

Durability of porous anodic alumina layers on AA1050 modified by incorporation of Cu, Ni and Cu/Ni

Ch. Girginov^{1*}, St. Kozhukharov², B. Tzaneva³

¹Department of Physical Chemistry, Faculty of Chemical Technologies, University of Chemical Technology and Metallurgy, Sofia, Bulgaria

²LAMAR Laboratory, University of Chemical Technology and Metallurgy, Sofia, Bulgaria

³Department of Chemistry, Faculty of Electronic Engineering and Technologies, Technical University of Sofia, Sofia, Bulgaria

Received: November 17, 2021; Revised: March 03, 2022

The resistance of referent porous AAO (anodic aluminum oxide) layers and such modified by incorporation of Cu, Ni and both Cu and Ni was evaluated by performing electrochemical measurements using electrochemical impedance spectroscopy (EIS) and linear sweep voltammetry (LSV). The reported results are obtained after 168 hours of exposure to a 3.5% NaCl model corrosive medium. The acquired EIS spectra were analyzed by fitting to a suitable model equivalent circuit (MEC). Further, the estimated impedance values, acquired by the performed EIS data evaluation were further verified by Tafel slope analysis of the respective LSV curves. The results have shown that the elaborated films are sufficiently durable and can successfully be employed as primers for the deposition of other types of advanced coating layers.

Keywords: AAO layers; Ni, Cu and Cu/Ni incorporation; Electrochemical characterization methods

INTRODUCTION

Low-doped Al alloys, such as AA1050, find various applications in both mass production and high-tech industries. One of the widest fields of use of these materials is the packaging of various nutrition products and soft drinks [1, 2]. However, reliable packaging requires additional protection of the surface of Al-based packaging materials before they come into contact with any food product. This requirement has arisen because the resorption of Al-ions from such packaging products was recently demonstrated [3, 4], which is dangerous to human health [5, 6]. The specific conjunction between electrical conductivity and the strength-to-weight ratio [7, 8] makes aluminum an indispensable material for high-voltage, long-distance electricity distribution [9, 10] as well. Among the most notable advantages of aluminum is its ability to form a highly ordered self-assembled porous surface by means of anodizing under certain conditions [11, 12]. The surfaces of the obtained textured *anodic aluminum oxide* (AAO) films are widely used for ink-printing on paper and plastic packaging materials [13, 14]. Also, anodized pure aluminum is used for manufacturing metal-oxide-semiconductor electronic components [15, 16], sensors [17, 18] and biosensors [19]. Other recently proposed important applications are for alternative energy sources, such as production of flexible solar cells [20] and fuel cell electrodes by anodization [21]. Recently, the

obvious advances of the multilayer coating systems elaborated by various electrochemical methods have been outlined in an extended review [22]. In this sense, AAO layers additionally modified by incorporation of Ce [23], Ag [24], and Cu and Ni [25] have shown superior corrosion-protective properties. In addition, these electrochemical modifications provide additional benefits, such as decorative color effects and even bactericidal ability. Undoubtedly, these modified AAO layers enable the deposition of other types of advanced coating layers, in order to produce various hi-tech components and multifunctional devices.

In this sense, the aim of the present research work is the performance of systematic comparative electrochemical measurements on porous AAO layers, after their modification by incorporation of Cu, Ni, and both Cu and Ni in their pores. The measurements were performed on two samples from each set: (i) reference AAO, (ii) AAO with incorporated Cu, (iii) AAO with incorporated Ni and (iv) AAO with incorporated Cu and Ni. All measurements were performed after 168 hours of exposure to a model corrosive medium (aqueous solution of 3.5% NaCl).

EXPERIMENTAL

Electrochemical elaboration of the investigated films

Eight square-shaped specimens (2×2 cm) of the low - doped AA 1050 alloy were cut in order to

* To whom all correspondence should be sent:
E-mail: girginov@uctm.edu

perform the planned systematic comparative study. The preliminary surface treatment was performed by etching in a NaOH solution (50 g dm^{-3}) for 2 minutes at $60 \text{ }^\circ\text{C}$ and subsequent activation in dilute nitric acid ($\text{HNO}_3\text{:H}_2\text{O} - 1\text{:}1$) for 2 minutes at room temperature, followed by a final vigorous washing with both tap and double-distilled water.

The specimens were then anodized in a 15 wt.% solution of H_2SO_4 under galvanostatic conditions (15 mA cm^{-2}) for 50 min at room temperature. The formed porous AAO layers were electrochemically modified by incorporation of Cu and/or Ni. This process was performed at the following conditions: AC-polarization at a constant voltage of 20 V and applied frequency of 60 Hz, for 15 min at $20 \text{ }^\circ\text{C}$. Both Cu- and Ni-containing electrolytes were composed by CuSO_4 or NiSO_4 (0.4 mol dm^{-3}), respectively. The combined Cu/Ni electrolyte was prepared by mixing these solutions in a volume ratio of 1:1. Each of these deposition electrolytes contained also $(\text{NH}_4)_2\text{SO}_4$ (30 g dm^{-3}) and H_3BO_3 (50 g dm^{-3}).

As a result, a set of: (i) reference AAO, (ii) AAO with incorporated Cu, (iii) AAO with incorporated Ni and (iv) AAO with incorporated Cu and Ni was prepared. In order to assess the repeatability of the results, each of these types of coatings was represented by two samples.

Electrochemical characterization of the obtained films

All samples were subjected to comparative electrochemical measurements after 168 hours of exposure to the model corrosive medium (MCM), which is essentially a 3.5 % aqueous NaCl solution. The electrochemical film characterizations were performed using an Autolab PGStat 30 potentiostat/galvanostat of "Metrohm" (Netherlands), equipped with FRA-2 frequency response analyzer. The measurements were performed in a standard, three-electrode "flat" cell (ISO 16773-2), equipped with a cylindrical platinum mesh as a counter-electrode and an Ag/AgCl/3M KCl reference electrode. Test areas of 2 cm^2 from the specimens served as working electrodes. The measurements included electrochemical impedance spectroscopy (EIS) and linear sweep voltammetry (LSV). The EIS spectra were acquired in the frequency range from 10 kHz to 0.01 Hz, distributed in 50 measurement points. The amplitude of the excitation signal was up to 35 mV in relation to the open circuit potential (OCP), in order to acquire

readable spectra. The linear sweep voltammetry (LSV) curve acquisitions were performed in the potential range from -150 to + 550 mV. OCP, at a sweep rate of 10 mV s^{-1} .

RESULTS AND DISCUSSION

EIS data acquisition

The electrochemical impedance spectra were acquired from all samples after 168 hours of exposure to the model corrosive medium, in order to obtain comparable results for all specimens. Figure 1 presents averaged EIS spectra plotted in Bode (a) and Nyquist (b) coordinates. The spectra resemble this of a capacitor, due to the excellent insulation properties of the elaborated AAO layers on the metallic surfaces. Only the phase shift of the reference AAO layers can be distinguished from those of the modified ones. Consequently, their modification by means of incorporation of Cu and/or Ni obviously results in further improvement of the formed AAO layers.

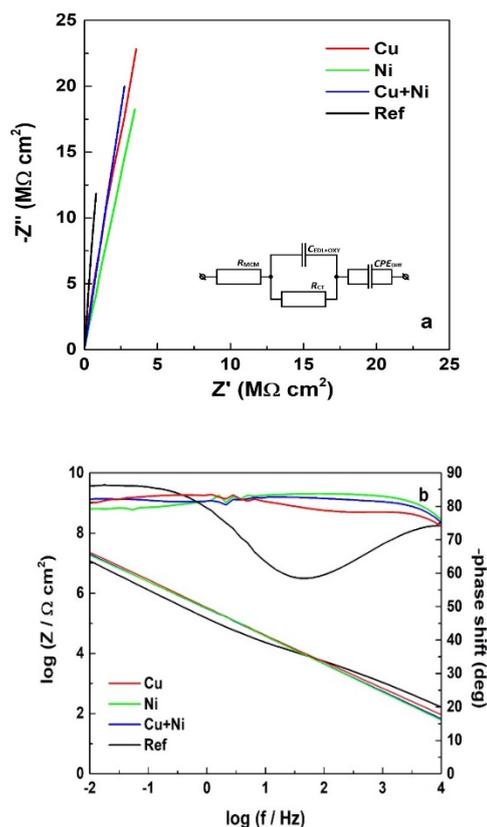


Fig. 1. Averaged EIS spectra of the investigated specimens, acquired after 168 hours of exposure to the 3.5% NaCl model corrosive medium.

Table 1. Results of the numerical analysis of the EIS spectra

Group	Sample	R_{MCM} $\Omega.cm^2$	$C_{EDL+OXY}$ $\mu F.cm^2$	R_{CT} $k\Omega.cm^2$	CPE_{diff} $(10^{-7})s^n \Omega^{-1} cm^{-2}$	n
G 1 – Ref	S1	90.40 ± 28.02	0.12 ± 0.01	6.590 ± 0.66	12.20 ± 0.63	0.88 ± 0.01
	S2	34.90 ± 8.49	0.36 ± 0.01	1.820 ± 0.22	11.56 ± 0.30	0.91 ± 0.01
G2 – Cu	S1	8.87 ± 1.40	1.22 ± 0.07	0.297 ± 0.030	5.53 ± 0.02	0.91 ± 0.01
	S2	5.79 ± 1.33	9.07 ± 1.27	0.219 ± 0.035	5.47 ± 0.01	0.93 ± 0.01
G3 – Ni	S1	8.73 ± 1.00	4.73 ± 0.46	275.184 ± 33.732	7.36 ± 0.05	0.91 ± 0.01
	S2	7.38 ± 1.05	3.47 ± 0.26	260.900 ± 37.332	6.73 ± 0.08	0.93 ± 0.01
G4 – Cu/Ni	S1	8.21 ± 0.85	7.65 ± 0.13	23.79 ± 6.13	6.47 ± 0.03	0.92 ± 0.01
		9.68 ± 0.58	5.02 ± 0.43	33.90 ± 10.70	6.08 ± 0.02	0.91 ± 0.01

The obtained spectra were further submitted to analysis using a suitable model equivalent circuit (MEC), illustrated in Fig. 1a. It is composed of resistance of the model corrosive medium R_{MCM} , connected to the capacitance of the electric double layer and the oxide film $C_{EDL+OXY}$ and the charge transfer resistance R_{ct} . Finally, a constant phase element CPE_{diff} was required in order to describe the diffusion of the electrolyte inside the pores of the AAO.

The results of the numerical analysis of the EIS spectra with the used MEC are presented in Table 1.

The comparative analysis of the data in Table 1 has revealed several obvious trends. The values of R_{MCM} , for the reference AAO layers are by entire order of magnitude higher than those of the modified layers. At the same time, there are no obvious differences between the R_{MCM} values of the AAO layers modified with incorporation of Cu and/or Ni. The capacitance $C_{EDL+OXY}$ of the reference samples is also lower than this of the modified layers by at least one order of magnitude. The biggest differences are in the charge transfer resistance R_{ct} . The electrochemical modification with Cu has led to a decrease by an entire order of magnitude, compared to the R_{ct} of the reference AAO layers. In contrast, the incorporation of Ni resulted in a sharp rise of R_{ct} by three orders of magnitude.

In the case of the AAO layer modified with both Cu and Ni, the R_{ct} values are with an entire order of magnitude higher than those of the reference AAO layers. Consequently, the beneficial effect of the Ni-incorporation is compensated by the weak detrimental effect of the Cu deposition. Both these effects are probable, because on one hand, the Cu and/or Ni incorporation enhances the barrier properties of the AAO layer by sealing the pore walls and bottoms. However, on the other hand, the AC-polarization during the electrochemical Cu and/or Ni incorporation results in pore widening, due to the cathodic dissolution commented elsewhere [26].

An additional analysis of the EIS spectra was performed, following the general concepts of Zheludkevich *et al.* [27]. It was performed by determination of the $\log|Z|$ values, acquired at 0.01 Hz (i.e., the last impedance data points). The corresponding values of the impedance modulus $|Z|$ (Table 2) should approximate those of the polarization resistance (R_p), commented in the next paragraph.

According to this parameter (i.e., $|Z|$), the AAO layers modified with Cu possess similar barrier properties to the reference ones. However, the other two trends commented above, regarding the obvious beneficial effect of the modification of the AAO layer with Ni and the weakening of this effect, are confirmed by the values of $|Z|$ presented in Table 2. Indeed, these values, estimated for the AAO layers with incorporated Ni are about three times higher, whereas the AAO modified with Cu and Ni have almost the same $|Z|$ -values as those of the other groups.

A rather interesting fact is that the $|Z|$ -values are by more than three orders of magnitude higher than those of R_{ct} . The discrepancy between the values of these parameters is a result of the fact that the value of $|Z|$ comprises the capacitive reactance, unlike R_{ct} .

Analysis of the data acquired by linear sweep voltammetry (LSV)

The EIS spectra, commented in the previous paragraph, were followed by recording of LSV curves, under the conditions described in the experimental section. The averaged LSV curves are presented in Fig. 2.

The anodic branches of all LSV curves are almost horizontal, revealing the lack of any corrosion processes. Consequently, the formation of the AAO layer results in efficient passivation of the surfaces of the AA1050 samples and serves as efficient barrier against access of corrosive species to the metallic surface.

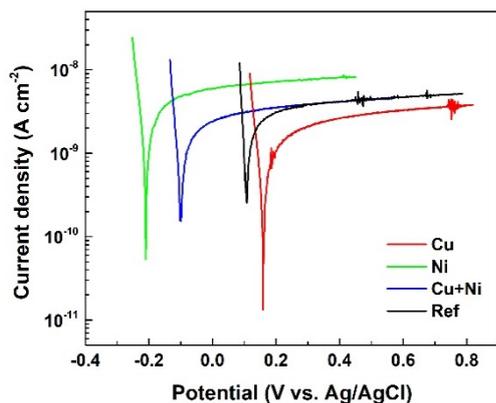


Fig. 2. Averaged LSV curves, acquired after 168 hours of exposure to 3.5% NaCl model corrosive medium

Again, the averaged LSV curve for the Ni-AAO samples falls below those of the other types of coatings, due to the already mentioned beneficial effect of the electrochemical treatment of the AAO layers in the electrolyte containing NiSO_4 . This curve is followed by the curves for Cu/Ni-AAO and for Cu-AAO. The LSV curves of the reference AAO layers are at the highest current. Besides, both modified with Ni and Cu AAO layers are shifted to more negative potentials, whereas the combined Cu and Ni AAO approaches the potential of the reference AAO layer. The LSV curves were submitted to further Tafel slope analysis, in order to acquire a clearer image regarding the corrosion characteristics of the investigated layers. The respective numerical data for the corrosion potential (calculated vs. SHE) and the polarization resistance are summarized in Table 3. The data for the corrosion potential in Table 3 reveal that the additional Cu and/or Ni modifications result in its shifting towards more negative values. Nevertheless, this shift is rather weaker for the combined Cu and Ni AAO layers.

The data for the polarization resistance (R_p) represented in Table 3 almost coincide with those for $|Z|$ in Table 2. Indeed, the data from both tables reveal the remarkable beneficial effect of the AC assisted electrochemical modification of the AAO

layers. Indeed, the average value for $|Z|^{\text{av}} = 27.00 \text{ M}\Omega\cdot\text{cm}^2$ approaches the average value for $R_p^{\text{av}} = 27.55 \text{ M}\Omega\cdot\text{cm}^2$, and both of them are three times higher than these of the other types of coatings.

CONCLUSIONS

The data, acquired from the electrochemical impedance spectroscopy (EIS), were fitted to appropriate model equivalent circuit (MEC). It was evinced that the main impedance components of the spectra are: resistance of the model corrosive medium (R_{MCM}), capacitance of the electric double layer and the oxide film ($C_{\text{EDL+OXY}}$), the charge transfer resistance (R_{ct}) and diffusion constant phase element CPE_{diff} . Further analysis was performed of the EIS spectra in order to acquire the values of the impedance modulus $|Z|$ at 0.01 Hz. It was established that these values are higher than those of R_{ct} by more than three orders of magnitude. The found discrepancy between the values of these parameters is a result from the fact that the value of $|Z|$ comprises the capacitive reactance as well.

Afterwards, linear sweep voltammetry (LSV) was applied, in order to determine the values of the corrosion potential and the polarization resistance (R_p).

The present research is based on the comparative analysis of data, acquired from systematic electrochemical measurements on AAO layers, after modification with Cu, Ni, and combination of them. Two independent electrochemical analytical methods were applied for data acquisition, after 168 hours of exposure of the specimens to 3.5% NaCl model corrosive medium.

Both analytical methods have revealed that the basic AAO layer behaves as almost perfect insulator. Further, the analysis of the obtained data has shown superior behavior of the AAO layers modified with Ni, compared to the other types. Besides, a weak deterioration of this behavior was registered for the AAO films modified with both Cu and Ni. As a main achievement of the present research could be pointed out the clear correspondence between $|Z|$ at the lowest frequency and the R_p from the LSV curves.

Table 2. Values of the total impedance modulus, acquired at 0.01 Hz.

Sample No.	S1		S2	
Unit	Log $ Z $	$ Z $ ($\text{M}\Omega\cdot\text{cm}^2$)	Log $ Z $	$ Z $ ($\text{M}\Omega\cdot\text{cm}^2$)
G1-Ref	7.118	13.12	7.066	11.65
G2-Cu	7.161	14.49	7.168	14.71
G3-Ni	7.454	28.42	7.408	25.58
G4-Cu/Ni	7.253	17.91	7.242	17.46

Table 3. Numerical data of the corrosion potential and the polarization resistance

Sample No.	S1		S2	
	Corrosion potential (mV versus Ag/AgCl)	Polarization resistance (MΩ.cm ²)	Corrosion potential (mV versus Ag/AgCl)	Polarization resistance (MΩ.cm ²)
G1-Ref	-102	13.79	-103	11.50
G2-Cu	-312	14.84	-332	15.56
G3-Ni	-293	29.06	-328	26.04
G4-Cu/Ni	-176	17.44	-125	17.55

In general, the Cu- and/or Ni-modified AAO layers, elaborated during the present research activities, can be efficiently used as a basis for deposition of other types of advanced coating systems. In particular, the approaches described here enable the elaboration of entire new generations of metal/dielectric/metal systems.

Acknowledgements: The authors gratefully acknowledge the financial support of the Bulgarian National Science Fund, under project KII06-H29/1.

REFERENCES

- M. Lamberti, F. Escher, *Food Rev. Internat.*, **23**, 407 (2007).
- O. Ayalon, Y. Avnimelech, M. Shechter, *Envir. Sci. Pol.*, **3**, 135 (2000).
- S. P. Joshi, R. B. Toma, N. Medora, K. O'Connor, *Food Chemistry*, **83**, 383 (2003).
- F. Bianchi, M. Careri, M. Maffini, A. Mangia, C. Mucchino, *Rapid Commun. Mass Spectr.*, **17**, 251 (2003).
- A. Becaria, A. Campbell, S. C. Bondy, *Toxicology and Industrial Health*, **18**, 309 (2002).
- J. Kandiah, C. Kies, *Biometals*, **7**, 57 (1994).
- S. S. Golru, M. M. Attar, B. Ramezanzadeh, *Appl. Surf. Sci.*, **345**, 360 (2015).
- R. Lukauskaitė, A. V. Valiulis, O. Černašėjus, J. Škamat, J. A. Rębiś, *J. Mater. Eng. Perform.*, **25**, 3493 (2016).
- D. E. Johnson, T. L. Anderson, US patent, US 6559385 B1 (2003).
- C. Hiel, G. Korzeniowski, D. Bryant, US patent, US 7179522 B2 (2004).
- Ch. A. Girginov, S. V. Kozhukharov, Chapter 1. Theoretical Bases and Mechanisms of the Electrochemical Alumina Films Formation, in: Aluminium Oxide. Structure Production and Application, A. Hermansen (ed.), NOVA Sci. Publ., 2020, p. 3.
- W. Stępniewski, J. M. Salerno, Chapter 12. Fabrication of nanowires and nanotubes by anodic alumina template-assisted electrodeposition, Manufacturing Nanostructures, in: Manufacturing Nanostructures, W. Ahmed, N. Ali (eds.), One Central Press –ISBN: 9781910086070, 2014, p. 321.
- R. E. Cleveland, US patent, US 2114072 A (1938).
- J. Curt, US patent, US 2780253 A (2008).
- P. Vachkov, D. Ivanov, Powerful MOS transistors and their application, Gov. Ed. "Tekhnicka", Sofia, 1990, p. 15.
- S. Iwauchi, T. Tanaka, *Jpn. J. Appl. Phys.*, **10**, 260 (1971).
- T. Kumeria, A. Santos, D. Losic, *Sensors*, **14**, 11878 (2014).
- I. Abrego, A. Campos, G. Bethencourt, E. Ching-Prado, *Mater. Proceed. Res. Soc. Symp.*, **1449**, 73 (2012).
- A. Santos, T. Kumeria, D. Losic, *Materials*, **7**, 4297 (2014).
- F.-C. Chen, M.-K. Chuang, S.-C. Chien, J.-H. Fang, C.-W. Chu, *J. Mater. Chem.*, **21**, 11378 (2011).
- P. Bocchetta, M. Santamaria, F. Di Quarto, *J. Mater. Sci. Nanotechnol.*, **1**, 1 (2014).
- M. Aliofkhaezrai, F. C. Walsh, G. Zangari, H. Koçkar, M. Alper, C. Rizal, L. Magagnin, V. Protsenko, R. Arunachalam, A. Rezvanian, A. Moein, S. Assareh, M. H. Allahyarzadeh, *Appl. Surf. Sci. Adv.*, **6**, 100141 (2021).
- S. Kozhukharov, Ch. Girginov, *J. Electrochem. Sci. Eng.*, **8**, 113 (2018).
- S. V. Kozhukharov, Ch. Girginov, D. Kiradzhyska, A. Tsanev, G. Avdeev, *J. Electrochem. Sci. Eng.*, **10**, 317 (2020).
- Ch. Girginov, S. Kozhukharov, A. Tsanev, A. Dishliev, *J. Electrochem. Sci. Technol.*, **12**, 188 (2021).
- T. T. M. Tran, B. Tribollet, E. M. M. Sutter, *Electrochim. Acta*, **216**, 58 (2016).
- M. L. Zheludkevich, I. M. Salvado, M. G. Ferreira, *J. Mater. Chem.*, **15**, 5099 (2005).