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Electrochemical methods for corrosion testing of Ce-based coatings prepared on AA6060 alloy by the dip immersion method

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Abstract: Dip-immersion is a simple and cost-effective method for the preparation of Ce-based conversion coatings (CeCCs), a promising alternative to toxic chromate coatings, on metal substrates. In this work, CeCCs were prepared on Al-alloy AA6060 from an aqueous solution of cerium chloride at room temperature. The effect of immersion time and post-treatment in phosphate solution on the microstructure and corrosion properties of the coatings was studied. The longer the immersion time was, the thicker but more non-homogeneous and cracked were the CeCCs. The post-treatment contributed to a sealing of the cracks, as proven by an increase in the corrosion resistance compared with the as-deposited coatings. The CeCCs prepared at longer deposition times and post-treated showed much better corrosion protection than those prepared at shorter deposition times. A detailed electrochemical impedance spectroscopy (EIS) study was undertaken to follow the evolution of the corrosion behaviour of the CeCCs with time of exposure to an aggressive chloride environment (3.5 % NaCl). For the sake of comparison, the EIS properties of bare AA6060 were also investigated. Linear voltammetry was performed to complete the study. The results confirmed the formation of protective CeCCs on the surface of AA6060. However, even CeCCs prepared at longer deposition times and post-treated provided short term protection in the aggressive environment, due to the small thickness of the coating.

Keywords: cerium; conversion coatings; aluminium alloy; EIS; linear voltammetry.

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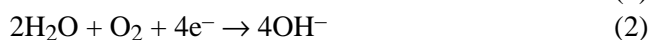
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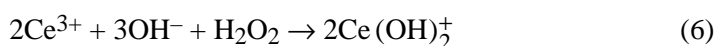
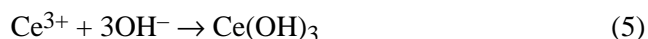
INTRODUCTION

Conversion coatings containing hexavalent chromium (chromate) have been widely used for decades as part of the corrosion protection system on aluminium alloys. However, chromates are prohibited in many fields due to their toxicity, and replacements that show promise have been extensively investigated.¹⁻⁶ Cerium-based conversion coatings (CeCCs) are among the most promising alternatives because of their anti-corrosion efficiency, environmentally benign nature and low cost. The effectiveness of cerium salts as corrosion inhibitors was highlighted in 1984. Hinton *et al.*^{7,8} reported that immersing an Al-alloy in a CeCl₃-containing solution for several days produced a yellowish Ce-based film that provided significant corrosion protection. Its deposition was driven by the natural electrochemical interactions between the Al matrix and inclusions of intermetallic compounds (IMCs) that make up structural alloys.⁹ Wilson and Hinton¹⁰ patented a commercially attractive process for the preparation of CeCCs in the order of minutes, using H₂O₂ to accelerate the deposition kinetics.

The deposition mechanism involves both anodic oxidation of Al, Eq. (1), and cathodic reduction of soluble oxygen and/or added H₂O₂, Eqs. (2 and 3), respectively, as follows:¹¹⁻¹⁵



The generation of hydroxide ions at cathodic sites leads to a strong local increase in the pH near the alloy surface, which promotes formation of a Ce(OH)₃ precipitate or/and soluble ionic complexes, such as Ce(OH)₂⁺. When H₂O₂ is added, the deposition of Ce(IV) is more favourable than Ce(III):^{14,15}



An inhibition effect was achieved by the insoluble Ce-oxide/hydroxide layer formed at the cathodic sites, which suppresses the oxygen reduction reaction (Eq. (2)), thereby providing cathodic inhibition.^{8,16}

The number of variables that influence the rate of CeCC deposition is large and includes solution chemistry (cerium salt used – chloride or nitrate, additives such as gelatine, glycerol to reduce cracking), concentrations of cerium and H₂O₂, pH, temperature, time of immersion, *etc.* In addition, the surface composition and electrochemical behaviour of the range of alloys, as a function of alloying elements, add to the complexity of the deposition mechanism. The most common

alloys studied are those rich in copper, AA2024 and AA7075, widely used in aerospace and military applications.^{7–10,17–29} According to the island growth model, precipitation of Ce-species commences on cathodically strong, Cu-containing IMCs,^{7,8,27–29} and the deposited film subsequently proceeds to grow over the Al matrix. It was shown later^{30,31} that, although the cathodic features of Cu enhance the deposition, its presence is not necessarily required. The deposition of Ce was also observed to occur on low Cu alloys (AA5xxx and AA6xxx), on IMCs of cathodic nature with respect to the matrix.^{32–35}

A limited number of studies report on the formation of CeCCs on AA6xxx.^{11,28,35–39} However, owing to the attractive combinations of properties, the AA6xxx series is of particular interest in the aerospace and automotive industry as potential replacements for the expensive AA2xxx and AA7xxx.^{39,40} The benefits include medium strength, formability and weldability, due to the Mg₂Si intermetallics formed when silicon and magnesium are added in appropriate amounts. They are also heat treatable.

CeCCs can be prepared by different chemical methods, such as spontaneous immersion, spraying and electrolytic routes. Major steps in the coating process are pre-treatment (acid or alkaline) of the substrate surface,^{12,20–24} deposition and subsequent post-treatment.^{12,25,26} Declaroy and Petitjean¹¹ showed that any etching sequence of AA6xxx must finish with an alkaline pre-treatment for successful CeCC deposition.

In this work experimental parameters for the preparation of ceria-based layers on the AA6060 by the dip immersion method were studied. In particular, the time of immersion of the substrate in the conversion solution was investigated, as well as the effect of subsequent post-treatment of the deposited coatings on their microstructure and corrosion properties. Electrochemical methods: linear voltammetry and electrochemical impedance spectroscopy (EIS) were applied for the corrosion testing. The time-dependent EIS behaviour of the CeCCs and of alkali etched AA6060, as the substrate, on exposure to an aggressive chloride environment (3.5 % NaCl) were detailed and compared with the aim of estimating the quality of CeCCs and the duration of protection.

EXPERIMENTAL

Pre-treatment of the substrate and coating deposition

Cerium conversion coatings were prepared on (50 mm×25 mm×0.8 mm) panels of commercial AA6060 alloy used as a substrate. Prior to deposition, the panels were abraded with SiC papers # 600 and #1000, ultrasonically desmutted in acetone for 2 min, rinsed with distilled water and then degreased and etched in alkaline solution (NaOH 7.5 g dm⁻³, Na₃PO₄·12H₂O, 45 g dm⁻³ Na₂SiO₃, 4 g dm⁻³, ethoxylate nonylphenol 13 g dm⁻³) at 70 °C for 2 min and rinsed again. The pre-treated panels were immersed for 5 and 20 min in the Ce-containing solution for deposition. An aqueous solution (0.05 M) of CeCl₃·6H₂O (Alfa Aesar), acidified to pH 2, was used, with the addition of 24 ml of 30 % H₂O₂ (Fisher Scientific). The coated samples were subjected for 5 min to a post-treatment in a phosphate

solution (2.5 % Na₃PO₄, pH 4.5) at 85 °C. The post-treated coatings were rinsed in deionised water and dried in air. All solutions were prepared with analytical grade chemicals and deionised water.

Electrochemical measurements

Electrochemical measurements were performed in an aqueous 0.5 mol dm⁻³ NaCl solution under ambient conditions using a Gamry Reference 600 Potentiostat/Galvanostat/ZRA. The classic three-electrode cell arrangement was used. The working electrode was a coated or bare AA6060 panel situated in a special 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). The cell assembly was located at a Faraday cage to prevent electrical interferences. The electrochemical impedance spectroscopy (EIS) measurements were performed at the open-circuit potential (OCP), over a frequency range from 300 kHz to 10 mHz, using a 10 mV amplitude sinusoidal voltage. The impedance spectra were analyzed using Gamry Elchem Analyst fitting procedure. The linear sweep voltammetry data were collected at a potential sweep rate of 0.5 mV s⁻¹, starting from the OCP, after a constant value was achieved (up to 30 min). Cathodic and anodic polarizations were performed independently.

Scanning electron microscopy with energy dispersive spectroscopy

A scanning electron microscope (SEM) JEOL JSM-5800, operated at 20 keV, equipped for energy dispersive spectroscopy (EDS) measurements, was used to analyze the morphology and composition of the CeCCs.

RESULTS AND DISCUSSION

The CeCCs microstructure

After 5 min of immersion in the conversion solution, the entire substrate surface underwent a noticeable change in colour, from initial metallic grey to light yellow. The colour turned evenly to dark yellow as the immersion time was increased to 20 min. The change in colour could be taken as an indication of different film thicknesses as a consequence of different deposition times. The CeCCs microstructure was characterized by SEM, a commonly used technique for morphology studies.^{3,4,9,41} SEM images of the as-deposited CeCCs, prepared at short and longer deposition times, are presented in Fig. 1.

As can be seen, the films covered, were adherent and had a rather rough surface. Polishing marks were noticeable after 5 min immersion, but they were no longer visible after the longer deposition time. The plan view of the coatings, illustrated in Fig. 2a for the CeCC deposited over 20 min, exhibited an inhomogeneous structure of deposited layers, with numerous defects and cracks. The cracks were more pronounced in the sample prepared at the longer deposition. However, the CeCCs microstructure visibly changed after the post-treatment: the majority of the cracks were effectively sealed, rendering a coating surface with fewer imperfections, as seen for the CeCC after 20 min deposition (Fig. 2b).

The EDS analysis (not shown) performed for CeCCs prepared at 5 and 20 min immersion confirmed a low amount of cerium deposited over the alloy sub-

strate. The weak Ce signals recorded at 0.9 and 4.9 keV were more pronounced for the CeCC prepared for a longer time, *i.e.*, the amount of Ce increased from 1.24 at. % for CeCC deposited for 5 min to 1.97 at. % Ce for the coating deposited for 20 min, which is in accordance with visual observations of the thicknesses of the coatings. After post-treatment in heated phosphate solution, a strong P signal appeared at 2 keV. Since the P content was quantified as 4.51 at. % (more than twice the Ce one) it is reasonable to believe that it allowed a conversion of the entire amount of Ce(CC) to the CePO_4 compound (see “Effect of post-treatment”).

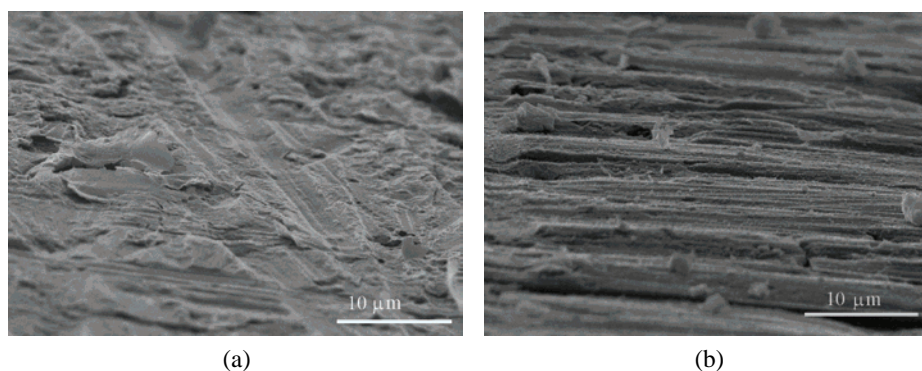


Fig..1. SEM microphotographs of CeCCs deposited for a) 5 min and b) 20 min (tilted view).

Electrochemical properties of the CeCCs

The electrochemical properties of the CeCCs exposed to 0.5 mol dm^{-3} NaCl were examined by EIS, a commonly used method in corrosion testing.^{9,31,34,38,42,43} The method was applied to measure the corrosion resistance of the coatings and to study the effect of the post-deposition treatment. A study was also undertaken to follow the evolution of the EIS properties of CeCC as well as those of alkali-etched AA6060, as the substrate for the deposition of CeCCs, with time of exposure to the corrosive agent. In addition, potentiodynamic measurements were performed to complete the corrosion behaviour study.

Effect of deposition time

The Nyquist plots in complex plane of CeCCs prepared by immersion in cerium-containing deposition solution for different periods (5 and 20 min), and of alkali-etched AA6060, as a reference, after 1 h of exposure to 0.5 mol-dm^{-3} NaCl solution are depicted in Fig. 3. No significant difference in the impedance plots was observed for CeCCs deposited for 5 and 20 min. A possible reason for the similar behaviour could be the cracked surface of the coatings. An increase in thickness, *i.e.* increase in deposition time, led to further crack propagation. How-

ever, the impedance values measured for both CeCCs were almost three times higher than that of bare AA6060.

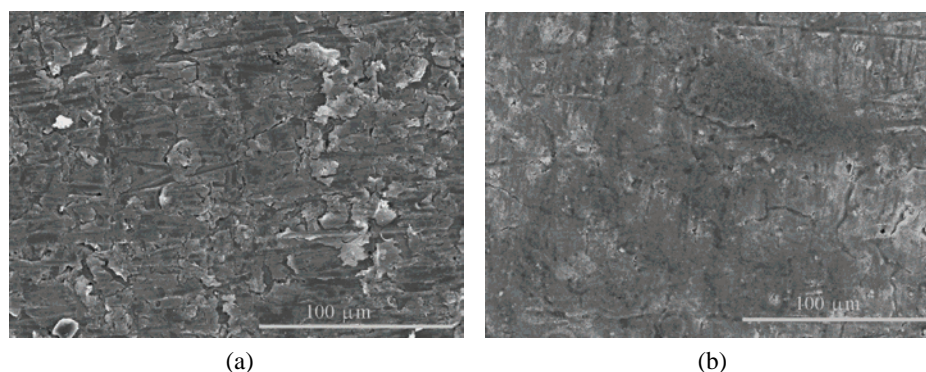


Fig. 2. SEM microphotographs of CeCCs deposited for 20 min, a) without and b) with post-treatment (plan view).

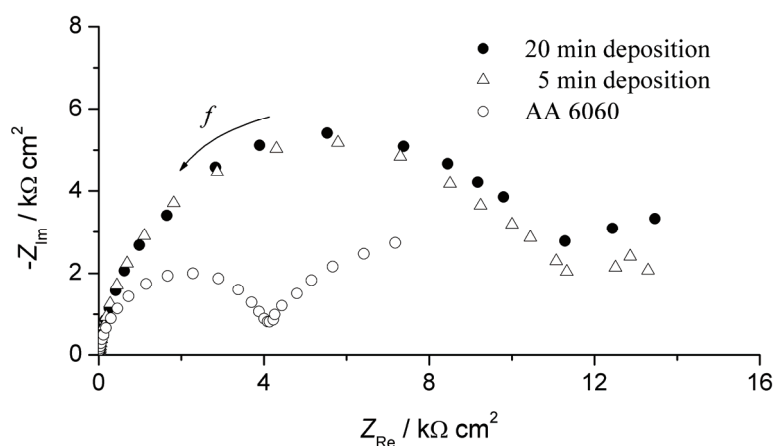


Fig. 3. Nyquist plots for CeCCs deposited for different deposition times and alkali-etched AA 6060, after 1 h of exposure to a 0.5 mol dm^{-3} NaCl solution.

Effect of post-treatment

The purpose of the post-treatment of CeCCs was to improve the corrosion resistance. As reported earlier,¹⁸ immersion of the coatings into a heated phosphate solution immediately after deposition sealed the present cracks, eliminated cerium-peroxide/hydroxide species and altered the chemical composition by converting most of the CeCCs to $\text{CePO}_4 \cdot \text{H}_2\text{O}$, all of which increased the corrosion protection. This study also confirmed (Fig. 2) that the post-treatment induced a change in the microstructure of the CeCCs. Accordingly, the post-deposition sealing of the cracks significantly increased the impedance of the coatings, as

illustrated in Fig. 4 for the CeCC prepared in a 20 min deposition; the impedance of the post-treated sample was around 4 times higher than that of the as-deposited one. A similar trend was also registered for the CeCCs deposited for 5 min (Figs. 3 and 4). Although both post-treated CeCCs (5 and 20 min deposition) had higher values of impedance in comparison with that of alkali-etched AA6060, the longer deposition offered much better corrosion protection than the shorter deposition (Fig. 4).

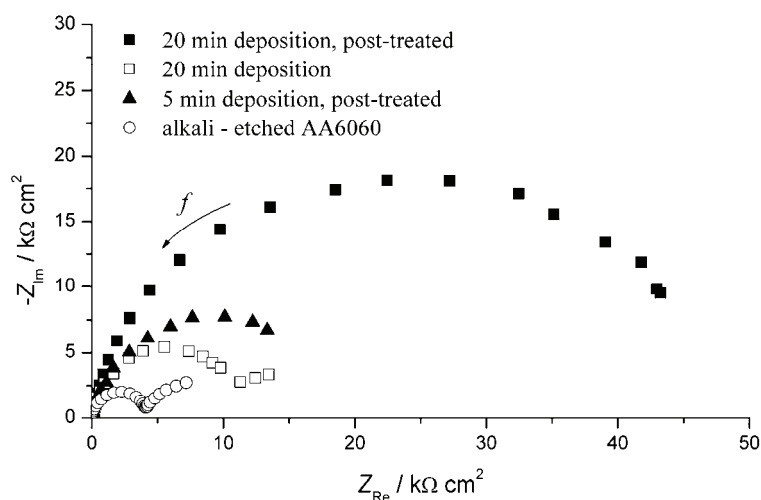


Fig. 4. Nyquist plots for CeCCs, 20 min deposition without and with post-treatment, and 5 min deposition with post-treatment, after 1 h of exposure to a 0.5 mol dm^{-3} NaCl solution.

Polarization measurements

The potentiodynamic polarization measurements gave further information on the behaviour of CeCCs in the corrosive agent (0.5 mol dm^{-3} NaCl). As it was shown that the post-treatment of CeCCs increased the corrosion protection of AA6060, only the post-treated samples were tested. The cathodic and anodic polarization curves registered for the CeCCs deposited for 5 and 20 min and for alkali-etched AA6060, as a reference, are shown in Fig. 5. As can be seen, smaller cathodic currents were measured for the CeCCs than for AA6060, since the CeCCs decreased the cathodic current density of oxygen reduction. The CeCC deposited for 20 min reduced the current more than the one deposited for 5 min, as a result of the diminution of the cathodic sites.^{2,44} The retarding effect of CeCCs on the anodic process of the alloy is more easily observed if the anodic curves are presented in a linear rather than in a semi logarithmic form (Fig. 5b). At a fixed potential, for instance -0.575 V , the anodic current densities were 2.73, 1.04 and 0.23 mA cm^{-2} for AA6060 and CeCCs deposited for 5 and 20 min, respectively. This clearly indicates a reduced anodic activity of the CeCCs on AA6060, which

was especially pronounced for the sample deposited for 20 min and post-treated. The results confirmed that the CeCCs affected both the cathodic and anodic behaviour of AA6060.

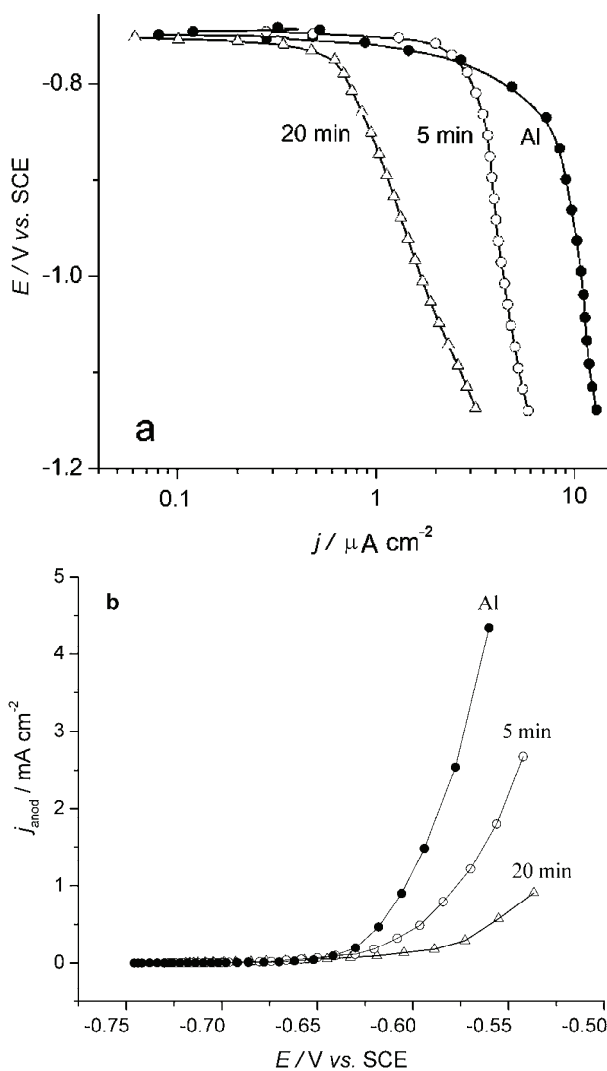
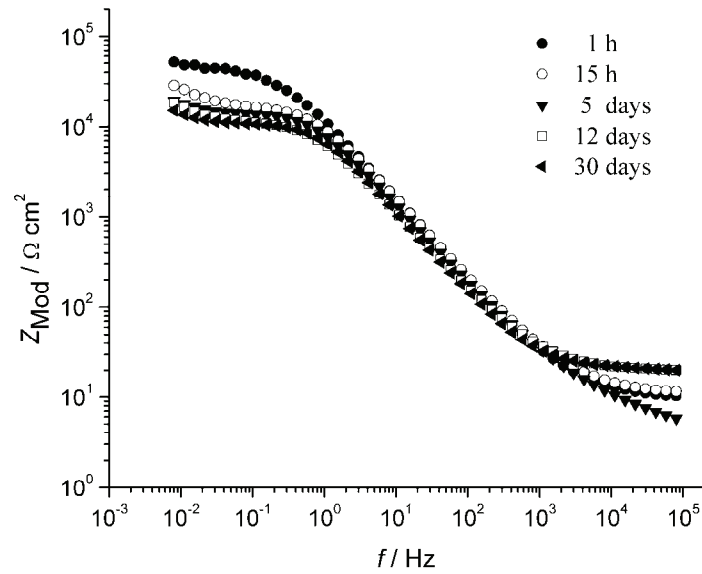


Fig. 5. Cathodic (a) and anodic (b) polarization curves for CeCCs deposited for 5 and 20 min and post-treated, and alkali-etched AA6060 in 0.5 mol dm⁻³ NaCl solution.

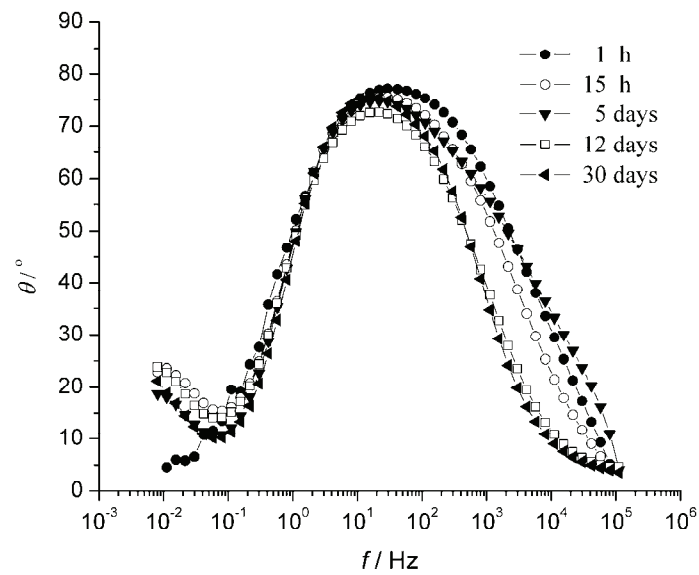
Time dependence of the EIS characteristics of CeCC and alkali etched AA6060

For an extensive EIS study, the CeCC deposited for 20 min and post-treated was submitted to a long-time immersion in a 0.5 mol dm⁻³ NaCl solution, since it showed the best protective properties. The evolution in corrosion behaviour of

CeCC, over a month period, is presented in the Bode module and phase plots, Figs. 6a and 6b.



(a)



(b)

Fig. 6. Bode module (a) and phase plots (b) for CeCC deposited for 20 min and post-treated after different times of exposure in 0.5 mol dm^{-3} NaCl solution.

The highest Z_{mod} value ($50 \text{ k}\Omega \text{ cm}^2$) was measured at the beginning of exposure (1 h), corresponding to a high pore resistance value of the coating. After 15 h immersion, there was a significant decrease in Z_{mod} . A much smaller change was registered after 5 days, followed by a small, gradual decrease up to 12 days of exposure. In the next 13–30 days, the Z_{mod} attained an almost constant value ($15 \text{ k}\Omega \text{ cm}^2$), which was more than 3 times smaller than the initial one. Two time constants could be seen in the EIS spectra, Fig. 6b. The first time constant, appearing at higher frequencies, is associated with the CeCC, while the other one refers to the AA6060 substrate.

The EIS data were fitted using the equivalent electrical circuits shown in Fig. 7. The circuits consist of electrolyte resistance, R_{Ω} , CeCC pore resistance, R_p , coating capacitance, C_c , charge-transfer resistance, R_{ct} , and CPE, a constant phase element which represents all frequency dependent electrochemical phenomena, namely the double layer capacitance, C_{dl} , and diffusion processes.

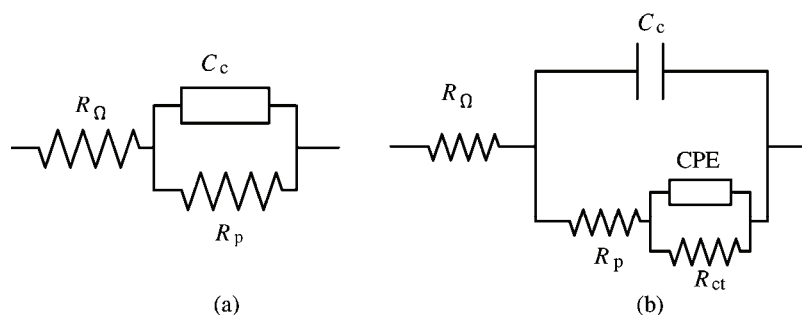


Fig. 7. Equivalent electrical circuits for CeCCs on the AA6060 alloy.

The results obtained are summarized in Fig. 8, which presents the evolution of CeCCs pore resistance and CPE with time. Fig. 8a shows that the highest value of the pore resistance ($R_p > 45 \text{ k}\Omega \text{ cm}^2$) was measured for the CeCC just after its immersion in the aggressive chloride solution. The result is in accordance with the cross-sectional SEM observation (inset in Fig. 8a), which indicates a small average thickness ($2 \mu\text{m}$) of the coating. After 15 h exposure, the R_p value had decreased significantly ($\approx 20 \text{ k}\Omega \text{ cm}^2$). During the following 15 days, the value gradually decreased. From 20 days to the end of tests, the R_p value was nearly unchanged ($\approx 10 \text{ k}\Omega \text{ cm}^2$). The value of the double-layer capacitance (more correctly, constant phase element, CPE) showed a tendency to increase during 20 days of immersion in NaCl solution and then gradually reached a constant value (Fig. 8b).

An EIS study of AA6060, used as the substrate, was also conducted (Figs. 9a and 9b). Prior to the CeCCs deposition, the substrate underwent alkaline etching, as detailed in the Experimental section. This treatment is known to induce the

formation of an alumina gel layer on the surface. This non-insulating layer was proven necessary for the deposition of Ce-species on the AA6xxx series, allowing faradic processes to occur. Hughes *et al.*⁴⁵ claim that the transfer of OH^- through the hydrated alumina layer assists the progress of the precipitation of cerium species. This layer is progressively substituted by a much more adherent $\text{CeO}_2 \cdot 2\text{H}_2\text{O}$ layer.

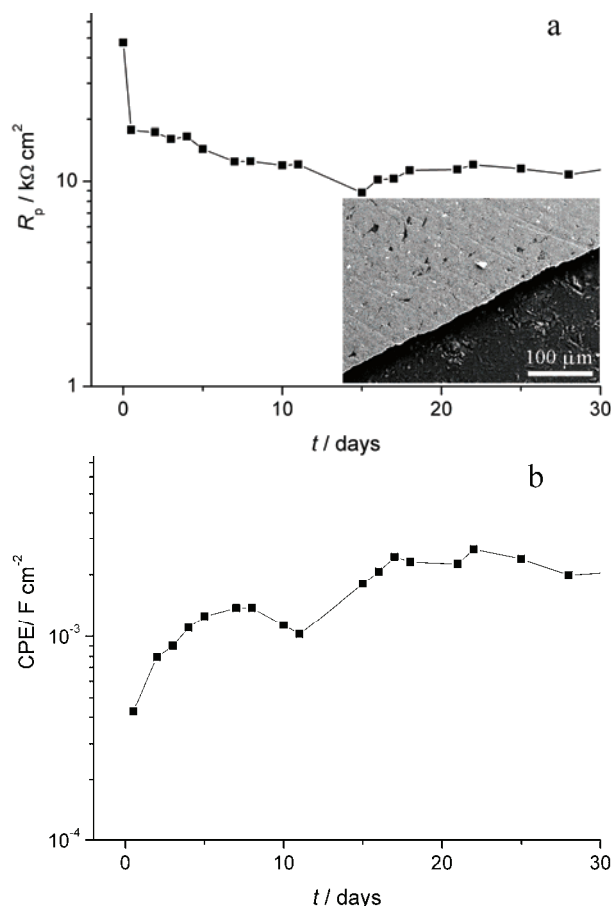


Fig. 8. The time dependences of a) pore resistance, R_p and b) constant phase element, CPE, for CeCC deposited for 20 min and post-treated, during exposure to a 0.5 mol dm^{-3} NaCl solution (inset shows cross-sectional SEM micrograph of CeCC).

The Nyquist plots in complex plane of alkali-etched AA6060 during different exposure times, as well as that of CeCC, given for comparison, are shown in Fig. 9a.

The relatively small impedance value of the alkali-etched AA6060, measured after immersion in the corrosive agent could be attributed to the cracked gel

structure, illustrated in Fig. 9b. In the following days (Fig. 9a), the impedance increased gradually. The increase in impedance value with immersion time can be related to the gel wetting and self-healing (crack sealing) and the growth phenomena. On the other hand, it can be seen that already after 12 days of exposure to the NaCl solution, the resistance of the CeCC approached the resistance of the alkali-etched AA6060. Thus, after about 2 weeks, the impedance value of the CeCC attained the impedance value of the alumina gel layer. This result suggests that the CeCC degrades with time, and provides only temporary corrosion protection to the AA6060 alloy, which could be expected for such a thin film in such an aggressive corrosion agent as 0.5 mol dm^{-3} NaCl solution.

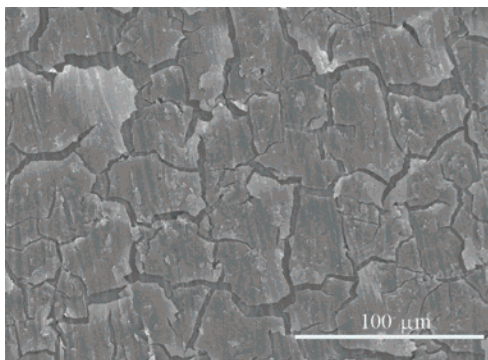
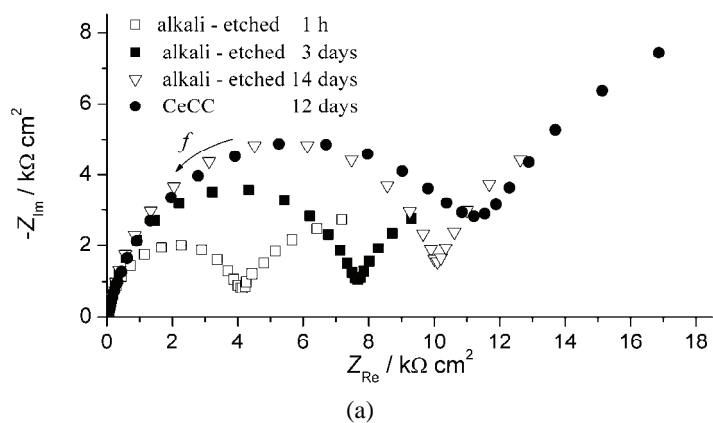


Fig. 9. a) Nyquist plots for alkali-etched AA6060 after different exposure times to 0.5 mol dm^{-3} NaCl solution and b) for CeCCs and microphotograph of alkali-etched AA6060.

CONCLUSIONS

Cerium conversion coatings (CeCCs) were deposited on AA6060 by immersion in an acidified aqueous solution CeCl_3 for 5 and 20 min at room temperature.

perature. To accelerate the deposition kinetics, H_2O_2 was added. Cracked layers with non-homogeneous and defect structures were produced. A subsequent post-treatment in a phosphate solution contributed to crack sealing, which improved the protective qualities of the coatings. The layers quality was evaluated from a corrosion perspective using linear sweep voltammetry and EIS, to assess the kinetics of the corrosion process and to estimate the duration of protection in a chloride-containing environment ($0.5 \text{ mol dm}^{-3} \text{ NaCl}$). The CeCCs increased the corrosion resistance of AA6060, slowing down the anodic and cathodic reaction rates with respect to the bare AA6060. The longer deposition time was more effective. However, the EIS study indicated that CeCCs provided only short term protection (2 weeks) to the AA6060 alloy.

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ИЗВОД

ЕЛЕКТРОХЕМИЈСКЕ МЕТОДЕ ЗА ИСПИТИВАЊЕ КОРОЗИОНЕ СТАБИЛНОСТИ ПРЕВЛАКА НА БАЗИ ЦЕРИЈУМА ДОБИЈЕНИХ ПОТАПАЊЕМ НА ЛЕГУРИ АА6060

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Наношење превлака потапањем у раствор је једноставна и економски прихватљива метода за припрему конверзионих превлака на бази церијума на металним супстратима, које су добра замена за токсичне хроматне превлаке. У овом раду превлаке на бази церијума су нанесене на алуминијумску легуру АА6060 из воденог раствора церијум-хлорида на собној температури. Испитиван је утицај времена потапања и утицај накнадног третмана у фосфатном раствору на микроструктуру и заштитна својства добијених превлака. Дужим потапањем су добијене дебље али нехомогене превлаке. Накнадни третман је повољно утицао на затварање прскотина, што је у сагласности са измереном већом корозионом отпорношћу у поређењу са превлакама без третмана. Превлаке добијене дужим наношењем су показале бољу корозиону заштиту од превлака добијених краћим наношењем. Корозиона стабилност превлака је испитивана у агресивној хлоридној средини (3,5 % NaCl) методама спектроскопије електрохемијске импеданције (СЕИ) и линеарне волтаметрије. Детаљно је праћено корозионо понашање превлака са временом деловања корозионог агенса. Поређења ради, СЕИ анализа је спроведена и за легуру АА6060 без превлаке. Резултати истраживања потврђују да добијене превлаке на бази церијума представљају добру корозиону заштиту легури АА6060. Међутим, чак и квалитетнија превлака (20 мин потапања и накнадно третирана у фосфатном раствору) обезбеђује легури краткорочну заштиту у агресивној средини услед своје мале дебљине.

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