Electrochemical properties and thermal stability of epoxy coatings electrodeposited on aluminium and modified aluminium surfaces[*]

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The corrosion behaviour of epoxy coatings electrodeposited on aluminium, as well as on electrochemically and chemically modified aluminium were investigated during exposure to 3 % NaCl. Electrochemical impedance spectroscopy (EIS) and thermogravimetric analysis (TGA) were used for the determination of the protective properties of epoxy coatings on aluminium, anodized aluminium, phosphatized and chromatized-phosphatized aluminium. The protective properties of epoxy coatings on anodized and chromatized-phosphatized aluminium are significantly improved with respect to the same epoxy coatings on aluminium and phosphatized aluminium: higher values of the pore resistance and charge-transfer resistance, lower values of the coating capacitance, double-layer capacitance and relative permittivity (from EIS) smaller amount of absorbed water inside the coating (From TGA). On the other hand, the lower values of the *ipdt* temperature indicate a lower thermal stability of the epoxy coatings on anodized and chromatized-phosphatized aluminium.

Keywords: electrodeposition, epoxy coatings, aluminium, anodized aluminium, phosphatized and chromatized- phosphatized aluminium, corrosion, EIS.

INTRODUCTION

Aluminium and aluminium alloys have attracted considerable attention because of their wide use in the architectural, aeronautic and car industries. However, when exposed to aggressive environments, aluminium and aluminium alloys react especially with oxygen and chloride ions to form complex interfaces. The corrosion rate of the reactions can be reduced if the metal is isolated from the aggressive environment by the formation of a thick inorganic layer or by applying an organic coating.[1–6]

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[*] Dedicated to Professor Dragutin Dražić on the occasion of his 70th birthday.

The aim of this work was to investigate the electrochemical and thermal properties of epoxy coatings on aluminium and modified aluminium surfaces (anodized aluminium, phosphatized and chromatized-phosphatized aluminium) ant to explain the effects of the surface modification on the protective properties and thermal stability of epoxy coatings electrodeposited on aluminium.

EXPERIMENTAL

The aluminium pretreatment and the chemical and electrochemical modification of aluminium are summarized in Table I.[7,8]

TABLE I. Aluminium pretratment and chemical and electrochemical modification of aluminium

Operation	Solution	τ/min	δ/μm	pH	t/°C
Degreasing	10 g dm^{-3} (NaOH + Na$_3$PO$_4$ · 10 H$_2$O + Na$_2$CO$_3$)	3	–	–	50
Pickling	5 % NaOH	3			50
Brightening	12 % HNO$_3$	0.5			Room temp.
Rinsing	Distilled water				–
Chromato - phosphating	58 g dm^{-3} H$_3$PO$_4$ 7 g dm^{-3} CrO$_3$ 4.5 g dm^{-3} NaF	2	0.5–1	1.85	Room temp.
Phosphating	5 % "Alfos" (based on Na-phosphates)	5	0.5–1	4.7	50
Anodizing	20 % H$_2$SO$_4$ (j = 1.8 A dm^{-2})	12.5	5		Room temp.
Hot sealing	H$_2$O	6.5		–	100

The protective epoxy coatings were formed during cathodic electrodeposition of an epoxy resin modified by amine and isocyanate, on aluminium and modified aluminium surfaces (Al 99.5), using the constant voltage method (CATOLAC emulsion 543.052, produced by Industrie Vernici Italiane under Pittsburg Paint and Glass (PPG) licence). The resin concentration in the electrodeposition bath was 10 wt.% solid dispersion in water at pH 5.7, the temperature was 27 ºC and the applied voltage was 250 V.[9] After coating for 3 min, the coatings were rinsed with distilled water and cured at 180 ºC for 30 min. The measured thickness of the coatings was 20 ⌈ 1 µm.

The electrochemical properties of the epoxy coatings on aluminium and modified aluminium surfaces were determined using electrochemical impedance spectroscopy (EIS). The coated samples were exposed to 3 % NaCl in distilled water for 100 days. A three-electrode cell arrangement was used in the experiments. The working electrode was a coated sample situated in a special Teflon holder. The counter electrode was a platinum mesh with a surface area considerably greater than that of the working electrode. The reference electrode was a saturated calomel electrode (SCE). A. C. impedance data ware obtained at the open-circuit potential using a PAR 273 potentiostat and PAR 5301 lock-in amplifier. The impedance measurements were carried out over a frequency range of 100 kHz to 5 mHz using a 5 mV amplitude of sinusoidal voltage. The impedance spectra were analyzed using a suitable fitting procedure.[10]

Thermogravimetric analysis (TGA) was carried out using a Perkin-Elmer TGS-2 instrument. The experiments were performed in a dynamic nitrogen atmosphere (30 cm3 min^{-1}) at a heating rate of 10 ºC min^{-1} over the temperature range of 20–600 ºC.

The rate of the hydrogen evolution reaction in the polymer solution on aluminium and the modified aluminium surfaces was determined on a rotating disc electrode using slow sweep voltammetry (rotation of 2000 rpm, sweep rate 1.0 mV s^{-1}). The counter electrode wa a Pt spiral wire and the reference electrode was a SCE.

The contact angle, φ, between the polymer solution and the different substrates was determined by the drop test.

RESULTS AND DISCUSSION

Electrochemical properties

EIS was used for the evaluation of the electrochemical properties of epoxy coatings on aluminium and modified aluminium surfaces. Fig. 1 represents the equivalent electrical circuit model for a polymer-coated metal in corrosive environments. The equivalent circuit consists of the electrolyte resistance, R_W, the coating capacitance, C_c, the pore resistance, R_p, the double-layer capacitance, C_d, the charge-transfer resistance, R_{ct}, and the Warburg impedance, Z_w. Fitting of experimental data in the complex plane, using the procedure elaborated by Boukamp,[10] enabled the determination of the parameters in the equivalent electrical circuit from Fig. 1.
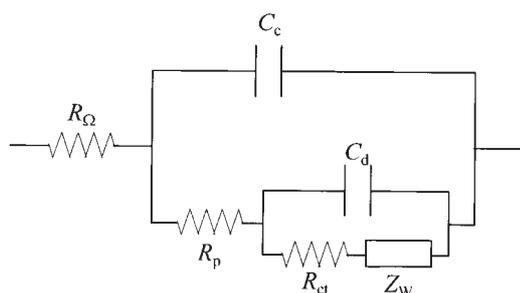
Fig. 1. Equivalent electrical circuit oa f polymer-coated metal.

The time dependences of the pore resistance, R_p and the coating capacitance, C_c, during exposure to a corrosive agent (3 % NaCl) are shown in Figs. 2 and 3, respectively. It can be seen that the pore resistance decreases and coating capacitance increases during the first few days, denoting the entry of electrolyte into the epoxy coating.[11,12] This is the first step of electrolyte penetration through an organic coating and it is related to water uptake, when molecules of pure water diffuse into the micropores of the polymer network according to Fick's law. After this initial period, the values of the pore resistance and the coating capacitance reach a plateau and remain almost unchanged over a long period of time, indicating the maintenance of good protective properties due to existence of the passive film on the aluminium surface. This is the second step of electrolyte penetration and it refers to the penetration of water and ions through the macropores of the coating which become deeper with time, until they finally pass through the epoxy coating and reach the metal surface.[13] This leads to the beginning of electrochemical processes on the metallic interface and, as a consequence, to the loss of

coating adhesion. The significantly higher values of R_p and lower values of C_c for the epoxy coatings on anodized and chromatized-phosphatized aluminium with respect to the same coatings on phosphatized aluminium and aluminium indicate the greater corrosive stability.
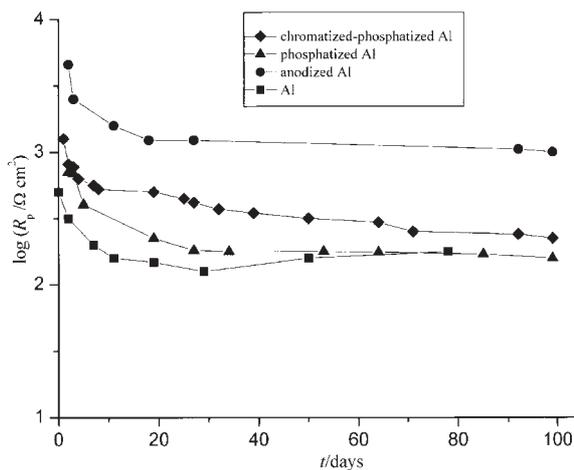
Fig. 2. The time dependence of the pore resistance for epoxy coatings electrodeposited on aluminium and on modified aluminium surfaces, durign exposure to 3 % NaCl.
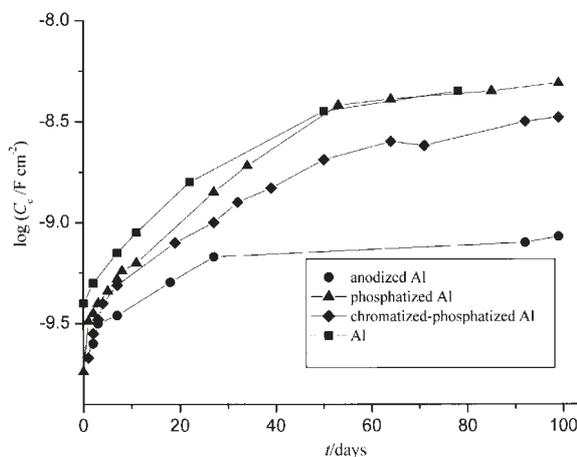
Fig. 3. The time dependence of the coating capacitance for epoxy coatings electrodeposited on aluminium and on modified aluminium surfaces, during exposure to 3 % NaCl.

The charge-transfer resistance, R_{ct} and double-layer capacitance, C_d, are plotted as a function of time (Figs. 4 and 5, respectively). Initially, for all coatings, the cahrge-transfer resistance decreases, while the double-layer capacitance increases. After this initial period, the values of the double-layer capacitance and the charge-transfer resistance remain unchanged during long exposure time. This behaviour confirmed the hypothesis of the existence of a passive film on the aluminium surface, which prevents the corrosion process at the substrate. The lower values of C_d and higher values of R_{ct}

for the same epoxy coatings on anodized and chromatized-phosphatized aluminium than on phospatized aluminium and aluminium also indicate that epoxy coatings on anodized and chromatized-phosphatized aluminium have greater corrosion stability due to existence of the passive anodic oxide and chromato-phosphate layer.
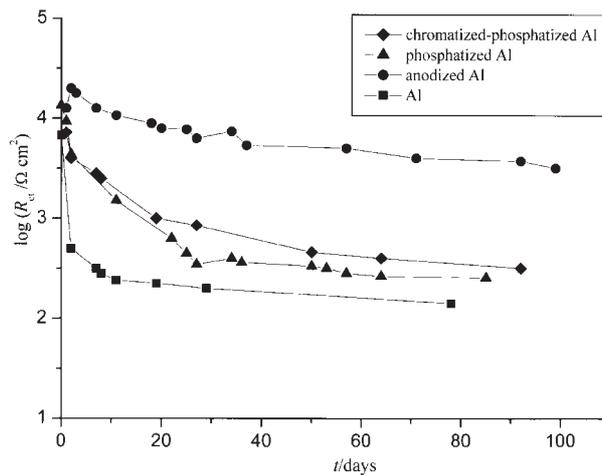
Fig. 4. The time dependence of the charge-transfer resistance for epoxy coatings electrodeposited on aluminium and on modified aluminium surfaces, during exposure to 3 % NaCl.
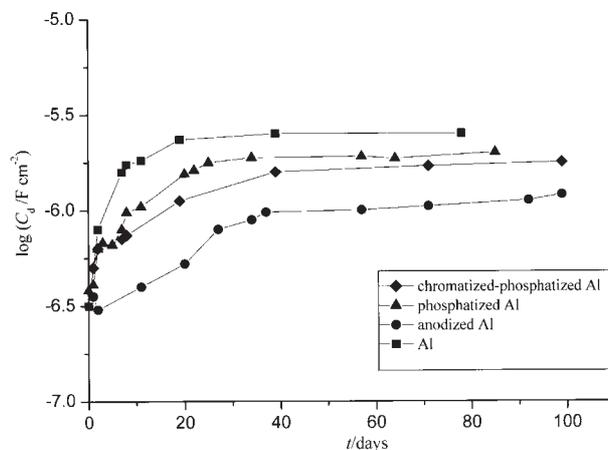
Fig. 5. The time dependence of the double-layer capacitance for epoxy coatings electrodeposited on aluminium and on modified aluminium surfaces, during exposure to 3 % NaCl.

The relative permittivity of an epoxy coating, ε_r, was calculated from the film thickness, δ and the coating capacitance, C_c, using the equation:

$$e_r = C_c d / \varepsilon_o \tag{1}$$

where $\varepsilon_o = 8.85 \times 10^{-12}$ F m^{-1} is the permittivity of a vacuum. The time dependence of the relative permittivities are presented in Fig. 6. The saturation values of relative

permittivity ' 10 indicate the low water content of the epoxy coating on anodized aluminium and its lower porosity and better corrosion stability compared to the coatings on the other substrates.
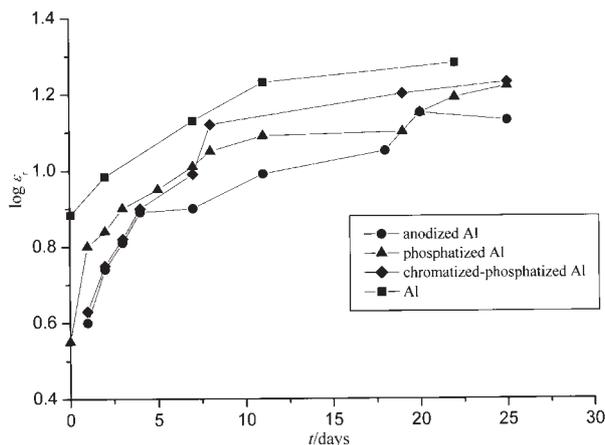
Fig. 6. The time dependence of the relative permittivity for epoxy coatings electrodeposited on aluminium and on modified aluminium surfaces, during exposure to 3 % NaCl.

The differences in the electrochemical properties can be explained by the different rates of hydrogen evolution during the deposition of the epoxy coating on different substrates (Fig. 7) and different wettability.[14,15] The faster H_2 evolution (Fig. 7) and lower wettability (Table II) on phosphatized aluminium and aluminium than is the case on anodized and chromatized-phosphatized aluminium cause an accumulation of hydrogen on the cathode during the subsequent electrodeposition of the epoxy coating. During the subsequent curing of the epoxy coating formation, hydrogen evolves, leav-
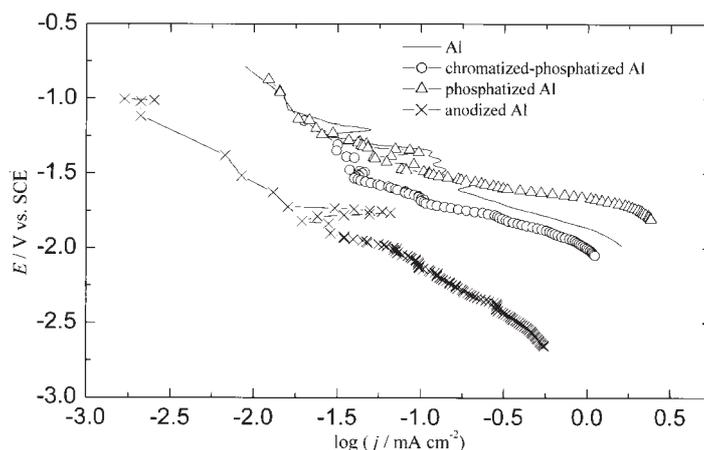
Fig. 7. Polarization curves for hydrogen evolution on aluminium and on modified aluminium surfaces in the polymer solution at 25 °C; N_2 saturated; $\omega = 2000$ rpm; $v = 1.0$ mV s^{-1}.

ing more vacancies in the polymer network, which results in a more porous structure of the epoxy coatings on phosphatized aluminium and on aluminium compared to the epoxy coatings on anodized and on chromatized-phosphatized aluminium. This explains the lower protective properties of these coatings: smaller values of R_p and R_{ct} and higher values of C_c, ε_r and C_d (From EIS).

Transport properties

The content of absorbed water inside the epoxy coating, as a measure of the corrosion stability of a coating, was determined from TG-curves. The TG curves for the dehydration process (Temperature range 20–200 ºC) are shown in Fig. 8. Two weight loss steps are observed with a total weight loss of ′ 1.2 % which is completed at temperature of ′ 1.2 % which is completed at temperature of 180 ºC. The first step takes place at temperature of ′ 50 ºC and is related to the loss of more or less free water. There is a further gradual slow decrease in weight (II step between temperatures of 50 ºC and 180 ºC) probably due to the loss of chemically linked water. From the weight loss at temperature of ′ 50 ºC, the free water content inside the coatings was calculated to be 0.160–0.450 wt.% for the different substrates (Table II).
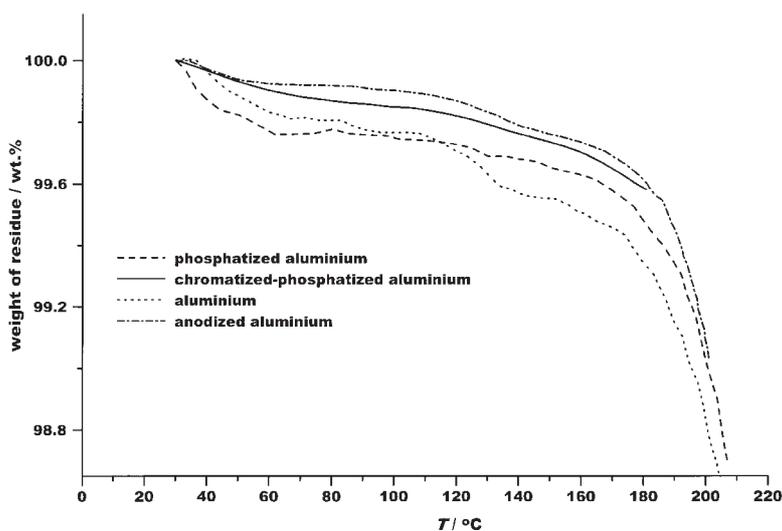
Fig. 8. TG curves for the dehydratation process of the epoxy coatings electrodeposited on aluminium and on modified aluminium surfaces (heating rate 10 ºC min^{-1}).

TABLE II. The values of the contact angle, φ, between the polymer solution and the investigated surfaces, the water content inside the coating and the integral procedure decomposition temperature (*ipdt*) for epoxy coatings electrodeposited on aluminium and modified aluminium surfaces

Substrate	Aluminium	Anodized aluminium	Chromatized-phosphatized aluminium	Phosphatized aluminium
j/ º	64	52	51	59
Water content/wt.%	0.348	0.160	0.237	0.450
ipdt/ºC	402.9	396.0	397.3	404.0

The lower values of the water content iside the epoxy coating on anodized and on chromatized-phosphatized aluminium compared to the same epoxy coatings on phosphatized aluminium and on aluminium (Table II), indicate again the less porous structure and a more stable system in a corrosive environment of the first two coating. These results are in accordance with the results obtained from impedance measurements.

Thermal stability

The thermal stabilities of the epoxy coatings electrodeposited on aluminium and on the odified aluminium were investigated by TGA over the temperature range of 10–600 ºC (Fig. 9). The tendency of a polymer to decompose on heating, as a measure of the thermal stability of the polymer, is expressed by the integral procedure decomposition temperature (*ipdt*), the temperature corresponding to a 50 % weight loss of the specimen.[16] The larger values of the *ipdt* temperature for the epoxy coatings on aluminium and on phosphatized aluminium (Table II) indicate that thermal stability of the
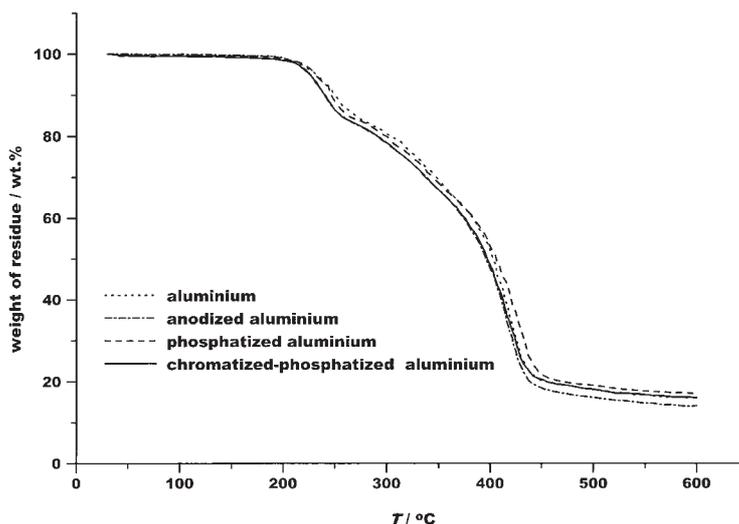
Fig. 9. TG curves for the determination of the thermal stability of the epoxy coatings electrodeposited on aluminium and on modified aluminium surfaces (heating rate 10 ºC min^{-1}).

epoxy coatings on these surfaces is improved. This is probably due to the increase number of hydrogen bonds inside the polymer network, as a consequence of the larger amount of hydrogen evolved on aluminium and on phosphatized aluminium compared to the aount evolved on anodized and on chromatized-phosphatized aluminium, which can react with the oxygen in the polymer chains.

CONCLUSIONS

Epoxy coatings were formed during the cathodic electrodeposition of an epoxy resin on aluminium and previously modified aluminium using the constant voltage method. From the experimental results obtained from electrochemical impedance

spectroscopy (pore resistance, coating capacitance, charge-transfer resistance, double-layer capacitance, relative permittivity of the coating) and thermogravimetric analysis (water content inside the coating and thermal stability), it can be concluded that the protective properties of the epoxy coatings on anodized and on chromatized-phosphatized aluminium are significantly improved with respect to the same epoxy coatings on aluminium and on phosphatized aluminium: higher values of pore resistance and charge-transfer resistance and lower values of coating capacitance, double-layer capacitance and relative permittivity of the coating (from EIS) and the smaller amount of absorbed water inside the coating (from TGA). On the other hand, the thermal stability of these coatings was somewhat lower (smaller values of the *ipdt* temperature). This behavior can be explained by the lower porosity of the epoxy coatings on anodized and on chromatized-phosphatized aluminium, resulting from the lower rate of H_2 evolution and the better wettability.

И З В О Д

ЕЛЕКТРОХЕМИЈСКЕ КАРАКТЕРИСТИКЕ И ТЕРМИЧКА СТАБИЛНОСТ ЕПОКСИДНИХ КАТАФОРЕТСКИХ ПРЕВЛАКА НА АЛУМИНИЈУМУ И МОДИФИКОВАНИМ ПОВРШИНАМА АЛУМИНИЈУМА

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Проучавано је корозионо понашање епоксидних превлака добијених катафоретским таложењем на алуминијуму и електрохемијски и хемијски модификованом алуминијуму током деловања 3 % раствора NaCl. За одређивање заштитних особина епоксидних превлака на злуминијуму, анодизираном алуминијуму, фосфатираном и хроматно-фосфатираном алуминијуму коришћене су методе спектроскопије електрохемијске импеданције и термогравиметријске анализе. Заштитне особине епоксидних превлака на анодизираном и хроматно-фосфатираном алуминијуму су значајно побољшане у односу на исте епоксидне превлаке на алуминијуму и фосфатираном алуминијуму: веће вредности отпорности у порама превлаке и отпорности преноса наелектрисања на граничној површини метал-електролит и мање вредности капацитивност превлаке, капацитивности електричног двојног слоја и релативне пермитивности превлаке (импедансна мерења) и мања количина абсорбоване воде у превлаци (термогравиметријска анализа). С друге стране, мање вредности ipdt температуре указују на мању термичку стабилност епоксидних превлака на анодизираном и хроматно-фосфатираном алуминијуму.

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