Corrosion Evaluation of Zirconium Doped Oxide Coatings on Aluminum Formed by Plasma Electrolytic Oxidation

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Abstract

The plasma electrolytic oxidation (PEO) of aluminum in sodium tungstate ($Na_2WO_4 \cdot 2H_2O$) and $Na_2WO_4 \cdot 2H_2O$ doped with Zr was analyzed in order to obtain oxide coatings with improved corrosion resistance. The influence of current density in PEO process and anodization time was investigated, as well as the influence of Zr, with the aim to find out how they affect the chemical content, morphology, surface roughness, and corrosion stability of oxide coatings. It was shown that the presence of Zr increases the corrosion stability of oxide coatings for all investigated PEO times. Evolution of EIS spectra during the exposure to 3% NaCl, as a strong corrosive agent, indicated the highest corrosion stability for PEO coating formed on aluminum at 70 mA/cm^2 for 2 min in a zirconium containing electrolyte.

Keywords: Aluminum; Plasma electrolytic oxidation; Oxide coatings; Zr; EIS; Corrosion

1. Introduction

Plasma electrolytic oxidation (PEO) is a processing technique in which the surfaces of metals such as aluminum, magnesium, titanium, zirconium, tantalum as well as their alloys are converted into oxide coatings.[1–8] The whole process involves anodizing of metals above the dielectric breakdown voltage where numerous transient short-lived discharges are generated continuously over the coating surface, accompanied by visible light emission and gas evolution.[9] Plasma-chemical, thermal, and anodic oxidation processes are induced at the discharge sites, due to increased local temperature and pressure, which modify the structure, composition, and morphology of such oxide coatings. The composition and concentration of electrolyte play a crucial role in obtaining the desired oxide coatings by PEO. The oxide coatings usually contain crystalline and amorphous phases with constituent species originating both from metal and electrolyte.

PEO of aluminum is a complex electrochemical process combining concurrent partial processes of oxide layer formation, dissolution, and dielectric breakdown. At the beginning of the anodization a thin barrier oxide layer is formed on the substrate.[10] The barrier oxide layer is produced at both aluminum/oxide and oxide/electrolyte interfaces as a result of migration of the O_2^-/OH^- and Al^{3+} ions across the oxide, assisted by a high electric field (~107 V/cm). Barrier oxide layers are amorphous featuring ionic conductivity and high electrical resistance. Thickness of the barrier oxide layer is limited to several hundred nanometers due to the dielectric breakdown. Three main steps lead to formation of PEO coatings.[11] In the first step, a number of separated discharge channels are formed in the oxide layer as a result of loss in its dielectric stability in a region of low conductivity. Due to the strong electric field, anionic components of electrolytes are drawn into the channels. Concurrently, aluminum is

melted out of the substrate, it enters the channels and becomes oxidized. Thus, plasma chemical reactions take place in the channels as a result of these processes. These reactions lead to an increase in pressure inside the channels. At the same time, a separation of oppositely charged ions occurs in the channels due to the presence of the electric field. The cations are ejected from the channels into the electrolyte by electrostatic forces. In the next step, the oxidized metal is ejected from the channels onto the coating surface. Finally, the discharge channels get cooled and the reaction products are deposited onto their walls. This process repeats itself at a number of discrete locations over the coating surface, leading to the increase of the coating's thickness.

One of the most desirable properties of oxide coatings obtained by PEO is their excellent corrosion resistance. In our earlier work we have shown that the presence of tungsten was beneficial for the corrosion stability of oxide coatings formed on aluminum by PEO process in sodium tungstate solution.[12] Since the incorporation of inhibitors into the protective coatings could improve their corrosion stability, the aim of this work was to analyze the possibility to further improve the corrosion stability of tungsten containing oxide coatings by incorporation of zirconium, i.e. more stable oxide, ZrO_2. Zirconium was chosen as a metal with excellant corrosion resistance. Morphology, chemical composition, and corrosion stability of oxide coatings containing both tungsten and zirconium were evaluated. The goal of this work was to identify the PEO parameters that result in improved corrosion stability of obtained oxide coatings.

2. Experimental

Oxide coatings were formed on cold-rolled aluminum samples (40 mm × 15 mm × 0.25 mm) of 99.5% purity. The working electrodes were sealed with insulation resin leaving only active surface with an area of 5 cm². Before the anodization, aluminum was degreased in acetone, ethanol, and distilled water, using ultrasonic cleaner, and dried in a warm air stream. The oxidation process was carried out in an electrolytic cell.[13] Two platinum wires (5 cm long and 1 mm in diameter) were used as cathodes. The power supply was a homemade DC power unit providing voltages of 0–600 V and a current of 0–1 A. For anodization of aluminum we used water solution of 0.01 M $Na_2WO_42H_2O$ with or without 1% Bonderite® (Henkel), Zr containing solution. The electrolyte was prepared using double distilled and deionized water and PA (pro analysis) grade chemical compound. Anodizing was carried out at current densities of 50–70 mA/cm². During anodization, the electrolyte circulated through the chamber–reservoir system. The temperature of the electrolyte was maintained during the anodization process at (20 ± 1) °C. After anodization, the samples were rinsed in distilled water to pre-

vent additional deposition of electrolyte components during drying.

Scanning electron microscope (SEM) JEOL JSM 5800 equipped with X – ray energy dispersive spectroscopy (EDS) was used to characterize surface morphology and chemical composition of formed oxide coatings.

The surface roughness of PEO coatings were determined by TR-200 Handheld roughness tester.

Electrochemical impedance spectroscopy measurements of the PEO coatings on aluminum were recorded in three-electrode cell arrangement, during the exposure to 3 % NaCl solution as corrosion agent. A coated sample, with a tested area of 1 cm², was used as a working electrode, the counter electrode was a platinum mesh, and the reference electrode a SCE. EIS data were obtained at the open-circuit potential using a Reference 600 potentiostat/galvanostat/ZRA (Gamry Instruments), over a frequency range of 100 kHz to 10 mHz using 7 mV amplitude of sinusoidal voltage.

The corrosion rates in aerated 3% NaCl solution of the PEO coatings were determined using extrapolation of anodic polarization curves to the open circuit potential. Potential sweep rate of 1.0 mV s^{-1} was applied starting from the open circuit potential (OCP), after the constant OCP was established (~1h).

3. Results and Discussion

3. 1. The Influence of Current Density

Although several current densities were investigated, it was only possible to reach the breakdown voltage at current densities ranging from 50 to 70 mA/cm². In tungsten containing electrolytes the breakdown voltage is typically reached at 15 mA/cm², but the addition of zirconium to commonly used electrolyte required application of much higher current densities. The influence of three dif-
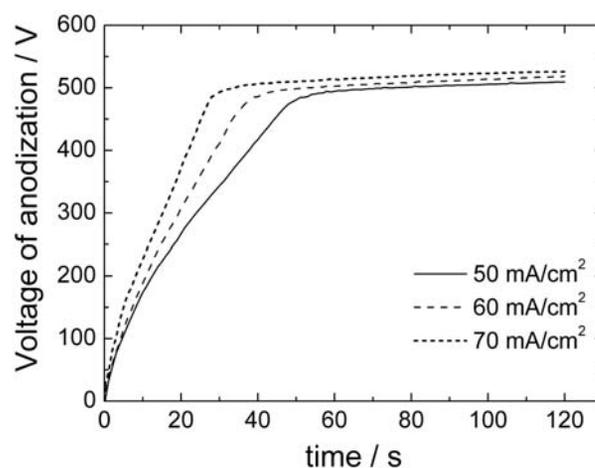
Fig. 1. Time variation of voltage during galvanostatic aluminum anodization in 0.01 M $Na_2WO_42H_2O$ containing Zr, at different current densities

ferent current densities on the voltage-time dependency is shown in Fig 1.

Typical voltage-time responses during galvanostatic aluminum anodization in 0.01 M $Na_2WO_42H_2O$ containing Zr were recorded for all three current densities. The time for reaching breakdown voltage was lower for higher current density.

The electrochemical properties of PEO coatings obtained at these three current densities, for PEO process time of 2 min, were determined by EIS analysis (Fig. 2), a commonly used method in corrosion testing.[3,14–18] The EIS response of bare Al is given as a reference in Fig. 2.
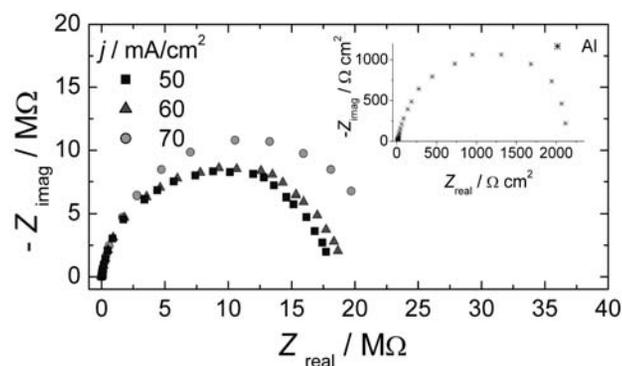
Fig. 2. Nyquist plots of bare Al (inset) and PEO coatings with Zr formed at different current densities during 2 min, after 1 h exposure to 3% NaCl

It can be seen that all PEO coatings showed significantly higher impedance values than bare Al surface (up to four orders of magnitude). Similar EIS response was recorded for PEO coatings formed at 50 and 60 mA/cm^2, whereas the overall impedance was increased for coating formed at 70 mA/cm^2. Since the aim of this work was to determine parameters for acquiring zirconium containing PEO coating with the increased corrosion stability the current density of 70 mA/cm^2 was chosen for further analysis.

3. 2. Morphology and Chemical Composition of PEO Coatings

SEM micrographs of oxide coatings formed in various stages of PEO process are shown in Fig. 3. Relatively uniform coatings are formed for short PEO times (Fig. 3 a–c). Clearly, at longer oxidation times the lacy surfaces were more pronounced, with an increasing diameter of pores.

Results of the EDS analysis of surface coatings (Fig. 3) are shown in Table 1. Main elements of the coatings are Al, O, W, and Zr, confirming that species from the electrolyte could be incorporated into the coating layer during the PEO process.
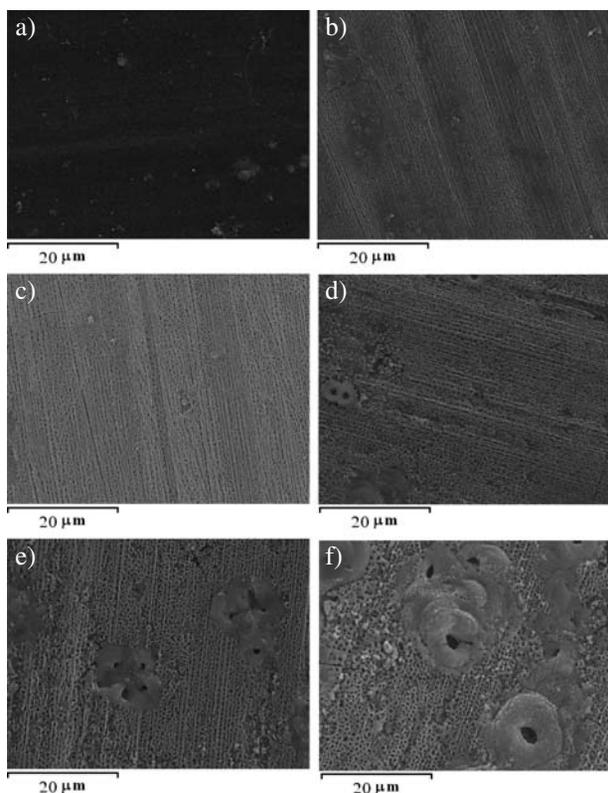
Fig. 3. SEM micrographs of oxide coatings formed in 0.01 M $Na_2WO_42H_2O$ containing Zr on aluminum at various stages of PEO process: (a) 0.5 min; (b) 1 min; (c) 2 min; (d) 3 min; (e) 4 min; (f) 5 min.

Table 1 – EDS analysis of surface coatings shown in Fig. 3.

Sample	PEO time/min	wt (%)			
		O	**Al**	**W**	**Zr**
Fig. 3a	0.5	19.31	80.69	/	/
Fig. 3b	1	28.14	71.86	/	/
Fig. 3c	2	30.96	63.43	3.02	2.59
Fig. 3d	3	36.79	57.22	1.23	4.77
Fig. 3e	4	35.35	56.74	2.14	5.78
Fig. 3f	5	36.52	49.95	6.84	6.80

Short PEO times of 0.5 and 1 min were not long enough for incorporation of W and Zr, although breakdown voltage was reached after about 20 s. Longer oxidation times generally result in higher amount of both W and Zr, while the amount of Al decreases. The amount of O also increases with the PEO time, confirming that W and Zr were predominately incorporated into the coating as oxides.

SEM cross-section micrograph of coating formed for 5 min is shown in Fig. 4. The EDS analysis of the cross-section showed quite homogenous distribution of W and Zr in the oxide coating. On the cross section micrograph two distinct layers could be observed: the thicker

outer layer and much thinner, but compact, inner layer. It is obvious that cracks and pores are not present just on the oxide surface but are distributed through the whole coating. It was shown that, typically for PEO process, the coating thickness increases with prolonged PEO process time,[12] reaching ~15 μm for 5 min oxidation.

Based on the SEM analysis it can be concluded that at oxide coatings containing Zr can be obtained at current density of 70 mA/cm^{2} for PEO times higher than 2 min. However, at this high current density even short oxidation times of 4 and 5 min result in a cracked oxide coatings with high porosity (Fig. 3 e and f).

The surface roughness of PEO coatings was also determined since it could be an important parameter for corrosion stability. The dependence of the values of surface roughness, R_a, on the PEO time in Zr containing electrolyte, is shown in Fig. 5.

The longer PEO time results in the increased surface roughness. This could be explained as follows: microdischarges are generated by dielectric breakdown through weak sites in the oxide coating. The number of weak sites

is reduced with increasing time of anodization, i.e. with increasing thickness of the coating.[19] The increased size of microdischarges with increasing time of PEO is ascribed to the reduced number of discharging sites through which higher anodic current is able to pass. As it was shown in Fig. 3 the surface morphology evolution of the coatings formed on aluminum during PEO process clearly demonstrates the decrease in the number of micropores and their increase in size. In a thicker layer of oxide coatings, higher energy is required for the current to pass through it. This is the reason why the diameter of the discharge channel increases. So, thicker coatings have higher surface roughness (Fig. 5). In initial stage of PEO, discharge channels are well distributed and oxide coatings exhibit lower surface roughness. As the number of discharge channels decreases with time of PEO, non-uniformities in the oxide coatings appear causing an increase in surface roughness.

Based on our experimental data, surface roughness increases with oxidation time from 0.216 μm for 1 min PEO process to 0.462 μm for 5 min PEO process.
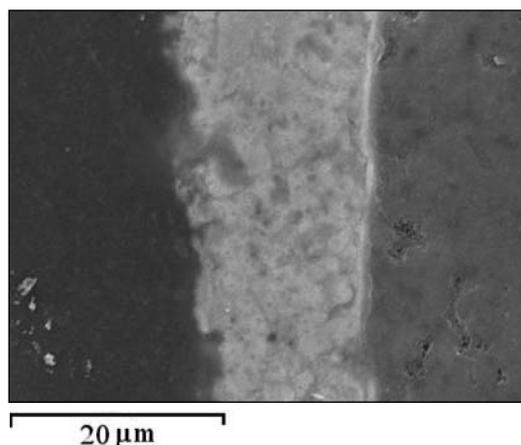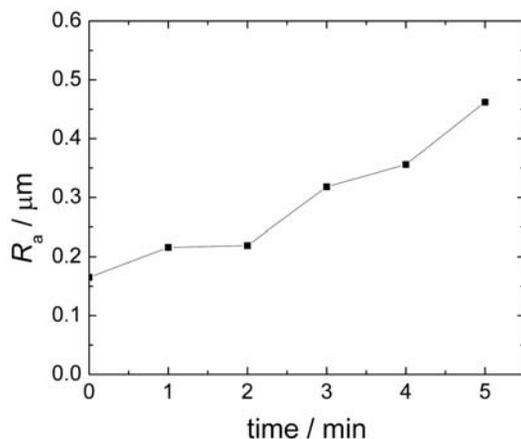
3. 3. Electrochemical Properties of PEO Coatings

An EIS study of PEO coatings on Al in 3% NaCl formed during various PEO times was performed in order to investigate the influence of process time on the EIS properties of zirconium containing oxide coatings. EIS plots for Zr-free oxide coatings are shown in Fig. 6a. All Zr containing samples showed only one time constant after a short immersion time in a corrosive solution (Fig. 6b), whereas Zr-free oxide coating formed during 4 min PEO process had two time constants (inset in Fig. 6a).

The increased impedance values of Zr containing oxide coatings could be seen from Figs. 6 a and b, for the same PEO parameters, suggesting that Zr-doped coatings are capable of reducing the corrosion processes. This could be the result of the incorporation of ZrO_2 into the mixed oxide coatings, as well as the reduced porosity of these coatings due to precipitation of ZrO_2 within the oxide coating. Namely, oxide coatings formed by plasma electrolytic oxidation have many cracks and pores that enable the ingress of the corrosive agent to the metal substrate, and, in turn, the initiation of corrosive processes. If, during the PEO process, zirconium ions bond with Al substrate and/or ZrO_2 precipitates at the walls of the discharge sites, oxide coatings with reduced corrosion activity can be formed.

According to our earlier results, as well as the results of other authors,[12,14,20–23] the EIS spectra for PEO coatings could be basically characterized by two time constants. One constant in the high frequency range, which is related to the porous outer oxide layer, and the second one in the lower frequency range, associated to the inner, barrier layer. It should be noted that even though the

Fig. 4. SEM cross-section micrograph of PEO coating formed for 5 min in 0.01 M Na$_2$WO$_4$2H$_2$O containing Zr on aluminum

Fig. 5 Influence of PEO treatment time on roughness of Zr containing oxide coatings

a)

b)
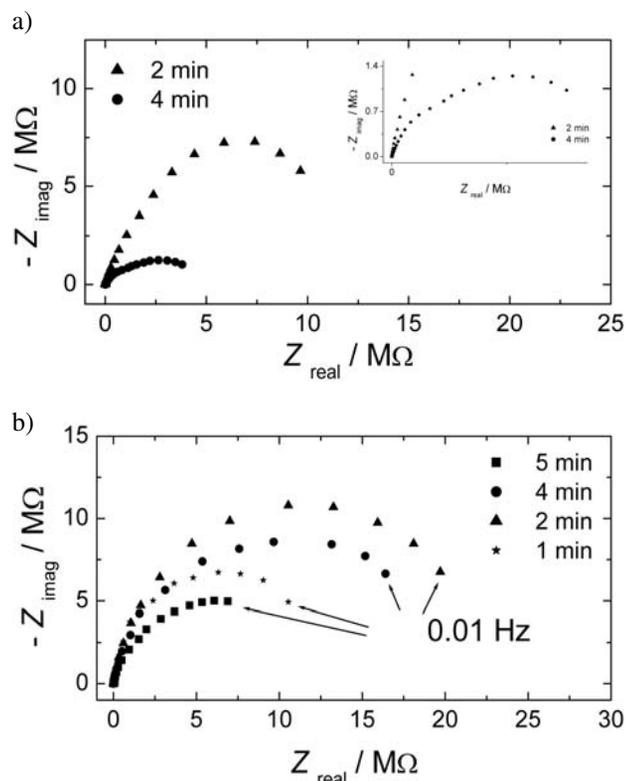
Fig. 6. Nyquist plots of PEO coatings formed at 70 mA/cm² a) without Zr, during 2 and 4 min and b) with Zr during different time, after 1 h exposure to 3% NaCl

outer oxide layer is usually much thicker than the inner oxide layer, the former is quite porous (Fig. 4) so its impedance is significantly smaller than the impedance of the inner barrier one. Therefore, the high impedance of the inner oxide layer often overlaps with the impedance of the outer layer, so one time constant EIS plots could often be fitted with only one time constant equivalent circuit (Fig. 7), which is related to the entire oxide coating.

The fitting of experimental data was accomplished using the appropriate equivalent electrical circuits (Fig. 7) and Gamry Instruments Echem Analyst fitting program, version 5.50. One time constant equivalent circuit shown in Fig. 7a was used for fitting the impedance plots of all oxide films for short time of exposure to NaCl (one time
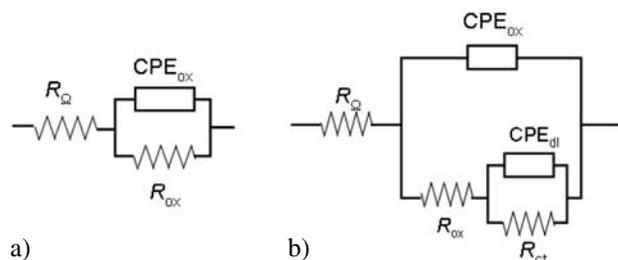
Fig. 7. Equivalent electrical circuits used for the impedance plots fitting of the PEO coatings on aluminum for a) short time of exposure to 3% NaCl and b) prolonged immersion in 3% NaCl.

constant plots). This equivalent circuit consists of the electrolyte resistance, R_Ω, the total oxide layer resistance, R_{ox}, and constant phase element CPE_{ox} related to the total oxide layer capacitance. Clearly this equivalent circuit corresponds to the oxide films with negligible resistance of outer porous layer compared to inner barrier layer.

The fitting results for all investigated samples after one hour of exposure to NaCl are shown in Table 2.

Table 2. Fitting results of EIS plots of the PEO coatings on Al and corrosion current density, j_{corr}, after 1h of exposure to 3% NaCl

PEO time / min	$R_{ox} \cdot 10^{-6} /\ \Omega$ cm²	CPE_{ox}		$j_{corr} \cdot 10^2 /$ μA cm⁻²
		$Y_o \cdot 10^7 /$ $s^n\ \Omega^{-1}$ cm⁻²	n	
Al	0.002160	56	0.86	7.9
1	11.6	0.41	0.96	0.11
2	21.9	$8.0 \cdot 10^{-5}$	0.98	0.070
3	12.8	4.5	0.79	0.63
4	18.6	4.4	0.81	0.10
5	10.4	6.2	0.78	0.14

It can be seen from Fig. 6 and Table 2 that, among all Zr containing oxide coatings, the smallest impedance values were obtained for the ones formed during the shortest and longest time, i.e. 1 and 5 min. Oxide coating formed for 1 min was quite homogenous, but did not contain Zr (Fig. 3, Table 1), which could also give evidence for the beneficial role of Zr in corrosion stability of oxide coatings. On the other hand, oxide coating formed for a long PEO time of 5 min was quite porous (great CPE value). As it was shown in Fig. 4 cracks and pores are interconnected at certain points, providing pathways for the penetration of corrosive agents towards the metal substrate, thus reducing the overall protective properties of such coatings. Although PEO coating formed for 2 min had the smallest amount of Zr it showed the highest impedance. These results suggest that the incorporation of Zr is beneficial for corrosion stability, but that it is not the sole factor determining good protective properties of these PEO coatings.

The corrosion behaviour of PEO coatings was also evaluated by potentiodynamic polarization after 1 h of exposure to 3% NaCl solution. Since it has been shown that the incorporation of Zr into PEO coatings resulted in increased corrosion protection of Al (Fig. 6a), only the samples containing Zr were tested. Some of the obtained E-log j dependences are shown in Fig. 8. The polarization curve for bare Al is also given in Fig. 8 for a reference. The corrosion current density (j_{corr}) determined from potentiodynamic polarization plots are shown in Table 2.

A clear difference among the samples could be seen just by looking at the potentiodynamic curves (Fig. 8). All PEO coatings doped with Zr have smaller corrosion rate compared to bare Al. The E_{corr} of oxide coatings was shifted to lower values, as well as both anodic and cathodic
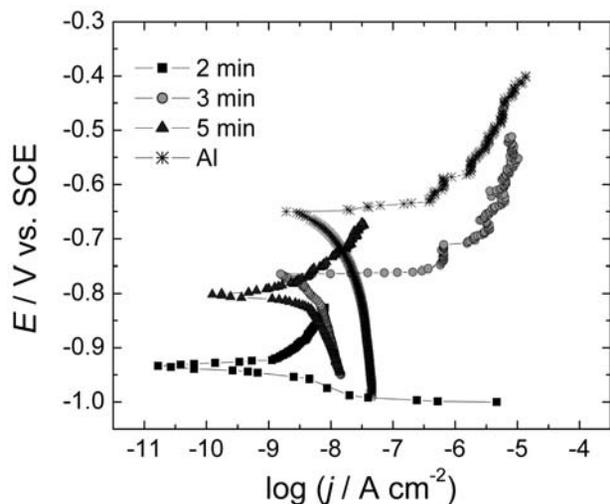
Fig. 8. Polarization curves in 3% NaCl for Al and zirconium containing PEO coatings formed during various PEO times

branches of the polarization curves, suggesting the protective effect of zirconium containing PEO coatings on the anodic process of metal dissolution. The j_{corr} of PEO coating obtained after 2 min is significantly lower than for coatings formed during longer times (Table 2). This is in agreement with previously discussed EIS results.

In order to further examine the corrosion behavior and the deterioration od PEO coatings on Al, the corrosion behavior of zirconium containing PEO coatings on Al was also examined by EIS measurements during prolonged immersion in 3% NaCl. The influence of Zr on the corrosion stability of oxide coatings was studied in two different ways. In one set of experiments oxide coatings were formed at 70 A/cm² in the tungsten and zirconium containing electrolyte for 2 and 4 min. In the second set, oxide layers were formed at the same current density, but in the tungsten only containing electrolyte for 2 and 4 min and then immersed in the zirconium containing solution for 1 min, with the aim of sealing the pores formed during PEO process with Zr film.

After longer exposure to NaCl solution (5 hours and up, depending on the PEO time), PEO films were fitted with two time constants equivalent electrical circuit that consisted of the electrolyte resistance, R_Ω, the oxide layer resistance, R_{ox}, the charge–transfer resistance, R_{ct}, and the constant phase elements, CPE_{ox} and CPE_{dl}, which are related to the oxide layer capacitance and double-layer capacitance, respectively (Fig. 7b). The evolution of R_{ox} and C_{ox} of these PEO coatings, during 192 h, is presented in Fig 9 a and b.

Initially, during the first day for all samples, the oxide layer resistance decreases (Fig. 9a) and oxide layer capacitance increases (Fig. 9b) as a consequence of the ingress of the electrolyte. The highest change (three orders of magnitude) could be observed for PEO coating formed for 4 min and sealed in Zr containing electrolyte. This is
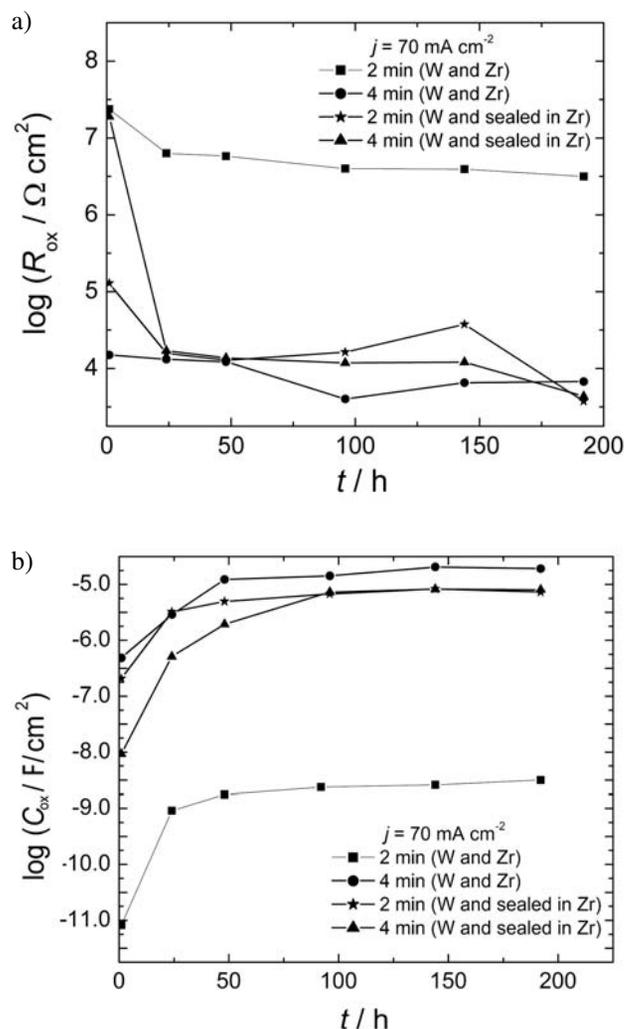
Fig. 9. Time dependences of oxide coating a) resistance, R_{ox}, and b) capacitance, C_{ox}, for different PEO coatings, during exposure to 3% NaCl

probably the result of the very porous coating, providing many pathways for the corrosive agent (Fig. 3e). It is interesting to note that there was no significant difference among other analyzed samples. This, again, suggests that the presence of Zr is not the only factor leading to the increased corrosion stability. It was shown to be beneficial in the early exposure to corrosive agent (Fig. 6, Table 2), but neither sealing, nor greater Zr content helped during longer exposure to a strong corrosive agent.

The highest R_{ox} and lowest C_{ox} values were obtained for oxide coating containing Zr and formed for 2 min. In addition, after the initial small drop, these values did not change much during the exposure to NaCl, suggesting the maintenance of good protective properties of this oxide coating. Such high corrosion stability is probably the result of both high compactness and thickness of this oxide layer. However, it is possible that a solid solution of three oxides (Al, W, and Zr -oxides) was formed under these conditions, which along with the compact layer strengthens the

protective behavior of this oxide coating on aluminum. Namely, it is well known that rapid cooling could result in widening of the range of solid solution compositions in a phase diagram. Since PEO coatings are formed under extreme conditions (the local temperatures and pressures during PEO process could be as high as $10^3 - 10^4$ K and $\sim 10^2$ MPa high[1]), this hypothesis seems probable.

So, under locally present high temperatures and pressures, which result from the appearance of the microdischarges at sites of dielectric breakdown, the solid solution of mixed oxides could be formed, resulting in a very high corrosion stability during long exposure to NaCl solution.

On the basis of all presented results it can be concluded that corrosion stability of bare Al was improved by mixed oxide layers investigated in this work, consisting of Al, W, and Zr –oxides, and PEO coating formed for 2 min showed the highest corrosion stability due to both its high compactness and thickness.

4. Conclusions

Plasma electrolytic oxidation (PEO) of aluminum was performed in sodium tungstate ($Na_2WO_4 \cdot 2H_2O$) and $Na_2WO_4 \cdot 2H_2O$ doped with zirconium at different current densities and different times. The corrosion stability of obtained oxide coatings was investigated by electrochemical impedance spectroscopy and polarization curves. It was demonstrated that the high current densities of 50–70 mA/cm^2 are required for incorporation of Zr in the oxide coatings, whereas the overall impedance was increased for coating formed at 70 mA/cm^2.

The PEO process time influences the coating thickness, roughness, and corrosion stability. The coating thickness, as well as coating roughness, increase with increasing PEO treatment time, while the presence of Zr increases the corrosion stability of oxide coatings for all investigated PEO times. The greatest corrosion stability, i.e. the highest resistance and the lowest capacitance and corrosion current density values, was achieved with 2 min PEO time in a zirconium containing electrolyte. The observed protective properties against corrosion are the consequence of both high compactness and thickness of oxide layer consisting of Al, W, and Zr –oxides. Longer PEO times resulted in porous oxide coatings enabling a fast ingress of a corrosive agent.

5. Acknowledgement

6. References

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Povzetek

Plazemsko elektrolitsko oksidacijo (PEO) aluminija v natrijem volframatu (Na$_2$WO$_4 \cdot$ 2H$_2$O) in Na$_2$WO$_4 \cdot$ 2H$_2$O, ki je dopiran z cirkonijem, smo uporabili kot način tvorbe oksidnih plasti z izboljšanimi protikorozijskimi lastnostmi. Analizirali smo vpliv gostote toka, časa oksidacije in dodatka cirkonija z namenom ugotoviti, kako ti dejavniki vplivajo na kemijsko sestavo, morfologijo, površinsko hrapavost in korozijsko stabilnost prevlek. Dodatek cirkonija izboljša korozijsko stabilnost prevleke ne glede na dolžino časa oksidacije. Na podlagi elektrokemijskih impedančnih spektrov, izmerjenih med potopitvijo vzorcev v korozivno 3 %-tno raztopino NaCl, smo ugotovili, da največjo korozijsko stabilnost izkazujejo PEO prevleke na aluminiju, ki so bile pripravljene pri gostoti toka 70 mA/cm^2 v času trajanja 2 minuti v raztopini, ki vsebuje cirkonij.