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Corrosion behavior of anodically formed oxide films on aluminum, sealed in cerium-ions containing solutions

R.A. Andreeva[1], E.A. Stoyanova[1], A.S.Tsanev[2], D.S. Stoychev[1*]

[1] "Rostislaw Kaischew" Institute of Physical Chemistry, Bulgarian Academy of Sciences,
"Acad. G. Bonchev" Str., bl. 11, Sofia 1113, Bulgaria
[2]Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences,
"Acad. G. Bonchev" Str., bl. 11, Sofia 1113, Bulgaria

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The corrosion behavior of anodically deposited oxide films on Al-1050 has been studied in 0.1M NaCl solution. The Al_2O_3 films have been formed in an electrolyte containing H_3PO_4 – 40 g/l under voltastatic conditions of anodization. The sealing has been carried out in 0.5M $CeCl_3$ solutions at temperatures 25°C and 60°C. The thickness of the coatings was 3-5µm.

The surface morphology and the composition of the sealed nano-porous anodic films have been studied by means of scanning electron microscopy (SEM) and energy dispersive analysis (EDS). It has been established that depending on the conditions of sealing the concentration of cerium inside the pores of the oxide films is growing up from 5.3 up to 10.4 wt.%. On the basis of the XPS spectra of the studied systems the chemical state of cerium in the nano-pores of the oxide film has been defined.

Potentiodynamic investigations have been carried out and the corrosion currents from polarization (E-i) curves have been determined for non-sealed and sealed in solutions containing Ce^{3+} ions anodic oxide coatings on aluminum. It has been shown that the filling up of the nano-pores of the formed Al_2O_3 anodic film with $Ce(OH)_3/Ce_2O_3$ is promoting its corrosion protection ability.

Key words: anodizing, aluminum oxide, sealing, corrosion.

INTRODUCTION

Anodizing is among the most widely applied methods for anti-corrosion surface treatment of aluminum and its alloys. It is known that the anodized oxide films consist of two layers: internal - barrier layer, and external - porous layer. An important step, aimed at improving of the protective ability of the porous oxide films, is the so called sealing process [1-4]. Taking into account the porosity of alumina films, the sealing step is indispensable [5,6] to enhance corrosion resistance. Sealing concepts involving various combinations of temperature and sealing bath chemical composition all promote 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 high temperature and slow kinetics, however, mean 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 to be the most effective sealing methods for corrosion prevention [6]. However, it is proved that Cr^{6+} ions have toxic effect [9, 11-13]. A number of sealants have been put forward for sealing applications and some new sealing processes are developed [14].

Nowadays studies on new types of sealants and sealing processes involve cold nickel acetate sealing [9], sodium silicate sealing [14], nickel fluoride sealing [6,14], Cr_2O_3 sealing [15], sodium acetate sealing [8, 10], cerium acetate sealing [13, 16], cerium nitrate and yttrium sulfate sealing [5], sol-gel sealing [12], and even an expensive sealing process using polytetrafluroethylene [15]. However these efforts to improve the performance seem to be insufficient. Therefore more convenient and effective processes are still needed [15].

The aim of the present work was to investigate and compare the influence of the composition of the sealing solution (aqueous solutions of $CeCl_3$, containing Ce^{3+} ions or boiling distilled water) and the conditions of sealing on the anodic oxide films, being formed in phosphoric acid on Al-1050 upon their corrosion-protection ability.

EXPERIMENTAL

In the present work we have applied a conventional procedure of anodization of Al in aqueous solution of H_3PO_4 [17]. High purity aluminium Al-1050 was used for anodization. The

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To whom all correspondence should be sent:
E-mail: stoychev@ipc.bas.bg

aluminium substrates (10x2x0.2 cm) were degreased in aqueous solution of NaOH at 60°C followed by etching and surface activation in aqueous solution of HNO_3 (50 wt. %) for 30s at room temperature. Anodization was conducted under constant cell potential in 4 wt.% H_3PO_4 aqueous solution. The temperature in each case was kept 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 aluminium sample was anodized from 60 to 120 min. After anodizing the samples were rinsed with distilled water and sealed.

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. $CeCl_3$ sealing: The specimens were dipped in 0.5M $CeCl_3$ solution (at 25°C or 60°C) for 60 and 120 min.

All the samples were rinsed by cold (25° C) water after sealing and air dried.

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 electronmicroscope 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 ~ 100 μA) and XPS studies. The XPS measurements were carried out on AXIS Supra electron- spectrometer (KratosAnalitycal Ltd.) using monoichromatic 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) were surrounding in the depth of the films 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 0.1 M 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 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

The polarization curves of the anodized aluminum samples, sealed by applying various sealing techniques, in the chosen corrosion medium (0.1M NaCl), are represented in Fig. 1 and Fig. 2. In the model solution of 0.1M NaCl the potentiodynamic studies prove that the sealing of the anodic films in 0.5M solution of $CeCl_3$ for 2 hours at room temperature leads to insignificant reduction of the corrosion currents in the system - Fig. 1, while upon increasing the time interval of sealing from 2 hours to 48 hours, the corrosion current of the system with about one order of magnitude (Table 1).

Table 1. Electrochemical parameters obtained from the potentiodynamic curves.

Anodic film	Corrosion potential, E_{corr}, V	Corrosion current, i_{corr} A.cm^{-2},
Unsealed	-0.710	1.75x10^{-6}
Sealed by boiling water	-0.701	1.65x10^{-6}
Sealed by cold $CeCl_3$ (2h)	-0.671	1.24x10^{-6}
Sealed by cold $CeCl_3$(48h)	-0.674	2.27x10^{-7}
Sealed by hot $CeCl_3$ (1h)	-0.718	7.97x10^{-7}
Sealed by hot $CeCl_3$ (2h)	-0.702	3.16x10^{-7}

The sealing of the anodic oxide films in 0.5M solution of $CeCl_3$ at 60°C (Fig. 2) results in a more substantial decrease in the corrosion current of the system Al/Al_2O_3 under the conditions of steady state (Table 1). The juxtaposition of the cathodic polarization curves, characterizing the depolarization reaction of oxygen reduction shows that the filling up of the pores of the anodic oxide film with $Ce(OH)_3$ and Ce_2O_3 is inhibiting the reaction of oxygen reduction, which is most strongly expressed in the case of time interval of the treatment 48 hours (at room temperature, Fig. 1) and respectively 2 hours (at 60ºC, Fig. 2). Similar effect is observed also with the respective anodic potentiodynamic curves, but it is more slightly expressed.

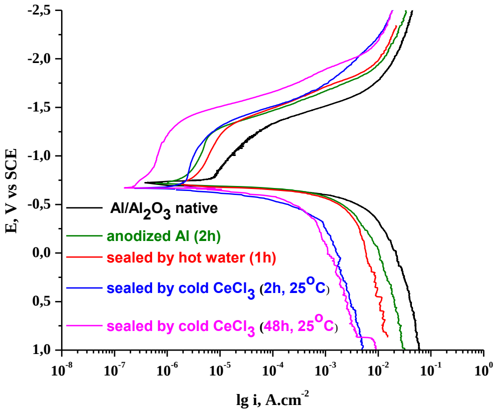

Fig.1. Polarization curves of systems tested in 0.1M NaCl at 25ºC.

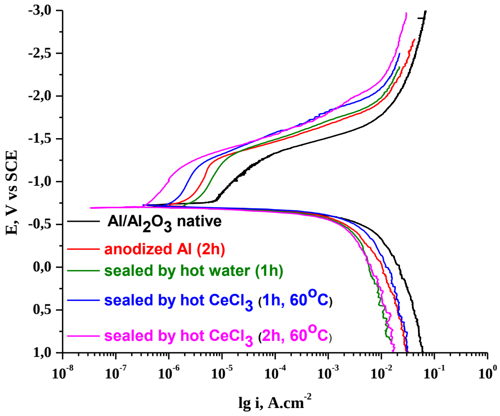

Fig. 2. Polarization curves of systems tested in 0.1M NaCl at 25ºC.

For comparison Figures 1 and 2 represent the anodic and the cathodic potentiodynamic curves for anodized samples, sealed in boiling distilled water for 60 min. In contrast to the sealing in solutions of 0.5M $CeCl_3$, the standard sealing in boiling distilled water consists in filling up of the pores by hydrated aluminum oxide-boehmite ($Al_2O_3 + H_2O \rightarrow 2AlO(OH)$), whose influence is expressed in a barrier effect and this leads to insignificant change in the kinetics of the corrosion process (Fig. 2) [1].

Fig. 3a illustrates the morphology of a non-sealed oxide film, formed by anodizing. It is seen that the film is strongly porous, with average diameter of the pores ~ 75 nm. Fig. 3b shows cross-section of the same film. The hexagonal (cellular) structure of the porous film is observable, formed in the electrolyte containing phosphoric acid. This result is in correspondence with the literature data on similar oxide films [17]. It should be noted, however, that in comparison with the anodic films, prepared by other researchers, the alumina obtained by us has some non-uniformity in the arrangement of the cells (Fig. 3b). One of the reasons for this non-uniformity is the fact that we used technically pure aluminum for our purposes. Another possible reason is that the higher degree of ordering is achieved by means of two consecutive oxidation steps – after dissolving the oxide film, obtained in the first step, during the second oxidation one obtains considerably more uniformly structure layer [18].

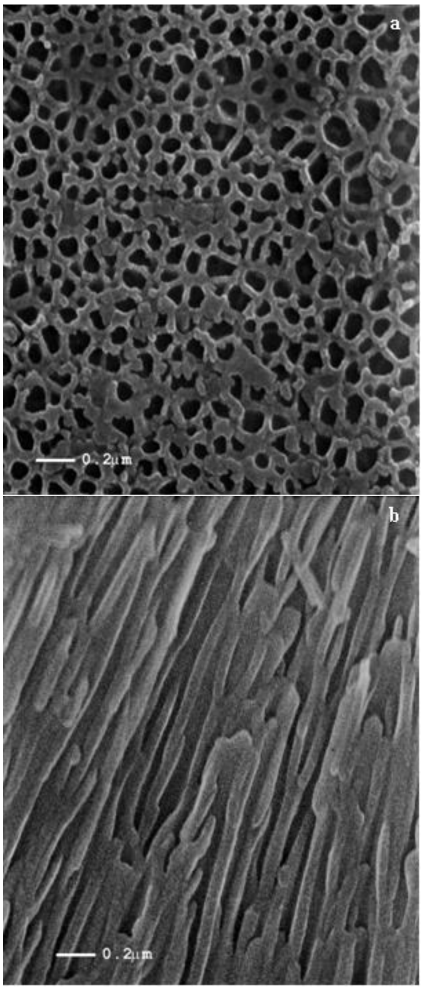

Fig. 3. SEM micrographs of the surface (a) and cross-section image (b) of unsealed Al_2O_3 film formed at 40V, for 2 hours (x50000).

Fig. 4a illustrates the morphology of the aluminum surface after anodic oxidation and sealing of the anodic layer in solution, containing Ce^{3+} at room temperature for 48 hours. In this case the influence of porosity of the oxide film is expressed by increase in the contact surface, interacting with the cerium ions, which is a prerequisite for promoting the rate of spontaneous formation of the cerium oxide film. Thereupon the film formed inside the pores has a complex nature. It consists of two layers, the internal one represents a mixture of alumina/hydroxides Ce_2O_3, and an external one, containing cerium oxides/hydroxides, which covers the cracks of the anodic film (Fig. 4a and b).

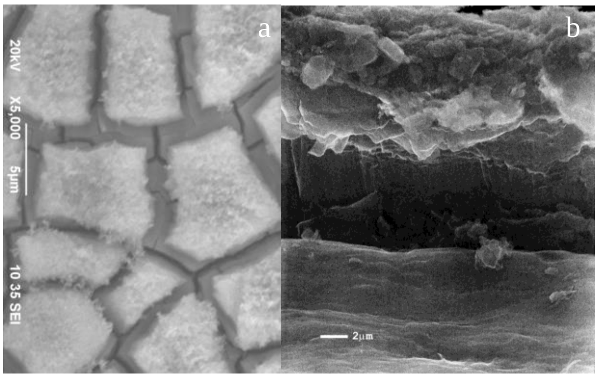

Fig. 4. SEM micrograph (a) and cross-section image (b) of the Al_2O_3 film sealed in cold solution of $CeCl_3$, for 48h (x5000).

For comparison Fig. 5a shows analogous surface of aluminum sample after anodic treatment upon changing the conditions of sealing. In this case the sealing has been carried out at 60ºC in the course of 2 hours in solution of 0.5M $CeCl_3$. Fig. 5b illustrates cross-section of the same sample and it follows thereof, that upon increasing the temperature of the solution for sealing exerts substantial effect on the rate of precipitation of the cerium oxides, whereupon during the time interval of sealing (2 hours) the formed protective layer on the aluminum sample is similar in its thickness to the one formed at room temperature for 48 hours.

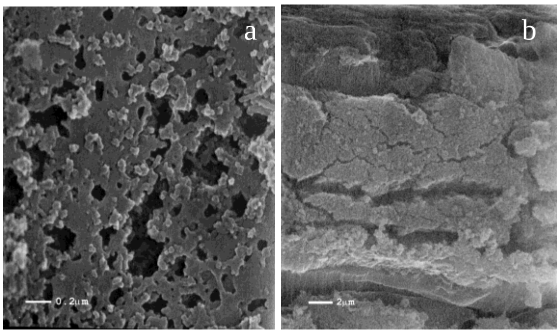

Fig. 5. SEM micrographs (a) and cross-section images (b) of the Al_2O_3 film sealed in hot $CeCl_3$ solution, for 2h (x50000, x5000).

By means of EDS analyses it was established that depending on the conditions of sealing the concentration of cerium on the anodized aluminum support grows up from 2.69 up to 6.18 wt.% upon increasing the time interval of sealing from 1 to 2 hours in hot solution (60ºC) of 0.5M $CeCl_3$, while in the case of sealing at room temperature the concentration of cerium reaches 10.4 wt.% for immersion time interval of 48 hours. This result is in accordance with the data from the potentiodynamic investigations, showing lower corrosion currents, respectively better protective ability, at time intervals of sealing 2 hours in hot solution of $CeCl_3$.

Fig. 6 demonstrates the surface morphology after corrosion test through anodic polarization (at potential +2.5 V) of samples subjected only to anodizing (Fig. 6a) and after consecutive sealing in solution of 0.5M $CeCl_3$ (Fig. 6b). It is known that the region of potentials more positive than 2.0V (vs. SCE) is the area, where the potential of pitting formation, characteristic of aluminum, has been surpassed [19]. It follows from Fig. 6a and b that the sealing changes the corrosion behavior of the system $Al/Al_2O_3/Ce_2O_3$ whereupon the type of corrosion passes over from pitting corrosion (Fig. 6a) into total corrosion (Fig. 6b). After the anodic polarization the external layer of the cerium oxide film loses its anti-corrosion properties, but the internal complex oxide layer has not been corroded, as a consequence of which there is no observation of any appearance of pitting corrosion damages on the surface of the sample.

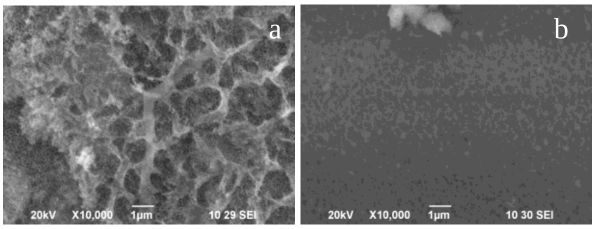

Fig.6. Surface morphology of theAl$_2$O$_3$ films unsealed (a) and sealed (in hot solution of $CeCl_3$) after anodic polarization to the zone of pitting formation (b) (~ +2.5 V).

Some additional light is shed upon the results, commented on above, by the data from the X-ray photoelectron spectroscopy study on the composition and chemical state of the elements comprising the formed protective films. Figures 7, 8 and 9 illustrate part of the results, obtained with the studied samples. Figure 7 a, b represents the typical Al2p and O1s - spectra for anodized and sealed in boiling distilled water sample. They characterize in a unique way the changes on the surface of the aluminum sample, which occur as a result of anodizing. The spectrum of Al2p (Fig. 7a) is characterized by a wide peak, consisting of several peaks. Its de-convolution leads to identification of four peaks, located at 74.6, 76.4, 78.0 and 80.7 eV. The presence of these peaks could be connected with the different in magnitude charging of the particles on the surface of the sample, determined by the presence of two separate phases [20]. On the basis of the values for the binding energy of the respective peaks and their integral peak area, and the comparison with the values of the oxygen peaks for the same sample, we can identify the valence state of the chemical elements, building up the separate phases on the surface. It follows from this juxtaposition that the peak, positioned at 74.6 eV, corresponds to Al^{3+} in Al_2O_3 [21]. Due to the above-mentioned charging a shoulder of this peak is formed, remotely positioned from it at about 3 eV, at 78.0 eV. Its corresponding peak in the spectrum of O1s (Fig. 7b) is located at 531.4 eV. The ratio between these two peaks indicates a certain deficit of oxygen in the formed compound.

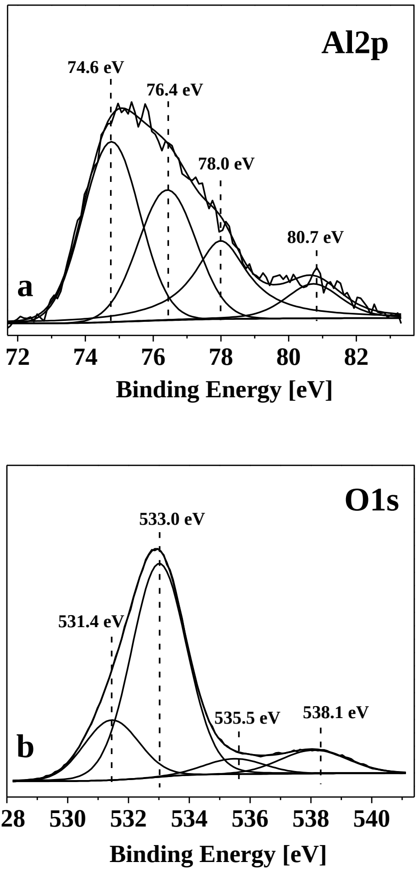

Fig. 7. Deconvoluted XPS – Al2p (a) and O1s (b) spectra of a film, obtained by anodization (after hot water sealing).

The peak, positioned at 76.4 eV, corresponds to Al^{3+}, connected with OH^- or H_2O ligands [22]. This peak has also a shoulder, which is located at 80.7 eV, whereupon the distance between the two peaks is 4 eV. An additional shifting of the peak at 76.4 eV towards higher energies could be attributed to formation of hydroxides and aqua-complexes having coordination number 6. A confirmation of this statement is the fact, that the ratio between the sum of total integrated areas of the two peaks and the area of the corresponding oxygen peak at 533.0 eV is 1:6. It is possible that the O1s peak at 533.0 eV is overlapped with the oxygen peak, corresponding to oxygen bonded in the carbonate groups. We can state that the ratio oxide/hydroxide is approximately 2:1. The remaining two peaks at 535.5 and 538.1 eV in the spectrum of oxygen possibly correspond to bonded oxygen in water molecules adsorbed on the surface as well as in phosphate groups.

The spectra of Al2p and O1s for the sample, sealed in solution of cerium ions (Fig. 8 a, b), are characteristic of all the prepared and studied samples of anodized aluminum, treated in solution of $CeCl_3$. They are also distinguished by complex structure, owing to the presence of different phases on the surface. The spectrum of Al2p (Fig. 8a) is similar to that of the sample, non-coated with cerium oxide. Here again there are four peaks present – at 74.5, 76.6, 78.5 and 80.6 eV, corresponding to Al^{3+} in the composition of Al_2O_3

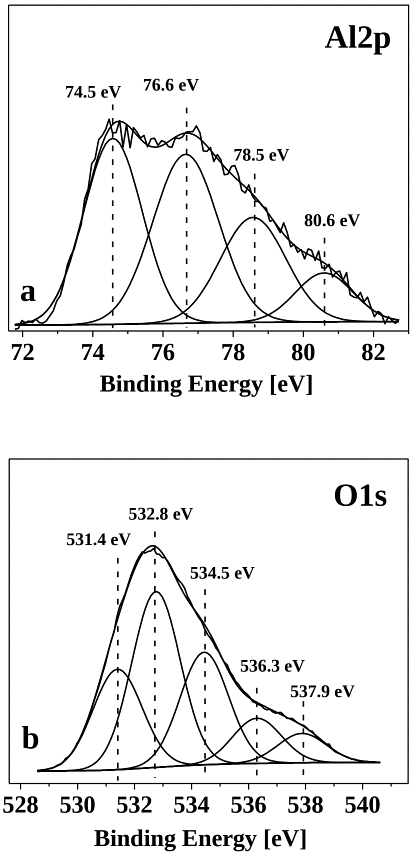

Fig. 8. Deconvoluted XPS – Al2p (a) and O1s (b) spectra of a film, obtained by anodization after hot $CeCl_3$ solution sealing.

and $Al(OH)_3$, whereupon again there are probably two different phases of these compounds present. The spectrum of O1s is more interesting (Fig. 8b). It is composed of five peaks. The first peak, located at 531.4 eV, is wider, due to its overlapping with the peak of the lattice oxygen in the composition of cerium oxide [23]. It is characteristic of Al_2O_3. Again due to the difference in charging of the separate phases, a shoulder of this peak is observable, shifted away from it with 3 eV at 534.5 eV. The second peak at 532.8 eV, corresponds to $Al(OH)_3$. The peak at 537.9 eV can be associated with the presence of phosphate groups [24, 25].

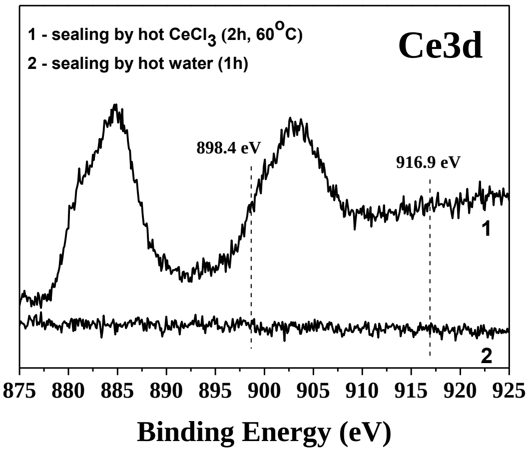

Fig.9. Ce3d - XPS spectra of a film, obtained by anodization after hot $CeCl_3$ solution sealing.

The spectrum of the cerium oxide formed (as a result of the sealing process) on the anodized surface layer, represented in Fig. 9, is characterized by complex structure, due to hybridization of cerium ion with the ligands of oxygen and partial occupation of the valence 4f orbital [26]. As a result of this spin orbital splitting occurs with the formation of doublets, whereupon each doublet has an additional structure, owing to the effect of the final state. The peaks at 916.9 eV and at 898.4 eV are characteristic of CeO_2 and they result from a $3d^{10}4f^1$ final state. The spectrum shows that as a result of the sealing process, a layer of Ce_2O_3 is being formed.

The results, obtained in the course of the studies carried out, show that the sealing of the anodic oxide films in solutions of $CeCl_3$ leads to formation of cerium oxide layers on the surface of the treated samples. These layers contribute to the formation of an efficient barrier against the occurrence of corrosion process influencing substantially the kinetics of the partial electrode reactions, determining its occurrence.

CONCLUSIONS

In this study, the effects of sealing process on the corrosion resistance of anodized aluminum (Al-1050) were investigated. We found out that the reaction products of cold and hot $CeCl_3$ solutions sealing contain $Al(OH)_3$, $Ce(OH)_3$ and Ce_2O_3. These products co-precipitate inside the micropores of the anodic films and they block the pores, so the anodic films have higher corrosion resistance compared to the films sealed by boiling water. Moreover the $CeCl_3$ sealing makes the surface structure and morphology of anodic films more uniform and compact.

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КОРОЗИОННО ПОВЕДЕНИЕ НА АНОДНО ФОРМИРАНИ ОКСИДНИ ФИЛМИ ВЪРХУ АЛУМИНИЙ, УПЛЪТНЕНИ В РАЗТВОРИ, СЪДЪРЖАЩИ ЦЕРИЕВИ ЙОНИ

Р. А. Андреева[1], Е. А. Стоянова[1], А. С. Цанев[2], Д. С. Стойчев[1*]

[1] *Институт по физикохимия „Академик Ростислав Каишев“, Българска академия на науките,*
ул. „Акад. Г. Бончев“ бл. 11, София 1113, България.
[2] *Институт по обща и неорганична химия, Българска академия на науките,*
ул. „Акад. Г. Бончев“ бл. 11, София 1113, България.

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(Резюме)

Изучено е корозионното поведение на анодно получени оксидни филми върху Al-1050 в разтвор на 0.1M NaCl. Оксидните филми са формирани в електролит, съдържащ H_3PO_4 – 40g/l, при волтастатични условия на анодиране. Уплътняването е осъществено в разтвори на 0.5M $CeCl_3$ при температури 25° и 60°C. Дебелината на филмите е 3-5μm.

Морфологията и съставът на формираните порьозни анодни филми са изследвани с помощта на сканираща електронна микроскопия (SEM) и енергийно дисперсионен анализ (EDS). Установено е, че в зависимост от условията на уплътняване, концентрацията на церий в порите на оксидните филми нараства от 5.3 до 10.4 тегл.%. Въз основа на проведени XPS изследвания на изучените системи е дефинирано химичното състояние на церия в порите на оксидния филм. Проведени са потенциодинамични изследвания и са определени корозионните токове на неуплътнените и уплътнените анодни оксидни покрития. Показано е, че запълването/уплътняването на порите на формирания Al_2O_3 аноден филм с $Ce(OH)_3/Ce_2O_3$ повишава неговата корозионно-защитна способност.