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STUDY OF THE CHEMICAL FORMATION OF CERIUM OXIDE CONVERSION LAYERS ON ALUMINIUM AD-3

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The effect of the concentration of cerium ions as a component of electrolytes, designed for conversion treatment, has been studied in view of the morphology and structure of the conversion films, formed on Al. The studies have been carried out in a complex electrolyte containing cerium and copper ions at temperature 25 °C and duration of the treatment 60 and 120 min. It has been found out that the presence of copper ions in the electrolyte leads to the formation of more compact and richer in cerium conversion films. The electrochemical characteristics (corrosion current, corrosion potential) of the formed films have been investigated applying potentiodynamic polarization method in 0.1 M NaCl solutions. The composition of the electrolytes has been optimized with respect to the concentrations of cerium and copper ions, aiming at obtaining conversion films having improved protection ability. Thereupon the influence of the microgalvanic couples copper/aluminium has been established.

Key words: cerium conversion films, aluminium, corrosion protection.

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1. Introduction

The wide application of conversion protective coatings on aluminium and on its alloys, formed in electrolytes containing hexavalent chromium Cr(VI), although it is beneficial in technological and economical aspect, is discontinued. This is determined by their high toxicity and carcinogenicity, respectively by changes in the legislation due to ecological considerations (Hagans & Haas 1994). In this connection intensive investigations are being carried out to replace the electrolytes, containing Cr^{6+} with other electrolytes, based on Cr^{3+} ions (Berger et al. 2007, Wen et al. 2008) or on inexpensive and less toxic salts of other metals, which are abundant in nature (Da Fonte & Mich 1982, Wilcox, Gabe & Warwick 1988, Hinton 1991, Deck & Reichgott 1992, Barbucci, Delucchi & Cerisola 1998, Delucchi et al. 2002). It is of special interest to study the electrolytes and the respective methods based on salts of metals, belonging to the lanthanide group, as the hardly soluble oxides and hydroxides, formed on them, are among the lowest toxicity compounds and their ingestion or inhalation is not considered harmful for human health (Montemor, Simões & Ferreira 2001, 2002, Montemor et al., 2006, Balasubramanian, Melendres & Mansour 1999). A substantial contribution in this direction is put forward by the studies of Hinton (Hinton 1992, Hinton & Wilson 2004). Aldykewicz et al. (Aldykiewicz, Jsaacs & Davenport 1995, 1996) also studied the deposition of cerium-containing oxide films on aluminium alloys and they proved that the trivalent cerium is oxidized into tetravalent ions by the oxygen dissolved in the electrolyte, leading to a final step of precipitating the insoluble CeO_2 on the cathode sections of the electrode surface. Montemor et al. (Montemor, Simões & Ferreira 2001, 2002) have investigated the influence of the composition of the electrolytes based on $Ce(NO_3)_3$ and the conditions of preparation on the composition and on the structure of conversion films, formed on steel surface. According to the same authors the conversion films, formed in $La(NO_3)_3$ solution are more efficient in view of their corrosion protection ability, in comparison to the films formed in electrolytes containing $Ce(NO_3)_3$ and $Y(NO_3)_3$ (Montemor, Simões & Ferreira 2002,).

In the study (A.Decroly & J. P. Petitjean, 2005) the authors investigate the effect of catalyzing additives upon the protection capacity of the conversion films, formed in electrolytes, which contain $CeCl_3$ and H_2O_2. They ascertained that insignificant amounts of $CuCl_3$ are catalyzing the formation of CeO_2. In addition to this fact, however, in the presence of catalyst in the electrolyte - ($CuCl_3$), a tendency is being observed to lower the protection ability of the conversion films.

The data on the role of copper have been used as the basis for elaborating a method to form conversion films on aluminium alloys rich in copper (Aldykiewicz, Jsaacs & Davenport 1996, Hinton, Arnott & Ryan 1986). As the authors claim, the process of formation of the oxides/hydroxides of Ce(III) and (CeIV) has an electrochemical nature, which is a consequence of and connected with the reaction of cathodic reduction of O_2 and/or H_2O_2. This means that the effect of the cathodic inter-metallic phases of the copper is expressed in promotion of the rate of the cathodic reaction, occurring on them, which is a prerequisite for the consecutive acceleration of the process

of deposition of cerium oxides/hydroxides on these sections themselves (E. Stoyanova et al. 2011). Campestrini et al (Campestrini et al. 2003) investigated in detail the influence of the intermetallic phases in aluminum alloy rich in copper AA2024 in view of development of applicable from technological point of view method for preparing conversion films from electrolytes, containing $CeCl_3$ and H_2O_2. In this context Campestrini and co-workers proposed a mechanism of Ce precipitation in the presence of Cu particles, suggesting that the amount of Cu and its distribution in the aluminum matrix influences the formation and the morphology of the Ce coatings.

In spite of the great number of studies, carried out until the present moment, the problem to optimize the composition of the electrolytes, containing cerium salts and the optimal conditions for immersion modification of the composition and structure of the surface of aluminum and its alloys, is still a controversial issue.

In this aspect the aims of the present investigation were: 1 – to optimize the composition (in regard to concentrations, respectively the ratio between Ce^{3+} and Cu^{2+} ions) of the electrolytes for chemical formation of cerium oxide films on aluminum, which would eventually lead to the formation of more compact and thick layers; 2 – to characterize the corrosion protection ability of these films, depending on the conditions of their preparation, on technically pure aluminum, chosen by us as the model object.

2. Experimental

Layers of cerium oxide were deposited on substrates of "technically pure" Al AD-3 selected by us as a model object, containing 0.40% Fe, 0.25% Si, 0.05% Mn, 0.05% Cu, 0.07% Zn, 0.05% Mg admixtures - Al 1050 finds wide application as a construction material. The studied samples of dimensions 1x1 cm, were cut out of Al sheets of thickness 0.1 cm. They were suspended on wire hangers, made of the same type of Al. Their preliminary treatment involved degreasing in organic solvent, degreasing in aqueous solution of NaOH (1.5 mol dm^{-3}) at 60°C (τ = 1 min), consecutive etching and surface activation in aqueous solution of HNO_3 (50 wt.%) 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 pretreated samples using different kinds of electrolytes containing: 1) $CeCl_3$-$1x10^{-1}$M; 2) $CeCl_3$- $1x10^{-1}$M + $CuCl_2$ - $1x10^{-5}$M, 3) $CeCl_3$- $1x10^{-1}$M + $CuCl_2$ – 8 $x10^{-5}$M; 4) $CeCl_3$- 0.5M; 5) $CeCl_3$ - 0.5M + $CuCl_2$ - $1x10^{-5}$M, 6) $CeCl_3$- 0.5M + $CuCl_2$ - $8x10^{-5}$M. The studies were carried out at temperatures of the deposition 25^{o} C, while the time interval of the deposition was varied between 60 and 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 JEM – 200 CX (Japan) (under the conditions of secondary electron image – SEI). The applied voltage was 120 kV, $I \sim 100$ μA).

The corrosion-electrochemical behavior of the samples was tested in 0.1 mol.dm^{-3} NaCl ("p.a." Merck) model medium at 25°C. Platinum electrode was used as the counter electrode having dimensions 10x10x0.6 mm, while the reference electrode was saturated calomel electrode (SCE), (E_{SCE}=+0.240 V versus SHE). All the potentials in this study are compared to SCE. The anodic and cathodic polarization curves were obtained by means of a potentiostat/galvanostat - Electrochemical Measurement System-Gamry, whereupon the obtained results were processed with the help of the "PHE 200" specialized software. The curves were recorded at a sweeping rate of the potential 10 mV.s^{-1} in the range of potentials from –2300 up to + 2200 mV.

The degree of protection (z, %) from corrosion was evaluated on the basis of the following equation (1):

$$z = \frac{\left(i_{corr(Al)} - i_{corr(CL/Al)}\right)}{i_{corr(Al)}}, \% \qquad (1),$$

where $i_{corr\ (Al)}$ is the corrosion current of Al electrode surface, non-coated with conversion film (but in all cases covered with very thin native layer Al_2O_3), determined from the potentiodynamic polarization curves, while $i_{corr\ (CL/Al)}$ is the corrosion current for the system conversion layer/Al.

3. Results and discussion

Figure 1 represents cathodic and anodic potentiodynamic curves, obtained in 0.1M NaCl solution, both for aluminum AD-3 and for the system aluminum/cerium oxide. The protective oxide layer is formed in electrolyte, containing only $CeCl_3$ (0.1M), at temperature 25°C. It can be seen from the figure that the presence of a conversion film on the aluminum surface shifts the cathodic potentiodynamic curve towards lower values of the corrosion currents and more negative values of the corrosion potentials, defined on the basis of the intersection point between the anodic and the cathodic potentiodynamic curves. This effect is more strongly expressed upon increasing the time interval of the conversion treatment from 60 to 120 minutes. The calculated degree of protection, achieved for time interval of conversion treatment 120 minutes reaches the value 87.5% (Table 1). In addition to this fact a characteristic tendency is observable in the course of the anodic potentiodynamic curves, describing the effect of increase in the corrosion currents in the vicinity of the stationary corrosion potential. Therefore the influence of the oxide film, deposited on the aluminum surface, is most probably due to its inhibiting effect on the rate of the occurring cathodic depolarization reaction of oxygen reduction, which will lead to lowering of the corrosion currents of the system $Al/Ce_2O_3 - CeO_2$ in comparison to those of the pure aluminum.

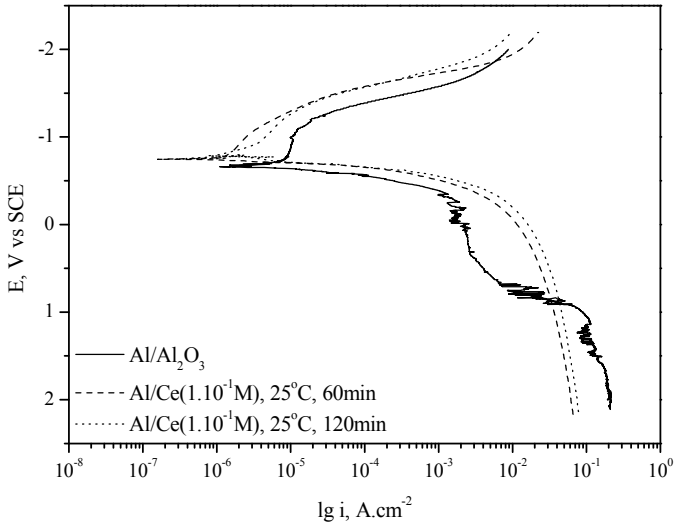


Fig. 1. Polarization curves of tasted systems in 0.1M NaCl at 25°C.

Analogous potentiodynamic curves, illustrating the corrosion behavior of the system aluminum/conversion film, obtained with layers, formed in electrolyte containing 0.5M $CeCl_3$, are represented in Figure 2. In this case the change in the character of the cathodic potentiodynamic curves of the system $Al/Ce_2O_3 - CeO_2$, compared to those of pure Al, is only slightly expressed. This result can be explained by the increase in the concentration of the chloride ions in the electrolyte from 24.3 g-ion /L for 0.1M $CeCl_3$, up to 121.5 g-ion /L, for 0.5M $CeCl_3$, which exerts unfavorable effect on the processes of chemical deposition of conversion films.

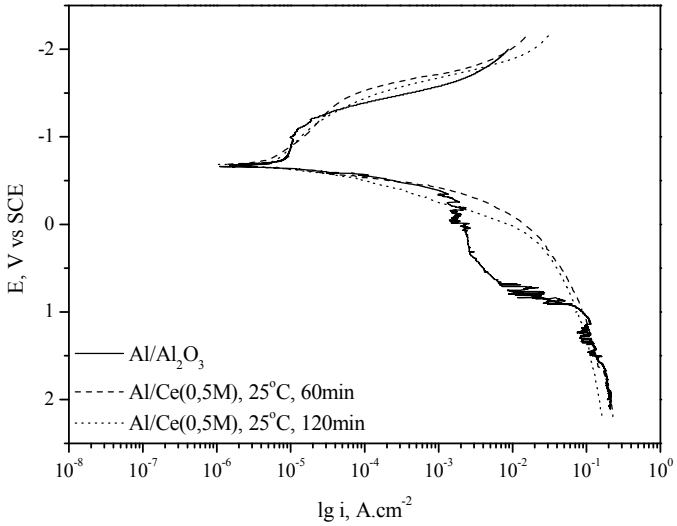


Fig. 2. Polarization curves of tasted systems in 0.1M NaCl at 25°C

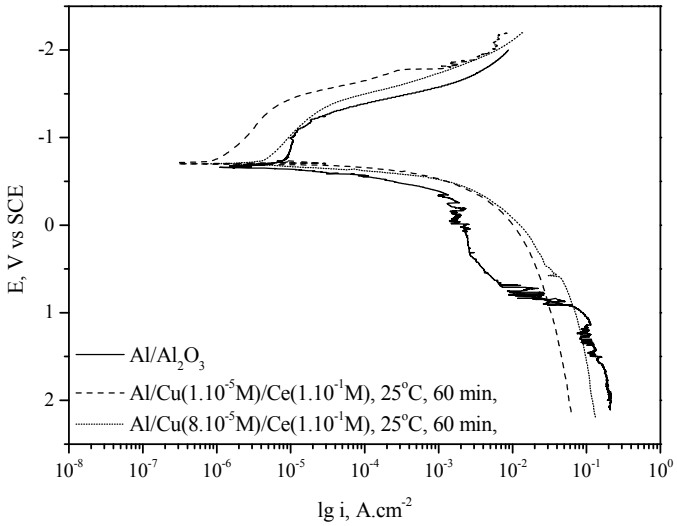


Fig. 3. Polarization curves of tasted systems in 0.1M NaCl at 25°C.

Aiming at optimization of the processes of conversion treatment, we carried out immersion treatment of aluminum samples in both electrolytes in the presence of Cu^{2+} - respectively 1.10^{-5}M and 8.10^{-5}M. Figure 3 illustrates the polarization curves, obtained with the system aluminum/cerium oxide for conversion films, which have been formed in electrolyte containing 0.1M $CeCl_3$ in the presence of various concentrations of Cu^{2+} - respectively 1.10^{-5}M and 8.10^{-5}M, for time interval of immersion treatment 60 minutes. It is seen that the presence of Cu^{2+} assists the formation of conversion films, which manifest stronger decrease in the corrosion currents of the system leading to shift in the cathodic potentiodynamic curves towards more negative potentials, resulting in stronger inhibition of the cathodic reaction of oxygen reduction, determining the occurring corrosion process. The degree of protection in this case reaches a value of 90% (Table 1). At the same time upon increasing the concentration of Cu^{2+} in the electrolyte for immersion treatment, the degree of protection of the deposited protective cerium oxide layers becomes lower – from 90% going down to 62.5%. For comparison Figure 4 represents analogous anodic and cathodic potentiodynamic curves for time interval of conversion treatment 120 minutes. It is noticeable that upon increasing the concentration of Cu^{2+} a more strongly expressed tendency of increase in the corrosion currents is established. The protection ability of the layers in this case is drastically decreased (from 92.5% down to 0% - Table 1) and practically it is missing completely.

Table1: Composition of the working electrolytes, conditions of formation of the protective immersion films and elecrochemical parameters in 0.1 M NaCl of selected coated samples

Composition of the electrolytes	**Concentration of components**	**Time of treatment, min**	**Corrosion current, i_{corr} ,A.cm^{-2}**	**Corrosion potential, E_{corr}, V**	**Degree of protection, z, %**
$CeCl_3$	0.1M	60	$1,5x10^{-6}$	-0.747	81.25
$CeCl_3$	0.1M	120	$1x10^{-6}$	-0.754	87.50
$CeCl_3$	0.5M	60	$3x10^{-6}$	-0.687	62.5
$CeCl_3$	0.5M	120	$2x10^{-6}$	-0.683	75.00
$CeCl_3$ $CuCl_2$	0.1M 1.10^{-5}M	60	$8x10^{-7}$	-0.716	90.00
$CeCl_3$ $CuCl_2$	0.1M 1.10^{-5}M	120	$6x10^{-7}$	-0.720	92.50
$CeCl_3$ $CuCl_2$	0.1M 8.10^{-5}M	60	$3x10^{-6}$	-0.700	62.50
$CeCl_3$ $CuCl_2$	0.1M 8.10^{-5}M	120	$1,5x10^{-5}$	-0.692	0
$CeCl_3$ $CuCl_2$	0.5M 1.10^{-5}M	60	$9x10^{-7}$	-0.706	88.75
$CeCl_3$ $CuCl_2$	0.5M 1.10^{-5}M	120	$4x10^{-7}$	-0.700	95.00
$CeCl_3$ $CuCl_2$	0.5M 8.10^{-5}M	60	$7x10^{-7}$	-0.720	91.25
$CeCl_3$ $CuCl_2$	0.5M 8.10^{-5}M	120	$5x10^{-7}$	-0.715	93.75

A question arises: what is the reason for the poorly expressed protective effect of the conversion films, formed in electrolyte containing $8.\ 10^{-5}$M Cu^{2+}, for time intervals of treatment 60 and 120 minutes. In our opinion the increase in the concentration of Cu^{2+} accelerates the process of contact deposition of copper on the alumina surface, which determines depolarizing effect on the cathodic reaction of oxygen reduction (Figures 3 and 4) and as a consequence of this fact the rate of the process of cerium oxide film formation is favored. However at the same time this effect will facilitate the appearance of a larger number of micro-galvanic couples Cu/Al, which will have dominating influence and they will determine an unfavorable effect upon the corrosion behavior of the system Al/Cu/Ce_2O_3 – CeO_2.

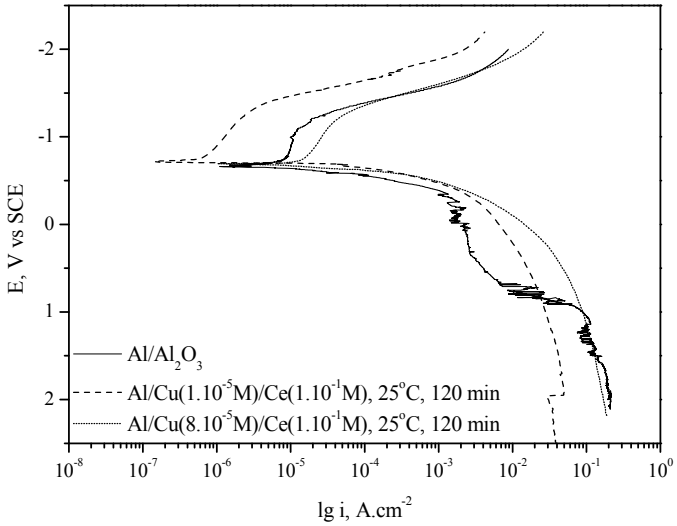


Fig. 4. Polarization curves of tasted systems in 0.1M NaCl at 25°C.

For comparison Figure 5 demonstrates the potentiodynamic curves, characterizing the electrochemical behavior of the systems aluminum/conversion films, formed in electrolytes, containing cerium ions (0.5 M) and copper ions - respectively 1.10^{-5}M and 8.10^{-5}M. It follows from the curves represented in the figure, without a doubt, that the observed decrease in corrosion currents comes as a result of the inhibiting effect of the formed mixed films, in regard to the cathodic depolarization reaction of oxygen reduction. When the concentration of cerium ions is sufficiently high (0.5M), the corrosion currents, respectively the degree of protection, are only slightly influence by the change in the concentration of Cu^{2+} in the electrolyte (Figure 5, Table 1), as the sections of the aluminum surface, which are covered by copper, are practically completely coated with cerium oxide film and the functioning of the galvanic couples Al/Cu is greatly hindered. This effect is preserved upon increasing the time interval of immersion treatment of the aluminum samples from 60 to 120 minutes (Figure 6).

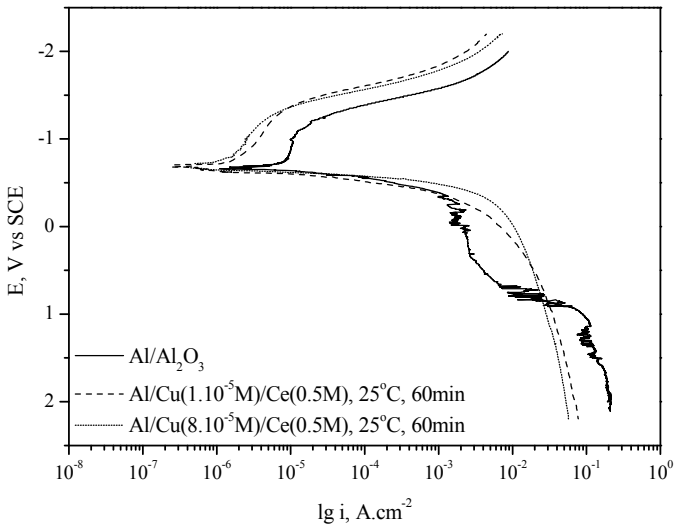


Fig. 5. Polarization curves of tasted systems in 0.1M NaCl at 25°C.

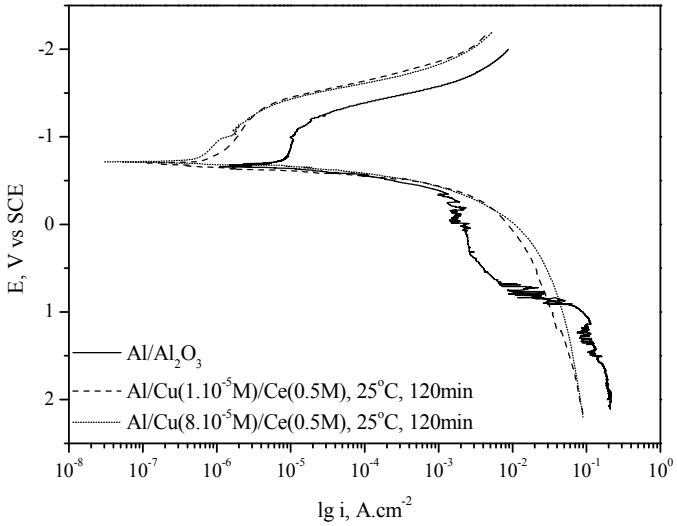


Fig. 6. Polarization curves of tasted systems in 0.1M NaCl at 25°C.

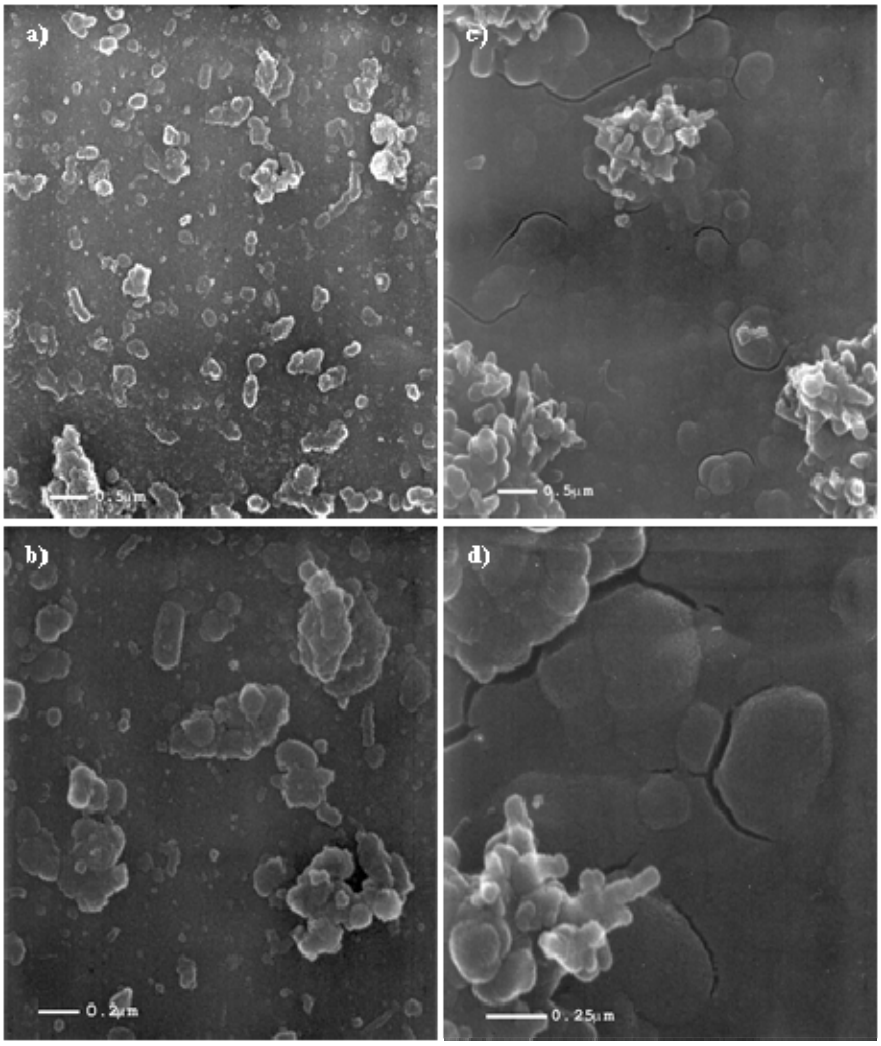


Fig.7. SEM micrograph of the surface of: a) Al/Ce_{ox} x 20000; b) Al/Ce_{ox} x 50000; c) Al/Cu/Ce_{ox} x 20000; d) Al/Cu/Ce_{ox} x 60000

Figure 7 shows the morphology and the structure of the formed conversion films in electrolyte containing only cerium ions (Fig. 7a and 7b) and in electrolyte containing cerium and copper ions (Fig. 7c and 7d). As it can be seen in Fig. 7a and 7b the structure of the cerium oxide film is uniform and it consists of agglomerates having size of about 150 nm. In the presence of Cu^{2+} (Fig. 7c and 7d) the structure of the oxide film is non-uniform, which is owing to the island structure contact-deposited copper on the aluminum surface, a process preceding the formation of the cerium oxide film. In this case the oxide film is built up of agglomerates having larger dimensions from 150 up to 250 nm. The activation of the aluminum surface as a result of increase in the number of the cathodic sections (contact-deposited copper), determines basically the increase in the rate of deposition of the cerium oxides on these sections, which will deteriorate the operation of the galvanic couples Al/Cu. In confirmation of this supposition are the established cracks in the cerium oxides film mainly around the zones of the copper agglomerates coated with this film (Fig. 7b).

4. Conclusions:

1. On the basis of the obtained results a conclusion can be drawn that the role of the copper ions in the working electrolyte has two aspects. On one side, the metallic copper being deposited on the surface of aluminum exerts catalyzing effect on the processes of formation of cerium oxide film. On the other side the formation of micro-galvanic couples Cu/Al deteriorates the corrosion stability of the system. This effect is more strongly expressed in electrolytes having low concentration of cerium ions and high concentration of Cu^{2+}- 8.10^{-5}M. As far as the rest of the electrolytes are concerned the role of copper is reduced most of all to its catalyzing action with respect to the processes of formation of cerium oxide film.

2. The composition of the electrolytes is optimized on the basis of the values of the corrosion currents of the systems aluminum/conversion film (criteria for general corrosion, respectively for the degree of protection from corrosion) with respect to the concentration of cerium and copper ions aiming at the formation of conversion films of improved protection ability.

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