

A high-performance Ti-Zr BASED conversion coating on 5556 aluminum alloy

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Abstract: *The process of deposition of titanium, zirconium-containing coatings at aluminum alloy 5556 is developed. In the process of performing the work, the basic patterns of coating formation were identified. The solution composition and process parameters were optimized, and the physicochemical properties were investigated. It is shown that passivation of aluminum alloy 5556 in a titanium, zirconium-containing solution increases its corrosion resistance to pitting corrosion. These coatings can replace chromate coatings because of good ability to resist corrosion.*

KEYWORDS: CORROSION PROTECTION, CONVERSION COATINGS, TITANIUM-CONTAINING COATINGS, ZIRCONIUM-CONTAINING COATINGS, SURFACE TREATMENT, CHROMATE-FREE PASSIVATION

1. 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.

Conversion chromate coatings are widely used as thin-layer adhesive layers under paint coatings before painting aluminum and its alloys.

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/m² of Cr⁶⁺, the legislation of many States significantly restricts or completely prohibits the use of conversion chromate coatings.

In the recent years in the world practice nanoscale particles obtained from hexafluorozirconic and hexafluorotitanic acids are more and more often used as an alternative to chromate layers [2-5]. Currently, world leading companies are actively developing the technologies necessary for production of such surfaces.

The development of protective and adhesive titanium, zirconium-containing conversion coating application methods on 5556 alloy with the aim replacing toxic chromating processes in automobile industry is the goal of the current work

2. Prerequisites and means for solving the problem

For the application of conversion coatings, samples of an aluminum alloy AA 5556 widely used in the automotive industry of the size of 3x4 cm were used.

Passivating coatings were formed by immersing aluminum samples 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 Na₂Cr₂O₇ and 60 g/l Na₂CO₃ (T= 95-100 °C; τ=20-30 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: CuSO₄·5H₂O 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° [6].

The composition of the surface layers was studied using X-ray photoelectron spectroscopy (Omicron, Taunusstein, Germany) (XPS). 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.

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 [ASTM D4541-17].

Pitting corrosion tests were carried out by simulating the effects of the maritime climate in constant contact with seawater. The test samples were immersed in a solution containing 3% sodium chloride and 0.1% hydrogen peroxide in accordance with GOST 9.913-90.

The study of the surface morphology of the coated samples was carried out using an MPLAPONLEXT 100 objective on a LEXT - OSL 4100 confocal laser microscope. To assess the layer structure, the degree of surface development, the depth and width of pitting corrosion spots, the surface images and profilograms of the samples after the formation of the conversion coating were investigated. The measurements were carried out in two-dimensional and three-dimensional coordinate systems.

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

3. Solution of the examined problem

As a result of this work, in order to replace the toxic chromating process in the automotive and other industries, a solution for applying protective titanium-, zirconium-containing coatings on the surface of the 5556 aluminum alloy based on H₂TiF₆, H₂ZrF₆, Ce(NO₃)₃ was developed.

In the process of research, the main patterns of the formation of coatings were revealed. Optimization of the composition of the solution and process parameters was carried out. The physicochemical properties of the coatings were investigated with the aim of their application as a substitute for chromate coatings.

Coatings with the best physical and chemical characteristics are formed in a solution with pH=4.0-5.0 at room temperature in 2 minutes of the process.

The chemical composition of the coatings was investigated with the help of X-ray photoelectron spectroscopy. The survey spectra of the coatings indicate the presence of titanium, zirconium, aluminum, cerium and oxygen in the coating.

Separate spectra of the elements made it possible to establish in which compounds the indicated elements are included in the coating (Fig. 1).

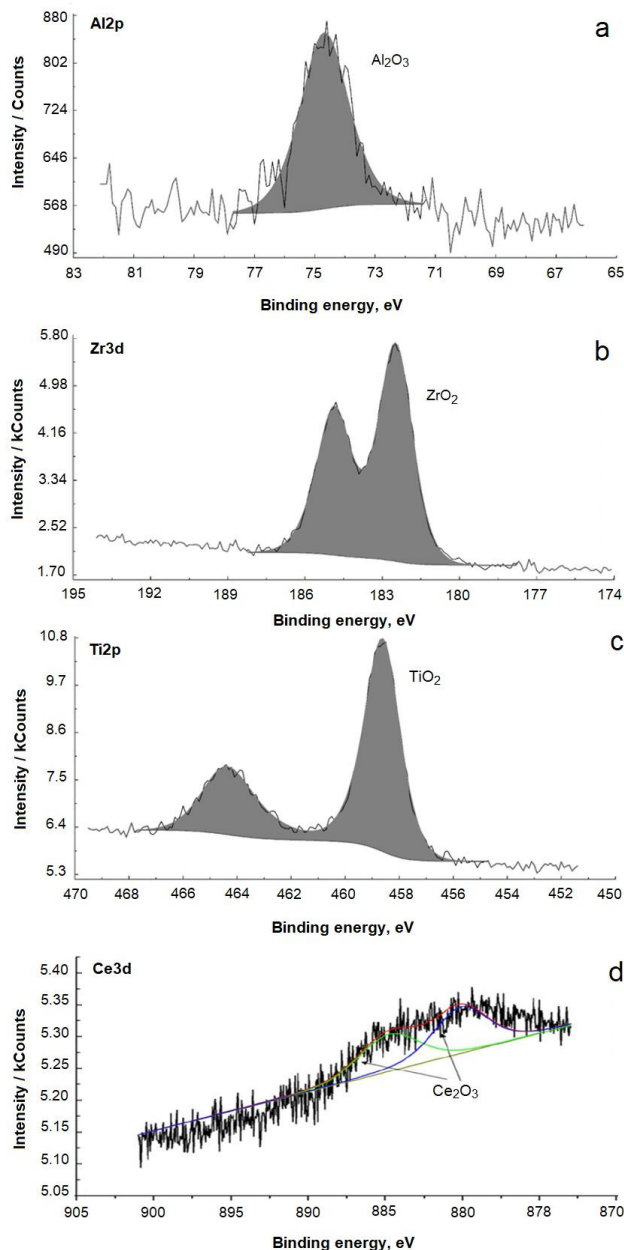


Fig. 1. Individual XPS spectra of aluminum (a), zirconium (b), titanium (c), cerium (d)

Aluminum is present in the coating in the form of Al_2O_3 oxide. Zirconium and titanium are present in the coating in the form of ZrO_2 and TiO_2 oxides. The position of the cerium energy peak corresponds to Ce_2O_3 .

Results and discussion

Corrosion tests (ASTM B117) in a salt spray chamber of painted samples of 5556 aluminum alloy with an adhesive Ti, Zr-containing coating were carried out. Tests have shown that Ti, Zr-containing coatings formed in the developed solution meet the

requirements in terms of protective ability, since the width of corrosion penetration from the notch does not exceed 2.0 mm after 750 hours of testing. It should be noted that in terms of corrosion properties these coatings are not inferior to chromate ones.

Corrosion tests of separate anticorrosive Ti, Zr-containing coatings showed that the coatings formed on the 5556 alloy in a Ti, Zr-containing solution have the highest resistance. The first corrosion spots appear after 170 hours of testing, while on the 5556 alloy with chromate coating they appear after 160 hours, and on the 5556 alloy after 24 hours of testing.

It was found that the inclusion of cerium-ions improves the resistance of the coating to pitting corrosion. The thickness of Ti/Zr/Ce-containing coatings is 120 nm.

With the help of confocal microscope the morphology and surface profile of the resulting coatings after corrosion tests in a $\text{NaCl}+\text{H}_2\text{O}_2$ solution were studied. It was found that the first pitting corrosion spots appeared in the unprotected 5556 alloy - 216 hours from the start of testing. Further pitting appeared on the Ti/Zr-containing coating - 1830 hours. After 2000 hours of testing corrosion was not observed on the Ti/Zr/Ce-containing and chromate coatings. During this time, the average depth of pitting corrosion spots was 206 μm for the 5556 alloy and 16 μm for the 5556 alloy with a Ti/Zr-containing coating.

4. Conclusion

The developed solution containing in its composition 1.2 g/l H_2TiF_6 and 1.2 g/l H_2ZrF_6 is a good alternative to toxic chromating solutions for protecting the aluminum surface from atmospheric corrosion and can also serve as an adhesive coating.

The developed solution containing in its composition 1.2 g/l H_2TiF_6 , 1.2 g/l H_2ZrF_6 and 1 g/l $\text{Ce}(\text{NO}_3)_3$ is a good alternative to toxic chromating solutions for protecting aluminum surface from pitting corrosion.

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