Influence of the surface pre-treatment of aluminum on the processes of formation of cerium oxides protective films

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Abstract. It is known that there is special interest in the contemporary investigations on conversion treatment of aluminum aimed at promoting its corrosion stability, which is focused on electrolytes on the basis of salts of metals belonging to the group of rare-earth elements. Their application is especially attractive, as it enables a successful substitution of the presently applied highly efficient, but at the same time toxic Cr6+ -containing electrolytes. The present paper presents a study on the influence of the preliminary alkaline activation and acidic de-oxidation of the aluminum surface on the processes of immersion formation of protective cerium oxides films on Al 1050. The results obtained show that their deposition from simple electrolytes (containing only salts of Ce3+ ions) on the Al surface, treated only in alkaline solution, occurs at a higher rate, which leads to preparing thicker oxide films having a better protective ability. In the cases when the formation of oxide films is realized in a complex electrolyte (containing salts of Ce3+ and Cu2+ ions), better results are obtained with respect to the morphology and protective action of cerium oxides film on samples that have been consecutively activated in alkaline solution and deoxidized in acidic solution.

Electrochemical investigations were carried out in a model corrosion medium (0.1 M NaCl); it was shown that the cerium protective films, deposited by immersion, have a cathodic character with regard to the aluminum support and inhibit the occurrence of the depolarizing corrosion process – the reaction of oxygen reduction.

1. Introduction

Cerium-based conversion coatings have been recognized as an environmentally friendly alternative to chromate conversion coatings for the corrosion protection of aluminum and aluminum alloys, such as the Al 1050 and Al 2024 alloys. Despite providing excellent corrosion protection, chromate conversion coatings contain hexavalent chromium, a known toxin and carcinogen. Federal mandates have required implementation of strict environmental controls to reduce workplace exposure to Cr6+, motivating the development of environmentally benign alternatives [1]. Rare earths conversion coatings, principally cerium-based conversion coatings, have been shown to improve the corrosion resistance of aluminum alloys [2,3]. The deposition of cerium-based conversion coatings occurs via a
precipitation reaction driven by an increase in the near surface pH that is formed by electrochemical reactions between the ions of coating solution and the alloy substrate. The cerium oxides conversion coatings are commonly considered environmentally friendly corrosion inhibitors for aluminum alloys. Nevertheless, the effectiveness of the cerium-based conversion coatings on the corrosion protection has been highly dependent on surface pre-treatment, deposition parameters, and post-treatment [4,5]. Recent results demonstrated a surface pre-treatment for deposition of cerium-based conversion coatings on aluminum alloys that consisted of acid then alkaline cleaning [6,7]. The corrosion performance of cerium-based conversion coatings can also be improved by using a subsequent weak acidic phosphate bath treatment after cerium oxides deposition. This additional bath treatment results in the formation of insoluble CePO₄ species that can provide long-term protection [8]. Although several authors have reported an increase in the corrosion resistance of certain aluminum alloys by using cerium-based conversion coatings, there is not a reliable common method of assessment. To date, no systematic studies have been reported that optimize the corrosion resistance of the cerium oxides coatings in terms of process parameters such as thickness, microstructure, composition, and bath temperatures, among others.

The purpose of the present study was to investigate the influence of the alkaline activation and acid deoxidation of Al 1050 on the formation and corrosion resistance of Ce-based conversion films on aluminum.

2. Experimental

Layers of cerium oxide (chemical conversion treatment) were deposited on substrates of “technical degree of purity” Al 1050 (0.40% Fe, 0.25% Si, 0.05% Mn, 0.05% Cu, 0.07% Zn, 0.05% Mg), widely applied as a construction material. The samples studied of dimensions 1×1 cm were cut out of Al sheets (thickness 0.1 cm). Their pre-treatment involved degreasing in an organic solvent, degreasing (chemical cleaning) in aqueous solution of NaOH (1.5 mol dm⁻³) at 60°C (τ = 1 min) or chemical cleaning in NaOH and consecutive etching and surface activation in aqueous solution of HNO₃ (50 wt %) (acid deoxidation) at room temperature (τ = 30 sec). After each one of these operations, the obligatory standard rinsing of the samples was accomplished with distilled water. The Ce-containing protective layers were deposited on the so pre-treated samples using two different kinds of electrolytes containing: 1) CeCl₃ - 5×10⁻¹ mol dm⁻³; 2) CeCl₃ - 5×10⁻¹ mol dm⁻³ + CuCl₂ - 1×10⁻⁵ mol dm⁻³. The studies were carried out at temperatures of deposition 25° and 60°C, while the time interval of the deposition was 120 minutes. The morphology, structure and chemical composition of the conversion films, as well as the distribution of the elements on the aluminum surface prior to and after the deposition of the protective layers, were observed by the electron microscope JEOL JSM 6390 (under the conditions of secondary electron image - SEI) and by X-ray photoelectron spectroscopy (XPS). The XPS measurements were carried out on an AXIS Supra electron spectrometer (Kratos Analytical Ltd.) using monochromatic AlKα radiation. The depth profile was performed by layer-by-layer sputtering (the energy of the Ar gun was 500 eV). The corrosion behavior of the samples was tested in 0.1 M NaCl model medium at 25°C. Platinum electrode was used as the counter electrode, while the reference electrode was saturated calomel electrode (SCE → +0.240 V vs. SHE). All the potentials in this study are compared to SCE. The polarization curves were obtained by means of a Gamry Interface 1000 potentiostat/galvanostat. The curves were recorded at a sweeping rate of the potential 10 mV s⁻¹ in the range of potentials from -2300 up to +1800 mV.

3. Results

The cathodic and anodic polarization curves (E-lgi), illustrating the electrochemical behavior of aluminum samples coated with a cerium oxide film from electrolyte containing also CeCl₃ (degreased in advance only in a hot solution of NaOH), as well as samples treated consecutively in NaOH and HNO₃ are represented in figure 1. It is seen that the conversion films, formed on samples activated only in NaOH, possess a better protective ability with regard to the cathodic depolarization reaction of the corrosion process in chloride solution – compared with the films formed on samples after activation
in solution of NaOH and deoxygenation in HNO₃. A considerable inhibition of the reaction rate of oxygen reduction is observed, which is connected with a substantial decrease in the cathodic currents (table 1). The calculated degree of protection \( \frac{I_{corr}}{I_{corr,Al}} \times \frac{I_{corr}}{I_{corr,Al}} \% \) on the basis of the values of the corrosion currents determined in the model potentiodynamic investigations, is reaching a value of 93.75 %. This value is a proof that the formed oxide layer is a more efficient barrier for the corrosion process in the case when the samples have been pretreated only in NaOH.

The analogous polarization curves, obtained with samples coated with ceria oxide film from electrolyte containing CeCl₃ and CuCl₂, are represented in figure 2. In this case, better results with respect to the protective ability of the ceria films are observed when the samples have been treated consecutively in NaOH and in HNO₃. As it was noted above, the conversion treatment is leading to an insignificant decrease in the corrosion current observed with the samples which have been treated in advance in NaOH only. At the same time, the additional acidic deoxygenation results in the formation of conversion films acting as an efficient cathodic inhibitor. In such a case, the degree of protection against corrosion reaches the value of 95 %, which is evident of the importance of the preliminary acidic treatment of the Al 1050 samples during the formation of conversion films on their surface from electrolyte containing CeCl₃ and CuCl₂.

Figures 3 and 4 illustrate SEM micrographs of the formed oxide films, showing the differences in the morphology of the deposited layers depending on the preliminary treatment procedures and on the composition of the electrolytes for chemical conversion treatment. The morphology of the coating, formed in electrolyte containing CeCl₃ on substrates which have been activated in advance only in NaOH, is more homogeneously distributed on the aluminum surface (figure 3a). This result is in correspondence with the data from the potentiodynamic investigations, showing lower corrosion currents, respectively better protection ability, in comparison with the coating which is being formed on substrates consecutively treated in NaOH and in HNO₃ (figure 3b).

**Table 1.** Pre-treatment solutions, operation conditions and electrochemical parameters obtained from the potentiodynamic curves.

| Pre-treatment                  | Electrolyte | \( C_{comp} \) M | Time, min | \( I_{corr} \), Acm⁻² | \( \% \) |
|-------------------------------|-------------|------------------|-----------|-----------------|-------|
| Activation in NaOH            | CeCl₃       | 0.5              | 120       | \( 5 \times 10^{-7} \) | 93.75 |
| Activation in NaOH and HNO₃   | CeCl₃       | 0.5              | 120       | \( 9 \times 10^{-7} \) | 88.75 |
| Activation in NaOH            | CeCl₃       | 0.5              | 120       | \( 1 \times 10^{-6} \) | 87.50 |
|                               | CuCl₂       | \( 1 \times 10^{-5} \) |           |                 |       |
| Activation in NaOH and HNO₃   | CeCl₃       | 0.5              | 120       | \( 4 \times 10^{-7} \) | 95.00 |
|                               | CuCl₂       | \( 1 \times 10^{-5} \) |           |                 |       |
One has the impression that in the case of the samples treated consecutively in NaOH and HNO₃ (figures 4a and 4b), the homogeneity of the distribution of the cerium oxide layer, being formed in a complex electrolyte (containing CeCl₃ and CuCl₂), displays a substantially more uniform distribution in comparison with the layers formed in electrolyte containing only CeCl₃. This effect is obviously associated with the availability of higher concentrations of copper/copper oxides on the surface of the sample treated by immersion in the solution containing cerium and copper ions, designed for conversion treatment [9]. Such kind of distribution is leading to a considerable increase in the overpotential of the cathodic reaction of oxygen reduction (figure 2). The activation of the aluminum surface (in NaOH and HNO₃) as a result of the increase in the number of the cathodic sections during the contact (electroless) deposition of Cu on the aluminum substrate leading to an increase in the rate of deposition of Ce oxides/hydroxides on these sections (figure 4b).

The surfaces of the substrates of Al, treated in solutions of NaOH and NaOH and HNO₃, was studied by means of XPS with the aim to establish the composition and the valence states of the elements on the surface after the preliminary treatment. The XPS analysis of the surface shows that peaks of aluminum, oxygen and sodium are only present, as well as the peak of C1s with a lower intensity. The spectra of Al2p of all the samples (figure 5 represents only the spectra of Al samples treated in solutions of: 1 - NaOH and 2 - NaOH followed by treatment in solution of HNO₃.) The Al substrates pretreated in this way were subjected to argon bombardment (etching) in the course of: 15 sec, 75 sec, 180 sec, 720 sec and 2050 sec. It is seen in the recorded spectra that they are composed of two components. The first peak, located at 72.8 eV, is a superposition of two peaks having a spin-orbital splitting of 0.44 eV, characteristic of Al2p₃/₂ and Al2p₁/₂ of metallic state Al[0] [10]. The second peak at 75.2 eV is wider than the first one. During its deconvolution for the sample treated in solution of NaOH (figure 5,
15 sec etching), it becomes clear that it is built up of two peaks (figure 5 with deconvolution of Al). By separating the two peaks we can determine the ratio between the oxide and the hydroxide on a given surface. Accounting for the energy of the respective peaks and their areas, as well as comparing them with the deconvoluted spectrum of O1s for the same sample (figure 6 – deconvolution of O1s), we can state that the first peak at 73.9 eV is corresponding to Al$^{3+}$ in Al$_2$O$_3$. Its respective peak in the spectrum of O1s is the one located at 530.6 eV [11].

The second peak in the spectrum of Al2p, located at 75.2 eV, is characteristic of Al$^{3+}$ in the composition of AlOOH. Its corresponding peak in the spectrum of O1s is the one at 531.9 eV [12]. The small peak in the spectrum of Al2p at 71.7 eV is owing to the peak of Na2s, to the availability of Na$^+$ - ions in the solution, in which the sample was treated. The oxygen peak at 533.3 eV is attributed to the availability of water molecules adsorbed on the surface.

Figure 6. Deconvolution of Al2p (a) and O1s (b) spectra on the surface of Al-sample etched for 15 sec. The sample has been treated in solution of NaOH only.

Figure 7. Depth profiles reflecting the change in the ratio between the elements Al and O in the layers obtained on the sample treated only in solution of NaOH (a) and the sample treated in solutions of NaOH and HNO$_3$ (b).

4 Accounting for the number of peaks and the magnitude of the areas of the deconvoluted peaks of Al2p and O1s, one can conclude that the surface consists mainly of AlOOH, and some smaller amounts of Al$_2$O$_3$, at a ratio of AlOOH/Al$_2$O$_3$ of approximately 3.6 : 1, whereupon this ratio between the oxide and the hydroxide is preserved in the depth of the layer.

A layer-by-layer XPS analysis was carried out in order to elucidate the influence of the pre-treatment on the composition and on the valence states of the elements in the so treated samples.

It becomes clear from figures 7a and 7b that upon increasing the time interval of etching (through argon bombardment) of the Al surface, the quantity of oxygen (respectively the oxide and the
hydroxide in the layer) is decreasing, while that of aluminum is increasing. Then an intersection point is reached, after which the increase in the concentration of Al, respectively the decrease in the O concentration take place in an abrupt way. This sharp change gives us reason to assume that this intercept point could serve as an indicator for the fact that the interphase boundary is reached between the layer formed during the pre-treatment and the aluminum substrate. In the case of the sample treated in solution of NaOH, this point is reached at the etching time interval of 160 sec, while in the case of the sample activated and deoxygenated in solutions of NaOH and HNO₃, this intercept point is reached after the etching time interval of 72 sec. Comparing the time intervals for reaching the interphase boundary with the two samples, which are proportional to the thickness of the layer, we can draw the conclusion that the thickness of the oxide/hydroxide layer for the sample treated with NaOH is much bigger (about 2-3 times) in comparison with that of the layer treated additionally in HNO₃.

The chemical composition on the surface of the samples with deposited conversion ceria layers was investigated by XPS as well, for both types of pre-treatments. It is as follows: Ce – 31.1÷39.6 at.%; O –56.6÷65.8 at.%; Al – 0.3 ÷ 3.8 at.% (and Cu – about 2.3÷3.8 at. %).

The results obtained on the basis of these analyses show that the preliminary treatment procedures of the Al substrates determine the formation of surface oxide layers differing in their thickness and in their composition. These layers, as it was shown by the above electrochemical investigations, possess a higher activity acquired during the immersion process of deposition of cerium oxide layers. This activity obviously influences the rate of formation and the homogeneity of the ceria layers. Moreover, they can contribute to the appearance of a more efficient barrier against the corrosion process.

4. Conclusions
The effect was investigated of alkaline activation and acid base deoxidation on the process of the deposition of cerium oxide conversion coatings on Al 1050 substrates. The results obtained prove that the conversion deposition of ceria on an alkaline-activated Al surface from electrolyte containing only CeCl₃ offers a high rate of deposition and a better option for cathodic protection.

In the case when the conversion coatings are formed in electrolyte containing CeCl₃ and CuCl₂ on an Al substrate pretreated by alkaline cleaning and acid deoxidation, the rate of the process of conversion deposition is much higher and the coatings exhibit an even higher cathodic protection. Moreover, the acidic pre-treatment decreases the amount of Al oxide/hydroxides on the surface of the Al 1050.

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