Influence of pH and modifying additives on the protective properties of ultrathin conversion coatings for AMg3 aluminum alloy

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Abstract

Aluminum alloys have low corrosion resistance due to the presence of intermetallic particles in the composition. The natural oxide layer on the metal surface adversely affects the adhesion of subsequent layers of a painting system. In this regard, special anti-corrosion primers surface are created on aluminum alloys, including by the method of chemical oxidation. In the present work, ultrathin conversion primers (coatings) were obtained in a converting composition containing environmentally friendly molybdates and phosphates. The protective properties of such coatings were studied depending on the pH of the converting composition and with addition of modifying additives in the composition. It has been shown that a decrease in pH has a positive effect on the protective properties of primers due to an increase in the oxide film thickness. Among the modifying additives studied, 1,2,3-benzotriazole (BTA) showed the best result. The coatings obtained in solution with addition of BTA effectively adsorb the corrosion inhibitor at the stage of filling the coating. The investigated coatings show good protective properties in corrosion tests in a moisture chamber and high adhesion of the painting system.

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1. Introduction

Due to the combination of the mechanical properties and low density, aluminum alloys have found wide application in various industries. However, due to the presence of intermetallic particles, aluminum alloys do not have high corrosion resistance [1, 2]. The natural oxide on the metal surface also does not contribute to the high adhesion of painting system [3]. In this regard, special primers for aluminum alloys are used. They must create an anti-corrosion barrier on the surface of metals and at the same time serve as adhesion promoters for the subsequent layer of painting system. One of the simple ways to create a primer is the chemical oxidation method, which results in the formation of a conversion coating on the surface.

Due to the toxicity of hexavalent chromium [4], on the basis of which conversion coatings have been obtained for a long time, alternatives to chromate treatments are being
actively studied. Along with expensive compositions containing rare-earth metals, primarily cerium \[5, 6\], and titanium and zirconium fluoride compounds \[7, 8\], it is possible to single out the development of molybdate and permanganate converting compositions. Molybdates and permanganates are well-known inhibitors of aluminum corrosion, whose mechanism of protective action is close to that of chromates. Both anions dissolve well and are reduced on the active surface of aluminum to insoluble compounds that can modify aluminum oxides, increasing their protective properties.

In \[9\], the general issues of growth of permanganate-based coatings on 2024 aluminum alloy were studied. It was shown that thicker oxide films have tend to crack on intermetallic alloy particles, so thin coatings obtained in a short oxidation time may be preferable. In \[10\], alkaline converting compositions containing Mn and Mo compounds were used. The resulting coating consisted of \(\text{Mn}_3\text{O}_4\), \(\text{Mn}_2\text{O}_3\) and a mixture of Mn, Mo, and Al oxides and showed good performance after exposure to a salt fog chamber for 168 h. It was noted in \[11\] that the presence of heterogeneous magnesium oxides in the coating composition can reduce the hydrophilic property of the oxide film, although this does not affect the subsequent adhesion of the painting system too much. In \[12\] molybdate coatings in an acidic solution containing fluorides were obtained. The oxide film obtained at 40°C showed the best protective properties, although the microphotographs show cracks on the surface up to 1 \(\mu\)m wide.

We have also studied permanganate and molybdate conversion coatings \[13, 14\], the advantage of which is modification with modern corrosion inhibitors \[15, 16\]. The addition of corrosion inhibitors to the converting composition and/or subsequent filling of coatings makes it possible to reach the level of traditional chromate coatings and at the same time ensure good adhesion of the painting system \[17\]. In this work, the study of modifications of molybdate inhibited conversion coatings is continued in order to increase their protective properties.

2. Experimental

Conversion coatings were produced on specimens of AMg3 aluminum alloy (Table 1). Specimens with the shape of 20×50 mm plates were sandpapered with papers of different grades, degreased in ethanol, etched in 10% NaOH solution for 1 min (at \(t=65–67^\circ\text{C}\)), washed in hot distilled water, refined in 50% HNO\(_3\) 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-2M conversion solutions for 60 min at \(t=80^\circ\text{C}\) and \(t=90^\circ\text{C}\). IFKhANAL-2M consists of \((\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\), \(\text{Al}_2\text{SO}_4\), \(\text{NiSO}_4\), \(\text{NH}_4\text{NO}_3\) and 1 g/l \(\text{Na}_2\text{HPO}_4\). After oxidation, the specimen was taken away from the solution, washed in distilled water, dried in air at room temperature for no less than 12 h, and weighed.
Table 1. The content of alloying elements (% mass) in the AMg3 according to GOST 4784–97.

<table>
<thead>
<tr>
<th></th>
<th>Fe</th>
<th>Si</th>
<th>Mn</th>
<th>Cu</th>
<th>Mg</th>
<th>Zn</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>less than 0.5</td>
<td>0.5–0.8</td>
<td>0.3–0.6</td>
<td>less than 0.1</td>
<td>3.2–3.8</td>
<td>less than 0.2</td>
<td>basis</td>
</tr>
</tbody>
</table>

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 CrO₃ + 50 g/L H₃PO₄ 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 as follows:

\[
h = \frac{m_1 - m_2}{S_{cc} \cdot \rho} \cdot 10^7
\]

where \( m_1 \) is the weight (g) of the specimen covered with the conversion coating, \( m_2 \) is the weight (g) of the specimens upon removing the conversion coating, \( \rho \) is the boehmite density (g/cm³), and \( S_{cc} \) is the surface area (cm²) of the conversion coating on the specimen.

Filling (compaction) of the coating was carried out by immersing specimens covered with the conversion coatings in hot distilled water (96–98°C), either containing corrosion inhibitor (natrium oleate), for an hour.

Anodic polarization curves of the alloy specimens covered with the conversion coatings (with a working surface of 0.5 cm²) were recorded in a borate buffer solution (pH 7.4) containing 0.01 M NaCl in a standard electrochemical cell under temperature control at \( t=20±2°C \). The auxiliary electrode was made of pyrographite. Electrodes were polarized (1 mV/s) starting usually from the free corrosion potential upon 20 to 30 min exposure to the studied solution.

Corrosion tests by GOST (State Standard) 9.913–90 on the alloy specimens covered with the conversion coatings were carried out in a G4 moist chamber under the following conditions: 8 hours the samples were in the chamber at 100% relative humidity and \( t=40°C \), and the next 16 hours at room temperature (\( t=20±2°C \)). A decrease in \( t \) caused abundant condensation of moisture on the samples. During the experiment, specimens were visually inspected every day, and the appearance of corrosion destruction was noticed.

X-Ray photoelectron (XPS) spectra were recorded using an Omicron+ (Germany) spectrometer. The analyzer chamber pressure was no higher than \( 10^{-8} \) Torr. The source was the polychromatic radiation of an X-ray Al anode (\( h=1486.6 \) eV, power 200 W). The analyzer transmission energy was set to 20 eV. Spectra were recorded with a step of 0.1 eV. The integral areas under the peak were determined after the background subtraction using the Shirley method and fitting the observed peaks by Gaussian curves with the contribution of the Lorentz component.
The application of Ecocolor PE RAL 9016/P polyester powder paint was carried out using a spray gun in a fume hood, achieving a uniform distribution of particles over the entire surface. The samples with paint were placed in a baking oven, where they were roasted at 200°C for 2 hours. At the end of the process, the equipment was turned off and the products cooled slowly and evenly. Quantitative determination of the adhesion strength of the paint with an aluminum base was carried out by the method of normal separation using a PosiTect AT-M digital adhesion meter.

3. Results and Discussion

Previously, it was shown [17] that the addition of phosphates to the converting composition favorably affects the protective properties of the IFKhANAL-2M coatings. Also, the composition is brought to a working pH 2.3 by adding phosphoric acid. Therefore, a decrease of pH affects the amount of phosphates in converting solution. In this regard, conversion coatings at various pH (from 2.3 to 1.7) of the converting composition were obtained. A decrease of pH leads to a negative shift of the corrosion potential during the oxidation of samples by approximately 25–50 mV (Figure 1a). This affects to the coating thickness. The coating thickness accordingly increases from 0.03 µm to 0.05 µm, but the protective properties of the coatings increase insignificantly (Figure 1b). The pitting potential ($E_{pt}$) is shifted to 50 mV in the positive direction for the coating obtained at pH 1.7 relative to the coating obtained at pH 2.3. Filling oxide films in a corrosion inhibitor solution is more effective for thicker oxide films obtained at pH 1.7. In this case, $E_{pt}$ is shifted by another 50 mV in the positive direction. It can be assumed that it is the increase in the thickness of such a thin oxide film that positively affects its protective properties.

According to XPS data (Table 2), the coatings obtained at different pH of the converting composition are heterooxide structure consisting of oxides, sulfates, and phosphates of magnesium, aluminum, and molybdenum. Nickel compounds are also present in the spectra, but the intensity of the nickel peak is very low, so it can be assumed that nickel ions somehow participate in oxidation reactions, beneficially affecting the properties of the coatings, but almost do not enter into the oxide film composition. The composition of the coating itself depends little on the pH of the converting composition. Table 2 shows that the elemental composition of coatings, rather, depends on which area of sample will be in the analysis area: enriched in magnesium oxides or not. In the first case, a large amount of magnesium compounds and a small amount of phosphorus compounds are observed in the coating, and vice versa in the second case. The amount of other elements changes insignificantly. This confirms that the increase in protective properties with a decrease in pH is more influenced by the thickness of the coating than its composition.
Figure 1. Dependence of the corrosion potential on the oxidation time of the AMg3 alloy (a) and anodic polarization curves (b) recorded in 0.01 M NaCl borate buffer solution (pH 7.4) on coatings without and with filling in a corrosion inhibitor solution (*), obtained in an IFKAnal-2M at various pH: 1 – 2.3, 2 – 2.1, 3 – 1.9, 4 – 1.7.

Table 2. Elemental composition of the IFKAnal-2M coatings according to XPS data, depending on the pH of the converting composition.

<table>
<thead>
<tr>
<th>pH of the converting composition</th>
<th>Content of elements in the coatings, at. %</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>O 1s</td>
</tr>
<tr>
<td>2.3</td>
<td>64.5</td>
</tr>
<tr>
<td>2.1</td>
<td>63.0</td>
</tr>
<tr>
<td>1.9</td>
<td>65.2</td>
</tr>
<tr>
<td>1.7</td>
<td>65.1</td>
</tr>
</tbody>
</table>
Increasing Na$_2$HPO$_4$ concentration from 1 to 2 g/l in the converting composition leads to an increase of the coating thickness. It changes from 0.12 µm to 0.17 µm in the pH range from 2.3 to 1.7. At the same time, according to XPS spectra, a higher concentration of Na$_2$HPO$_4$ does not lead to significant changes in the composition of the coatings, that is, this method fails to increase the amount of hardly soluble phosphates in the oxide film composition, but the increased thickness increases its protective properties. The results of polarization measurements confirm this (Figure 2a). It can be seen from them that with an increase in the concentration of Na$_2$HPO$_4$, $E_{pt}$ shifts by ~100 mV in the positive direction relative to the coatings obtained at a lower concentration of Na$_2$HPO$_4$ for pH 2.3 and 2.1 and by 200 mV for pH 1.9 and 1.7. $E_{pt}$ symbatically shifts in the positive direction for filled coatings.

**Figure 2.** Anodic polarization curves recorded in 0.01 M NaCl borate buffer solution (pH 7.4) on AMg3 samples with coatings obtained in an IFKhANAL-2M solution with the addition of 2 g/l Na$_2$HPO$_4$ (a) and 1 g/l Zn(H$_2$PO$_4$)$_2$ (b) at various pH, without and with filling in a corrosion inhibitor solution (*): 1 – 2.3, 2 – 2.1, 3 – 1.9, 4 – 1.7.
The addition of Zn(H₂PO₄)₂ to the converting composition leads to the appearance of a Zn2p intensity peak in the XPS spectra. However, this peak is very weak, and the concentration of zinc compounds in the coating does not exceed 0.5 at. %. In this case, the intensity of the P2p peak decreases, and the content of phosphorus compounds decreases to 1 at. %. This negatively affects the coatings obtained in the composition with the addition of Zn(H₂PO₄)₂, especially after filling in a corrosion inhibitor solution (Figure 2b).

The best result was obtained when BTA was added to the converting composition. In this case, an increase in the coating thickness to 0.40–0.45 μm is observed. A nitrogen peak appears on the XPS spectra and a carbon peak increases significantly (Figure 3a and 3b). However, due to the features of XPS spectroscopy, it is practically impossible to determine which carbon belongs to BTA and which carbon from carbon contamination on the coating surface. It is likely that both C–H and C–N belong to BTA. Although such a large amount of carbon in the coating composition has little effect on the protective properties of the initial coatings, it has a positive effect on the subsequent adsorption of the corrosion inhibitor (Figure 4). The increased thickness of the oxide film also contributes to this. Polarization curves show that \( E_{pt} \) shifts to the range of positive potentials for all coatings modified with BTA and filled with a corrosion inhibitor solution.

These data are confirmed by the results of corrosion tests in the moisture chamber. For all the studied modifications of the IFKhANAL-2M composition, the first pits for unfilled coatings appeared on the 4–5th day of testing, which is significantly less than for the coating obtained in the traditional chromate composition. Filling coatings in a corrosion inhibitor solution increases the time until the first corrosion pits up to 8 days for the initial coating, up
to 12 days for coatings obtained in a composition with a higher concentration of Na$_2$HPO$_4$ and in a composition with the addition of Zn(H$_2$PO$_4$)$_2$, and up to 16 days for coatings obtained in the composition with the addition of BTA. The latter result exceeds the protective properties of the traditional chromate coating (Table 3).

![Figure 4. Anodic polarization curves recorded in 0.01 M NaCl borate buffer solution (pH 7.4) on AMg3 samples with coatings obtained in an IFKhANAL-2M solution with the addition of 1 g/l BTA at various pH, without and with filling in a corrosion inhibitor solution (*): 1 – 2.3, 2 – 2.1, 3 – 1.9, 4 – 1.7.](image)

**Figure 4.** Anodic polarization curves recorded in 0.01 M NaCl borate buffer solution (pH 7.4) on AMg3 samples with coatings obtained in an IFKhANAL-2M solution with the addition of 1 g/l BTA at various pH, without and with filling in a corrosion inhibitor solution (*): 1 – 2.3, 2 – 2.1, 3 – 1.9, 4 – 1.7.

**Table 3.** The results of corrosion tests of coatings obtained at pH 1.7 in IFKhANAL-2M with various modifying additives in the moisture chamber.

<table>
<thead>
<tr>
<th>Modifying additives</th>
<th>Time to the first corrosion pits, days</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 g/l NaH$_2$PO$_4$</td>
<td>4</td>
</tr>
<tr>
<td>1 g/l Na$_2$HPO$_4$ (filling in corrosion inhibitor)</td>
<td>8</td>
</tr>
<tr>
<td>2 g/l NaH$_2$PO$_4$</td>
<td>4</td>
</tr>
<tr>
<td>2 g/l NaH$_2$PO$_4$ (filling in corrosion inhibitor)</td>
<td>12</td>
</tr>
</tbody>
</table>

In addition to corrosion tests, the comparison of the IFKhANAL-2M coatings with a traditional chromate coating was evaluated during their interaction with powder paint (Table 4). The results of adhesion tests show a significant variation in the adhesion strength of the paint system for samples without coating. This indicates uneven adhesion of the paint system, which confirms the data from the literature [3]. With a conversion coating, the variation of adhesion does not exceed 5–10%. The greatest adhesion of the powder paint to the substrate was obtained for the chromate coating and the IFKhANAL-2M conversion coating modified with BTA.
Table 4. The results of adhesion tests of powder paint in relation to coatings obtained at pH 1.7 in IFKhANAL-2M with various modifying additives.

<table>
<thead>
<tr>
<th>Modifying additives</th>
<th>Adhesion, MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>without coating</td>
<td>1.63 ± 0.60</td>
</tr>
<tr>
<td>traditional chromate coating</td>
<td>2.21 ± 0.15</td>
</tr>
<tr>
<td>1 g/l Na$_2$HPO$_4$</td>
<td>1.76 ± 0.08</td>
</tr>
<tr>
<td>2 g/l Na$_2$HPO$_4$</td>
<td>1.54 ± 0.10</td>
</tr>
<tr>
<td>1 g/l Zn(H$_2$PO$_4$)$_2$</td>
<td>1.49 ± 0.20</td>
</tr>
<tr>
<td>1 g/l BTA</td>
<td>2.24 ± 0.20</td>
</tr>
</tbody>
</table>

Conclusions

1. Reducing the pH of the converting composition from 2.3 to 1.7 has a positive effect on the protective properties of the conversion coatings, primarily due to an increase in the thickness of the oxide film.

2. The addition of BTA into the converting composition promotes the adsorption of the corrosion inhibitor at the stage of filling the coating and thereby significantly increases the protective properties of the resulting coatings.

3. Corrosion tests and measurement of powder paint adhesion show that the IFKhANAL-2M coating modified with BTA is close to the traditional chromate coating in its characteristics.

References


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