

## Formation of protective films on Al in electrolytes containing no Cr<sup>6+</sup> ions

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Received November 22, 2007, Revised February 25, 2008

Compositions and methods of formation of thin ceria films on aluminum have been studied, whereupon their protective effect is compared with that of chromate films obtained from Cr<sup>6+</sup>-containing electrolytes. It has been established that the chemically and electrochemically formed ceria films improve the corrosion stability of Al in regard to both general and pitting corrosion. It has been shown that the degree of protection of the deposited ceria films in the course of the corrosion process in 0.1 M NaCl reaches 99.9% and it exceeds that of Cr<sup>6+</sup>-containing conversion coatings – about 99.3%. A characteristic feature of the ceria films is that being cathodic coatings with respect to the aluminum support they inhibit the occurrence of a cathodic depolarization reaction during the corrosion process. On the basis of the investigations carried out, a conclusion is drawn that the prepared Ce-containing protective films represent a promising alternative of the Cr<sup>6+</sup>-containing coatings.

**Key words:** aluminum, ceria protective films, corrosion, Cr<sup>6+</sup>-free electrolytes.

### INTRODUCTION

The present wide application of conversion protective layers on Al and on its alloys, obtained in Cr<sup>6+</sup>-containing electrolytes, although it is beneficial from technological and economic point of view, has to be terminated. This is determined by their high toxicity and carcinogenicity, respectively by the strict labour legislation and ecological regulations [1]. In this respect intensive investigations are being carried out to replace Cr<sup>6+</sup> with Cr<sup>3+</sup> [2–7] or with some other less toxic and inexpensive metal salts, which are widely occurring in nature. Special interest is focused on the electrolytes and the respective methods, based on salts of the lanthanide group metals [8–19], as the hardly soluble oxides and hydroxides of these metals are among those of lowest toxicity and their ingestion or inhalation is not considered harmful to health [20].

In the above-cited data, it is shown convincingly that there is an extraordinarily favourable protective effect of the oxides and hydroxides of Ce, which is a strong impulse to intensify the investigations in this field. To be more specific, the options to simplify the methods for depositing cerium-containing protective layers on aluminum and its alloys and to transfer them into technologies are being studied intensively.

In view of these considerations, the aim of the

present work was to select, investigate and juxtapose various approaches, based on different compositions and methods for the formation of thin ceria layers having good adhesion on Al, whereupon their protective action was compared with that of conversion chromate layers, formed in Cr<sup>6+</sup>-containing electrolytes [21, 22].

### EXPERIMENTAL

The present article represents the results, obtained with ceria layers, deposited on the widely used construction material “technically pure” aluminium AD-3. The studied samples of dimensions 1×1 cm, were cut out of Al sheets with thickness 0.1 cm. The samples were hung on wires, made of the same type of Al. Their preliminary treatment consisted in degreasing using an organic solvent, etching in aqueous solution of NaOH (60 g/l) at 60°C ( $\tau = 1$  min) and consecutive lighening in aqueous solution of HNO<sub>3</sub> (50%) at room temperature ( $\tau = 30$  s). After each one of these operations, the necessary standard washing of the samples with distilled water was carried out.

Cerium-containing protective layers were deposited chemically upon the so-prepared samples, reproducing the method, proposed in [18], according to which the formed layers possess a maximum protection ability. A series of electrochemical treatment procedures of the aluminum samples were carried out in electrolytes under conditions, elaborated by us, which had given good results in the

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deposition of cerium-containing protective oxide films on stainless steels [23, 24].

Ceria films as well as immersion chromate films were obtained from electrolytes, having high  $\text{Cr}^{6+}$  concentration ("standard") [21], low  $\text{Cr}^{6+}$  concentration ("Alodine 1200") [22] or  $\text{Cr}^{6+}$ -free electrolytes, containing  $\text{Ti}^{4+}$  ions ("Alodine 400") [25], aimed at comparing their protective properties.

The morphology and structure of the layers were examined by scanning electron microscopy, using a JEOL JSM 6390 electron microscope (Japan), equipped with ultrahigh resolution scanning system (ASID-3D) in a regime of secondary electron image (SEI). The accelerating voltage was 25 kV,  $I \sim 65 \mu\text{A}$ . The pressure was of the order of  $10^{-6}$  Torr. The distribution of the elements on the Al surface before and after deposition of protective layers was investigated using back-scattered electrons and energy-dispersive X-Ray techniques (EDS).

The colouring of the layers was determined visually, while their thickness was estimated by profile-metering (step test at the interphase boundary between coated and noncoated zone of the sample) using Profile-meter "TelyStep" (Hybson-Taylor, England).

The electrochemical (*corrosion*) behaviour of the samples was studied in 0.1 M NaCl (p.a. Merck) model medium without deaeration at 25°C. A counter-electrode, representing a platinum plate ( $10 \times 10 \times 0.6$  mm) and a saturated calomel reference electrode (SCE), ( $E_{\text{SCE}} = +0.240$  V vs SHE) were used. All potentials in the text are given with respect to SCE. The anodic and cathodic polarization curves were obtained using a 273A EG&G potentiostat/galvanostat (Germany) and computer-aided processing of the results using an "Echem" programme, with a potential sweeping rate of 10 mV/s within a potential range from -2300 to +1800 mV. The steady-state corrosion potential ( $E_{\text{st}}$ ) of the samples under investigation was also determined by direct measurement of the function " $E_{\text{st}}$ -time" (recorded by X-t recorder "Endim" 621.02 (Germany)) at open circuit (with respect to the same reference electrode) after immersing the samples in 0.1 M NaCl. The time interval for the appearance of pitting corrosion spots was judged by the appearance of strong oscillations on the  $E$ - $\tau$  curve. The protection coefficient ( $\gamma$ ), respectively the degree of protection ( $z$ , %), were determined in accordance with equations (1) and (2):

$$\gamma = \frac{i_{\text{cor(Al)}}}{i_{\text{cor(CL/Al)}}} \quad (1)$$

$$z = \frac{(i_{\text{cor(Al)}} - i_{\text{cor(CL/Al)}})}{i_{\text{cor(Al)}}}, \quad \% \quad (2)$$

where  $i_{\text{cor(Al)}}$  is the corrosion current of Al non-coated with conversion layer, determined by poten-

tiodynamic polarization curves and  $i_{\text{cor(CL/Al)}}$  is the corrosion current for the system conversion layer/Al. These experimental investigations were juxtaposed with the observations of the surface of the samples with optical microscope "EPIQUANT" (Carl Zeiss, Germany) and electron microscope, respectively the quantitative estimate for the appearance and development of pitting corrosion.

## RESULTS AND DISCUSSION

### Colouring and thickness of the films

The results in regard to colouring and thickness of the formed films are represented in Table 1.

**Table 1.** Composition of the electrolytes, conditions of formation, colour and thickness of the protective films.

No	Electrolytes	Concentration	Time	$T$ , °C	Colour	$\delta$ , $\mu\text{m}$
1	Al in air media (with native oxide film)	Air	hours	room temperature	Colourless	$3 \times 10^{-3}$ [30]
2	$\text{CrO}_3$ $(\text{NH}_4)\text{HF}_2$ $\text{K}_3[\text{Fe}(\text{CN})_6]$	8 g/l 2 g/l 1.5 g/l	1.5 min	20	golden brown	1.0
3	Alodine 1200	9 ml/l A 8 g/l B	1 min	20	light yellow	1.1
4	Alodine 400	15 ml/l	1.5 min	40	Colourless	1.05
5	$\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ $\text{H}_2\text{O}_2$ $\text{CuCl}_2$	$2 \times 10^{-2}$ M 15 ml/l $10^{-3}$ M	5 min	20	dark grey	1.02
6	$\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ $\text{C}_2\text{H}_5\text{OH}$	66 g/l	60 min $i=1$ $\text{mA/cm}^2$	12	pale yellow	2.1

### SEM and EDS investigations

The changes in the structure, morphology and composition of the studied samples, after the respective surface treatment (Table 1), are represented in Figure 1. The morphology, structure and distribution of the elements on the Al surface, non-treated in conversion solution, after preliminary treatment of the samples in degreasing solution, (6% NaOH) and lightening solution (50%  $\text{HNO}_3$ ) are characterized in Figure 1a. It is seen that the surface is "decorated" with the well distinguishable iron agglomerates (the light-coloured zones) of dimensions  $\sim 0.5$ –1  $\mu\text{m}$ . The following elements are registered: Al (99.67%) and Fe (0.33%). Figure 1b represents the SEM image of the same surface, after its immersion treatment in a standard solution for chromating of Al (Table 1, No. 2). The formed chromate film is uniformly cracked, which is typical of a thick conversion film and it is the result of stresses, induced in the film during the drying process, whereupon the

width of the cracks is about 1–2  $\mu\text{m}$ . At the bottom of the cracks we observed a layer, which is less cracked with analogous structure [26], which gave us the reason to suppose that the conversion film has a bi-layer structure. The upper, thicker part of the film is more cracked than the lower one (having width of the cracks about  $\sim 0.1 \mu\text{m}$ ), attached directly to the Al substrate. The integral values, obtained at magnification  $\times 30000$  and  $\times 180000$  are given below Fig. 1b. They give a good idea about the average concentrations and the distribution of the elements, deposited on the Al surface, in the characteristic zones – in the thicker sections of the film (A) and inside the cracks (B).

The analyses of the thin chromate films formed within short time intervals in a spot or along a line showed that their deposition starts and it is accomplished prevalently on Fe segregates. Upon reaching the thickness, representing practical interest, no Fe segregates are being detected. Figure 1c represents Al surface, after its treatment in low- $\text{Cr}^{6+}$ -content composition for chromating Alodine 1200 [22]. The impression is that the size of the cracks of these films is smaller. Thereupon the concentration of Cr, respectively the thickness of the film, both in the thick parts of the film as well as in the cracks, is smaller compared to the films, formed in highly concentrated chromate solution, and the registering of iron in the support is an indication of this. Figure 1d illustrates the Al surface, after its treatment in the  $\text{Cr}^{6+}$ -free electrolyte Alodine 400 [25]. In this case the conversion film contains  $\text{TiO}_2$ . It is uniform without any cracks and the iron agglomerates, characteristic of the Al surface prior to the immersion treatment, have remained partially non-coated by the deposited conversion layer. Figure 1e illustrates the Al surface after chemical conversion treatment in a solution, proposed by Decroly and Petitjean [18] (Table 1, No. 5), that contains also  $\text{Cu}^{2+}$  ions and  $\text{H}_2\text{O}_2$  in addition to  $\text{Ce}^{3+}$ . The obtained layer has a specific morphology. Uniformly distributed light zones of cerium oxide with dimensions varying within the interval  $\sim 1\text{--}8 \mu\text{m}$  are observed in it. The presence of copper and high concentration of Ce is registered in the centre of the light zones with a high degree of aggregation (denoted by point A). According to the opinion of these authors the influence of  $\text{Cu}^{2+}$  ions is based mainly on their catalytic effect on the formation of  $\text{Ce}(\text{OH})_3$ , respectively the formation of  $\text{CeO}_2$ . It is considered that the couple  $\text{Cu}^{2+}/\text{Cu}^+$  is an oxidation-reduction mediator. The formation of Cu clusters does not provoke acceleration of the reaction of ceria formation [18]. The results that we obtained do not confirm this statement. It follows from Fig. 1e

and from the results of EDS measurements given below it that definite concentrations of Cu are registered both in the centre (Cu 10.36%; Ce 32.04%), as well as in the periphery (Cu 13.37%; Ce 8.59%) of the light zones. The complete absence of Fe in the EDS spectra, which is obviously an effect of the prevailing reduction of  $\text{Cu}^{2+}$  ions on Fe segregates, correlates completely with the results, obtained and explained by us earlier by “contact” separation of ions of more noble metals on the iron segregates in such systems [27, 28]. A new and important moment, in our opinion, in this case is the fact that the reduction of the cerium ions is occurring in the Cu-rich zones, which have screened completely Fe. Judging by the amount of Ce deposited in the center of the light zones and on their periphery, it can be supposed that the deposited copper clusters have a definite catalytic effect in regard to the reaction of  $\text{Ce}(\text{OH})_4/\text{CeO}_2$  formation. The concentration of Ce in point A is about four times higher than in point B. In point C, in which the analysis registers only Al, Cu is missing, as well as Ce. Obviously, the process of immersion coating on the Al surface with a protective film is occurring mainly on the active sites of this surface, while in the spots, on which the natural protective  $\text{Al}_2\text{O}_3$  film is not dissolved, a conversion layer is not formed (the dark zones – point C). In the grey zones (between point B and point C) the concentration of Cu and Ce varies within the interval 0.5–4 and 0.1–0.2%, respectively. The reason for this lack of correspondence with the data in [18] is probably the availability of Fe in the Al substrate, determining the occurrence of a conjugated reaction of dissolution of Al and reduction of  $\text{Cu}^{2+}$  ions and the energy barrier for it in this case is very low.

Figure 1f illustrates the surface morphology and structure of the ceria layer, deposited electrochemically upon the Al substrate (after carrying out in advance the operations of the preliminary treatment) from non-aqueous electrolyte (Table 1, No. 6) and reported in [29]. The layer is compact and non-cracked, with good adhesion to the substrate surface, characterized by a specific distribution of Ce on the Al surface. The deposited layer contains sphere-like zones and next to them, the layer is very thin. The data from EDS analyses show that in analogy to the layer, obtained by the method of Decroly, the formation of a Ce film starts and grows prevalently upon Fe segregates of the Al substrate. No Fe is registered in the zones of thicker Ce coating (item A), while the concentration of Ce reaches up to 65%. In the periphery of Ce “drops” the concentration is decreased ( $\sim 25\%$ ), whereupon the detector registers also Fe (item B), while next to

them (the grey zones) the Ce film is very thin (Ce 0.25% and Fe 0.19%). It is worth to note that there are no zones non-coated with Ce.

*Corrosion investigations*

The results from the comparative corrosion tests of the studied systems are represented in Fig. 2 and

Table 2. The analysis of the potentiodynamic cathodic and anodic polarization curves and chrono-potentiograms shows that:

A – The first spots of pitting corrosion in the natural passive film of Al AD1 are observed after about 180 min, upon immersion of the samples in 0.1 M NaCl (Fig. 2a);

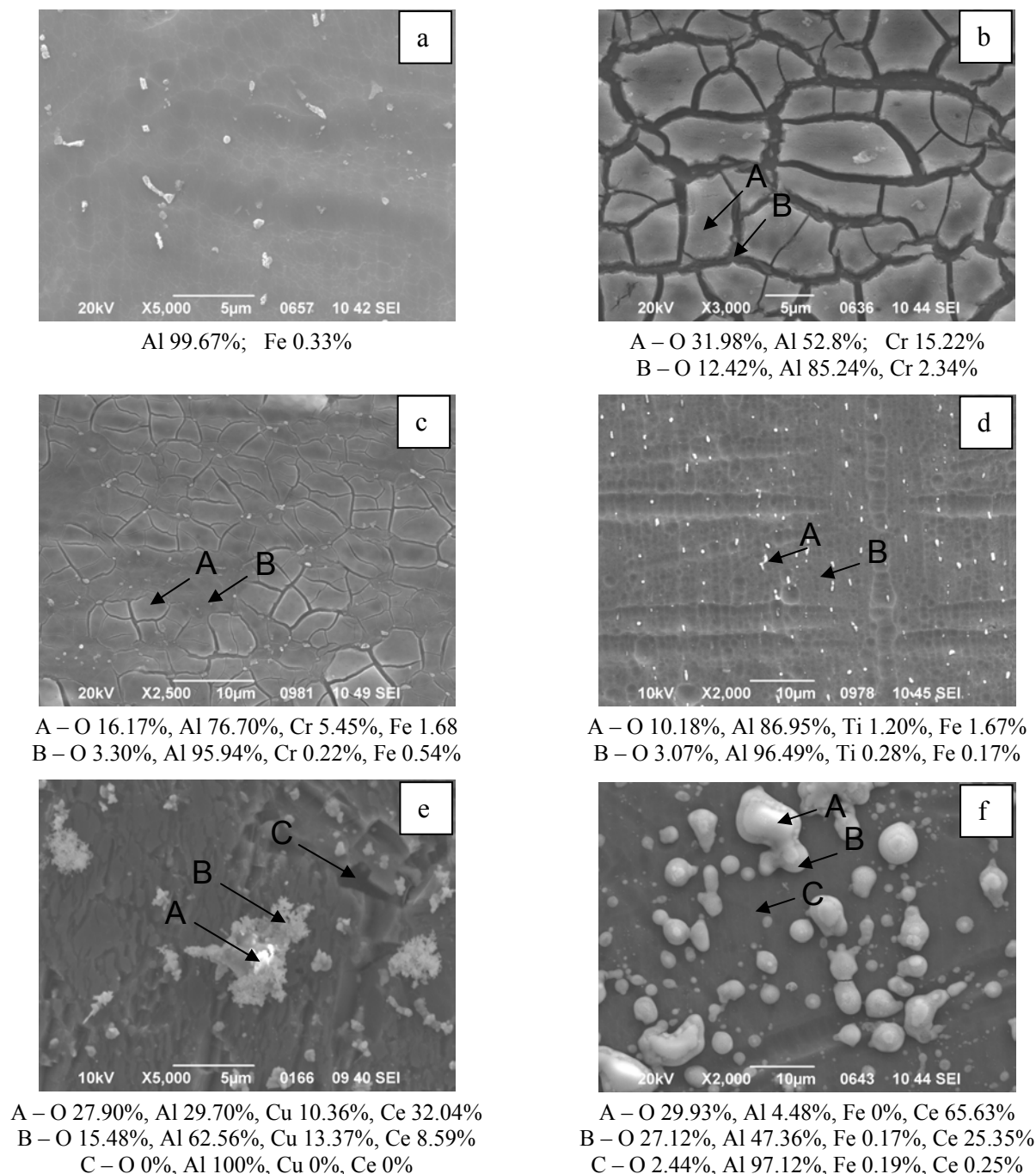


Fig. 1. SEM micrographs of the surface of: (a) Al/Al<sub>2</sub>O<sub>3</sub>; (b) Al/Cr<sub>2</sub>O<sub>3</sub> “standard”; (c) Al/Cr<sub>2</sub>O<sub>3</sub> Alodine 1200; (d) Al/TiO<sub>2</sub> Alodine 400; (e) Al/Cu<sub>ox</sub>/Ce<sub>ox</sub>; (f) Al/Ce<sub>ox</sub> (electrodeposited).

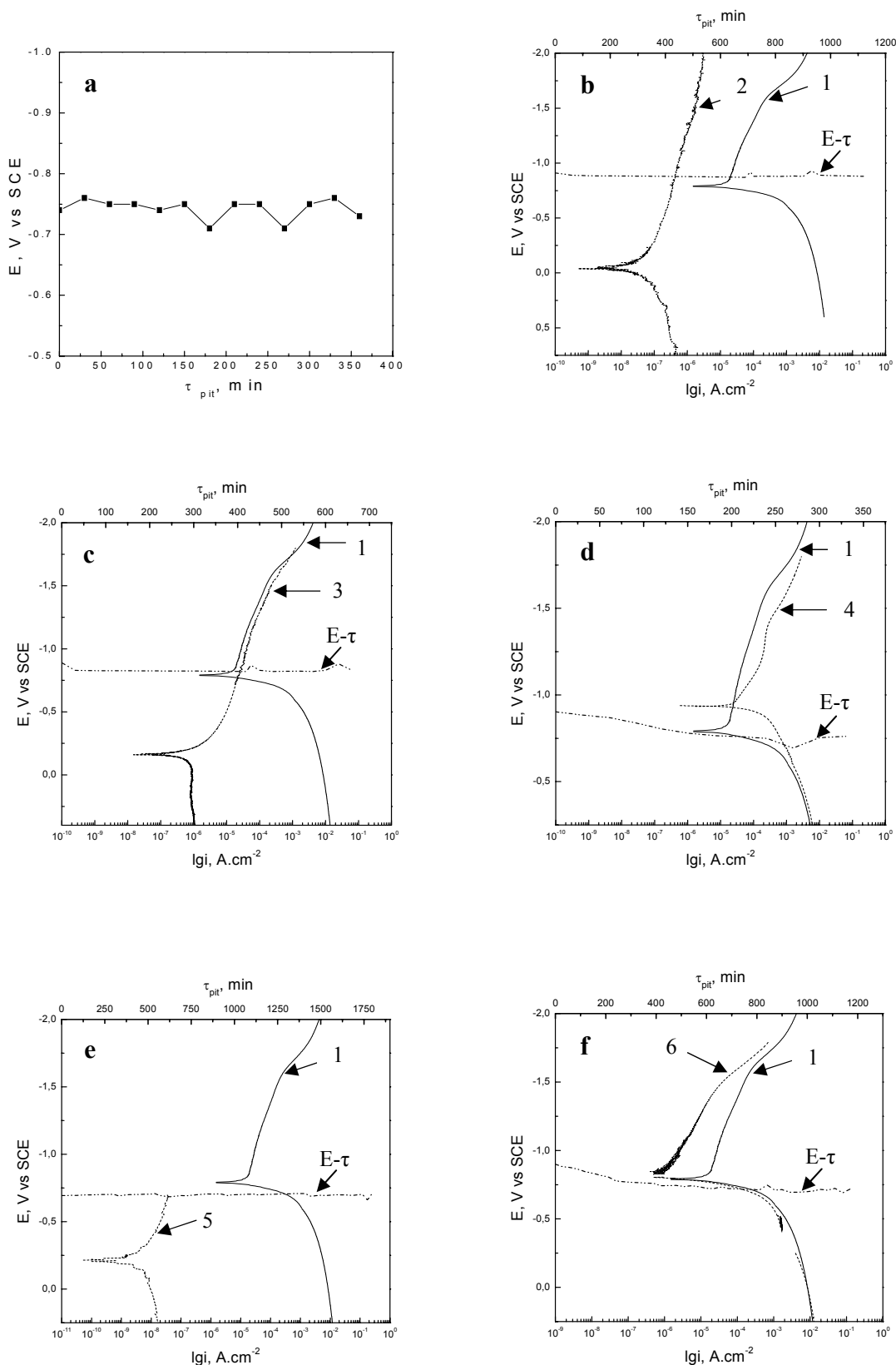


Fig. 2.  $E-\tau$  curves for the system: Al/Al<sub>2</sub>O<sub>3</sub> (a); potentiodynamic  $E-lgi$  curves for the same system (curves 1 in Fig. 2 b, c, d, e and f); and for the systems: Al/Cr<sub>2</sub>O<sub>3</sub> "standard" (curves 2 in Fig. 2b); Al/Cr<sub>2</sub>O<sub>3</sub> Alodine1200 (curves 3 in Fig. 2c); Al/TiO<sub>2</sub> Alodine 400 (curves 4 in Fig. 2d); Al/Cu<sub>ox</sub>/Ce<sub>ox</sub> (curves 5 in Fig. 2e); Al/Ce<sub>ox</sub> (electrodeposited) (curves 6 in Fig. 2f) in 0.1 M NaCl.

**Table 2** Rate of corrosion ( $i_{\text{cor}}$ ,  $\text{A}\cdot\text{cm}^{-2}$ ), degree of protection ( $z$ , %) and time interval of appearance of the first pitting spots for non-treated Al and for aluminum, coated with protective films in the studied electrolytes.

No	Electrolytes	$i_{\text{cor}}$ , $\text{A}\cdot\text{cm}^{-2}$	$z$ , %	$\tau_{\text{pit}}$ , min
1	Al without conversion treatment	$1.05\times 10^{-5}$	-	180
2	$\text{CrO}_3+(\text{NH}_4)\text{HF}_2+$ $+\text{K}_3[\text{Fe}(\text{CN})_6]$	$7\times 10^{-8}$	99.3	710
3	Alodine 1200	$1\times 10^{-6}$	90.4	430
4	Alodine 400	$1\times 10^{-5}$	4	270
5	$\text{CeCl}_3 + \text{H}_2\text{O}_2 + \text{CuCl}_2$	$1.05\times 10^{-8}$	99.99	1770
6	$\text{CeCl}_3\cdot 7\text{H}_2\text{O} + \text{C}_2\text{H}_5\text{OH}$	$7\times 10^{-7}$	93	840

B – The chromate oxide conversion layers, obtained from highly concentrated in  $\text{Cr}^{6+}$  ions solution, shift strongly (from  $-0.790$  to  $-0.036$  V) the corrosion potential ( $E_{\text{cor}}$ ) of the system “chromate film/Al substrate” in the positive direction and decrease the corrosion current ( $i_{\text{cor}}$ ) from  $1.05\times 10^{-5}$   $\text{A}\cdot\text{cm}^{-2}$  (for the non-protected Al) to  $7\times 10^{-8}$   $\text{A}\cdot\text{cm}^{-2}$ . Thereupon they promote strongly the overpotential both of the cathodic depolarization reaction of oxygen reduction, as well as that of the anodic reaction of Al dissolution (Fig. 2b). The first pitting spots for this system are registered after  $\sim 700$  min time interval of exposure to 0.1 M NaCl solution.

In the case of layers, obtained with the commercially available solution Alodine 1200, containing a lower concentration of  $\text{Cr}^{6+}$ , these effects are considerably weaker ( $E_{\text{cor}}$  is shifted from  $-0.790$  to  $-0.160$  V, respectively  $i_{\text{cor}}$  from  $1.05\times 10^{-5}$   $\text{A}\cdot\text{cm}^{-2}$  to  $1.05\times 10^{-6}$   $\text{A}\cdot\text{cm}^{-2}$ ). It should be noted that in this specific case the conversion film has a positive effect only on the polarization of the anodic reaction, while it has practically no effect upon the cathodic process of oxygen reduction (Fig. 2c). As a consequence, the time interval for the appearance of the first spots of pitting corrosion is increased from  $\sim 180$  min for the non-treated Al samples up to  $\sim 430$  min;

C – The conversion film, obtained in Alodine 400 solution, practically does not change the course of the cathodic and anodic polarization curves. However, it shifts the potential of the system “conversion layer/Al” with  $\sim 0.180$  V in the negative direction at the moment of immersion of the sample in 0.1 M NaCl, afterwards  $E_{\text{cor}}$ , for the time interval of exposure  $\sim 270$  min, is shifted again in the positive direction reaching the values ( $\sim -710$  mV), which are characteristic for the system  $\text{Al}_2\text{O}_3/\text{Al}$ . The fact that  $i_{\text{cor}}$  does not change gives us the reason to suppose that the relatively thick ( $\sim 1.05$   $\mu\text{m}$ ) conversion film is insufficiently compact (Fe segregates remain partially uncovered – Fig. 1d) and the nature of the corrosion process, dominated by the

functioning of the galvanic couples Fe/Al, remains practically the same as that of the unprotected Al surface. A confirmation of this conclusion is the appearance of the first pitting spots during exposure to 0.1 M NaCl  $\sim 270$  min – relatively close to those for the non-treated Al. The reason for such a behaviour is obviously the very small thickness of the conversion film on Fe segregates. The concentration of  $\text{TiO}_2$  registered on them is very low (Fig. 2d).

D – The cerium-containing conversion layer, obtained by the method of Decroly [18], shifts  $E_{\text{cor}}$  from  $-0.790$  to  $-0.240$  V, decreasing simultaneously  $i_{\text{cor}}$  from  $1.05\times 10^{-5}$   $\text{A}\cdot\text{cm}^{-2}$  to  $1.05\times 10^{-8}$   $\text{A}\cdot\text{cm}^{-2}$ , which is  $\sim 7$  times lower than the corrosion current, achieved with the chromate conversion film, formed in solution with high concentration of  $\text{Cr}^{6+}$ . The formed layer increases strongly the change of the over-potential both of the cathodic depolarization reaction of oxygen reduction, as well as of the anodic reaction of Al dissolution (Fig. 2e). In the case of presence of such a protective film the highest protective ability was registered. The appearance of the first pitting corrosion spots is detected at time intervals of about 1770 min (Table 2).

E – The ceria layer electrodeposited from non-aqueous electrolytes practically does not change the value of  $E_{\text{cor}}$ , but it makes  $i_{\text{cor}}$  one order of magnitude lower (from  $1.05\times 10^{-5}$   $\text{A}\cdot\text{cm}^{-2}$  up to  $7\times 10^{-7}$   $\text{A}\cdot\text{cm}^{-2}$ ). This type of conversion films inhibits the cathodic reaction of oxygen reduction, while there is practically no effect on the anodic process of Al oxidation (Fig. 2f). The time interval of appearance of pitting corrosion spots in it is  $\sim 840$  min (Table 2).

## CONCLUSION

The obtained results show that the formation of Ce-containing corrosion-protective layers on Al surfaces is a promising alternative to the chromate conversion treatment. The application of electrolytes based on harmless from ecological and health-protection point of view  $\text{Ce}^{3+}$  ions obviously can allow the substitution of the toxic  $\text{Cr}^{6+}$ -containing electrolytes and the respective technologies. The investigations carried out so far and the comparative analysis of the properties of the existing electrolytes, respectively the conversion layers corresponding to them, show that it is possible to deposit these layers both chemically and electrochemically. The choice of the technological approach should be made on the basis of the already achieved protective-decorative indexes, as well as on economic technical considerations and calculations. In our next communication we shall represent the results of analogous invest-

tigations, where the conversion layers are formed both electrochemically and chemically from aqueous solutions, in the presence of  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  ions. There we shall consider in details their catalytic action.

**Acknowledgements:** *The electrochemical measurements have been performed by means of scientific equipment donated to Prof. A. Milchev (Inst. Phys. Chem., Bulg. Acad. Sci.) by the Alexander von Humboldt Foundation, Germany.*

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## ФОРМИРАНЕ НА ЗАЩИТНИ ФИЛМИ ВЪРХУ АЛУМИНИЙ ОТ НЕСЪДЪРЖАЩИ $\text{Cr}^{6+}$ ЕЛЕКТРОЛИТИ

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Постъпила на 22 ноември 2007 г., Преработена на 25 февруари 2008 г.

(Резюме)

Изучени са състави и методи за формиране на тънки слоеве от цериеви оксиди върху алуминий, като тяхното защитно действие е сравнено с това на хроматни слоеве, получени от  $\text{Cr}^{6+}$  съдържащи електролити. Установено е, че формираните химично и електрохимично цериеви оксидни филми подобряват корозионната устойчивост на алуминия към обща и питингова корозия. Показано е, че степента на защита на отложените цериеви филми при протичането на корозионен процес в 0.1 М NaCl достига 99.9% и има по-висока стойност от тази от тази на  $\text{Cr}^{6+}$  съдържащите покрития около 99.3%. Характерна особеност на цериевите оксидни филми е, че те са катодни покрития по отношение на алуминиевата подложка и инхибират протичането на деполяризиращата катодна реакция на корозионния процес. Въз основа на проведените изследвания е направен извод, че получените Се съдържащи защитни филми са перспективна алтернатива на  $\text{Cr}^{6+}$  съдържащите такива, което ще позволи замената на токсичните  $\text{Cr}^{6+}$  съдържащи електролити за конверсионна обработка на алуминия.