Protective chromate-free conversion coatings on AMg6 aluminum alloy with different types of surface treatment

Ya.A. Kuzenkov, D.O. Chugunov, S.V. Oleynik† and V.L. Voititsky

A.N. Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, Leninsky pr. 31, 119071 Moscow, Russian Federation
**E-mail: osvpkz@outlook.com*

Abstract

Al-Mg alloys with a high Mg content (above 4.5%) are more sensitive to corrosion than alloys with a low Mg content. Pretreatment of the alloy also affects its sensitivity to corrosion. Previously, it was shown that the alkaline chromate-free converting composition IFKhANAL-3 makes it possible to obtain conversion coatings with high protective properties, regardless of the heat treatment. In the current work, the protective properties of IFKhANAL-3 conversion coatings on AMg6 aluminum alloy were studied for annealed samples and for samples after rolling. It was shown that an increase in the temperature of the converting composition and addition of corrosion inhibitors to the composition reduces the amount of Si-containing oxides in the conversion coating and removes the difference in the protective properties of coatings obtained on annealed samples and on samples after rolling.

Received: March 5, 2022. Published: April 8, 2022 doi: 10.17675/2305-6894-2022-11-2-5

Keywords: *aluminum alloys, conversion coatings, pitting corrosion, corrosion inhibitors.*

Introduction

Increasing the magnesium amount in an aluminum alloy (above 4.5%) leads to an increase in its strength. Therefore, such alloys are classified as "semi-hard" and even "hard" alloys. However, they can be susceptible to exfoliation corrosion and intergranular corrosion. The sensitivity to these types of corrosion depends on the heat treatment of the alloy and on the environment where it is used [1, 2]. Although annealing and mechanical hardening increase the resistance of Al-Mg alloys to pitting corrosion, the presence of Mg and Si intermetallics in the alloy leads to a potential difference between the intermetallics and the base metal, what initiates the corrosion process [3]. In maritime climate, the pits formed on such alloys are three times deeper than on alloys with low magnesium content [1].

Conversion coatings (CC) obtained by chemical oxidation is one of the ways to protect aluminum alloys from corrosion. Phosphates [4, 5] and solutions based on cerium [6] and zirconium salts [7, 8] are actively studied as an alternative to toxic Cr(VI) converting compositions. However, these compositions are often not free from toxic compounds. For example, hexafluorozirconic acid (H_2ZrF_6) is used in zirconium converting compositions [8–10].

In order to avoid the use of toxic reagents (chromates, fluorine-containing compounds, etc.), environmentally friendly converting compositions of IFKhANAL series were developed earlier [11–13]. They were developed to obtain CC on aluminum alloys of various alloying systems, including alloys with different heat treatment. It has been shown that pretreatment of the alloy can affect the heterooxide structure of the coatings [13]. One of these converting compositions is IFKhANAL-3, which is based on non-toxic borates. Inhibited coatings obtained using IFKhANAL-3 make it possible to obtain CC with high protective properties on aluminum alloys of various alloying systems. In this work, we continue the study of the properties of CC obtained on aluminum alloy AMg6 in the IFKhANAL-3 converting composition. The purpose of which investigation to identify the possibility of high protective properties of CC with different surface treatment of the alloy.

Experimental

Conversion coatings were produced on specimens of AMg6 aluminum alloy. 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°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 different conversion solutions for 60 min at t = 80°C and t = 90°C. 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.

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 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, ρ is the boehmite density g/cm^3), and S_{cc} is the surface area (cm^2) 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) containing IFKhAN-25 corrosion inhibitor [14] for an hour.

Anodic polarization curves of the alloy specimens covered with the conversion coatings (with a working surface of 0.5 cm^2) 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) usually starting from the free corrosion potential after exposure for 20 to 30 min to the solution being studied.

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

Microslices of samples were prepared by pouring samples with epoxy resin, grinding on sandpaper of different grain sizes, polishing with felt and cerium oxide, and etching the microslices in Keller's reagent.

Compositions of the conversion coatings on the alloy surfaces were studied by X-ray spectral microanalysis (CAMEBAX) at an electron beam power of 15 keV, a size of the analyzed surface spot of 50×50 μm^2, and an analysis depth of 1 μm.

Results and Discussion

Previously, it was shown that surface pretreatment, including heat treatment, can affect the protective properties of CC obtained on aluminum alloys [13]. In the present work, we studied two types of state of samples from the AMg6 alloy: annealed without cladding and after rolling with cladding (the cladding was removed during the etching of the samples). As can be seen from Figure 1, the grain size of the surface layer depends on the surface pretreatment. The grain boundaries of the alloy are clearly visible for annealed samples, and the grain is much finer and it is not always possible to clearly determine its boundaries in samples after rolling. This leads to the fact that the protective properties of CC obtained at t = 80°C in the IFKhANAL-3 converting composition differ for annealed samples and for samples after rolling (Figure 2). The value of local anodic activation (E_{pitt}) for CC on samples after rolling is in a more negative range than on electrodes with CC obtained on annealed samples. The second feature of the AMg6 alloy is the presence of Si in the composition of the alloy (up to 0.4%), and, consequently, Si-containing intermetallics. The protective properties of the CC are unstable, which is probably due to the enrichment of the coating with Si-containing oxide particles (Figure 3). For coatings obtained on annealed samples, the spread in the values of E_{pitt} is 0.19 V, while for CC on samples after rolling, it is 0.15 V.

It is known that homogenizing the composition of a CC and reduce the amount of heterogeneous oxides is possible by modifying the converting composition using complexing additives (Trilon B), corrosion inhibitors (1,2,3-benzotriazole (BTA) and 5-methyl-BTA or activators (NaF). As can be seen from Figure 4, which shows CC on annealed samples, only the addition of BTA shifts E_{pitt} in the positive direction relative to the E_{pitt} of a similar electrode but with a CC obtained in an unmodified converting solution. However, the results of these polarization measurements are still unstable, and according to X-ray spectral microanalysis data (Table 1), the modified coatings still comprise Si-containing oxide particles.

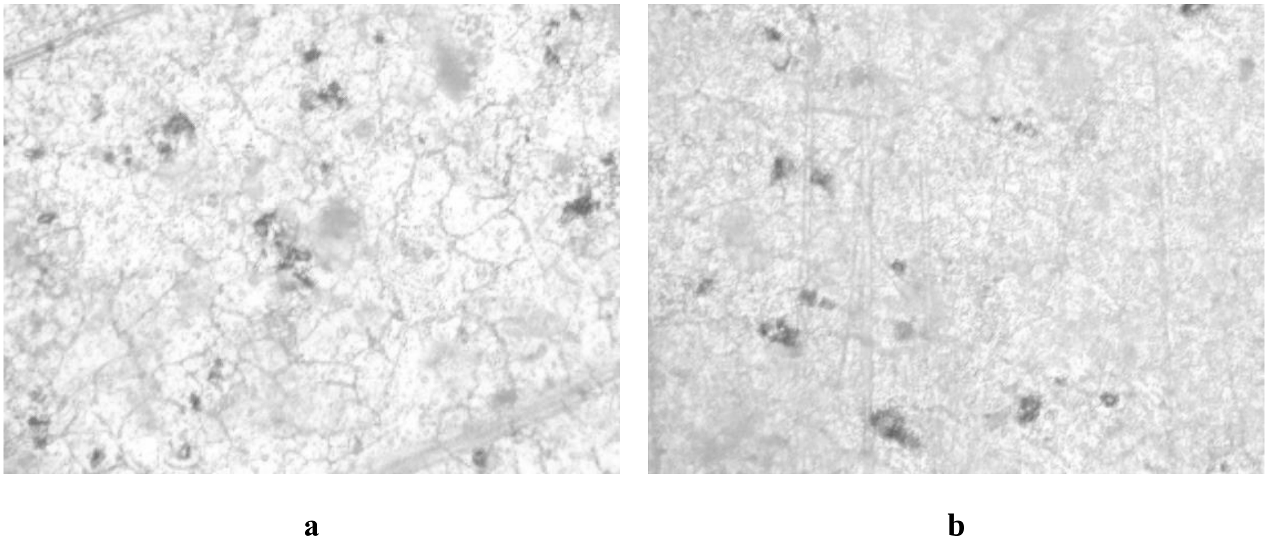

Figure 1. Photographs (x400) of microslices of AMg6 alloy samples after etching in Keller's reagent: a) annealed samples, b) samples after rolling.

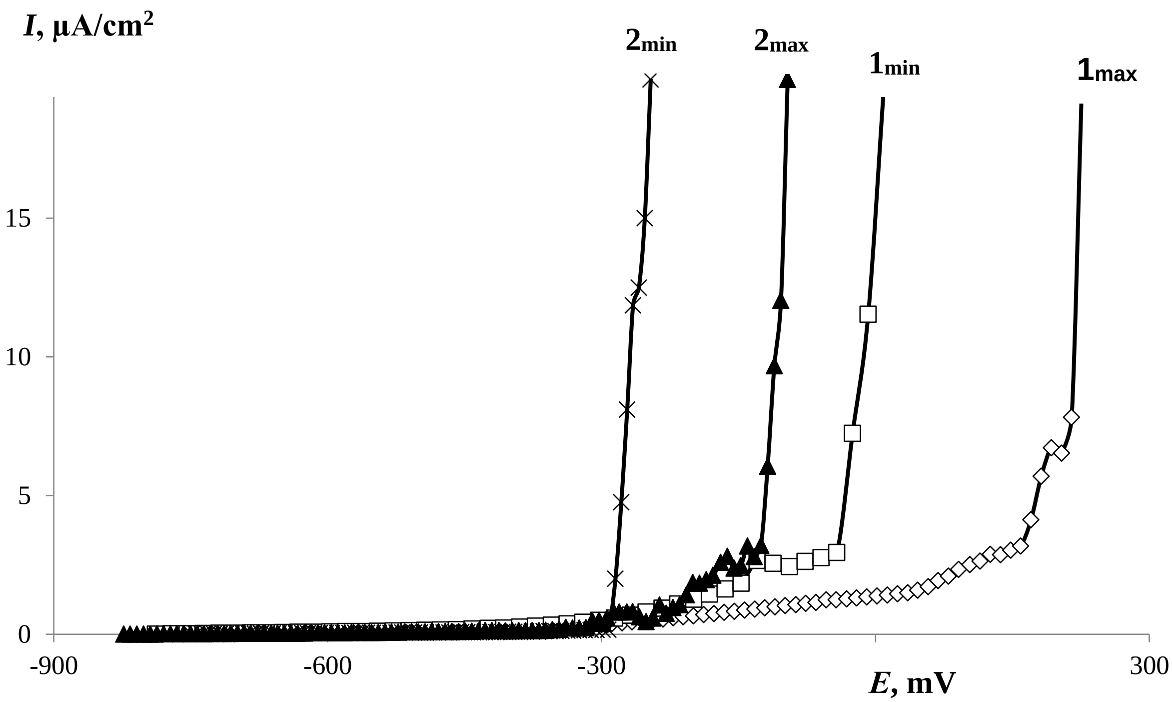

Figure 2. Anodic polarization curves recorded in 0.01 M NaCl borate buffer solution (pH 7.4) on AMg6 alloy covered with a CC obtained in IFKhANAL-3 (80°C) solution and filled in IFKhAN-25 inhibitor solution: 1 – annealed samples, 2 – samples after rolling. Polarisation curves with maximum (max) and minimum (min) E_{pitt}.

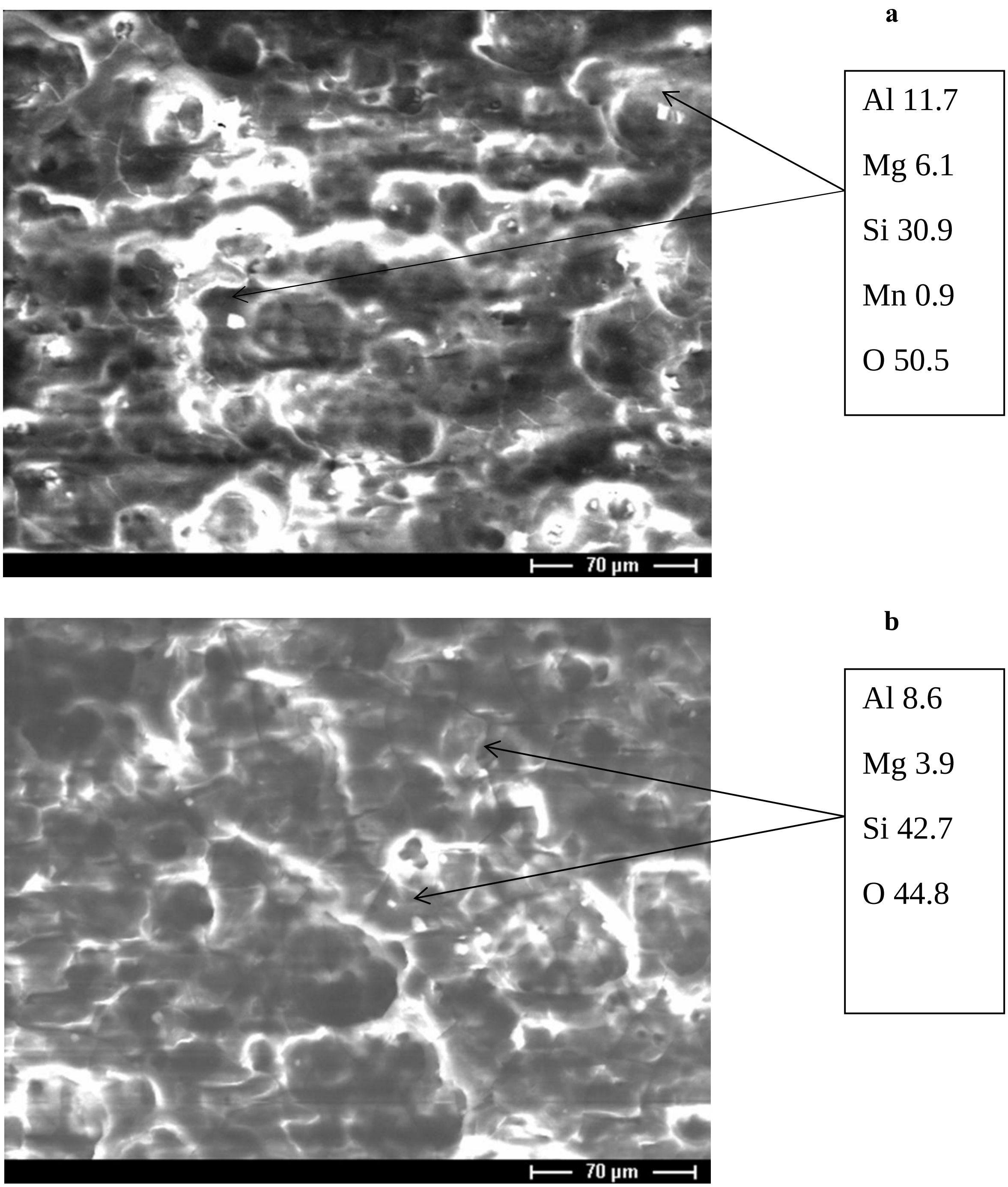

Figure 3. Microphotos of IFKhANAL-3 CC surface obtained at 80°C and elemental composition of Si-containing oxide particles: a) annealed samples, b) samples after rolling.

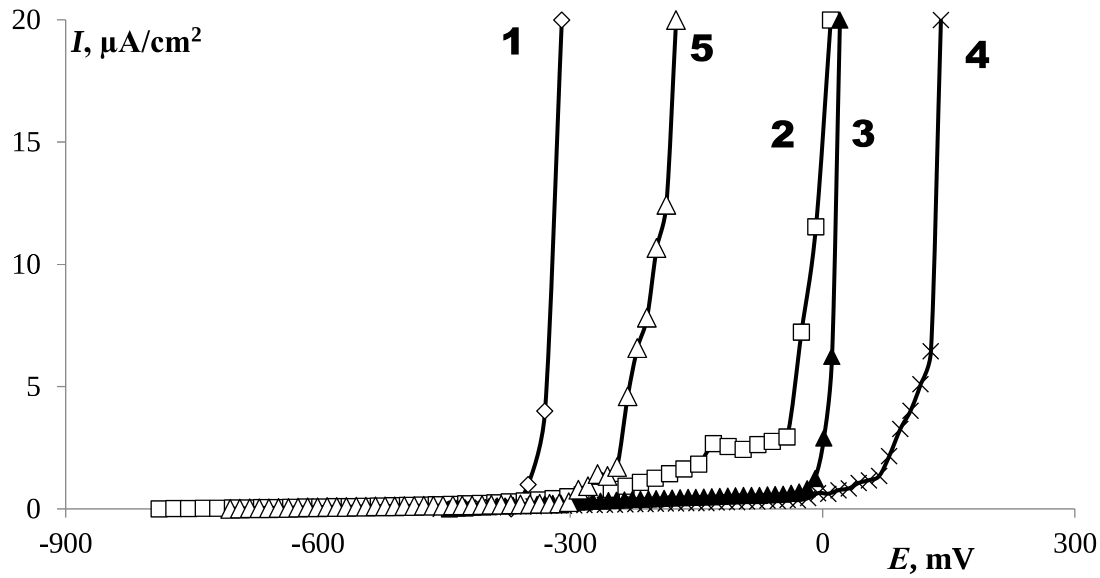

Figure 4. Anodic polarization curves recorded in 0.01 M NaCl borate buffer solution (pH 7.4) on AMg6 annealed samples covered with a CC obtained in IFKhANAL-3 (80°C) solution with modifications and filled in IFKhAN-25 inhibitor solution: 1 – without CC, 2 – IFKhANAL-3, 3 – IFKhANAL-3 + Trilon B, 4 – IFKhANAL-3 + BTA, 5 – IFKhANAL-3 + NaF.

The efficiency of modifying substances can be increased by raising the temperature of the converting composition. Changing the temperature from 80°C to 90°C accelerates the alloy dissolution rate and, accordingly, the coating growth rate. This is evidenced by an increase in the coating thickness: from 3 μm (at 80°C) to 5 μm (at 90°C). At the same time, the processes of interaction of modifying substances with intermetallics in the alloy are also accelerated.

The increased coating thickness also contributes to an increase in inhibitor adsorption during the CC filling process. In the case of annealed samples (Figure 5), this has a positive effect on CC obtained in converting solutions with the addition of 5-methyl-BTA and with the addition of mixture of sulfosalicylic acid and NaF. For them, E_{pitt} shifts in the positive direction by 0.35 V relative to the coating obtained in the unmodified composition. The addition of only NaF to the converting composition does not lead to any effect, and the addition of Trilon B and BTA shifts E_{pitt} in the negative direction relative to the coating obtained in the unmodified composition. The negative effect of the addition of Trilon B, apparently, is due to the fact that only in this case the coating thickness practically does not change with an increase in temperature to 90°C. As can be seen from Table 1, the coatings that showed good protective properties on the polarization curves contain a large number of heterogeneous oxides, but no Si-containing oxides were found on their surface. This confirms that the modifying additives effectively cope with Si-containing oxide particles for an increase of the temperature of the converting composition.

Table 1. Elemental composition of the obtained CC. The temperature of the converting composition is indicated in parentheses.

IFKhANAL-3 CC with modifications	**Contents of elements in CC, wt %**						
	Al	**Mg**	**Si**	**Mn**	**O/S**	**C**	**The presence of Si-containing oxide particles**
Annealed samples							
IFKhANAL-3 * (80°C)	21.7	9.4	2.8	0.5	45.1	20.4	Yes
IFKhANAL-3 + BTA* (80°C)	28.9	14.0	6.2	2.2	35.0	13.6	Yes
IFKhANAL-3 + BTA* (90°C)	25.9	8.2	3.6	2.6	35.2	24.5	No
IFKhANAL-3 + 5-methyl BTA * (90°C)	29.7	7.5	2.7	1.8	28.9	29.5	No
IFKhANAL-3 + sulfosalicylic acid and NaF * (90°C)	26.1	13.4	5.6	6.6	30.3/0.5	17.6	No
Samples after rolling							
IFKhANAL-3 * (80°C)	19.8	8.6	2.8	0.9	41.2	25.8	Yes
IFKhANAL-3 + BTA* (90°C)	14.1	7.0	2.8	8.2	34.9	33.0	No
IFKhANAL-3 + 5-methyl BTA * (90°C)	26.6	8.5	2.2	1.7	18.5	42.4	No
IFKhANAL-3 + sulfosalicylic acid and NaF * (90°C)	30.4	11.4	2.0	2.5	35.2/0.4	16.2	No

* filled in IFKhAN-25 inhibitor solution.

If we compare the elemental composition of the CC obtained on annealed samples at a converting composition temperature of 90°C and coatings obtained on samples after rolling, then it is almost the same (Table 1). CC obtained on samples after rolling also show a large amount of heterogeneous oxides in the coatings and the absence of Si-containing oxide particles. The polarization curves (Figure 6) show that all the studied modifying additives, with the exception of Trilon B, significantly shift E_{pitt} in the positive direction. In this case, the difference between E_{pitt} of the unmodified coating and E_{pitt} of coatings with modifiers reaches 0.60 V in the case of BTA, 5-methyl BTA, and a mixture of sulfosalicylic acid and

NaF. The greater positive effect for the coatings obtained on samples after rolling is due to the fact that E_{pitt} of the unmodified coating lies in a more negative area than E_{pitt} of the unmodified coating obtained on annealed samples. Consequently, an increase in the temperature of the converting composition to 90°C and the introduction of modifying additives (BTA, 5-methyl BTA, and a mixture of sulfosalicylic acid and NaF) levels out the difference in the protective properties of the CC for both types of surface treatment of the AMg6 alloy, which exists for unmodified coatings.

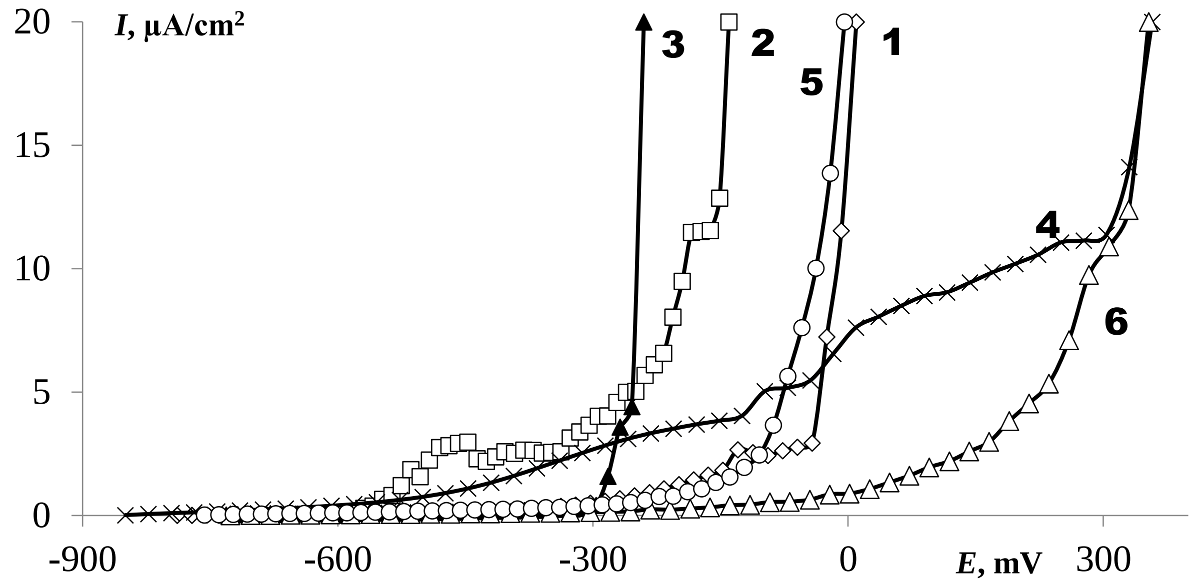

Figure 5. Anodic polarization curves recorded in 0.01 M NaCl borate buffer solution (pH 7.4) on AMg6 annealed samples covered with a CC obtained in IFKhANAL-3 (90°C) solution with modifications and filled in IFKhAN-25 inhibitor solution: 1 – IFKhANAL-3, 2 – IFKhANAL-3 + Trilon B, 3 – IFKhANAL-3 + BTA, 4 – IFKhANAL-3 + 5-methyl BTA, 5 – IFKhANAL-3 + NaF, 6 – IFKhANAL-3 + sulfosalicylic acid and NaF.

This is also seen in the cathodic potential region (Figure 7). CC are often used as an anticorrosion primer for paint coatings. So it is necessary that CC inhibit not only the anodic but also the cathodic processes on the surface. It can be seen from Figure 7 that the studied electrodes with modified CC, which performed well in the anodic potential region, are also more efficient than electrodes with unmodified CC in slowing down the cathodic process. Moreover, the region of deceleration of the cathodic process when using modifying additives is practically the same for coatings obtained on samples after rolling and for annealed samples.

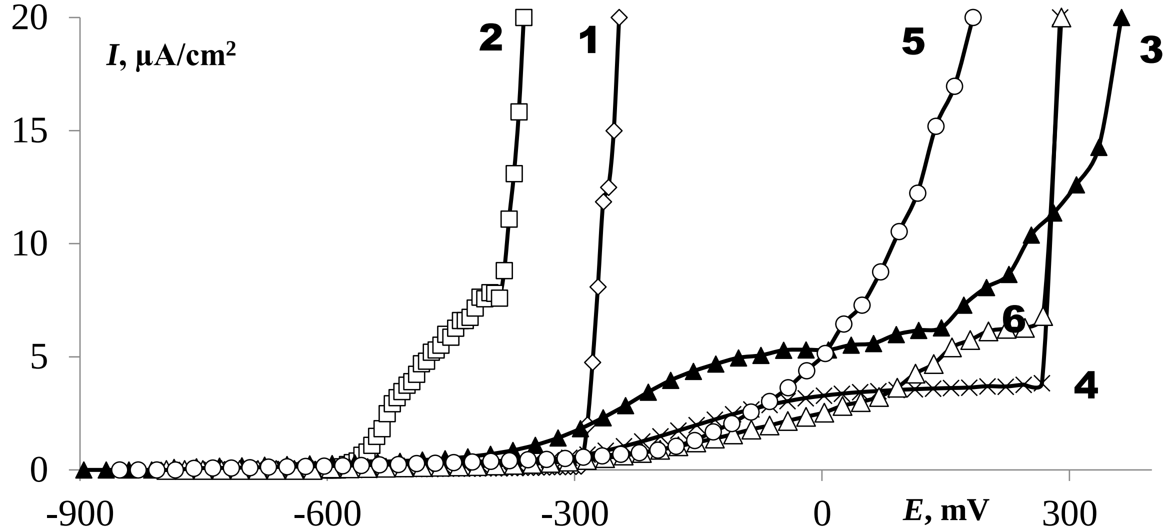

Figure 6. Anodic polarization curves recorded in 0.01 M NaCl borate buffer solution (pH 7.4) on AMg6 samples after rolling covered with a CC obtained in IFKhANAL-3 (90°C) solution with modifications and filled in IFKhAN-25 inhibitor solution: 1 – IFKhANAL-3, 2 – IFKhANAL-3 + Trilon B, 3 – IFKhANAL-3 + BTA, 4 – IFKhANAL-3 +5-methyl BTA, 5 – IFKhANAL-3 + NaF, 6 – IFKhANAL-3 + sulfosalicylic acid and NaF.

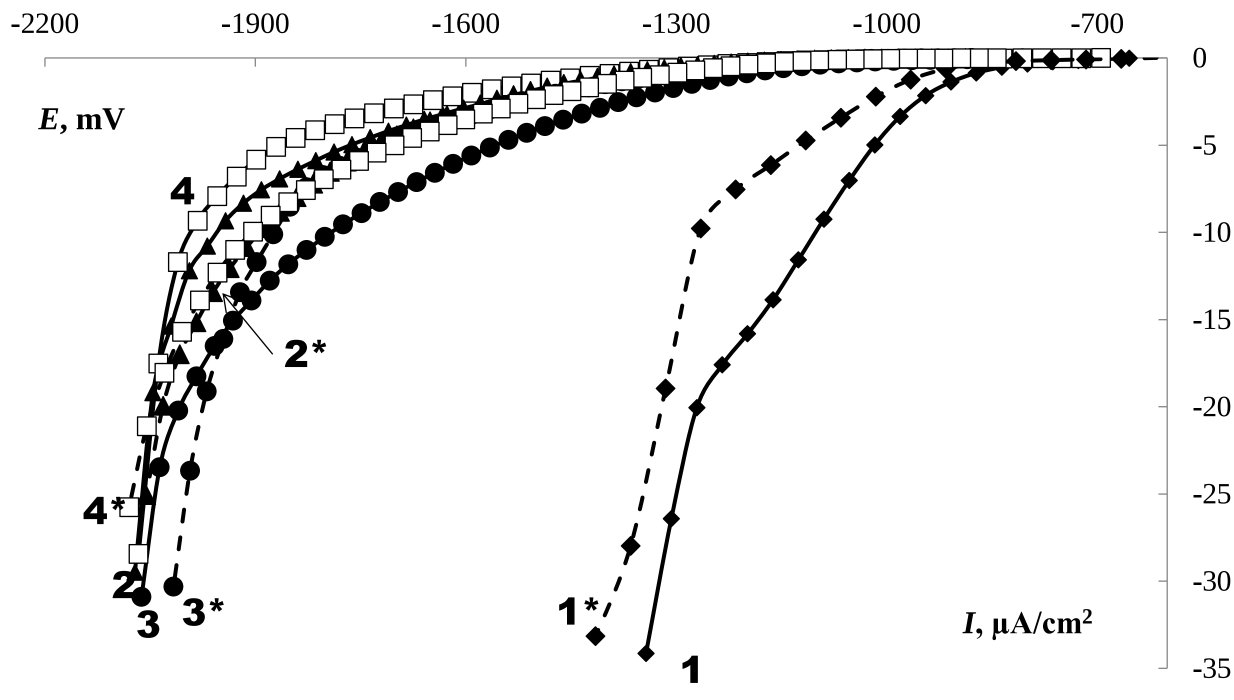

Figure 7. Catodic polarization curves recorded in 0.01 M NaCl solution (pH 7.4) on AMg6 annealed samples and samples after rolling (*) covered with a CC obtained in IFKhANAL-3 (90°C) solution with modifications and filled in IFKhAN-25 inhibitor solution: 1 – IFKhANAL-3, 2 – IFKhANAL-3 + BTA, 3 – IFKhANAL-3 + 5-methyl BTA, 4 – IFKhANAL-3 + sulfosalicylic acid and NaF.

Table 2. Results of corrosion tests of IFAHNAL-3 CC in G-4 moisture chamber. The temperature of the converting composition is indicated in parentheses.

IFKhANAL-3 CC with modifications	**Time before the appearance of the first pits, days**	
	Annealed samples	**Samples after rolling**
IFKhANAL-3* (90°C)	28	26
IFKhANAL-3 +BTA* (90°C)	34	38
IFKhANAL-3 +5-methyl BTA * (90°C)	34	38
IFKhANAL-3 + sulfosalicylic acid and NaF * (90°C)	32	32
IFKhANAL-3 +BTA* (80°C)	28	28

* filled in IFKhAN-25 inhibitor solution.

Corrosion tests were carried out in a G4 moisture chamber, with all samples preliminarily filled with an IFKhAN-25 inhibitor solution. The results of these tests and polarization measurements are in good agreement with each other. As can be seen from Table 2, CC obtained on annealed samples in an unmodified converting composition at 90°C prevent the appearance of the first pits on days 28 and 26 in the case of a coating obtained on samples after rolling. This coincides with the protective properties of the modified coating obtained at 80°C. The protective properties increase for modifying CC obtained at 90°C. The best result is shown by the modification of CC with BTA and 5-methyl BTA. Such CC completely protects the alloy from local corrosion for 34 days (for annealed specimens) or for 38 days (for specimens after cladding rolling).

Conclusions

1. Relatively weak protective properties of IFKhANAL-3 CC obtained in the converting composition at t = 80°C on aluminum alloy AMg6 are associated with the enrichment of coatings with Si-containing oxide particles.
2. Increasing the temperature of converting composition to 90°C, the introduction of modifying additives and filling of IFKhAN-25 inhibitor solution makes it possible to stabilize the composition of the CC and increase their protective properties, both on annealed samples and on samples after rolling and cladding.
3. The best results are shown by CC modified with BTA and 5-methyl BTA and filled in IFKhAN-25 inhibitor solution.

References

1. V.S. Sinyavsky, V.D. Valkov and V.D. Kalinin, *Corrosion and protection of aluminum alloys*, Moscow, Mettallurgiya, 1986, p. 368 (in Russian).
2. Corrosion of aluminum and aluminum alloys, Ed. J.R. Davis, Moscow, NP "APRAL", 2016, p. 333 (translated into Russian).
3. K. Hirayama, H. Tod, D. Fu, R. Masunaga, H. Su, K. Shimizua, A. Takeuchi and M. Uesugi. Damage micromechanisms of stress corrosion cracking in Al-Mg alloy with high magnesium content, *Corros. Sci*., 2021, **184**, 109343. doi: 10.1016/j.corsci.2021.109343
4. X. Sun, D. Susac, R. Li, K.C. Wong, T. Foster and K.A.R. Mitchell, Some observations for effects of copper on zinc phosphate conversion coatings on aluminum surfaces, *Surf. Coat. Technol*., 2002, **155**, 46–50.
5. V. Burokas, A. Martushene, A. Ruchiskene, A. Sudavichus and G. Bikulchus, Deposition of amorphous phosphate coatings on aluminum alloys, *Prot. Met*., 2006, **42**, 339–344.
6. J.J. Alba-Galvín, L. González-Rovira, M. Bethencourt, F.J. Botana and J.M. Sánchez-Amaya, Influence of aerospace standard surface pretreatment on the intermetallic phases and CeCC of 2024-T3 Al-Cu alloy, *Metals*, 2019, **9**, 320. doi: 10.3390/met9030320
7. B. Liu, Y. Zhao, L. Li, Y. Feng, Z. Fang, H. Liu, and Y. Guan, Formation and properties of Zr/Ti based nano-sized non-chromium chemical conversion coating on AA 5083, *J. Nanosci. Nanotechnol*., 2019, **19**, 3487–3494. doi: 10.1166/jnn.2019.16462
8. P. Zhou, Y. Liu, L. Liu, Yu. Baoxing, T. Zhang and F. Wang, Critical role of pretreatment on the corrosion resistance of Zr conversion coating on 6061 aluminum alloy: The combined effect of surface topography and potential difference between different phases, *Surf. Coat. Technol*., 2019, **377**, 124904. doi: 10.1016/j.surfcoat.2019.124904
9. G. Šekularaca, J. Kovač and I. Milošev, Prolonged protection, by zirconium conversion coatings, of AlSi7Mg0.3 aluminium alloy in chloride solution, *Corros. Sci*., 2020, **169**, 108615. doi: 10.1016/j.corsci.2020.108615
10. Commission Directive 2001/59/EC of 6 August 2001 Adapting to technical progress for the 28th time Council Directive 67/548/EEC on the approximation of laws, regulations and administrative provisions concerning the classification, packaging and labeling of hazardous substances relation to the EEA). Official Journal L 225, 21/08/2001, pp. 0001–0333.
12. A.S. Koryakin, Ya.A. Kuzenkov, S.V. Oleynik and V.L.Voiticky, Protective chromate-free conversion coatings on 1424 aluminum alloy, *Corrosion: materials, protection*, 2019, no. 1, 27–32 (in Russian). doi: 10.31044/1813-7016-2019-0-1-27-32

13. Ya.A. Kuzenkov, S.V. Oleynik, V.L. Voiticky, I.A. Archipushkin and L.P. Kazansky, Chromate-free conversion coatings on 1105 aluminum alloy, *Korroz.: Mater., Zashch. (Corrosion: Materials, Protection)*, 2020, **3**, 32–38 (in Russian). doi: 10.31044/1813-7016-2020-0-3-32-38
14. Ya.A. Kuzenkov, S.V. Oleynik, S.A. Karimova and T.I. Tararaeva, Chromate-free conversion coatings on V95 aluminum alloy with different heat treatments, *Korroz.: Mater., Zashch. (Corrosion: Materials, Protection)*, 2010, **5**, 39–44 (in Russian).
15. Y.I. Kuznetsov, S.V. Oleynik and A.V. Khaustov, Chemical Oxidation of an AMг-3 Type Alloy in Alkaline Molybdate-Containing Solutions, *Prot. Met.*, 2003, **39**, 352–356. doi: 10.1023/A:1024978911178

♦ ♦ ♦