FORMATION OF CERIUM-CONTAINING CONVERSION COATINGS ON ALUMINIUM AND ITS ALLOYS AS ALTERNATIVE TO CHROMATE (Cr^{6+}) CONVERSION COATINGS

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Abstract: *Studies, focused on elucidating the options of cerium oxide conversion films formation, have been carried out with the view to replace the toxic Cr^{6+}-containing electrolytes in the case of surface treatment of aluminium and its alloys. Aiming at accelerating the processes of chemical deposition of cerium the composition of the electrolytes has been optimized ($CeCl_3$, $LaCl_3$), as well as the conditions of deposition (the temperature). The influence of copper (as component of the electrolyte-$CuCl_2$) was also investigated in view of the formation of active cathode zones in the course of depositing the cerium oxide films. It has been found out that the heterogeneous nature of the aluminium surface determines an island-like structure of the deposited cerium oxide film. It has been shown that the corrosion process of reduction of oxygen in 0.1M NaCl solutions, occurring on the cerium oxide cathode, leads to a conjugated anodic process of oxidation of the aluminium matrix and formation of mixed oxide film. The protective ability of the formed films has been studied, whereupon the dependence between the potential (E) and the current intensity (i) was monitored by the potentiodynamic method. The cerium–containing conversion films were shown to have values of the electrochemical corrosion parameters - corrosion currents and corrosion potentials, which makes them an appropriate alternative to the chromium-containing films. SEM micrographs of the formed cerium-containing films on aluminium were made and analysed.*

Keywords: ALUMINIUM, CERIUM CONVERSION COATINGS, CORROSION, Cr^{6+}- FREE ELECTROLYTES

1. Introduction

The use of salts of rare-earth metals as basic components in electrolytes for the formation of cerium, lanthanum and other oxide films is a desired alternative of the chromate films and one of the modern methods for protection of metals and alloys from corrosion. The oxide films can be formed based either on a chemical or an electrochemical approach [1-3]. In spite of the growing number of investigations in the current literature, during the last years, devoted to the mechanism via which the presence of oxides of rare-earth metals (mainly cerium) leads to improvement of the corrosion stability of the systems and number of questions remain controversial. The first attempts in this direction have been made by Hinton [4,5]. He supposed in his works that the cathodic reactions (reduction of oxygen and liberation of hydrogen) lead to alkalization of the layer near to the electrode surface, which in its turn leads to precipitation of oxides of the rare-earth elements, respectively to formation of protective film on the electrode surface. Davenport and co-workers [6,7] also studied the deposition of cerium on aluminum alloys and they reported that the trivalent cerium is oxidized into tetravalent state by the oxygen, dissolved in the electrolyte. This leads, as a final step, to precipitation of insoluble CeO_2 on the cathodic sections of the electrode surface. Montemor et al. [1,2] studied the influence of the composition of the electrolyte (based on $Ce(NO_3)_3$) and the regime of preparation of the conversion layers on galvanized steel. The increase in the thickness of the cerium conversion film is connected with their enrichment in Ce^{4+}. According to the same authors the conversion films formed in $La(NO_3)_3$ are more efficient in view of the anticorrosion protection in comparison to those formed in electrolytes containing $Ce(NO_3)_3$ and $Y(NO_3)_3$ [2]. The mechanism of corrosion inhibition of zinc, treated in solutions of cerium salts has been studied by Aramaki [8-11]. He ascertained the formation of hydrated or hydroxylated Ce-rich layer. This process, in its turn, leads to the formation of Ce_2O_3 on the electrode surface, respectively to inhibition of the cathodic reactions of the corrosion process in solutions of NaCl.

The different mechanisms, supposed in the literature, show that the role of the rare-earth elements as inhibitors of corrosion and as protective coatings is not yet completely elucidated. It is accepted that they lead to improvement in the corrosion stability of metals and alloys and therefore they are a promising alternative, taking into account the environmental protection requirements in regard to the conventional Cr^{6+} conversion treatment.

In this respect the aim of the present study was to compare the protective action of conversion films, formed by immersion, in three electrolytes, containing cerium and lanthanum and a mixed electrolyte with the action of commercial electrolytes, not-containing Cr^{6+} too, known under the name ALODINE 160 and ALODINE 161.

2. Experimental

The present study represents the results, obtained with conversion layers of Ce and La oxides, deposited on the widely used construction material "technically pure Al AD-3, containing 0.40% Fe, 25% Si, 0.05% Mn, 0.05% Cu, 0.07% Zn, 0.05% Mg.

The studied samples of dimensions 2x2 cm were cut out of aluminum sheets of thickness 0.1 cm. The samples were hung on wire hooks, made of the same type of aluminum. Their pretreatment consisted in degreasing with organic solvent, etching in aqueous solution of NaOH (60g/l) at 60ºC for 1 min and consecutive discoloration in aqueous solution of HNO_3 (50%) at room temperature for 30 sec. After each one of these operations the necessary standard washing was done with flowing and distilled water. On the so prepared samples a cerium oxide conversion film was deposited or lanthanum-containing conversion film, as well as a mixed film. The compositions and the conditions of treatment of the aluminum samples are given in Table 1. For comparison some conversion films were also obtained with commercial electrolytes (ALODINE 160 and ALODINE 161) – Table 1. The time interval of deposition for all the compared conversion films was 5 min. The morphology and structure of the layers were examined by scanning electron microscopy using JEOL JSM 6390 electron microscope (Japan), equipped with ultrahigh resolution scanning system (ASID-3D) in a secondary electron image (SEI). The accelerating voltage was 25 kV, I was 65 μA. The pressure was of the order of 10^{-6} Torr. The electrochemical (corrosion) behavior of the samples was studied in 0.1M NaCl (p.a. Merck) model medium without de-aeration at 25ºC. A counter-electrode, representing a platinum plate (10x10x0.6 mm) and a saturated calomel reference electrode (SCE), (E_{SCE}=+0.240 V versus SHE) were used. All the potentials in the text are related to SCE. The anodic and cathodic polarization curves were obtained using a GAMRY potentiostat/galvanostat (Germany) and computer aided processing of the results by an "Echem" program at a potential sweeping rate of 10 mV/s within a potential range from -2200 to +2000 mV.

Table 1: *Composition of the electrolytes, conditions of formation of the protective films.*

Electrolytes	Concentration	Time [min]	Temperature [°C]
Alodine 160	13 g/l	5	20
Alodine 161	15 g/l	5	20
$CeCl_3$ $CuCl_2$	$4x10^{-2}$ M $4x10^{-4}$ M	5	20
$CeCl_3$ $CuCl_2$	$4x10^{-2}$ M $4x10^{-4}$ M	5	90
$LaCl_3$ $CuCl_2$	$4x10^{-2}$ M $4x10^{-4}$ M	5	20
$LaCl_3$ $CuCl_2$	$4x10^{-2}$ M $4x10^{-4}$ M	5	90
$CeCl_3$ $LaCl_3$ $CuCl_2$	$4x10^{-2}$ M $4x10^{-2}$ M $4x10^{-4}$ M	5	20
$CeCl_3$ $LaCl_3$ $CuCl_2$	$4x10^{-2}$ M $4x10^{-2}$ M $4x10^{-4}$ M	5	90

3. Results and discussion

Fig. 1 represents the cathodic and anodic potentiodynamic curves of the pure aluminum and of the systems Al/conversion film, obtained in the Alodine commercial electrolytes. It is interesting to note that the formed conversion films inhibit the cathodic reaction of oxygen reduction in the studied model corrosion medium 0.1M NaCl. This effect is more strongly expressed in the case of Alodine 160 conversion films. As far as the corrosion currents and the complete passivation currents are concerned – they have values close to those of the pure aluminum.

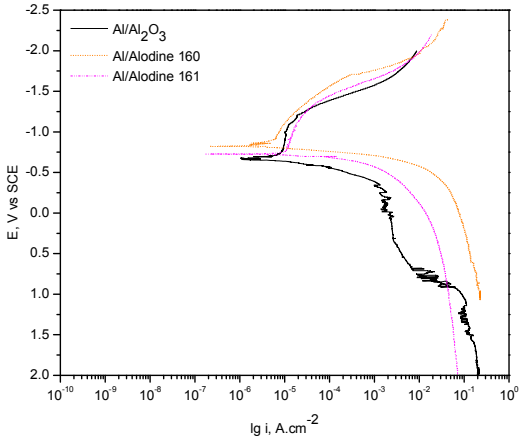

Fig.1 *Polarization curves of tasted systems in 0.1M NaCl at 25°C.*

For comparison Fig. 2 shows analogous potentiodynamic curves for the conversion layers obtained by immersion in electrolytes, containing cerium and lanthanum salts. In all three kinds of studied electrolytes the obtained conversion films lead to changes both in the anodic and cathodic behavior of aluminum in regard to the occurring corrosion processes (see Table 1). While for the systems $Al/Cu/La_{ox}$ and $Al/Cu/Ce_{ox}/La_{ox}$ the deposition of lanthanum oxide and mixed oxides of La and Ce on the active cathodic sections of copper leads to promotion of the effectiveness of the cathodic process of oxygen reduction. The change in the kinetics of the cathodic corrosion process improves the oxidation of the active anodic sections, which is manifested in the improvement of the passivation ability of the system and results in a lowering of the values of complete passivation currents.

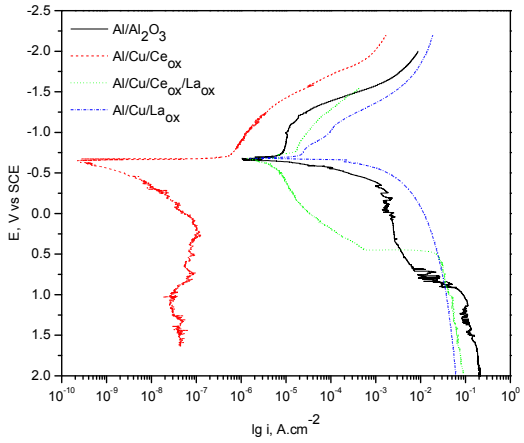

Fig.2 *Polarization curves of tasted systems in 0.1M NaCl at 25°C.*

The most strongly expressed protective effect with respect to the aluminum matrix is displayed by the cerium oxide film and as it follows from Fig. 2 it appears in the inhibition of the cathodic reaction of oxygen reduction, as well as in a strong decrease of the corrosion currents and the currents of complete passivation of the system. In this case the corrosion current of pure aluminum is decreasing from $2{,}12.10^{-6}$ down to $2{,}63.10^{-10}$ $A.cm^{-2}$ for the system $Al/Cu/Ce_{ox}$ under conditions of steady state.

Analogous polarization curves are represented in Fig. 3 and in this case the conversion films were being formed in the same electrolytes, but at different temperature (90°C). The obtained curves are in accordance with those illustrated in Fig. 2, whereupon an increase in the effectiveness of the cathodic process of oxygen reduction is observed with all three types of conversion layers. This is reflected on the conjugated anodic process of aluminum oxidation and it leads to formation of mixed oxide films of Al_2O_3 and lanthanum and cerium oxides and hydroxides. The so prepared oxide films are characterized by lower values of the currents of complete passivation having respectively better protective properties. An evidence for this is the tendency for shifting the corrosion potential of the system in positive direction (see Fig. 3).

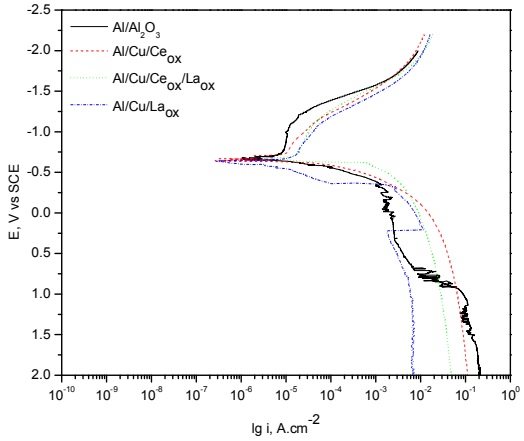

Fig.3 *Polarization curves of tasted systems in 0.1M NaCl at 25°C.*

The changes in the structure and in the morphology of the aluminum surface, after the respective surface treatment (Table 1), are represented in Fig. 4a – c. The Fig. 4a characterizes the morphology and the structure of Al surface non-treated in conversion solution, after the preliminary treatment of the samples

in degreasing NaOH solution and discoloration HNO_3 solution. It can be seen that it is "decorated" by the appearance of iron agglomerates (the light spots) of size ≈0.5 μm. Fig. 4b and 4c represents the SEM image of the same surface after its immersion treatment in a solution for cerium oxide formation. It is seen that the deposited layer has island structure and it is relatively homogeneous. No copper crystallites, which represent the active cathodic zones, are observable.

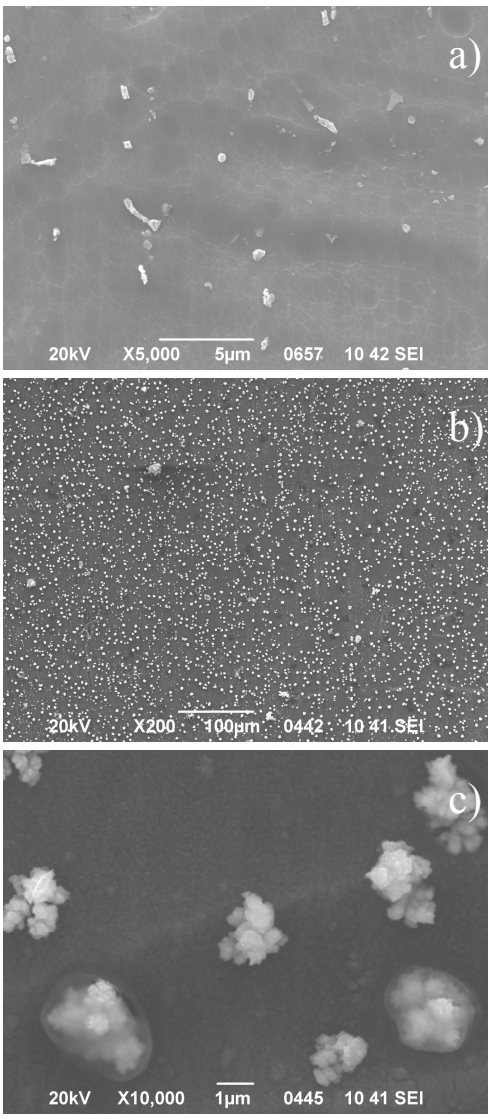

Fig.4 *SEM micrograph of the surface of: (a) Al/Al_2O_3; (b) Al/Cu/Ce_{ox}×200; (c) Al/Cu/Ce_{ox}×10000.*

4. Conclusions

The obtained results show that the formation of Ce-containing corrosion-protective layers on Al surface is a promising alternative to the chromate conversion treatment. The use of electrolytes based on Ce^{3+} ions, harmless from ecological and health-care point of view, could obviously enable the substitution of the toxic Cr^{6+} - containing electrolytes and technologies. The investigations carried out and the comparative analyses of the data, available from the current literature, give us the reason to state that it is possible to deposit such films by immersion. It has been shown that in most cases cerium oxides fulfill the role of effective cathodic coating in regard to the aluminum matrix facilitating the processes of its passivation. Evidently the selection of the technological approach should be made on the basis of technical and economical estimations and considerations.

The application of electrolytes, which contain in addition to the cerium ions also other heavy metal ions (Cu^{2+} etc.) results in obtaining of mixed oxide films, which are richer in Ce (La) and aluminum – this fact determines their better protection ability.

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