CERIUM-BASED CONVERSION COATINGS ON ALUMINUM ALLOY 5556

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Abstract

In recent years, the cerium-based conversion coatings have been increasingly used as one of the more promising chromate coatings substitutes on aluminum alloys, as cerium compound do not pose environmental problems and the coatings provide an efficient corrosion protection close to that of chromium. The cerium-based layer was prepared from simple immersion of aluminium alloy sheets in a solution composed of a 4 - 8 $g \cdot L^{-1}$ $Ce(NO_3)_3 \cdot 6H_2O$; 30 - 50 $ml \cdot L^{-1}$ H_2O_2 (37 %) and 0.5 - 1,5 $g \cdot L^{-1}$ tannin at room temperature. After optimization of several parameters as deposition bath composition, immersion time, drying temperature and so on, the corrosion resistance was evaluated mainly by means of salt spray tests (SST). It was established that the thickness of cerium-containing coatings is about 280 - 320 nm.

Keywords: Corrosion protection, conversion coatings, cerium-containing coatings, chromate-free passivation, rare earths

1. INTRODUCTION

Conversion chromate coatings are widely used as adhesion sub-layers for paint coatings before staining of aluminum and its alloys. High anticorrosion and adhesion characteristics of coatings, as well as ease of implementation of the process, provided their wide application in industry [1,2].

Chromate solutions, like the chromate coatings themselves, are highly toxic due to the hexavalent chromium ions they contain. For this reason, their use is limited or completely prohibited by law in the EU countries and the EEA, South Korea, China, etc. (Directives 2000/53 / EC, RoHS and WEEE) [3-6].

Analysis of scientific, technical and patent literature has shown that the process of depositing cerium, titanium, zirconium-containing coatings can be a promising replacement for aluminum chromating processes. Solutions for the application of these coatings are low-toxic, do not require heating and are easy to use [7-9].

The present study is devoted to the development of technologies for applying protective-adhesive cerium-containing conversion coatings on the surface of AA 5556 to replace toxic chromating processes in the automotive and other industries.

2. EXPERIMENTAL MATERIALS

For the application of conversion coatings, samples of an aluminum alloy AA 5556 widely used in the automotive industry of the size of 3 x 4 cm were used. Solutions were prepared of pure and pro analysis grades of chemicals and distilled water.

Developed cerium-containing coatings were compared in characteristics with chromate coatings, for application of which solutions based on Cr (VI): $Na_2Cr_2O_7$ 15 g/l were used; Na_2CO_3 60 g/l; T = 95-100 °C; 20 - 30 minutes; and based on Cr^{3+}: INTERLOX 338-A 160 ml/l; INTERLOX 338-B 50 ml/l; pH 3.3-4.3; T = 20-25 °C; 3 min.

To accelerate the evaluation of the protective ability of conversion coatings, a drop-express method was used using an Akimov solution containing: $CuSO_4 \cdot 5H_2O$ 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 ellipsometric method using the spectroscopic ellipsometer SENreseach 4.0 from SENTECH.

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 [10].

To determine the self-healing ability, samples with conversion coatings were incised and placed in a 0.003 M NaCl solution. After 24 and 80 hours of exposure in this solution, a surface area with scratches in the same place was examined with the OLYMPUS LEXT-OSL 4100 laser confocal microscope with MPLAPONLEXT 10 (x216) and MPLAPONLEXT 50 (x1069) objectives.

To evaluate the thermal stability of coatings, the samples were heated for 1 hour at a temperature of 160 °C, after which their protective ability was determined. Corrosion tests were carried out in a salt fog chamber Ascott S450iP in accordance with the international standard ASTM B117.

3. EXPERIMENTAL

The object of the study was a solution for the chemical oxidation of aluminum containing cerium ions, which were introduced into the solution as its nitric acid salt [$Ce(NO_3)_3 \cdot 6H2O$].

3.1. Determination of the cerium-containing coatings depositing process parameters

The effect of the concentration of cerium nitrate on the appearance and the protective ability of the coatings obtained is studied. The experiments were carried out for 5 minutes at room temperature.

In the aqueous solution of cerium nitrate (solution 1) at pH = 2.5 and temperature of 18 - 25 °C, the layers with the greatest protective ability according to Akimov (PAA = 40 s) are formed at salt concentration in the range of 4 - 8 g/l in 60 minutes of the process. It should be noted that at a concentration of more than 8 g/l, the protective ability (PAA) of coatings is reduced from 40 to 20 seconds. The experiments carried out made it possible to determine the optimal concentration range of solution components.

The addition of 30 - 50 ml/l of an oxidizing agent into the solution, such as H_2O_2 (solution 2), promotes the formation of more uniform coatings with PAA up to 80 s. The duration of coatings formation is reduced to 10 - 15 minutes in this case.

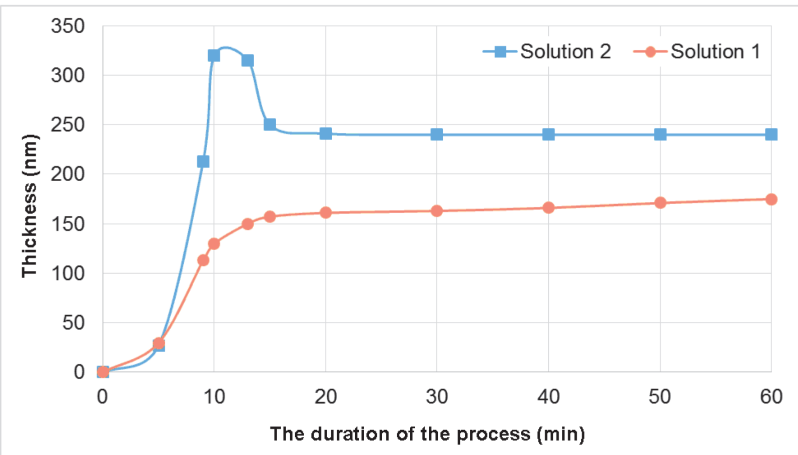

Figure 1 The thickness of coatings obtained in solutions 1 and 2, depending on the duration of the process

The thickness of the coatings obtained was determined by ellipsometry, depending on the duration of their formation (**Figure 1**). It was found that the thickness of the coatings obtained by solution 2 reaches a maximum value (320 nm) in 10 minutes; while in solution 1 the thickness of coatings does not reach such values even after

60 minutes of the process. The maximum thickness of coatings obtained from a solution without hydrogen peroxide is only 160 nm.

It was found that formation of coatings at room temperature and pH = 2.5 is over within 10 minutes, the thickness of the coatings and their protective ability during this time reaches maximum (110 s, 320 nm). The immersion of the coating in this solution for more than 20 minutes is undesirable, since it results in a slight decrease in the PAA (from 110 to 100 s).

The effect of solution temperature on the protective ability of the coatings obtained was studied. It was found that heating of solution above 35 °C promotes a sharp deterioration in the protective capacity of the emerging coatings (from 80 to 40 sec). Thus, the operation temperature range 18 - 25 °C was chosen, and it was noted that it is allowed to warm the solution, for example in the summer, up to 35 °C.

It was found that optimal pH values of the solution are in the range 2.0 - 3.0 units. It is known that in this region the following reactions occur [11]:

$Al \rightarrow Al^{3+} + 3e^-$ (1)

$H_2O_2 + 2e \rightarrow 2OH^-$ (2)

OH^- ions alkalize the solution near the sample surface, resulting in formation of cerium (IV) oxide according to the following reactions:

$Ce^{3+} + OH^- + \frac{1}{2} H_2O_2 \rightarrow Ce(OH)_2^{2+}$ (3)

$Ce(OH)_2 + 2OH^- \rightarrow Ce(OH)_4$ (4)

$Ce(OH)_4 \rightarrow CeO_2 + 2H_2O$ (5)

The influence of the drying temperature on the appearance and protective ability of the coatings is studied. Drying at a temperature of 170 - 190 °C favorably affects the properties of the coating - protective ability is increased from 110 to 150 s.

The possibility of increasing the protective ability of cerium-containing coatings was established by introducing into the working solution tannin, an ester of gallic acids with polyhydric alcohol. It is established that the introduction of 2-8 g/l tannin allows to increase the protective ability of coatings from 150 to 180 s.

3.2. Tests of the coatings

In order to identify the possibility of coatings application under high-temperature conditions, the samples were heated for 1 hour at a temperature of 160 °C. It was found that the protection of the coating after thermal shock increased from 180 to 220, while the protective ability of chromate coating, as expected, declined from 150 to 12 seconds.

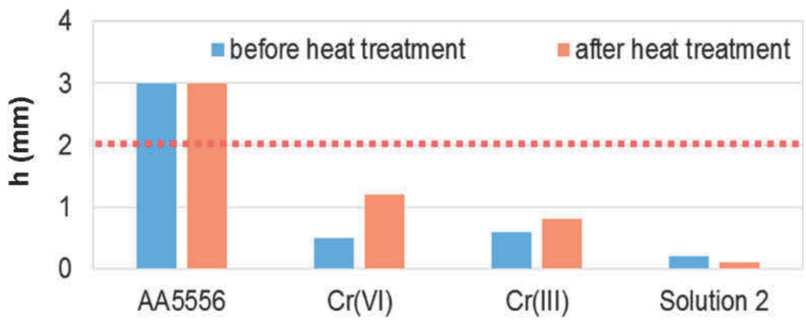

Figure 2 Results of corrosion tests (ASTM B117) of AA5556 samples with an adhesive coating painted with polyester powder; h is the width of the peeling of the paint from the notch.

Corrosion tests (ASTM B117) of painted samples with an adhesive cerium-containing coating were carried out. The tests have shown that cerium-containing coating satisfy the requirements for the adhesive layers, since the width of penetration of the corrosion under paint coating does not exceed 2.0 mm after 750 hours of testing. In addition, cerium-containing coatings are superior to chromate and chromite analogues in terms of their protective ability and are resistant to high temperatures without deterioration in performance.

The strength of paint adhesion for coatings on aluminum alloy with and without various adhesion sub-layers was determined by the detachment method (**Table 1).** The measurements were carried out before and after corrosion tests.

Table 1 The results of tests for the adhesion strength of coatings were determined by the method of normal detachment using the PosiTest AT digital adhesion meter

	Adhesion strength (MPa)		**Adhesion change, %**
	Before corrosion tests	**After corrosion tests (750 h)**	
Solution 2+Thermal treat	2.41	2.21	8.3
Solution 2	2.38	2.07	13.0
Cr(VI)	2.25	1.94	13.8
Cr(III)	2.25	2.05	8.9
AA5556	1.97	1.51	23.4

Tests showed that the adhesion properties of the developed coatings formed in solution 2 are comparable with chromate analogs. In addition, heat-treated cerium-containing coatings have a minimum adhesion loss value of 8.3 % after corrosion tests.

The self-healing ability of the developed cerium-containing coatings is illustrated in **Figure 3**.

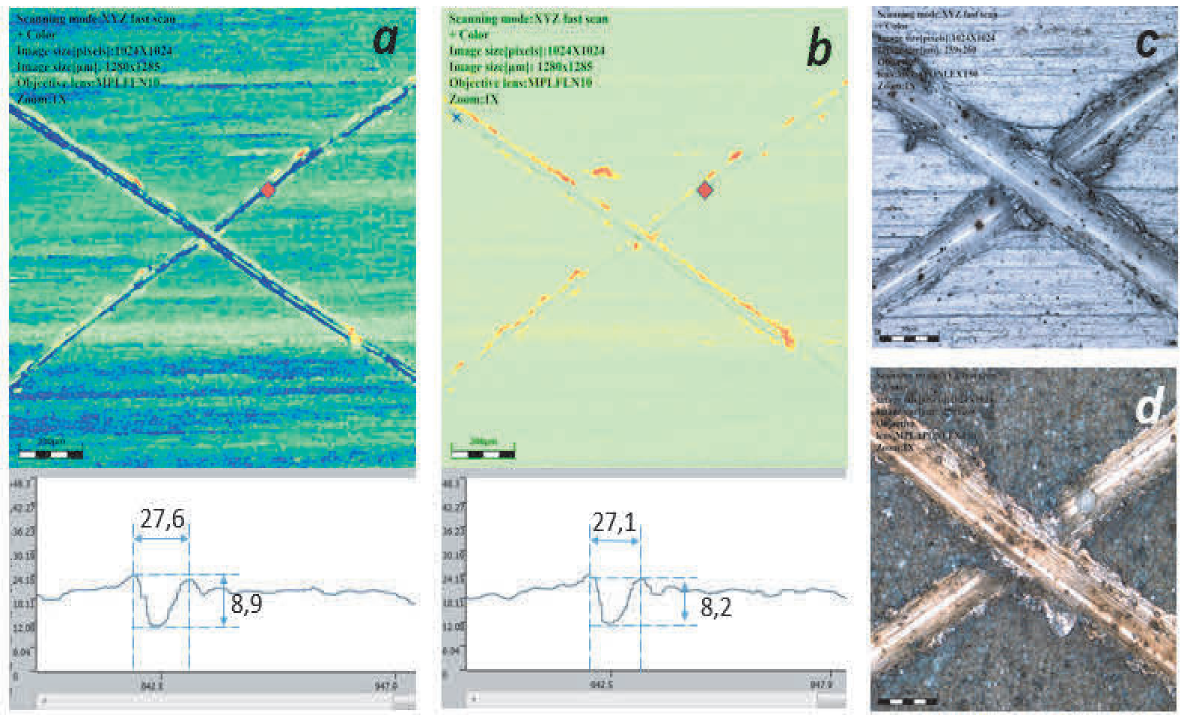

Figure 3 Pictures of scratched areas (solution 2 (a, b, c), Cr (VI) (d)) after immersion in 0.003 M NaCl solution: a - 24 h; b, c, d - 80 h

It is obvious that after 80 hours of testing the depth and width of the applied scratch are reduced by approximately 0.6 µm, which is most likely due to the repeated formation of a protective film whose thickness is approximately 0.3 µm (**Figures 3a, b**). The surface of the metal at the scratch site is again covered with a thin layer of coating and, compared to the chromate coating, less corrodes in a 0.003M NaCl solution (**Figures 3c, d**).

4. CONCLUSION

As a result it was shown that the developed cerium-containing coatings on aluminum alloy AA5556 in terms of their protective ability and adhesion properties are comparable to chromate coatings and can be an alternative to toxic chromate coatings in the automotive and other industries. It has been found that cerium-containing coatings, like chromate coatings, have the ability to self-heal and, in contrast to them, withstand thermoshocks without deteriorating characteristics.

ACKNOWLEDGEMENTS

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