Protective properties of chromate-free conversion coatings for copper-containing aluminum alloys in tropical climates

Y.A. Kuzenkov,[1] D.O. Chugunov,[1] V.A. Karpov,[2] T.T. Trang,[3] S.V. Bel'skii[3] and N.V. Thang[3]

[1]A.N. Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, Leninsky pr. 31, 119071 Moscow, Russian Federation
[2]Severtsov Institute of Ecology and Evolution, Russian Academy of Sciences, 119071, Moscow, Russian Federation
[3]Joint Russian–Vietnamese Tropical Research and Technology Center, Hanoi, Socialist Republic of Vietnam
**E-mail: osvpkz@outlook.com*

Abstract

Copper-containing aluminum alloys have low corrosion resistance due to the presence of copper-rich intermetallic phases in the alloy composition. In the case of atmospheric corrosion, increased humidity and the presence of chlorides can significantly accelerate the corrosion processes for these alloys. In this work, V95T3 and 1105 copper-containing aluminum alloys and IFKhANAL-3 chromate-free inhibited conversion coatings (CC) for their protection were studied for 2 years in tropical climate. Full-scale corrosion tests were carried out at the corrosion test station of the Joint Russian–Vietnamese Tropical Research and Technology Center in the suburbs of Hanoi, Hoa Lac station, Vietnam. It was shown that in these climatic conditions, IFKhANAL-3 chromate-free CC can protect 1105 alloy for 12 months, and V95T3 alloy for 24 months. To increase protective properties of the alloys, additional treatment of these coatings was carried out with acrylate varnish and a layer of low molecular polytetrafluoroethylene (PTFE). This makes it possible to completely protect the 1105 and V95T3 aluminum alloys for 2 years in tropical climates.

Received: July 19, 2024. Published: August 5, 2024 doi: 10.17675/2305-6894-2024-13-3-17

Keywords: *aluminum alloys, conversion coating, pitting corrosion, corrosion inhibitors, atmospheric corrosion testing, tropical climate, field tests.*

Introduction

Aluminum alloys are widely used in various industries due to their low density and high specific strength. At the same time, some copper-containing aluminum alloys are not inferior to steels in terms of strength properties. However, they are characterized by reduced corrosion resistance due to the presence of copper-rich intermetallic phases in the alloys composition [1, 2]. In the case of atmospheric corrosion of aluminum alloys, the key factors are high humidity and the presence of chlorides in the atmosphere [3, 4]. For example, full-scale tests of high-strength aluminum alloys in Beijing, China, where the rate of chloride deposition was 4.9 mg/(m^2·day) and the average annual relative humidity was 57%, showed that the corrosion rate of alloys with 4% copper in the alloy composition was 2 times higher than for alloys with 2% mass of copper in the alloy composition during 2 years of testing [5]. Studies of aluminum corrosion at 10 corrosion stations in India have confirmed a direct relationship between the amount of chloride in the atmosphere and the rate of aluminum corrosion. Thus, at a corrosion station in Mumbai, with a chloride deposition rate of 30 mg/(m^2·day) and an average maximum humidity of 94%, the aluminum corrosion rate was 2.6 μm/year, and in Mangalore, with a chloride deposition rate of 69 mg/(m^2·day) and an average maximum humidity of 90%, the aluminum corrosion rate was 5.3 μm/year [6].

One of the simple and economically advantageous ways to protect aluminum alloys is conversion coatings (CC) obtained by chemical oxidation. In the present days, research in this area is aimed at replacing toxic Cr(VI) [7], converting compounds based on which have been used for a long time. The most studied alternative to chromates are Ce-based compounds. However, the processes for obtaining CC in these compounds are often complex and are also not free from the use of toxic compounds. In [8, 9] it is noted that in the case of copper-containing aluminum alloys, alkaline etching of samples before applying Ce-based coatings is not enough, and for better deposition of Ce oxides it is necessary to use acid-base etching, including using concentrated sulfuric or hydrofluoric acids. In [10, 11] it is said that Ce-based coatings are very often heterogeneous, because Ce is deposited predominantly on intermetallic phases, and most of the coating does not contain Ce compounds. In this case, the use of more effective $Ce(NO_3)_3$ instead of $CeCl_3$ may require a long oxidation time and even the use of boiling oxidation solutions. There are also virtually no studies in which conversion coatings demonstrate their anti-corrosion properties under fields test. In this regard, it is of interest to evaluate the protective properties of the IFKhANAL-3 chromate-free composition for the chemical oxidation of aluminum alloys [12, 13, 14], which is based on non-toxic organic corrosion inhibitors [15, 16], in the humid tropical climate of Vietnam.

Experimental

CC were obtained on flat samples (50×50 mm) on 1105 and V95T3 aluminum alloys (Table 1). Samples prepared in the standard manner were oxidized in the IFKhANAL-3 conversion composition (borate based) according to the methodology described in [12]. The thickness of the obtained coatings on the samples was 3–4 μm. After process of oxidation, the coatings were filled by immersing the samples for 1 h in hot distilled water (98–100°C) in the presence of the IFKhAN-25 corrosion inhibitor (carboxylates based). Some of the coated samples were treated with "AC-16" (TU-6-10-814-80) acrylate varnish, and some were coated with a layer by applying a solution of low-molecular-weight PTFE. The thickness of these layers did not exceed 10 μm.

Table 1. Aluminum alloys composition (GOST 4784–97).

Alloy	Component, wt.%						
	Al	**Mg**	**Cu**	**Zn**	**Si**	**Mn**	**Fe**
1105	base	0.4–2	2–5	<1	<3	0.3–1	<1.5
V95	base	1.8–2.8	1.4–2	5–6.5	<0.2	0.2–0.6	0.05–0.25

Field tests of the effectiveness of the CC for protecting aluminum alloys were carried out for 24 months, from November 2021 to November 2023, at the corrosion test station (CTS) of the Joint Russian–Vietnamese Tropical Research and Technology Center, Hoa Lak station, Socialist Republic of Vietnam. As shown in [17], its atmosphere can be classified as humid tropical in accordance with GOST 9.03-749. The average climatic characteristics of the test site for the field test period correspond to the data in Table 2.

Table 2. Climate characteristics at corrosion test station of Tropical Center in Hanoi, Hoa Lak station, November 2021 – November 2023.

Climate characteristics	2021	2022	2023
Air temperature, °C			
Average	20	25	25
Average maximum	25	29	30
Average minimum	17	21	23
Average maximum absolute	29	34	35
Average minimum absolute	13	18	18
Relative humidity, %			
Average	86	89	87
Average maximum	98	99	98
Average maximum	66	70	71
Average maximum absolute	100	100	100
Average minimum absolute	40	46	49
Rainfall, mm	21	3263	1024

Before testing, experimental and control samples had no corrosion damage. To conduct field tests in a tropical atmosphere, the experimental samples were placed in an open area at an angle of 45° to the horizon in the north-south direction. The samples did not come into contact with material that could have affected the course of their degradation. Control samples were stored in a laboratory cabinet with a relative humidity of 40% without light.

During the tests, first once a month and then once every three months, control examinations of the samples were carried out. In this case, changes in the state of the coating (in comparison with the control ones) and degree of corrosion damage to the samples were monitored. The protective and decorative properties of the coating were assessed by visual determination of the type of corrosion damage to the samples, followed by measurement of the area occupied by corrosion according to GOST 9.311-87.

The anode polarization curves on the coated electrodes (working surface 0.5 cm^2) were removed in a borate buffer solution (pH 7.36) containing 0.01 M NaCl at $t = 20 \pm 2$°C. Electrode polarization (1 mV/s) began with the potential for free corrosion (E_c) after 10–20 min of their exposure in the test solution.

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

Results and Discussion

CC on 1105 and V95T3 aluminum alloys are complex heterogeneous oxide films consisting of Al, Mg, Cu, Si, Zn and Mn oxides (Table 3). This leads to low protective properties of CC, according to polarization studies (Figure 1). For CC on the V95T3 alloy, the value of local anodic activation (E_{pt}) shifts in the positive direction relative to the uncoated sample only by 140 mV, and for coatings on the 1105 alloy – by 100 mV. In this regard, filling CC in a solution of corrosion inhibitors plays a decisive role in ensuring the anti-corrosion properties of coatings. Filling results in a large percentage of carbon appearing in the coating composition (Table 3). Inhibition of coatings results in shifts E_{pt} by 2 V in the positive direction relative to the uncoated sample for inhibited CC on V95T3 alloy, and by 1.5 V for inhibited CC on 1105 alloy. It is the inhibited coatings that were studied for 2 years in a tropical climate in Hanoi, Vietnam, including additional treatment of conversion coatings with acrylate varnish and PTFE.

Table 3. Elemental composition of the IFKhANAL-3 CC.

Alloy	**Contents of elements in CC, wt.%**						
	Al	**Mg**	**Cu**	**Si**	**Zn**	**Mn**	**C**
1105	31.6	1.9	5.2	4.1	0.7	1.6	
B95T3	22.6	7.9	4.0	2.9	14.0	–	
	After filling in the corrosion inhibitor solution						
1105	21.8	1.5	4.2	3.1	0.7	0.9	31.5
B95T3	15.0	6.1	4.5	2.2	6.9	–	32.6

Note: the rest is oxygen.

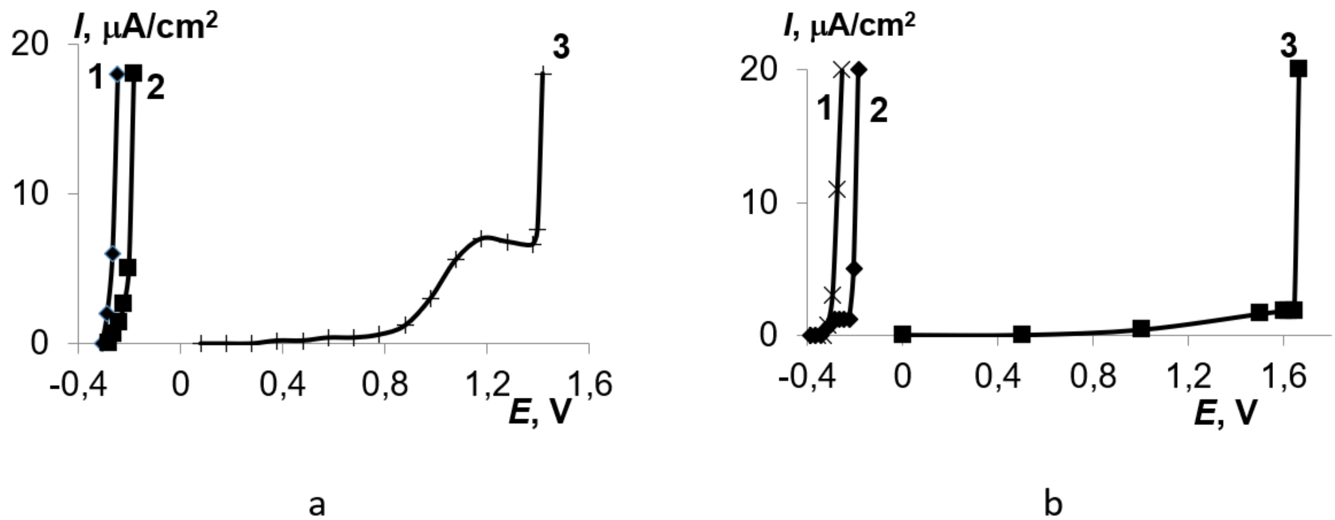

Figure 1. Anodic polarization curves recorded in 0.01 M NaCl borate buffer solution (pH 7.4) on 1105 (a) and V95T3 (b) aluminum alloys without coating (1), with IFKhANAL-3 CC (2) and with inhibited IFKhANAL-3 CC (2).

Samples of 1105 aluminum alloy without coatings are subject to active corrosion in humid tropical climates. The pits appeared on the samples already during the first month of testing. The average number of pits was 10–15 per square centimeter of surface. During further testing, the pits began to merge together to bigger pits. This happened in the third month of testing. By the end of the first year of testing, corrosion damage occupied about 10% of the surface of samples, by the end of the second year – from 20 to 35% for different samples. However, it should be noted that these data refer to the front surface of the samples. On the reverse side, corrosion damage spreads to a lesser extent. Here, predominantly individual small pits are formed, rather than big areas of corrosion damage, and the total area of corrosion damage by the end of the second year of testing was 8 to 15% of the surface (Table 4).

Table 4. Appearances of 1105 alloy samples without CC during field tests.

Test time, months			
1	12	24	
Front side	Front side	Front side	Reverse side
			

IFKhANAL-3 inhibited CC protects 1105 alloy for 9 months in humid tropical climates. During 9 months testing, only lightening of the front side of the coated samples due to exposure to ultraviolet radiation was noted, and pits wasn't detected on the coating. Only after 12 months of testing, corrosion pits on the CC were observed. They are concentrated on the edges of the samples, while no pits were observed in the center of the samples. During the second year of testing, the front side of the coated samples was gradually covered with corrosion products, which eventually occupied 50–60% of the surface of the samples. However, only isolated pits were observed on the reverse side, the number of which did not exceed 1–2 pits per square centimeter of surface. On samples coated with acrylate varnish and PTFE, for 18 months of testing the corrosion damage, as well as peeling, were not found. Only after 21 months of testing on individual samples did peeling of the varnish and PTFE along the edges and minor under-film corrosion begin (Table 5).

Table 5. Appearances of 1105 alloy samples with IFKhANAL-3 CC during field tests.

Test time, months		
IFKhANAL-3 CC		
12	24	
Front side	Front side	Reverse side
		
IFKhANAL-3 CC + acrylate	IFKhANAL-3 CC + PTFE	
24	24	
Front side	Front side	
		

Samples of V95T3 aluminum alloy without coating resist corrosion better than samples of 1105 alloy because they contain less copper in the alloy composition. This is confirmed in the total number of pits after the 24 months of testing and in the fact that the pits do not form big corrosion damage. However, the first corrosion pits on the samples were also observed during the first month of testing. During further tests, the number of pits gradually increased, both on the front and reverse sides of the samples, and their number at the 24th month of testing was 1–2 pits per square centimeter of surface (Table 6).

Table 6. Appearances of V95T3 alloy samples (front side) without CC during field tests.

Test time, months		
1	12	24
		

IFKhANAL-3 inhibited CC effectively protects V95T3 aluminum alloy for 24 months. Only after 2 years of testing did several pits appear on the coating, mainly along the edges of the samples. The number of pits was no more than 3–6 pits over the entire area of the sample. However, it should be noted that the coating itself is subject to general corrosion during the second year of testing. The appearance of dark and greenish spots of varying sizes on the surface of the samples was observed. Additional treatment of conversion coatings with acrylate varnish or PTFE makes it possible to completely protect V95T3 samples from corrosion during 2 years of testing. At the 24th month of testing, no corrosion damage was detected on the samples, with the exception of slight peeling of the varnish on the corners of two samples (Table 7).

Table 7. Appearances of V95T3 alloy samples (front side) with IFKhANAL-3 CC during field tests.

Test time, months		
IFKhANAL-3 CC		
6	12	24
		

IFKhANAL-3 CC + acrylate	IFKhANAL-3 CC + PTFE
24	24
	

Conclusions

1. The studied 1105 and V95T3 copper-containing aluminum alloys have low corrosion resistance in tropical climates. The first corrosion lesions appear on samples during the first month of testing. However, it should be noted that 1105 alloy, which contains more copper in its alloy composition, have more corrosion damage than V95T3 alloy.
2. In tropical climate, the IFKhANAL-3 chromate-free inhibited CC is capable of maintaining the passive state of alloys for 12 months for 1105 alloy and for 24 months for V95T3 alloy. In this case, corrosion occurs more actively on the front side of the samples than on the back side.
3. Additional treatment of the IFKhANAL-3 CC with acrylate varnish and PTFE helps prevent the appearance of corrosion damage on the conversion coating for 24 months. Active peeling of varnish and PTFE is not observed during this time, which indicates the high adhesive properties of the IFKhANAL-3 CC.

References

1. V.S. Sinyavsky, V.D. Valkov and V.D. Kalinin, Corrosion and protection of aluminum alloys, Moscow, Mettallurgiya, 1986, 368 pp. (in Russian).
2. *Corrosion of aluminum and aluminum alloys*, Ed. J.R. Davis, ASM International, 1999 (Russian translation, Moscow, NP “APRAL”, 2016, 333 pp).
3. A.A. Mikhailov, Yu.M. Panchenko and Yu.I. Kuznetsov, *Atmospheric Corrosion and Protection of Metals*, Pershin R.V. Publishing House, 2016, 555 pp. (in Russian).
4. Z. Dan, S. Takigawa, I. Muto and N Hara, Applicability of constant dew point corrosion tests for evaluating atmospheric corrosion of aluminium alloys, *Corros. Sci.*, 2011, **53**, no. 5, 2006–2014. doi: 10.1016/j.corsci.2011.02.027
5. L. Tao, S. Song, X. Zhang, Z. Zhang and F. Lu, Image analysis of atmospheric corrosion of field exposure high strength aluminium alloys, *Appl. Surf. Sci.*, 2008, **254**, no. 21, 6870–6874. doi: 10.1016/j.apsusc.2008.04.088
6. M. Natesan, G. Venkatachari and N. Palaniswamy, Kinetics of atmospheric corrosion of mild steel, zinc, galvanized iron and aluminium at 10 exposure stations in India, *Corros. Sci.*, 2006, **48**, no. 11, 3584–3608. doi: 10.1016/j.corsci.2006.02.006

7. 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*, 2001, **225**, 0001–0333.
8. S. Sainis and C. Zanella, A localized study on the influence of surface preparation on the reactivity of cast Al-7Si-1Fe and Al-7Si-2Cu-1Fe alloys and their effect on cerium conversion coating deposition, *Appl. Surf. Sci*., 2022, **585**, 152730. doi: 10.1016/j.apsusc.2022.152730
9. C.M. Rangel, T.I. Paiva and P.P. da Luz, Conversion coating growth on 2024-T3 Al alloy. The effect of pre-treatments, *Surf. Coat. Technol*., 2008, **202**, no 14, 3396–3402. doi: 10.1016/j.surfcoat.2007.12.017
10. J.M. Sánchez-Amaya, G. Blanco, F.J. Garcia-Garcia, M. Bethencourt and F.J. Botana, XPS and AES analyses of cerium conversion coatings generated on AA5083 by thermal activation, *Surf. Coat. Technol*., 2012, **213,** 105–116. doi: 10.1016/j.surfcoat.2012.10.027
11. M. Dabalà, L. Armela, A. Buchberger and I. Calliari, Cerium-based conversion layers on aluminum alloys, *Appl. Surf. Sci*., 2001, **172,** no. 3–4, 312–322. doi: 10.1016/S0169-4332(00)00873-4
12. Ya.A. Kuzenkov, D.O. Chugunov, S.V. Oleynik and V.L. Voititsky, Protective chromate-free conversion coatings on AMg6 aluminum alloy with different types of surface treatment, *Int. J. Corros. Scale Inhib*., 2022, **11**, no. 2, 541–552. doi: 10.17675/2305-6894-2022-11-2-5
13. Y.A. Kuzenkov, C.D. Hong and V.A. Karpov, Corrosion protection of aluminum alloys with chromate-free inhibited conversion coatings in a tropical climate, *Int. J. Corros. Scale Inhib*., 2022, **11**, no. 4, 1692–1702. doi: 10.17675/2305-6894-2022-11-4-18
14. D.O. Chuguno and Yu.A. Kuzenkov, Inhibited chromate-free conversion coatings on aluminum alloys AMg5 and AMg6, *Corrosion: material protection and research methods*, 2024, **1**, 119–126 (in Russian). doi: 10.61852/2949-3412-2024-2-1-119-126
15. Yu.I. Kuznetsov, Organic corrosion inhibitors: where are we now? A review. Part II. Passivation and the role of chemical structure of carboxylates, *Int. J. Corros. Scale Inhib*., 2016, **5**, no. 4, 282–318. doi: 10.17675/2305-6894-2016-5-4-1
16. Yu.I. Kuznetsov, Triazoles as a class of multifunctional corrosion inhibitors. Review. Part III. 1,2,3-Benzotriazole and its derivatives. Aluminum alloys *Int. J. Corros. Scale Inhib*., 2020, **9**, no. 4, 1142–1168. doi: 10.17675/2305-6894-2020-9-4-1
17. V.A. Karpov, V.N. Ivonin, T.M. Tien, V.A. Timonin, O.L. Mikhailova, Yu.L. Koval'chuk, F.Z. Nam and K.K. Shon, Determination of atmospheric corrosivity at the test stations of the Tropical Center and in some areas of Vietnam, *Korroz.: Mater., Zashch. (Corrosion: Materials, Protection)*, 2014, **9**, 1–7 (in Russian).

♦ ♦ ♦