Studies of the mechanism of adhesion of polymer coatings on the oxidized surface of aluminum and magnesium alloys

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Abstract

The mechanism of adhesion of styrene-acrylic polymer on the oxidized surface of aluminum alloy AMg3 and magnesium alloy MA20 is investigated. It is shown that the adhesion of the polymer coating to the chemically oxidized surface of the aluminum alloy is much higher than to the anodic film on the magnesium alloy. The relationship between the adhesive strength of the substrate and the concentration of hydroxyl ions capable of participating in condensation reactions in it has been established. To explain the observed patterns, the chemical composition and morphology of the alloys were studied using photoelectron XPS spectroscopy and EMS analysis. Methods of modification of conversion coatings on magnesium and aluminum alloys with ethylene glycol, which significantly improve the adhesion of polymer layers to them, are proposed. It has been established that ethylene glycol actively interacts with ions of these alloys to form macromolecules of magnesium and aluminum ethylene glycolate embedded in the hydroxide lattice of the conversion coating. These coatings contain a significant amount of hydroxyl ions involved in the formation of chemical bonds. Mechanical and electrochemical tests of the modified coatings were carried out in order to optimize the compositions and modes of their formation.

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Introduction

Aluminum and magnesium alloys are widely used as structural materials in aviation, electronics, automotive and other industries due to their low density and high strength. The disadvantage of these alloys is their low corrosion resistance in aqueous electrolytes, which limits their use without special preparation. To protect aluminum and magnesium alloys from corrosion, paint and varnish materials are usually used, which are applied on hydroxide conversion coatings, which have a porous structure providing strong mechanical adhesion to the substrate [1–7]. At the same time, the increase in adhesion force is due to the chemical interaction of surface metal hydroxides with the components of the paint coatin [8–11]. Most paints contain monomers with the general formula R–OH and R–COOH, where R stands for aliphatic or cyclic hydrocarbon radicals. In this case, the chemical interaction between the paint and the metal occurs as a result of a condensation reaction, which can be represented in the form of Equations:

$$Me-OH+R-OH=Me-OR+H_2O \quad (1)$$

$$Me-OH+R-COOH=MeCOR+H_2O \quad (2)$$

Thus, in order for the paint to form chemical bonds with the conversion coating, chemically active hydroxyl groups of atoms must be present in its composition. Most studies on modifying conversion coatings are aimed at changing their structure rather than their chemical composition, assuming that the main factor that increases adhesion is the mechanical bonding of the paint to the pore walls [12–14]. However, the rapid development of technologies based on the use of organosilane primers indicates the significant role of chemical interaction in the formation of strong bonds between coating materials and metal surfaces [15, 16]. Conversion coatings on aluminum and magnesium alloys are formed in alkaline or acidic electrolytes and consist mainly of metal oxides and hydroxides [17, 18]. Only metal hydroxides are involved in the formation of chemical bonds by the mechanism of hydrolytic condensation, so the adhesion strength should depend on the MeO/MeOH ratio in the conversion coating. In this work, the chemical composition of anodized layers on aluminum and magnesium alloys will be investigated by XPS methods and the barrier properties by electrochemical impedance spectroscopy EIS. The impregnation of the coatings was carried out with Lakroten E-244 styrene-acrylic dispersion. The copolymer of this dispersion is acrylic acid, which can interact with metal hydroxides by reaction 2. The modified composite coatings were obtained by introducing ethylene glycol into the oxidation electrolytes, followed by analysis of the chemical composition and thickness of the coatings.

Experimental

Materials

Samples from aluminum and magnesium alloys were used in the work, the composition of which is presented in Table 1.

The following substances were used to compose inhibitory compositions:

– styrene-acrylic dispersion Lakroten E-244 (Chemservice Russia);
– Ethylene glycol (EG), HO-CH_2-CH_2-OH (RusHim);
– Super adhesive glue EDP (NPK Astat).

Table 1. Compositions of AMg3 aluminum alloy and MA20 magnesium alloy according to GOST 14957-76 and GOST 4784-97.

	Mass fraction of elements, %							
Alloy	**Fe**	**Cu**	**Mn**	**Mg**	**Cr**	**Zn**	**Ce**	**Al**
AMg3	0.5	0.1	0.3–0.6	3.2–3.8	0.05	0.2	–	93.8–96
MA20	0.05	0.03	0.04	97.9–98.8	–	1.5	0.02	0.2

Specimen Preparation

Specimens of AMg3 aluminum alloy were sandpapered with papers of different grades, degreased in ethanol, etched in 10% NaOH solution for 1 min (at t = 65–67°C), washed in hot distilled water, refined in 50% HNO3 solution, washed once more, and dried. Upon exposure in a desiccator over calcium chloride for a day, the specimens were weighed with analytical balances (±0.0001 g) and immersed in IFKhANAL-3 conversion solutions for 60 min at t = 80°C. After oxidation, the specimen was taken away from the solution, washed by distilled water, dried in air at room temperature for no less than 12 h, and weighed.

The thickness of the conversion coating was estimated from the weight loss upon 30 min of etching in a conventional chromate–phosphate solution (20 g/L CrO_3 + 50 g/L H_3PO_4 at t = 80°C) taking into account the correction for the weight loss of the reference specimen. Then, the specimen was washed in distilled water, dried, and, in a day, weighed. The thickness of the conversion coating (μm) was calculated by the Formula:

$$h = \frac{m_0 - m_c}{S_s \cdot \rho} \cdot 10^7 \qquad (3)$$

where m_0 is the weight (g) of the specimen covered with the conversion coating, m_c is the weight (g) of the specimens upon removing the conversion coating, ρ is the boehmite density (g/cm^3), and S_s is the surface area (cm^2) of the conversion coating on the specimen.

Anodized coatings on MA20 magnesium alloy samples were formed under direct current. The effective density of anodic currents was 2.5 A/dm^2 during 30 min at t = 20–23°C. After oxidation, samples with coatings were washed by distilled water, and dried in air. The thickness of the formed coatings was determined with the use of a PosiTector 6000 (NS) thickness measuring device (USA).

The compositions of the oxidation electrolytes for AMg3 aluminum alloy and MA20 magnesium alloy are shown in Table 2.

Table 2. Compositions of oxidation electrolytes of AMg3 aluminum alloy and MA20 magnesium alloy.

Alloy	**Conversion Coating**	**Modified conversion coating**
AMg3	IFKhANAL-3 (pH 12)	IFKhANAL-3 (pH 12), 50 g/l EG
MA20	NaOH, Na_2HPO_4, $Al(NO_3)_3$	NaOH, Na_2HPO_4, $Al(NO_3)_3$, 50 g/l EG

Adhesion measurement

The coating adhesion test during separation was carried out using an electronic adhesion meter PSP-MP4 (Russia), shown in Figure 1. Samples with conversion coating were placed in a fixed holder. Super glue was applied to the surface of an aluminum rod with a diameter of 10 mm and then brought into contact with the test samples. After curing the glue, the joint was stretched at a constant speed of 5 mm/min. For each test, five repeating samples with the specified mean value were used.

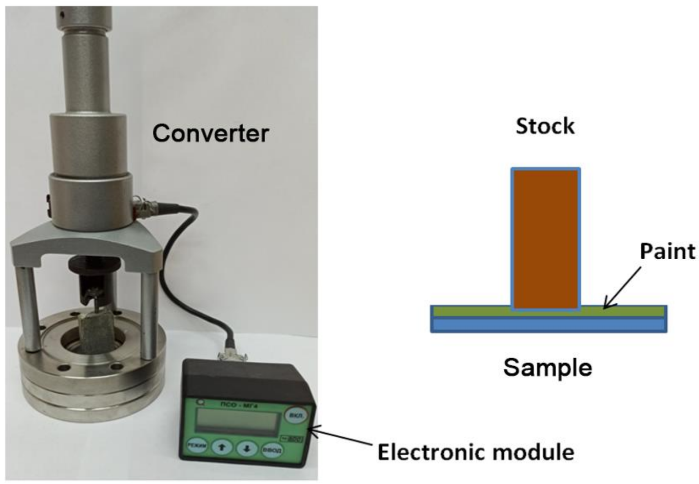


Figure 1. Electronic adhesion meter: PSO-MG4g.

X-Ray photoelectron spectroscopy (XPS) study

X-Ray photoelectron spectra (XPS) were recorded using the Omicron+ X-ray photoelectron spectrometer (Germany). The pressure in the analyzer chamber did not exceed 10^{-8} Torr. The radiation of an X-ray Al-anode (radiation energy 1486.6 eV, power 200 W) was used as a source. The transmission energy of the analyzer is set to 20 eV. The binding energy of the electrons was calibrated according to the XPS peak of C1s electrons, the binding energy of which was assumed to be 285.0 eV and which is due to the settled layers of diffusion oil vapor. Photoionization cross sections of the corresponding electron shells taken from [19] were used for quantitative evaluation. The integral peak intensities were obtained after subtracting the background using the Shirley method [20] and by fitting the observed peaks with Gauss curves with the contribution of the Lorentz component. To obtain information about the thicknesses of the layers formed on the surface, the MultiQuant program was used [21], the photoionization sections of the corresponding electron shells given by Schofield [22] were selected. To calculate the thicknesses of the layers, the values of electron free path lengths (or average attenuation coefficients) calculated by the method proposed by Kampson and Sih were used [22].

SEM study

SEM images were obtained by a JSM-6400 scanning microscope with an electron beam intensity of 20 keV, unless stated otherwise. Analysis of the elements was performed with SEM equipped with energy-dispersive X-ray analysis (EDX) with a WinEDS EUMEX analyzer (Germany). The thickness of the polymer siloxane coatings was determined using the ZAF correction algorithm for K_a ratios for samples with a known coating thickness.

Results and Discussion

The adhesion of coating materials to metal surfaces depends mainly on the chemical composition of the surface, the thickness and porosity of the adhesion layer. The thickness and porosity of conversion coatings for aluminum and magnesium alloys differ to a lesser extent than the chemical composition. Anodic coatings on AZ91D magnesium alloy contain mainly MgO, Al_2O_3 and $MgAl_2O_4$ [23, 24]. The adhesion of the paint to such a surface should depend on the thickness and porosity of the conversion coating, since the chemical interaction is minimized. The addition of reagents to anodizing electrolytes that are susceptible to hydrolysis increases the hydroxide ion content of the conversion coating and thus, according to Equation (1, 2), the adhesion of the coating to the alloy surface. Since the adhesive strength of the coating depends on the chemical composition of the substrate, XPS studies of conversion coatings were carried out.

XPS and SEM investigation of the chemical composition of the conversion coating on MA20 alloy

Samples after magnesium oxidation were thoroughly washed in running water and distilled water. They were then ultrasonically cleaned in double distilled water until the electrolyte residues were completely removed. The purity of the cleaning was assessed by the presence of sodium ions in the XPS spectra. The elemental composition of the conversion coating obtained by anodizing the MA20 alloy in an alkaline solution is shown in Table 3.

Table 3. The elemental composition of the conversion coating on the MA20 alloy.

Alloy	Mg, at.%	Al, at.%	C, at.%	O, at.%	Thickness, μm
MA20	30.3	8.4	19.2	42.1	23.0±5.0

From the results of the chemical analysis given in Table 3, it can be seen that the composition of the conversion coating includes significant amounts of aluminum compounds that fall into the coating from the substrate during oxidation. Figure 2 shows the XPS spectra of Mg2p and Al2p in the conversion coating.

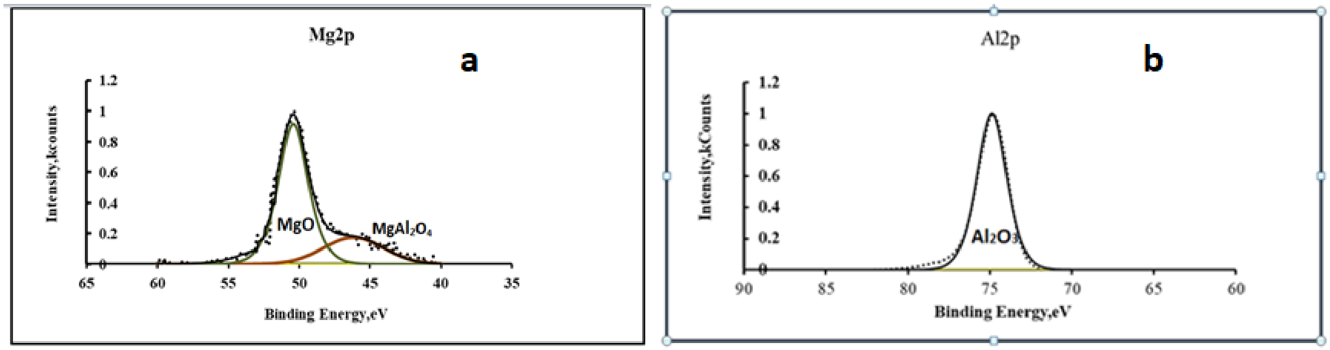


Figure 2. XPS spectra of Mg2p (a) and C1s (b) in the MA20 conversion coating.

After decomposition of the spectra into components, it is seen that the conversion coating consists mainly of magnesium and aluminum oxides. A study of the adhesion of acrylic paint on anodized magnesium alloy surfaces showed extremely low adhesion strength. To increase the adhesive strength of aluminium and magnesium alloys, it is often recommended to hydroxylate the surface by treatment in alkaline solutions. It is possible to increase the concentration of adhesively active R–OH radicals in the conversion coating by adding polyfunctional alcohols to the anodizing electrolytes. In the articles [25, 26], studies were carried out on the anodizing of magnesium alloys in aqueous solutions of ethylene glycol and glycerin. The authors of these works found that the conversion coatings obtained in these solutions are formed at sufficiently high speeds, have a porous structure, have high hardness and wear resistance. However, studies of the chemical composition and adhesive strength were not carried out in these works. Morphology and chemical composition of the magnesium layers obtained with ethylene glycol additives in anodizing solutions were studied. Figure 3 shows SEM images of the surface of the anodized alloy before and after modification with ethylene glycol.

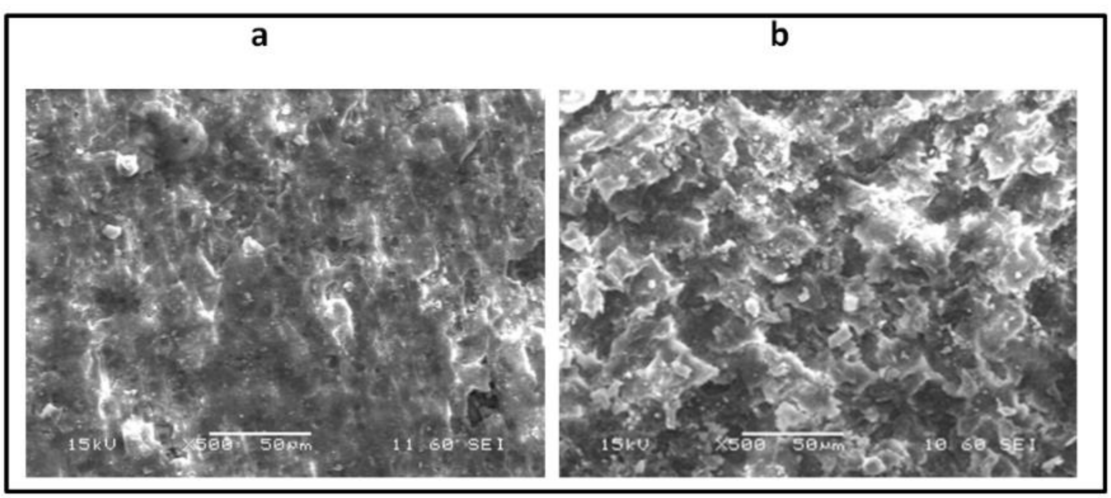


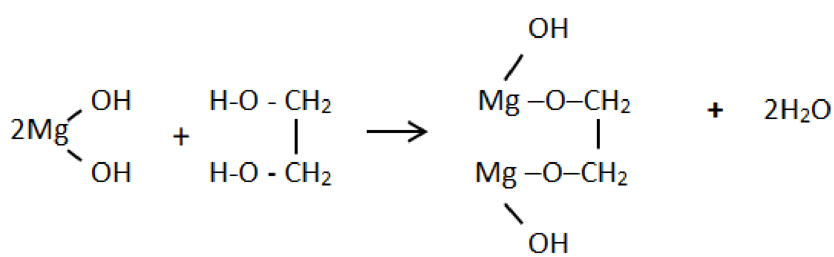
Figure 3. SEM images of the surface of the MA20 anodized alloy before (a) and after (b) modification with ethylene glycol.

The addition of ethylene glycol to the electrolyte leads to an increase in the roughness and thickness of the coating. The increase in roughness is apparently due to the formation of magnesium glycolate macromolecules linked together by a bridging bond. Table 4 shows the chemical composition of the modified composite coating.

Table 4. Elemental composition of the modified conversion coating on the MA20 alloy.

Alloy	Mg, at.%	Al, at.%	C, at.%	O, at.%	Thickness, μm
MA20	22.3	2.4	43.2	32.1	32.4.0±5.0

The results of chemical analysis show that the composite coating contains a significant amount of carbon. According to [27], magnesium hydroxide molecules interact with ethylene glycol to form magnesium ethylene glycolate by reaction (4). Magnesium glycolates can interact with each other to form macromolecules by reaction (5)



(4)

$$n\ [HO\text{-}MgO(CH_2)_2OMg\text{-}OH] \rightarrow [\text{-}\ O\text{-}Mg\text{-}O(CH_2)_2OMgO\text{-}]n\ \ +nH2O \qquad (5)$$

Macromolecules, together with magnesium oxides, are embedded in the structure of globules that make up conversion coating [28, 29]. Polyglycolates contain in their composition adhesive active groups –OH, through which interaction with paints and individual globules is carried out. On the XPS spectra of Mg2p, magnesium ethylene glycolates can be observed by the appearance of a peak with E_b = 53.5 eV (Figure 4), and on the spectra of C1s with E_b = 288.2 eV (Figure 5).

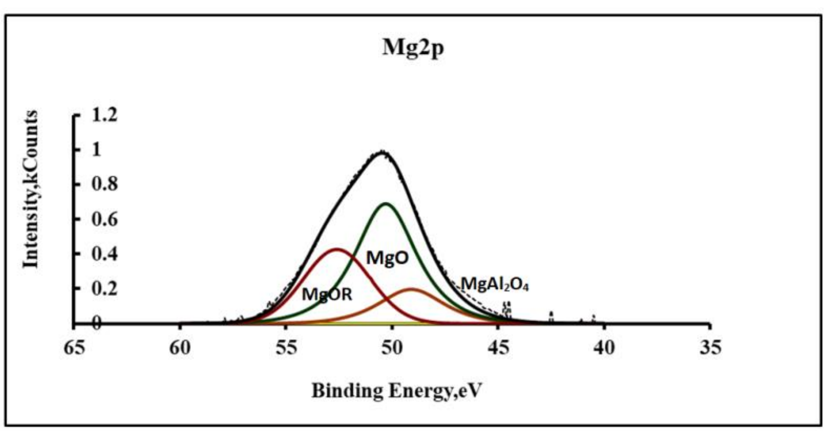


Figure 4. XPS spectra of Mg2p in a modified conversion coating on the MA20 alloy.

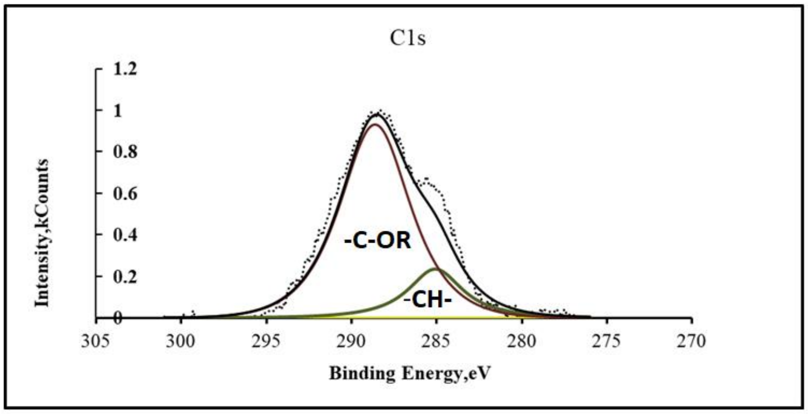


Figure 5. XPS spectra of C1s carbon in a modified conversion coating on the MA20 alloy.

The amounts of ethylene glycolates and magnesium hydroxides in the original and modified conversion coating are shown in Table 5.

Table 5. Chemical composition and adhesion strength of the initial and modified MA20 conversion coating.

Type of coating	MgO, at.%	Mg glycolate, at.%	$MgAl_2O_4$, at.%	Adhesion strength, kPa
Initial coating	84,6	–	15.4	300±50
Modified coating	57.2	36.2	18.6	1180±50

The inclusion of magnesium glycolates in the conversion coating should change the concentration of chemically active groups –OH. Figure 6 shows the XPS spectra of O1s oxygen in the modified conversion coating.

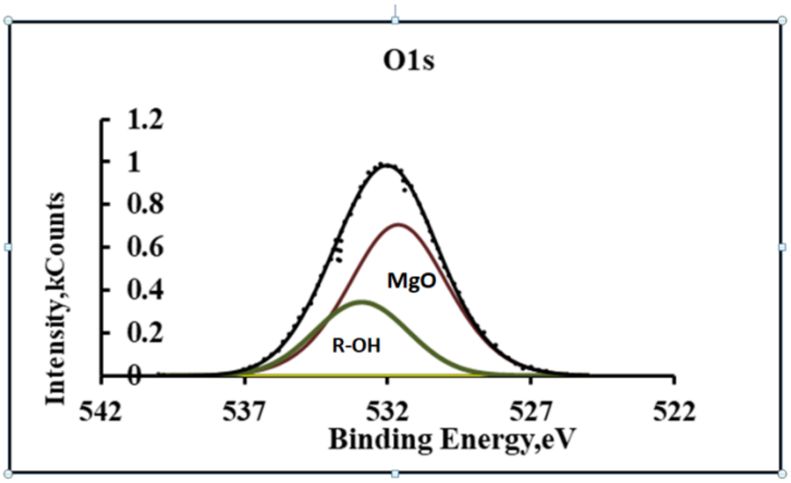


Figure 6. XPS-spectra of O1S oxygen in the modified conversion coating on the MA20 alloy.

Quantitative calculations showed that the concentration ratio of [O]/[OH] in the conversion coating changes toward increasing hydroxide ions mainly due to magnesium ethylene glycolate.

XPS and SEM study of the cchemical composition of the conversion coating on AMg3 aluminum alloy

Conversion coatings on aluminum alloys are usually obtained by chemical or electrochemical oxidation. The oxide layer on oxidized aluminum has a microporous structure and as a result has a high adsorption capacity, which increases the adhesion of paint coatings to the surface of parts. Electrochemically oxidized aluminum alloys have better performance characteristics such as microhardness, wear resistance, heat resistance. However, electrochemical oxidizing is used for products with simple shapes or to give them different electrical properties (electrical insulating or conductive). Chemical oxidation is the most commonly used method for conversion coatings. Films obtained by chemical oxidation of aluminum are inferior in performance characteristics to anodic ones, but they have technological and economic advantages when coating complex profile and large-sized products, internal surfaces of long and thin-walled pipes, large welded structures, as well as in those cases when electrical conductivity on the surface of oxidized aluminum is required. Conversion coating on chemically oxidized AMg3 alloy consists mainly of aluminum hydroxides and boemite AlOOH. A sufficiently large number of methods of obtaining and compositions of electrolytes for the formation of conversion coatings on the surface of aluminum alloys on the basis of compounds, molybdates [30, 31], permanganates [32] and vanadates [33, 34]. The main drawbacks of the proposed methods are the multistage process, complex composition and small resource of electrolytes, which makes their introduction into production unprofitable. By analogy with magnesium alloys, it is of interest to use electrolytes with ethylene glycol additives to improve the adhesion and performance properties of conversion coatings. The main advantage of ethylene glycol is the presence in its composition of two reactive -capable functional groups –OH, capable of interacting with aluminum hydroxides to form organometallic structures forming additional chemical bonds in loose hydroxide structures of conversion coatings. The conversion coating on AMg3 alloy was modified with ethylene glycol by adding it to the oxidation solutions. Figure 7 shows the SEM photograph of the surface of the conversion coating on the original and modified alloy.

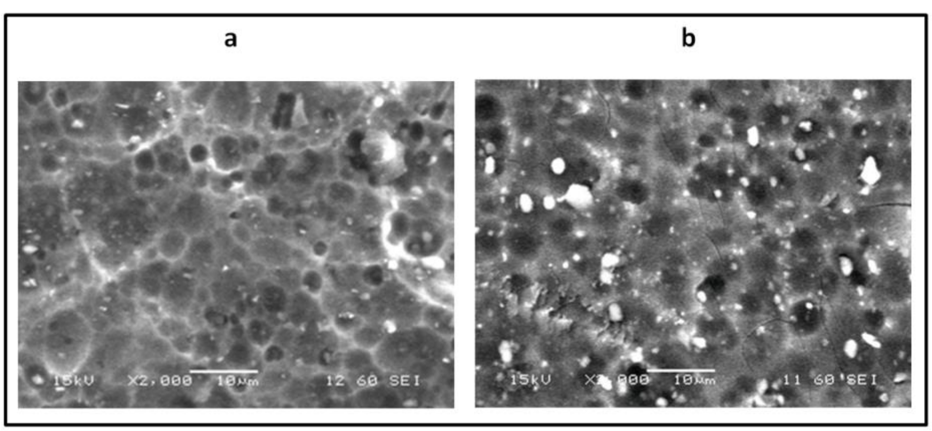


Figure 7. SEM images of the surface of the AMg3 conversion coating before (a) and after (b) modification with ethylene glycol.

It can be seen that the structure of AMg3 conversion coating is fine-grained with vertical pores of 5–10 microns in size, in contrast to MA20 alloy. On the modified alloy the structure is also granular but the number and diameter of the pores are larger. Inclusions of white color according to X-ray microanalysis data are microphases of magnesium glycolate. The chemical composition of the alloys is given in Table 6.

Table 6. Chemical composition of the initial and modified conversion coating on AMg3 alloy.

Type of coating	Mg, at.%	Al, at.%	C, at.%	O, at.%	Thickness, μm
Initial coating	2,3	14.4	25.1	58.2	3.2
Modified coating	1.8	11.6	42.8	43.8	2.8

Comparing the chemical analysis data of the original and modified coating, it is clear that the latter contains a significant amount of carbon belonging to magnesium and aluminum glycolates. Aluminum glycolates can be detected by the appearance of a peak on the Al2p spectra with an energy of 71.4 eV and a peak with an energy of 288.2 eV on the C1s spectra (Figure 8).

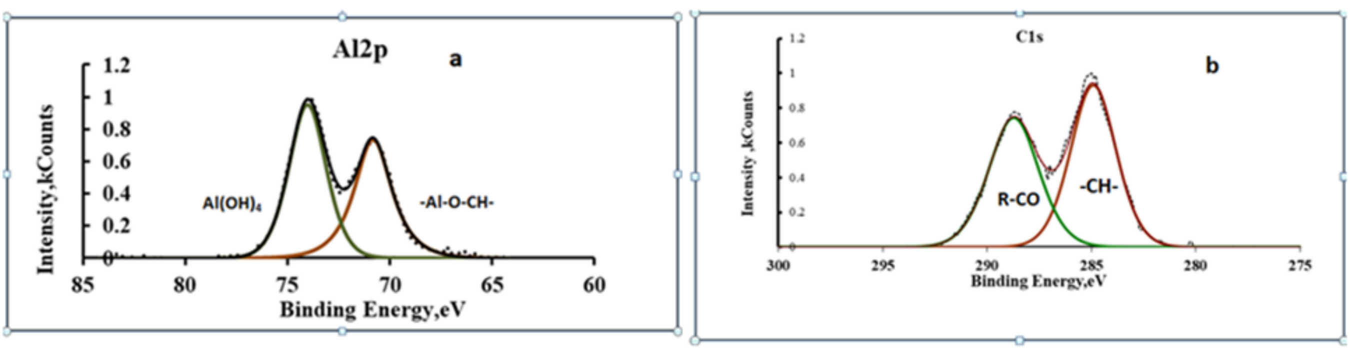
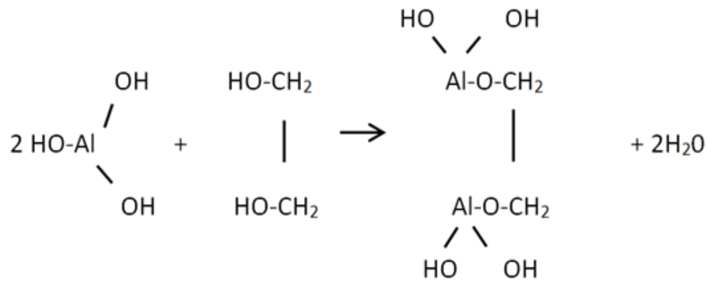


Figure 8. XPS spectra of Al2p (a) and C1s (b) for a modified conversion coating on AMg3 alloy.

A symmetrical doublet on the Al2p spectrum indicates the existence of two types of chemical compounds of aluminum distributed in the conversion coating as separate phases. One of these phases is $Al(OH)_3$, the other is aluminum glycolate. Quantitative calculations of the XPS spectra belonging to aluminum glycolates have shown that two aluminum atoms account for approximately the same number of carbon atoms. This ratio corresponds to the reaction of the formation of aluminum glycolate according to Equation 6:



(6)

Aluminum glycolate molecules can interact with each other to form macromolecules and separate phases in the conversion coating. Significant amount of aluminum glycolate in the substrate indicates high chemical activity of ethylene glycol to aluminum hydroxides. The inclusion of aluminum glycolate in the composition of the conversion coating changes its structure and possibly mechanical properties in the direction of increasing strength due to the formation of new chemical bonds. Table 7 shows the results of adhesion tests of original and modified aluminum and magnesium alloys.

Table 7. Adhesion strength of the initial and modified MA20 and AMg3 conversion coatings.

Type of coating and alloy	Adhesion strength, kPa
Initial coating on MA20	300±20
Conversion coating on Ma20 with ethylene glycol modification	1180±50
Initial coating on AMg3	1600±100
Conversion coating on AMg3 with ethylene glycol modification	1850±100

The data shown in Table 7 shows that the adhesion of Lacroten E-244 on the modified conversion coating of Ma20 alloy is 5–6 times greater than on the conventional one. Modification of conversion coating on AMg3 alloy does not lead to a significant increase in adhesion strength, because the content of hydroxyl ions in the coating does not change as noticeably as in magnesium alloy.

Most studies of paint adhesion to metal conversion coatings attribute the increase in adhesion force to mechanical adhesion in pore volumes. At the same time, our studies have shown that the adhesive force of paint adhesion to the surface of these alloys can differ by an order of magnitude. From the point of view of the theory of mechanical adhesion of paints with the alloy surface, conversion coatings on MA20 alloy are more preferable because they have a more developed structure on the surface and inside the oxide layer. However, studies have shown that the adhesion force on aluminum alloys is 5–6 times greater than on magnesium alloys. It was assumed that this is due to the chemical composition of the conversion layers. On anodized magnesium alloys conversion layers consist mainly of magnesium oxides, and on chemically oxidized aluminum alloys of aluminum hydroxides. According to Equations (1, 2) the formation of strong chemical bonds with paints is possible only on chemically oxidized aluminum alloy. It is possible to increase the concentration of hydroxides in the coating by adding compounds that form –R–OH groups of atoms upon hydrolysis to the anodizing electrolyte. Modification of the conversion coating on magnesium alloys with ethylene glycol leads to an increase in the concentration of –OH groups in it as a result of which the adhesion force increases. The amount of magnesium glycolate in the conversion coating is about 30% of the oxide layer, and the adhesion force increases by about 5–6 times and the coating thickness by 50%. Modification of aluminum alloys with ethylene glycol does not result in a significant increase in adhesion strength, since the conversion coating consists of aluminum hydroxides. However, there is an increase in the number and size of pores due to the incorporation of aluminum glycolate macromolecules into the coating composition. As a result, the adhesion strength increases ~10–15%.

Conclusions

Studies of the adhesion of the Lakroten E-244 acrylic paint to AMg3 aluminum and MA20 magnesium alloys have been carried out. Significant differences in the adhesive activity of these alloys to polymer coatings were found. With the help of XPS and SEM studies of the chemical composition and morphology of alloys were carried out. It is shown that the adhesion of coatings to the surface of alloys depends mainly on the ratio of MeO/MeOH in the conversion coating. Modification of the conversion coating on a magnesium alloy with ethylene glycol significantly increases the adhesive strength of the alloy to paints. The addition of the ethylene glycol increases the thickness of the conversion coating and its strength due to the formation of additional chemical bonds of magnesium ethylene glycol macromelecules with inside and on the border of globules. Studies of the chemical composition, morphology and adhesive activity of conversion coatings on the surface of aluminum alloys modified with ethylene glycol have been carried out. It is shown that the increase in the adhesive activity of modified aluminum alloys is mainly due to an increase in the number and size of pores. The chemical composition and quantity have been established macromolecules of aluminum ethylene glycolate in the conversion coating of aluminum alloy. Modification of the conversion coating with ethylene glycol on magnesium and aluminium alloys changes their structure and chemical composition, which contributes to a significant increase in their adhesive activity.

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