

Effect of cerium ions on the protective ability of Al₂O₃ films formed anodically during their sealing in aqueous solutions

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The influence of the process of sealing has been studied in aqueous solutions of Ce(III) ions in regard to the protective ability of Al₂O₃ film prepared anodically on aluminum. The oxide film was being formed on aluminum Al-1050 in electrolyte, containing H₃PO₄ – 40g/l, under voltostatic conditions of anodizing. The sealing of the films has been carried out in 0.5M CeCl₃ solution at 25° and 60°C. The composition, the morphology, the structure and the chemical state of the elements of the investigated systems have been characterized by means of scanning electron microscope (SEM), energy dispersive analysis (EDS) and X-ray photoelectron spectroscopy (XPS). Potentiodynamic and chronoamperometric studies have also been carried out aiming at establishing the influence of the Ce³⁺ ions, Ce₂O₃ phase respectively, involved and appearing in the anodically formed porous Al₂O₃ film upon its corrosion protective ability. It has been ascertained that as a result of the so accomplished sealing of the Al₂O₃ film both inside the pores, as well as on its surface Ce(OH)₃ and/or Ce₂O₃ are formed and occluded, which determines the decrease in the corrosion currents of the system Al₂O₃/Al in the model corrosive medium (0.1M NaCl) and this fact leads to promoting its stability with respect to pitting corrosion.

Keywords: anodization, aluminum and cerium oxides, sealing, corrosion

INTRODUCTION

Aluminum has been used in many fields, such as aerospace systems, aviation systems, auxiliary parts of locomotives and so on. However, aluminum alloys manifest many disadvantages, such as poor corrosion resistance and lower mechanical strength. It is of essential importance to improve the corrosion stability of aluminum alloys through anodization technology or passivation directly [1].

The anodization is among the most widely applied methods for surface treatment of aluminum and its alloys aiming at enhancement of the corrosion stability. It is known that the protective anodic oxide films consist of two layers: an internal one – barrier layer and an external one – porous layer. The porous layers could be the defects reducing corrosion resistance of anodized aluminum. Pitting corrosion could be easily developing in porous layers due to electrochemical processes occurring between intermetallics and grain boundaries [2]. Hence, it is necessary to develop such kind of methods leading to sealing of the pores within porous layers, which would help to improve mechanical and chemical properties [3-5].

Sealing concepts involve various combinations of temperature and sealing bath chemical composition – all of them promoting the corrosion resistance to a certain degree [6]. Sealing traditionally is being done through immersion in boiling water – the so called “hot water sealing” method [7-9]. The need of applying high temperature to achieve slow kinetics, however, means considerable energy consumption [10]. As a result the hot water process has been gradually replaced since 1980s by cold sealing [8]. Dichromate and nickel acetate sealing are well established now to be the most effective sealing methods for corrosion prevention [6]. However, it has been proved that Cr⁶⁺ ions have toxic effect [9, 11-13]. A number of sealants have been put forward for sealing applications and some new sealing processes are also developed [14]. In spite of these efforts to improve the performance, more convenient and effective processes are still needed [15].

The aim of the present work was to study the influence of the cerium ions, included as component of the solution for sealing of anodically formed oxide films, respectively the role of cerium oxides/hydroxides being deposited from this solution inside the pore and on the surface, in

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regard to the corrosion behavior of the system Al/Al₂O₃ in aggressive medium containing chloride ions.

EXPERIMENTAL

In the present work we have applied a conventional procedure of anodization of Al in aqueous solution of H₃PO₄. High degree of purity aluminum Al-1050 was used for anodization. The aluminum substrates (10x2x0.2 cm) were degreased in aqueous solution of NaOH (6wt. %) at 60°C followed by etching and surface activation in aqueous solution of HNO₃ (50 wt. %) for 30s at room temperature. Anodization was conducted under constant cell potential in 4wt.% H₃PO₄ aqueous solution. The temperature in each case was maintained constant at 25°C. The DC voltage in each case was 40 V. The current density was varied from 2 to 0.2 mA.cm⁻². The aluminum sample was anodized for 120 min. After anodizing the samples were rinsed with distilled water and then sealed. The thickness of the formed Al₂O₃ layers varied between 5 and 7 μm.

Two different sealing techniques were applied to the anodic films after anodizing:

1. Boiling distilled water sealing (pH 6–7.5) for 60 min.
2. CeCl₃ sealing: The specimens were dipped in 0.5M CeCl₃ solution (at 25°C for 48 h and at 60°C for 2 h).

All the samples were rinsed by cold (25° C) water after sealing and air dried. The thickness of formed conversion layers was about 2 μm.

The morphology, structure and elemental composition of the aluminum oxide films, as well as the distribution of the elements on the aluminum surface, prior to and after the deposition and sealing of the protective layers, were observed by the electron microscope JEOL JSM 6390 (under the conditions of secondary electron image - SEI, back-scattered electrons - BEC and characteristic energy dispersive X-rays EDS, the applied voltage was 20 kV, $I \sim 100 \mu\text{A}$) and XPS studies. The XPS measurements were carried out on AXIS Supra electron- spectrometer (Kratos Analytical Ltd.) using monochromatic AlK_α radiation with a photon energy of 1486.6 eV. The energy calibration was performing by normalizing the C1s line of adsorbed adventitious hydrocarbons to 285.0 eV. The binding energies (BE) characterize the surrounding in the depth of the films and they were determined monitoring the areas and binding energies of C1s, O1s, Al2p, Na1s and N1s photoelectron peaks. Using the commercial data-processing software of Kratos Analytical Ltd. the concentrations of the

different chemical elements (in atomic %) were calculated by normalizing the areas of the photoelectron peaks to their relative sensitivity factors.

The corrosion behavior of the samples was tested in 0.1M 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), ($E_{\text{SCE}}=+0.240\text{V}$ vs. 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 Gamry Interface 1000, whereupon the obtained results were processed with the help of specialized software. The curves were recorded at a sweeping rate of the potential 1.0 mV.s⁻¹ in the range of potentials from –2500 up to + 2500 mV.

RESULTS AND DISCUSSION

Figure 1 illustrates SEM images of as deposited anodically formed protective Al₂O₃ films on aluminum Al-1050 (Fig. 1a); the same films after their sealing in boiling distilled water (Fig. 1b) and those sealed in 0.5M CeCl₃ solution (Fig. 1c -1f), respectively at 25° and 60°C. Figure 1a illustrates the porous structure of Al₂O₃ prior to subjecting the anodically prepared film to the so called “sealing procedure”, with the purpose to enhance its protective ability. As a result of the process of sealing in boiling distilled water (the widely applied standard sealing procedure) one can observe a definite decrease in the size of the pores of the oxide film (Figure 1b). Obviously, the reason for this effect is owing to the fact that the sealing in boiling distilled water results in partial filling up of the pores by the hydrated aluminum oxide - boehmite ($\text{Al}_2\text{O}_3 + \text{H}_2\text{O} \rightarrow 2\text{AlO}(\text{OH})$) [1].

Figure 1c – e illustrates the morphology on the surface of the treated samples after sealing of the anodic layer in aqueous solution of 0.5M CeCl₃ at temperature 25°C in the course of 48 hours. It can be seen in the figure that in the case of such treatment on the surface of the anodic film a thick coating has been formed, which was screening the pores of the anodic film. It is built up of segments having macro-cracks (Fig.1c), whereupon the boundaries between them (the darker zones Fig.1d) are also formed by a layer of similar structure, but having smaller thickness. The EDS analyses of these layers in the bright spots and in the dark spots of the formed layer shows that a coating of cerium oxide has been deposited [16]. Evidently, as a result of the processes of sealing a cerium oxide layer is being deposited, which initially is filling up the

pores on the surface of aluminum oxide and there after a conversion film is being formed, which is covering up the treated surface entirely. Figure 1f

shows SEM image of the anodized aluminum surface after the sealing process in the course of 2 hours in aqueous solution of 0.5M CeCl₃ at

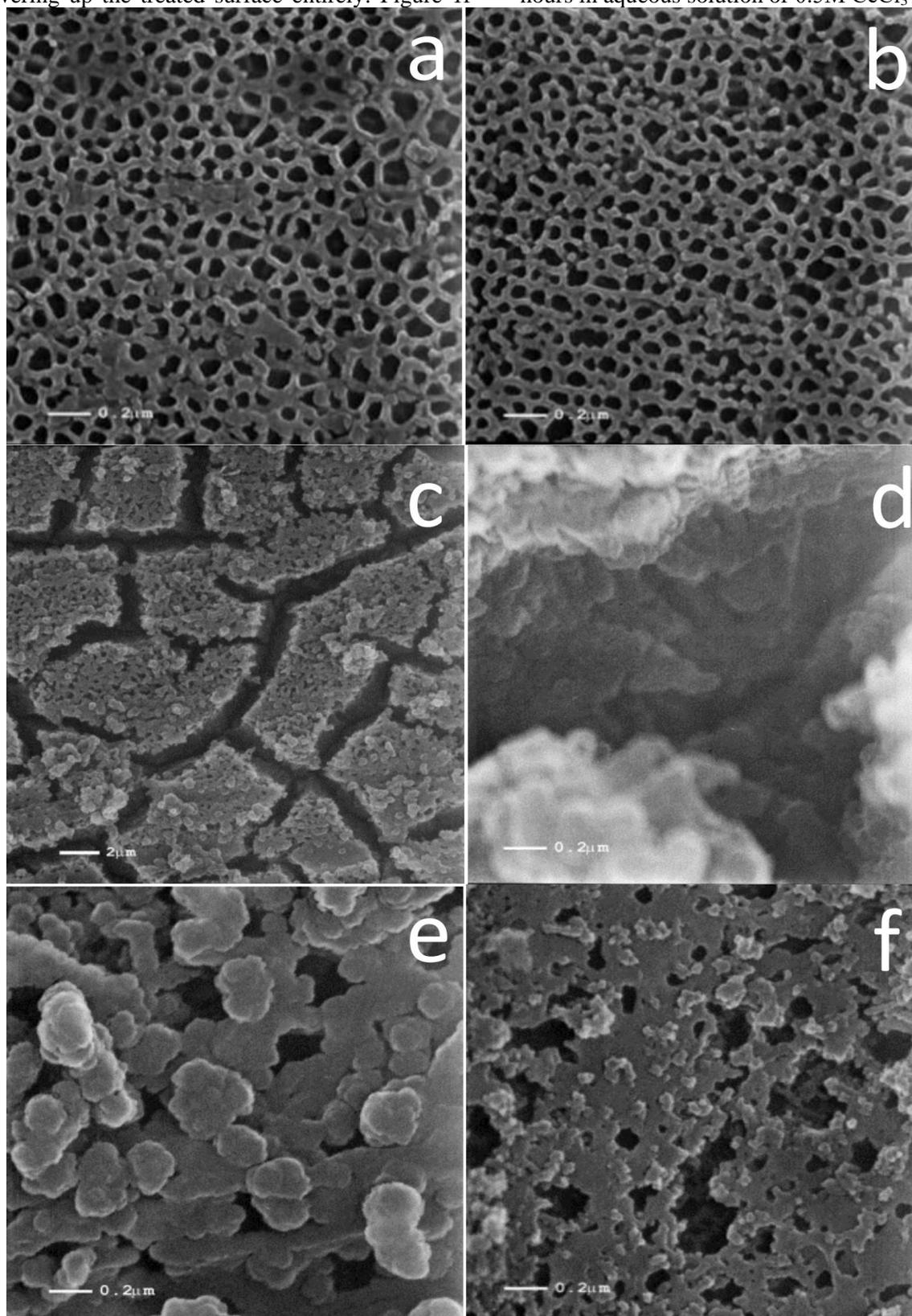


Fig.1. Surface morphology of anodically formed films: (a) unsealed Al₂O₃ film formed at 40V for 2 hours, X 50 000; (b) sealed in boiling water (1h), X 50 000; (c) sealed in cold CeCl₃ (48h), X 5000; (d and e) sealed as in (c) at magnification X 50000; (f) sealed in hot CeCl₃ (2h), X 50000.

temperature of 60°C. The so obtained conversion film on the anodized surface in this case is continuous and uninterrupted and it consists of some smaller aggregates. The EDS proved that depending on the conditions of sealing the thickness of the conversion film grows up,

respectively the concentration of cerium on the anodized aluminum substrate is growing up from 5.29% after time interval of sealing 120 minutes in hot solution (60°C) of 0.5M $CeCl_3$, up to 10.42 wt.% in the case of sealing at room temperature for 48 hours of immersion time interval [16].

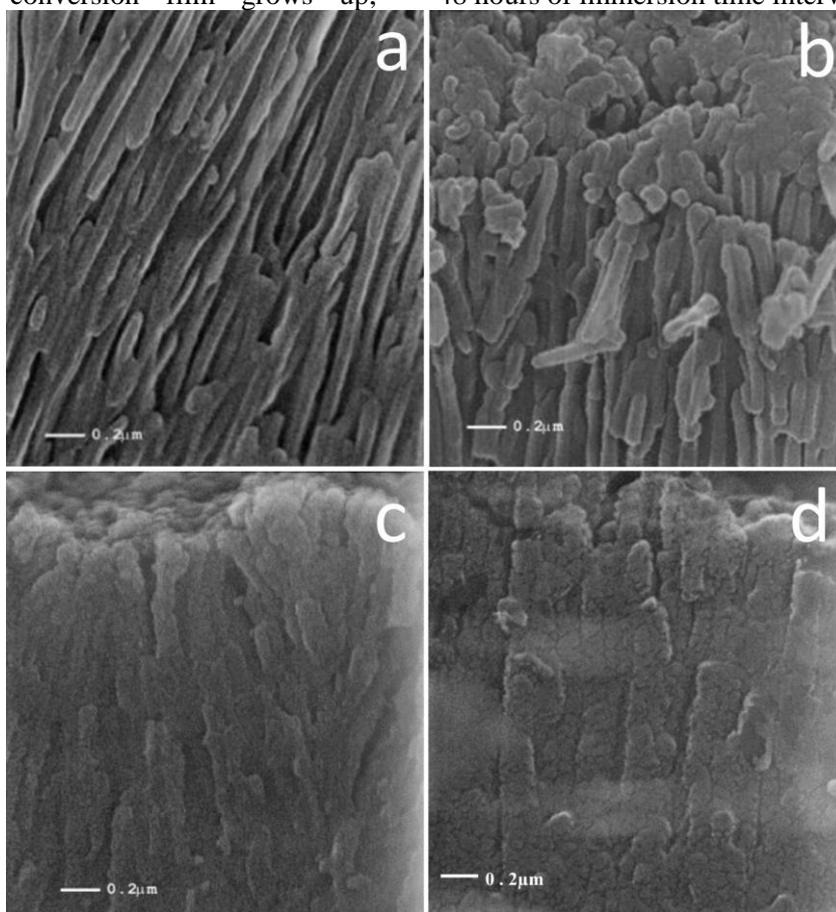


Fig. 2. The cross section structures of: (a) unsealed as deposited Al_2O_3 film formed at 40V for 2 hours on Al-1050; (b) the same layer sealed for 1h in boiling water; (c) sealed in cold $CeCl_3$ for 48h; (d) sealed in hot $CeCl_3$ for 2h.

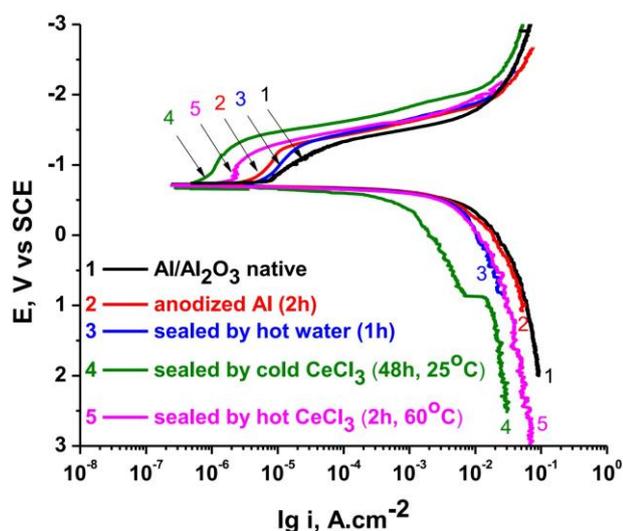


Fig. 3. Polarization curves of systems tested in 0.1M NaCl at 25°C.

Figure 2 presents the morphology of the cross section of the anodic film, obtained in phosphoric acid before and after its treatment in boiling

distilled water or in aqueous solution of 0.5M $CeCl_3$. It is seen that as a result of the sealing carried out in boiling distilled water the anode layer becomes more compact (Figure 2b). In the case of the samples, sealed in 0.5M $CeCl_3$ (Figure 2c and 2d), in addition to the even stronger sealing of the porous part of the anodic film one can observe also difference in the thickness of the formed surface film. This effect is the result of occurring of the processes of sealing–filling up of the pores of Al_2O_3 by cerium oxides and hydroxides and deposition of a superficial conversion cerium oxide film upon the anodically formed Al_2O_3 layer.

Figure 3 presents the anodic and cathodic potentiodynamic curves for: non-anodized aluminum (Al-1050) sample; anodized aluminum sample, as well as for the anodized aluminum sample, sealed respectively in boiling distilled water and in aqueous solution of 0.5M $CeCl_3$ (at temperatures 25° and 60°C) in corrosive medium of 0.1M NaCl.

Judging from the changes in the course of the polarization curves one can conclude that the sealing of the anodic oxide films in 0.5M aqueous solution of CeCl₃ at temperature 60°C (Fig. 3)

leads to more substantial decrease in the corrosion current of the system Al/Al₂O₃ under the conditions of a steady state, observed at the chosen rate of sweeping the potential (Table 1).

Table 1. Electrochemical parameters (E_{corr} and i_{corr}) obtained from the potentiodynamic curves.

Investigated samples	Corrosion potential, E_{corr} , V	Corrosion current, i_{corr} , Acm ⁻²
Al/Al ₂ O ₃ native system	-0.660	8x10 ⁻⁶
Unsealed anodically formed Al/Al ₂ O ₃ system	-0.710	1.75x10 ⁻⁶
Anodically formed Al/Al ₂ O ₃ system sealed in boiling water	-0.701	1.65x10 ⁻⁶
Anodically formed Al/Al ₂ O ₃ system sealed in cold CeCl ₃ (48h)	-0.674	2.27x10 ⁻⁷
Anodically formed Al/Al ₂ O ₃ system sealed in hot CeCl ₃ (2h)	-0.702	3.16x10 ⁻⁷

The juxtaposition of the cathodic polarization curves, characterizing the depolarization reaction of reduction of oxygen, shows that the filling up of the pores of the anodic oxide film with Ce(OH)₃ and Ce₂O₃ (see Fig.5b) inhibits the reaction of reduction of oxygen, which is most strongly expressed for treatment time intervals respectively 48 hours, at room temperature – Fig. 3 and 2 hours– at temperature 60°C. A similar effect, although weakly expressed, is observed also with the respective anodic potentiodynamic curves. For comparison Fig. 3 gives the anodic and the cathodic potentiodynamic curves for anodized samples, sealed in boiling distilled water for 60 minutes. Obviously, the standard sealing in boiling distilled water, leading to filling up of the pores of the anodic film by hydrated aluminum oxide (boehmite) [1], whose influence has a barrier effect, is resulting in insignificant changes in the kinetics of the corrosion process (Fig.3) and it is characterized by significantly weaker protective effect comparing with sealing in solutions of 0.5M CeCl₃.

In order to check the validity of this conclusion, we carried out a parallel cycle of chronoamperometric measurements with analogous samples, where upon the samples were exposed to corrosive medium for 60 minutes at a potential, close to the potential of pitting formation [17] of aluminum Al-1050. This cycle was accomplished by recording the chronoamperometric curves for each one of the studied samples. After conducting this set of experiments, the samples were washed thoroughly with distilled water and subjected to XPS analyses, with the aim to establish the occurring changes in the chemical composition and in the chemical state of the elements in the surface layer of the systems Al/Al₂O₃ and Al/Al₂O₃/Ce₂O₃.

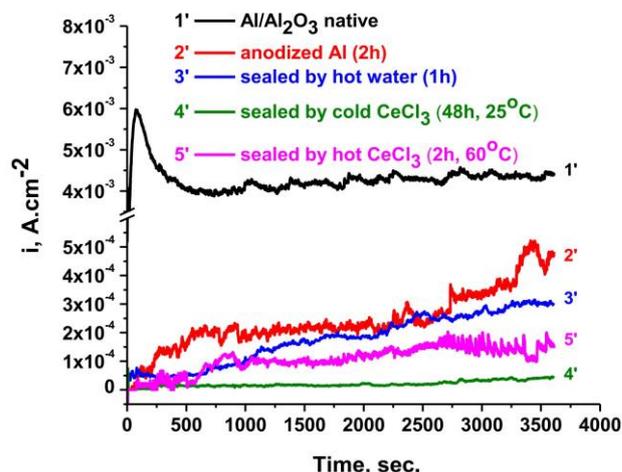


Fig. 4. Chronoamperometric curves of the systems tested in 0.1M NaCl at 25°C

Figure 4 represents the results of chronoamperometric measurements, carried out at potential -0.5V (SCE), close to the potential of pitting formation of the studied aluminum in 0.1M NaCl. Based on the course of the separate curves we can derive the character of the corrosion attack judging from the type of the appearing pitting defects. It is seen that in the case of non-treated aluminum (Al-1050) sample, after its immersion at the potential in the corrosive medium, the density of the corrosion current is increasing sharply (curve 1'), which is an indication of the appearance and development of pitting corrosion, after 75 seconds of interaction with the chloride ions. No substantial fluctuations of the current density are observed with the sample, upon which anodic film is formed, but it is not subjected to consecutive sealing procedure, until about 3400 seconds time interval (curve 2'). Thereupon the current density relatively low values

– of the order of 5.2×10^{-4} A.cm⁻², which is an indication for the appearance of pittings, which, however undergo quickly repassivation and they do not reach the stage of further development. It can be seen in the chronoamperogram that the relatively thick porous layer Al₂O₃, which had been formed during the anodic treatment, is prolonging the incubation period for the appearance of pitting corrosion on aluminum from ~75 to ~3400 seconds. The samples, sealed in boiling distilled water (curve 3'), both in cold solution (curve 4') and in hot solution (curve 5') of CeCl₃, are characterized by stable protective film. The proofs for this conclusion are the low values of the corrosion currents and the lack of fluctuations of their values in the respective chronoamperograms (Fig.4).

It follows from the results, obtained with the additionally subjected to sealing procedure samples, that in accordance with the established stability of the studied systems with respect to the appearance and development of general and pitting corrosion, they can be arranged in the following order: Al<Al/Al₂O₃<Al/Al₂O₃ (sealed in boiling

distilled water) <Al/Al₂O₃/Ce₂O₃ (sealed in 0.5M CeCl₃ at 60°C for 120 minutes) <Al/Al₂O₃/Ce₂O₃ (sealed in 0.5M CeCl₃ at 25° C for 48 hours).

On the basis of the XPS analyses, carried out with the studied samples, including the corrosion products being formed on their surface under the conditions of anodic polarization at potential close to that of the pitting formation on aluminum in 0.1M NaCl, an attempt was made to explain the character of the corrosion process of the studied systems, when during the sealing process of the anodically formed Al₂O₃ layer cerium ions are also participating. It was based on juxtaposition of the data for the composition and the chemical state of the elements on the surface of the samples. This includes comparison of the data on as deposited samples, the samples after applying the sealing procedure and those after the occurring changes, which appear on their surface during anodic polarization (the chronoamperometric measurements), simulating corrosion process under conditions close those for pitting formation.

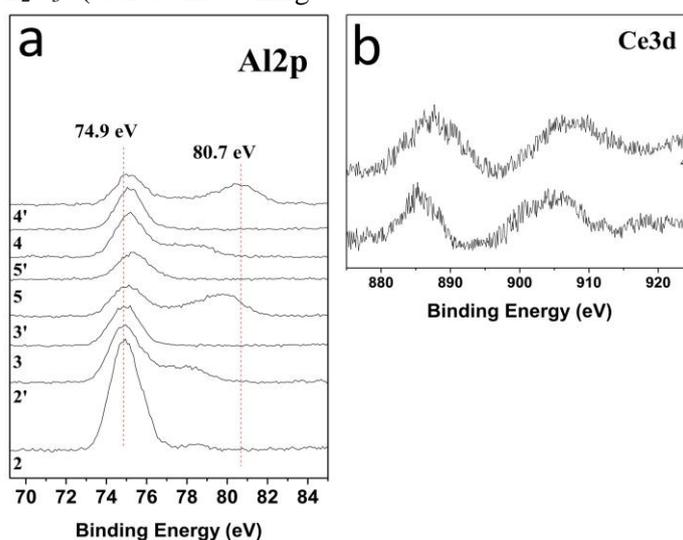


Fig. 5. a) Al₂p spectra of the investigated samples: 2 – Al/Al₂O₃ unsealed; 2' – the same system after chronoamperometry; 3 – Al/Al₂O₃ sealed in boiling water; 3' – the same system after chronoamperometry; 4 – Al/Al₂O₃ sealed in cold CeCl₃ for 48h; 4' – the same system after chronoamperometry; 5 – Al/Al₂O₃ sealed in hot CeCl₃ for 2h; 5' – the same system after chronoamperometry; b) Ce₃d spectra of the films: 4 – corresponds to the curve 4 on Fig.3 – Al/Al₂O₃ sealed in cold CeCl₃ for 48h; 4' – corresponds to the curve 4' on Fig.4 – the same system after chronoamperometry measurements.

Figure 5a represents the spectra of Al₂p for the studied samples. It can be seen in the figure, that the spectra of the samples, non-treated by anodic polarization at potential close to that of pitting formation (i.e. after the chronoamperometric measurements) are comparatively widely extended. The spectra of the samples, subjected to chronoamperometric investigation, are considerably different. Most of them (spectrum 2', 3', 4', 5') display additional peaks at higher binding energies. Aiming at more precise identification of the nature

and the quantity of the separate chemical compounds on the surface of the films, a deconvolution of the basic peaks of Al₂p (Fig.6 a-h) and O1s was made (not given here).

It is seen in the deconvoluted spectrum of Al₂p for the anodized Al sample (Fig.6a) that it can be divided into three peaks – two of them have binding energies of 74.7 eV, 76.0 eV and there is a small peak at 78.5 eV. In this way the presence mainly of Al₂O₃ on the surface of the sample not undergoing chronoamperometric investigation is proven

(characteristic peak at 74.7 eV) [18] and also some small quantities of Al(OH)₃ (the characteristic peak 76.0 eV) [19]. The third peak at BE 78.5 eV is owing to the presence of agglomerates of Al(OH)₃ having various sizes, which determines the different extent of their charging [20]. For all the samples we have compared the areas of the deconvoluted peaks of Al2p, normalized with respect to corresponding value of Relative Sensitivity Factors (RSF), with the areas of the peaks normalized in regard to the respective value of RSF for the deconvoluted peaks of O1s. The obtained ratio between them is in correspondence with the stoichiometry of the

respective compounds: Al₂O₃ and Al(OH)₃. The spectrum of Al2p (Fig.6b) on the surface of the same sample, subjected to anodic polarization up to a potential close to the potential of pitting formation (i.e. after the chronoamperometric characterization) shows that the surface consists again of Al₂O₃ and Al(OH)₃ mainly, however here, as a result of the occurred corrosion processes of anodic dissolution, the quantity of Al(OH)₃ is smaller (see Table 2, sample of anodized aluminum prior to and after the chronoamperometry). One samples decreases from 4.55 to 1.19.

Table.2. Comparison of the areas of the integrated peaks, calculated after deconvolution of the spectra of Al2p

Different treatment methods	Area of the integrated peak(s) associated with Al ₂ O ₃ , [a. u.]*	Area of the integrated peak(s) associated with AlOOH (and Al(OH) ₃), [a. u.]*	Ratio of the areas of Al ₂ O ₃ to AlOOH (or/and Al(OH) ₃), [a. u.]*
Al/Al ₂ O ₃ unsealed	4653	1023	4.55
Al/Al ₂ O ₃ unsealed – after chronoamperometry	2294	1923	1.19
Al/Al ₂ O ₃ sealed in boiling water	1280	730	1.75
Al/Al ₂ O ₃ sealed in boiling water– after chronoamperometry	1784	1618	1.10
Al/Al ₂ O ₃ sealed in hot CeCl ₃ for 2h	0	1443	-
Al/Al ₂ O ₃ sealed in hot CeCl ₃ for 2h– after chronoamperometry	0	3191	-
Al/Al ₂ O ₃ sealed in cold CeCl ₃ for 48h	0	1852	-
Al/Al ₂ O ₃ sealed in cold CeCl ₃ for 48h– after chronoamperometry	0	3174	-

*arbitrary units

A similar picture is also observed with the anodized sample, subjected to sealing in boiling distilled water (in the course of 1 hour at 100°C – Fig. 6c). In the Al2p-spectrum of the studied sample again peaks are observable, characteristic of Al₂O₃ and Al(OH)₃, but here the ratio Al₂O₃/Al(OH)₃ is substantially different from that of the sample, not subjected to this treatment. In the case of the anodized sample, sealed in boiling distilled water, the amount of Al(OH)₃ is significantly higher than that of the anodized but not sealed sample, whereupon the ratio Al₂O₃/Al(OH)₃ for the latter sample is 4.55, while in the case of former sample it is 1.75. No peaks are displayed by this sample, which could be associated with the presence of particles having different extent of charging, i.e. the surface is more homogeneous. After carrying out chronoamperometric measurements with this sample, one

can observed again on the surface the presence of Al₂O₃ and Al(OH)₃, and in this case also the quantity of Al(OH)₃ is decreasing again (from 1.75 down to 1.10 – see Fig. 6c, d). In contrast to the sample, not subjected to chronoamperometric investigation, here the presence of phases is observable having different extent of charging, due to particles of various sizes (hence different charging) both of Al₂O₃ (the peak at 76.2 eV), as well as that of Al(OH)₃ (the peak at 79.9 eV). This splitting of the peaks is visible also in the spectrum of O1s (not given here).

In the case of the sample, sealed in solution of CeCl₃ in the course of 2 hours at 60°C – Fig. 6e and 6f, the presence of one basic peak is observable at 75.0 eV, characteristic of AlO(OH). Considering this peak, after carrying out the chronometric investigation, again an additional splitting of the basic peak at 75 eV is observed – splitting into two additional peaks. Their presence is again due to the

appearance (after the chronoamperometric investigation) of agglomerates of AlO(OH) on the surface having different charge.

The spectrum of Al2p for sample anodized and sealed in 0.5 M CeCl₃ for 48h at temperature 25°C, indicates the presence of a single peak at 75.1 eV, characteristic of AlO(OH) (Fig. 6g). A specific feature of this samples is the fact that after subjecting it to chronoamperometric investigation,

a multitude of agglomerates of AlO(OH) appears on the surface having various sizes and therefore different charging (Fig. 6h). This phenomenon is observed also in the spectrum of O1s of these samples. The spectra of Ce3d for these samples – before and after the chronoamperometric investigation (Figure 5b) – prove the formation of Ce₂O₃ layer.

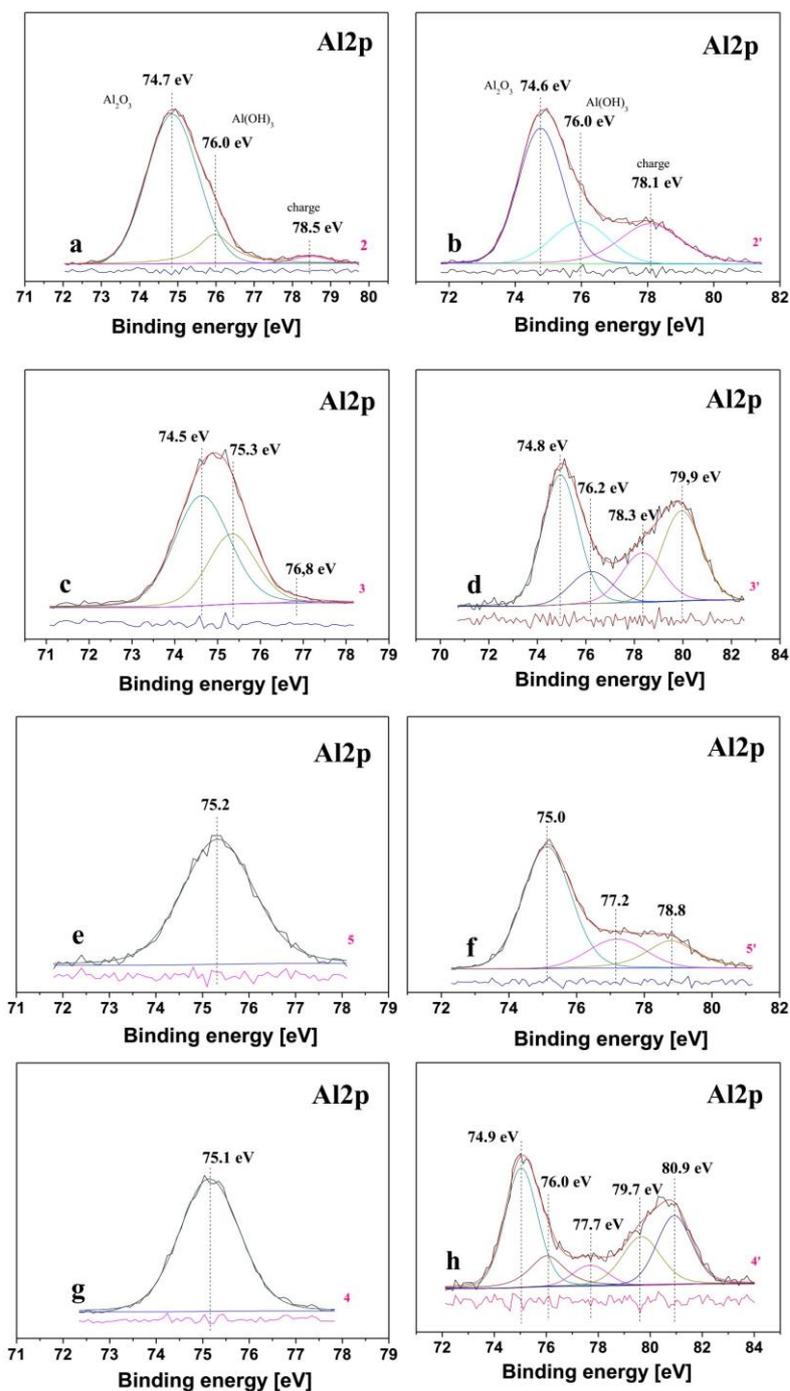


Fig 6. Deconvoluted Al2p spectra of the films: (a) Al/Al₂O₃ unsealed; (b) – the same system after chronoamperometry; (c) – Al/Al₂O₃ sealed in boiling water; (d) – the same system after chronoamperometry; (e) Al/Al₂O₃ sealed in hot CeCl₃ for 2h; (f) the same system after chronoamperometry; (g) Al/Al₂O₃ sealed in cold CeCl₃ for 48h; (h) – the same system after chronoamperometry.

Table 3. Concentrations of the chemical elements in the investigated films. The concentrations are calculated from XPS spectra of the elements, presented in atomic percents.

Different treatment methods	Amount of Al in the layer [at.%]	Amount of Ce in the layer [at.%]	Amount of O in the layer [at.%]
Al/Al ₂ O ₃ sealed in hot CeCl ₃ for 2h	9.5	0.9	89.6
Al/Al ₂ O ₃ sealed in hot CeCl ₃ for 2h– after chronoamperometry	18.7	0.9	80.4
Al/Al ₂ O ₃ sealed in cold CeCl ₃ for 48h	14.0	0.8	85.2
Al/Al ₂ O ₃ sealed in cold CeCl ₃ for 48h – after chronoamperometry	18.5	0.8	80.7

The spectrum of the cerium oxide layer, formed on the surface of the oxidized Al substrate, sealed in CeCl₃ solution in the course of 2 hours at temperature 60°C, is characterized by complex structure, owing to hybridization of cerium ions with the ligand orbitals of oxygen and partial occupation of the 4f valence orbital [21]. As a result of this there occurs spin-orbital splitting of the doublet peaks, whereupon each doublet as an additional structure, owing to the effect of the final state. The peaks, denoted by u''' and v''' at 916.9 eV and 898.4 eV are characteristic of CeO₂ and result from a 3d¹⁰4f¹ final state. The spectrum shows that as a result of the process of immersion treatment, a layer of Ce₂O₃ has been formed.

It is seen in Table 3 that the relative concentrations of cerium oxide of both samples, prior to and after the chronoamperometric investigation, remain constant. In the case of the sample, sealed in solution of CeCl₃ in the course of 2 hours at 60°C, the concentration of Ce₂O₃ prior to the chronoamperometric investigation is 0.9 at.% (see Table 3). No change in the concentration of Ce₂O₃ after chronoamperometric investigation. In the case of the sample anodized and sealed in 0.5M CeCl₃ for 48h at temperature 25°C, the concentration of Ce₂O₃, before the chronoamperometric investigation, is 0.8 at.% (see Table 3). After the investigation it is again 0.8 at.%. This fact gives evidence that as a result of the chronoamperometric measurements, the chemical composition with respect to the concentration of ceria on the surface of the samples is preserved unchanged. Therefore we can conclude that the corrosion attack in this case does not lead to any disruption of the integrity of the oxide films and no localization of the corrosion process has been registered.

CONCLUSIONS

The obtained results show that the sealing of the anodic oxide films in boiling water or in aqueous solution of CeCl₃, determines different corrosion-protection behavior of the systems

Al/Al₂O₃ and Al/Al₂O₃/Ce₂O₃. It follows from these results that the anodic formation of porous protective layers of Al₂O₃ on Al-1050 improves to a considerable extent its corrosion behavior. The accomplishment of an additional post-treatment “sealing procedure” in boiling water improves even better the protective effect of the anodic film in regard to the processes of pitting corrosion and general corrosion. The XPS analyses, registering changes in the composition on the surface of the studied samples as a function of the different treatment procedures carried out, showed that under conditions close to the appearance of pitting corrosion, depending on the type of these treatment processes, during the corrosion process changes in the chemical composition are occurring (in favor of increasing the concentration of Al(OH)₃), which improve the corrosion behavior of the system Al/Al₂O₃.

In the course of sealing procedure accomplished in the presence of cerium ions, in addition to the partial blocking of the pores of the anodic Al₂O₃ layer, there appears also a barrier action of the conversion formed cerium oxide layer upon the anodic coating. There upon the conversion cerium oxide layer is not influenced practically by the corrosion attack of the aggressive medium. The changes occurring in the zone of potentials close to the potential of pitting formation on aluminum, consist mainly in increasing the concentration of the corrosion products being formed (AlOOH and Al(OH)₃). As a result of these two effects the corrosion stability of the system Al/Al₂O₃/Ce₂O₃ promoted, inclusively in respect to the appearance and development of pitting corrosion.

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ЕФЕКТ НА ЦЕРИЕВИТЕ ЙОНИ ВЪРХУ ЗАЩИТНАТА СПОСОБНОСТ НА АНОДНО ФОРМИРАНИ Al₂O₃ СЛОЕВЕ ПРИ УПЛЪТНЯВАНЕТО ИМ ВЪВ ВОДНИ РАЗТВОРИ

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(Резюме)

Изучено е влиянието на процеса на уплътняване във водни разтвори на Се(III) йони върху защитната способност на анодно получен Al₂O₃ филм върху алуминий. Оксидният филм е формиран върху алуминий Al-1050 в електролит, съдържащ 40g/l H₃PO₄, при волтастатични условия на анодиране. Уплътняването на филмите е осъществено в 0.5M разтвор на СеCl₃ при температури 25° и 60°C. Съставът, морфологията, структурата и химичното състояние на елементите на изследваните системи са охарактеризирани с помощта на сканираща електронна микроскопия (SEM), енергийно дисперсионен анализ (EDS) и рентгенова фотоелектронна спектроскопия (XPS). Проведени са и потенциодинамични и хроноамперометрични изследвания, с цел установяване на влиянието на включващите се в анодно формираня Al₂O₃ филм цериеви йони, респ. формираща се Се₂O₃ фаза, върху корозионно-защитната му способност. Установено е, че в резултат на проведеното уплътняване на Al₂O₃ филм както в порите, така и на повърхостта му се формират и включват Се(OH)₃ и/или Се₂O₃, което обуславя понижаване на корозионните токове на системата Al₂O₃/Al в моделната корозионна среда (0.1M NaCl) и води до повишаване на устойчивостта ѝ към питингова корозия.