of coatings with a hardness 3–13 times higher than the hardness of the substrate (HV = 600 MPa).

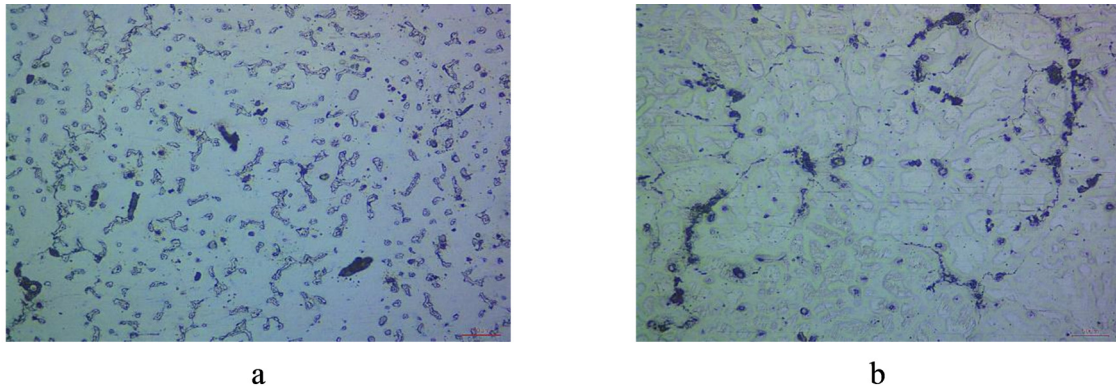


Fig. 4. Microstructure of magnesium alloys a – AZ91(x 200), b – MA60B (x 200)

Microplasma treatment also ensures high adhesion of the coating to the substrate. This is evidenced by adhesion tests by tearing the tape off the coating after its transverse cut with a step of 1 mm [18]. The results showed that in no case, both in the initial state and after immersion in water for 240 hours, not a single area (1x1 mm) was cleaned.

To determine the corrosion resistance of the coatings, a droplet method was used; a NaCl solution containing phenolphthalein was used as a reagent. The research showed that the coatings obtained in the 5th type of electrolytes showed the highest resistance (Table 2). Also, the coatings obtained in the 6th and 7th types of electrolytes showed great stability. For the 1st, 2nd and 3rd types of electrolytes, the coating resistance is lower, which can be attributed to the defectiveness of the coatings (the presence of through pores and cracks, which is a consequence of the lower specific volume of the coating compared to the substrate). Such coatings are subjected to tensile stresses, which increases its defectiveness and reduces corrosion resistance.

Analysis of the results showed that the protective properties of the coating depend on its phase composition. Thus, the presence of $MgAl_2O_4$ spinel in the coating along with MgO increases the protective properties of the coating. This result can be explained by the fact that the presence of spinel in the coating increases the specific volume of the coating relative to the substrate (the ratio of the specific volume of MgO and the volume of $MgAl_2O_4$ spinel to the volume of Mg is 0.79 and 2.83, respectively). An increase in the specific volume of the coating relative to the substrate causes the occurrence of compressive stresses in the coating and, as a result, contributes to the formation of more continuous oxide films.

The research also included a salt spray corrosion test, which consisted in measuring the maximum corrosion width along the X-shaped

cut line on the sample coating. The corrosion cycle included irrigation (1 hour) and drying (1 hour) for 2 months. The following conditions were used: salt solution 5 wt. % NaCl (0.5 wt. % water); temperature in the treatment area of 50°C; pH from 6.5 to 7.2.

The results showed that in the case of the AZ91 cast alloy (Mg–9%Al–0.7%Zn–0.3%Mn), no signs of corrosion were detected under specified electrolysis conditions (corrosion width < 0.5 mm), while for the MA60V alloy the corrosion width reaches > 1 mm).

Thus, the corrosion resistance of the coatings on the alloy AZ91 is higher than that of MA60V. This fact can be explained by the different aluminum content and distribution of the Al_3Mg_2 phase in the alloys (Fig. 4). The microstructure of magnesium alloys should influence the formation of the oxide phases of the coating.

High corrosion properties of coatings on magnesium alloys can be obtained by increasing the spinel content during MAO treatment, which is achieved by increasing the aluminum content in the alloy or in the electrolyte.

4. Conclusions

1. The use of multicomponent electrolytes allows for a stable implementation of the microarc oxidation process in the microarc discharge mode and ensures a growth rate of MAO coatings of 50-200 $\mu\text{m/h}$;

2. It has been established that as a result of MAO treatment, ceramic coatings are formed containing the following crystalline phases: magnesium oxide MgO, spinel $MgAl_2O_4$, and Mg_2SiO_4 and $Mg_3(PO_4)_2$ compounds. The phase composition of the coatings is determined by the composition of the electrolyte;

3. The electrolysis conditions used in the work provide high hardness of the coatings of 1500-7300 MPa, which is 3-13 times higher than the hardness of the base (600 MPa), as

well as high corrosion resistance, which exceeds the standard.

4. The presence of MgAl_2O_4 and $\text{Mg}_3(\text{PO}_4)_2$ phases along with MgO increases the protective properties of the coating by increasing its specific volume.

5. The obtained results showed that modification of the surface of magnesium alloys by MAO method allows obtaining coatings that can be used both as an outer (functional) layer with high adhesion to the substrate and as a sublayer for the subsequent application of protective coatings (varnishes, polymers, in particular polytetrafluoroethylene).

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