Surface passivation of 5556 aluminum alloy in solutions based on cerium nitrate

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Abstract

A solution has been developed for applying protective-adhesive cerium-containing coatings to the surface of the 5556 aluminum alloy in order to replace the toxic chromating process in the automotive and other industries. The developed solution contains: 5–10 g/l $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 30–40 ml/l H_2O_2 and 0.5–1.5 g/l gallic acid ester. Coatings with the best physicochemical characteristics are formed in a solution with $\text{pH}=2-3$ at a temperature of 18–25°C and a process duration of 10–15 minutes. The optimum drying temperature is 120–160°C. The coatings formed under these conditions consist of cerium oxides CeO_2 , Ce_2O_3 and aluminum oxide Al_2O_3 . The addition of a gallic acid ester (in an amount of 0.5–1.5 g/l) to the working solution leads to a change in the chemical composition of the forming coatings, namely, to the exclusion of CeO_2 compounds in their composition. This increases the protective ability of coatings. Corrosion tests in a salt-spray chamber have shown that the developed cerium-containing coatings are superior in protective ability to the currently widely used chromate coatings. The developed coatings have good adhesion properties and withstand exposure to high temperatures without degradation of their protective properties. Adhesion after 750 hours of salt-spray corrosion tests decreased by 13.0 and 13.8% for cerium-containing and chromate coatings, respectively. The thickness of cerium-containing coatings is 280–320 nm. The developed solution for the formation of protective adhesive coatings on aluminum is an alternative to toxic chromating solutions.

Keywords: corrosion protection, conversion coatings, cerium-containing coatings, surface treatment, chromate-free passivation, rare earth metals.

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Introduction

Aluminum alloys are widely used as a structural material in various fields of technology, in industrial and civil construction for the manufacture of building frames, window frames, stairs, in the automotive industry, in shipbuilding, aviation and space technology, in electrical engineering, in nuclear reactor construction, *etc.* [1]. Due to the presence of a thin

natural oxide film on the surface, aluminum and its alloys are sufficiently resistant to corrosion, therefore, in some cases, they are used without special anti-corrosion protection. However, due to its low thickness, the natural film on the surface of aluminum often does not provide reliable protection against corrosion, for example, in a humid industrial atmosphere or in sea water.

Depending on the alloy grade, product design, its purpose, working conditions and other factors, protective-decorative electrochemical oxidation (anodizing), paint coatings, complex coatings consisting of an oxide film and a paint coating applied to it are most often used for corrosion protection. However, for details that are subjected to loads, for example, periodic bending loads, in many cases anodic oxidation is not applicable because cracks appear in the coatings. According to, on the surface of samples anodized in sulfuric acid electrolyte to a thickness of 10 μm , cracks in the coating appear even when bent by 4° ; when the thickness of the oxide film decreases to 5 μm , cracks are formed at a bending angle of 30° . Under bending loads, cracks also appear in anodic oxide films deposited in a chromic acid electrolyte, although their number is less [1, 2]. In these cases, before applying the LPC, thin conversion adhesive layers with a thickness of 0.1–0.3 μm are deposited, for example, chromate layers, on the surface of which cracks are not observed even when bending at 180° [2]. Chromate adhesive coatings are also preferable for painting complex-shaped products, since their anodization is associated with difficulties and requires additional techniques and costs [2–5].

Due to the high toxicity of chromating solutions, which include highly toxic hexavalent chromium compounds, and the conversion coatings formed in them, which also contain up to 200 mg/m^2 of Cr^{6+} , the legislation of many States significantly restricts or completely prohibits the use of conversion chromate coatings.

In the Russian Federation, similar directives have not yet been adopted, but the problem of replacing solutions containing hexavalent chromium is no less acute. The current SanPiN 2.1.5.980-00 regulates that the maximum concentration limit for Cr^{6+} compounds in industrial wastewater should be 0.02–0.05 mg/l , which is an order of magnitude lower than in the EU countries, *i.e.*, 0.1–0.5 mg/l [6–9].

Among the alternative corrosion inhibitors of aluminum alloys to chromates, the literature describes salts of rare earth metals, in particular cerium, which is an environmentally friendly and quite effective corrosion inhibitor of metals such as aluminum and zinc [10–13]. In this regard, cerium-containing conversion coatings can become a possible replacement for adhesive chromate conversion coatings.

This work is devoted to the development of the process of applying adhesive protective cerium-containing conversion coatings under paintwork on the surface of the 5556 aluminum alloy in order to replace the environmentally hazardous chromating processes.

Experimental procedures

For the application of conversion coatings, samples of an aluminum alloy AA 5556 widely used in the automotive industry of the size of 3×4 cm were used.

To prepare the solutions, the chemical reagents of grades “pure”, “chemically pure”, and distilled water were used.

Passivating coatings were formed by immersing samples of an aluminum alloy AA 5556 in the test solution for a specified time, after which the samples were removed and dried by blowing hot air at a temperature of 80°C for 10 minutes. For the deposition of chromate coatings, which were selected as objects of comparison, a solution containing 15 g/l $\text{Na}_2\text{Cr}_2\text{O}_7$ and 60 g/l Na_2CO_3 ($t = 95\text{--}100^\circ\text{C}$; $\tau = 20\text{--}30$ min) was used.

To accelerate the evaluation of the protective ability of conversion coatings, a drop-express method was used using an Akimov solution containing: $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ 82 g/l, NaCl 33 g/l, 0.1 N HCl 13 ml/l. The PAA (Akimov’s protective ability) of conversion coatings on aluminum or its alloys is estimated by this method as time (in seconds) before the color change at the surface under a drop from gray to black.

The thickness of the coatings was determined by an ellipsometric method using a spectroscopic ellipsometer by Sentech SENreasech (SENTECH Instruments GmbH, Krailling, Germany) 4.0 SER 800 with a high-speed monochromator. The measurements were carried out in the spectral range of wavelengths of 240–1000 nm at a goniometer angle of 70° [25]. For calculations, a three-layer model was used, including 2 Drude–Lorentz layers and 1 Cauchy layer. The model parameters (thickness d , refractive index n_2) from the measured values Ψ and Δ (inverse problem of ellipsometry) were determined by the software of the device in accordance with the selected mathematical model. The calculated result was considered valid if the result of the parameters of the physical model corresponded to the mathematical model and did not exceed the limits of the established errors [19].

The composition of the surface layers was studied using X-ray photoelectron spectroscopy (Omicron, Taunusstein, Germany) (XPS) [20–23]. The panoramic spectra were also recorded after argon-ion etching of the coating in different depths. Thus, the composition of the coating at different distances from the substrate was determined. The pressure of the inert gas in the working chamber was maintained at this level, so that the ion energy and the ion current rate, and consequently, the etching rate, were constant. When analyzing the obtained spectra, it was considered that the analyzing beam penetrates the material to the depth of 5 nm, *i.e.*, the resulting spectra correspond to a layer of material 5 nm thick [24].

In order to reveal the possibility of using the coatings at a high temperature, the samples were exposed in a ShS-80-01 SPU drying cabinet for 1 h at a temperature of 160°C and subsequent cooling in air. After that, the protective ability of the coatings was determined using the method described above. Coatings are considered heat-resistant if the decrease in protective ability as a result of thermal shock is insignificant (up to 5%).

The adhesion of the coatings was determined by the normal detachment method using the PosiTest AT digital adhesion meter. The method is based on measuring the minimum breaking tension required to separate or rupture the coating in a direction perpendicular to the substrate surface [25].

Corrosion tests were carried out in a salt spray chamber Ascott S450iP in accordance with the international standard ASTM B117.

Results and Discussion

Cerium salts such as phosphates, cinnamates, and cerium silicates [26–28], as well as water-soluble salts of cerium, such as $\text{Ce}(\text{NO}_3)_3$ and CeCl_3 [29], are described in the literature as corrosion inhibitors of aluminum alloys.

Taking into account the processability, safety, availability in the present work, cerium nitrate $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was chosen as the main component of the conversion solution.

According to the literature, the formation of a coating on the surface of aluminum in a solution based on cerium salts begins at the cathode areas of the surface as a result of an increase in pH in the solution adjacent directly to the metal surface due to oxygen reduction. The degree of protection depends on the duration of the dive. The formation of films can be accelerated by introducing oxidizing agents into the solution, which catalyze the cathodic reaction [14–17].

The dependence of the protective ability of the formed conversion coatings (Akimov Express test) on the duration of treatment in the test solution (10 g/l $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, pH=3.0) was studied.

As can be seen from Figure 1a, the coating formation is completed under these conditions by the 20th minute of the process. The protective ability of the coatings is stabilized (60 s), and the coating thickness reaches 250 nm. It should be noted that the thickness of chromate coatings is usually 500–1000 nm, and their protective ability according to the Akimov method is 80–100 s.

The coating with the maximum protective ability (60–70 s) is formed in the range of cerium nitrate concentrations of 6–16 g/l (Figure 1b). When the salt concentration is more than 16 g/l, the protective ability (PAA) of coatings decreases from 61 to 47 s. In the optimal range of salt concentration, the coating thickness reaches 250 nm, and when the salt concentration is higher than 16 g/l, the coating thickness is significantly reduced (up to 193 nm), which leads to a deterioration of the protective characteristics.

To improve the protective characteristics of the coating and reduce the duration of its formation, an oxidant H_2O_2 was introduced into the solution, taking into account the information in the literature. The concentration range of the solution components was determined (in Figure 2 highlighted by a black frame), in which coatings with the maximum protective ability according to Akimov (up to 80 s) were formed. In addition, it should be noted that the introduction of 30–40 ml/l of hydrogen peroxide into the solution promoted the formation of coatings that were more uniform in appearance.

Figure 3 shows that, in the presence of hydrogen peroxide in the solution, the thickness of the forming coatings increases to 320 nm, and the duration of the process is reduced to 10 min.

Figure 1. Dependence of the protective ability (a) and thickness (b) of coatings on the duration of the process and the concentration of cerium nitrate in the solution.

		Concentration of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, g/l				
		4	8	12	16	20
H_2O_2 (ml/l)	0	28	34	40	29	26
	3	42	20	46	53	38
	5	46	28	46	64	44
	10	51	43	51	62	50
	15	66	58	59	58	55
	20	68	64	67	53	52
	30	74	79	75	50	46
	40	78	80	78	50	39
	50	67	69	65	43	24
	60	64	62	49	37	18

	-	good quality coatings
	-	poor quality coatings

Figure 2. Dependence of the protective ability of cerium-containing coatings on the concentration of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and H_2O_2 .

The experiments described above were carried out at a working solution temperature of 18–25°C. It was found that heating the solution to 40°C practically does not affect the properties of coatings, further heating is undesirable, since it leads to a certain decrease in the thickness and protective ability of coatings. Thus, the solution can be heated up to 30°C in the summer.

The study of the effect of the acidity of the solution on the protective ability of coatings showed that the acceptable pH values are in the range of 1.5–3.5, and the optimal values are in the range of 2–3 pH units. When the pH of the solution rises to $\text{pH} \geq 4$, a precipitate of slightly soluble Ce^{4+} compounds precipitates in the solution.

Taking into account possible transformations in accordance with the Pourbaix diagram for the Ce– H_2O_2 system (Figure 4), the mechanism of coating formation in a solution with hydrogen peroxide at $\text{pH}=2\text{--}3$ may be described by the following reactions:

At the same time, the aluminum base is dissolved and the solution is alkalinized at the interface:

Figure 3. Dependence of the protective ability and thickness of the coatings on the concentration of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and H_2O_2 .

Figure 4. Pourbaix diagram of the Ce–H₂O₂ system.

Aluminum ions, as well as Ce³⁺ ions unoxidized by hydrogen peroxide, form aluminum and cerium hydroxides:

During subsequent drying, the resulting coatings are dehydrated and a mixed oxide is formed:

According to the above mechanism, the forming coating would appear to consist of oxides: Ce₂O₃, CeO₂ and Al₂O₃.

This is confirmed by the results of the chemical composition of the coatings. The survey XPS spectra of the coating formed in the working solution Ce/H₂O₂ (Figure 5) indicate the presence of 40.67% oxygen, 4.68% cerium, 13.82% aluminum, 39.02% carbon in the coating (Table 1). From the individual spectra of cerium (Figure 6a) and aluminum (Figure 6b), it can be seen that cerium is present in the coating in the three- and four-valent state, and aluminum in the trivalent state, which is consistent with the above mechanism of coating

formation. The presence of a carbon peak in the spectrum is explained by the deposition of diffusion oil vapor in the pre-chamber of the spectrometer.

Table 1. Chemical composition of the coatings (X-ray photoelectron spectroscopy (XPS)).

Name	Quantitative composition, %
Aluminum	22.66
Oxygen	66.69
Cerium	7.68
Others	2.97

Figure 5. Survey spectrum of the cerium-containing coating obtained from the working solution Ce/H₂O₂.

The possibility of improving the characteristics of the coating was investigated by introducing organic additives into the solution, such as polyethylene glycol (PEG 1500), gallic acid, gallic acid ester and glycerin, which, according to the literature, have proven themselves well in the processes of film formation on metal surfaces. The introduction of gallic acid ester into the solution in an amount of 0.5–1.5 g/l increased the protective ability of the forming coatings up to 140 seconds. When other organic additives were introduced, the protective ability of the coatings either did not change (PEG 1500) or decreased (gallic acid, glycerin), and their continuity was disrupted.

Figure 6. Individual XPS spectra of cerium (a) and aluminum (b) in the coating.

In order to reveal the possibility of using the coatings at a high temperature, the samples were exposed in drying cabinet for 1 h at a temperature of 160°C. As can be seen in Figure 7, cerium-containing coatings withstand high temperatures without reducing their protective ability, while chromate coatings, as expected, are destroyed, as evidenced by the degradation of their protective ability.

Figure 7. Test results of samples with conversion coatings at high temperatures.

Corrosion tests (ASTM B117) in a salt-spray chamber of 5556 aluminum alloy samples with an adhesive cerium-containing coating without heat treatment and after it, painted with polyester powder paint (Ecocolor PE RAL 9016/P), were carried out. Tests have shown that the developed cerium-containing coatings in terms of protective ability satisfy the requirements for adhesive layers under the paintwork, since the width of corrosion penetration from the place of incision in these cases does not exceed 2 mm after 750 hours of testing (Figure 8). It should be noted that after heat treatment the protective ability of the developed coatings not only did not deteriorate, but even improved, while in chromate coatings, the width of corrosion penetration from the place of incision increased 2 times.

Figure 8. Results of corrosion tests (ASTM B117) of samples with an adhesive coating painted with polyester powder paint; h – width of corrosion penetration from the place of incision: 1 – before heat treatment, 2 – after heat treatment.

Using the PosiTest AT digital adhesion tester, the adhesion of paint coatings with adhesive cerium-containing sublayers on the surface of 5556 aluminum alloy was determined (Table 2).

It was revealed that LPCs with cerium-containing conversion coating have a higher adhesion strength to the base compared to chromate coatings: 2.38 vs. 2.25 MPa. It should be noted that the decrease in adhesion (%) after 750 hours of corrosion tests in a salt-spray chamber is 13% and 13.8% for samples with cerium-containing and chromate coatings, respectively.

Table 2. The results of determining the adhesion strength of coatings to the substrate.

	Adhesion strength, MPa		The decrease in adhesion, %
	Before corrosion tests	After corrosion tests (750 h)	
Developed solution	2.38	2.07	13.0
Solution without H ₂ O ₂	2.28	1.97	13.1
Cr(VI)	2.25	1.94	13.8
5556 AA	1.97	1.51	23.4

Conclusion

A solution containing 5–10 g/l Ce(NO₃)₃·6H₂O, 30–40 ml/l H₂O₂ and 0.5–1.5 g/l gallic acid ester was developed. At pH = 2.0–3.0 and at a temperature of 18–25 °C, it allows for 10 minutes to form on the surface of the 5556 aluminum alloy adhesive layers under the paintwork, not only are not inferior to chromate adhesive layers, but also surpassing them in protective ability, heat resistance and adhesion strength with LPCs.

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