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A review on cerium-based conversion coatings on aluminium surfaces

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Abstract: Conversion coatings containing hexavalent chromium (chromate) have been widely used for decades as part of corrosion protection systems on aluminium alloys. However, chromates are prohibited in many fields due to their toxicity and should be replaced by "green" environmentally friendly alternatives. Cerium-based conversion coatings (CeCCs) are among the most prospective alternatives because of their anticorrosion efficiency, environmentally friendly characteristics, and low cost. This review is focused on the protective properties of CeCCs on aluminium as a sole protecting coating or as a conversion one in combination with top organic coating.

Keywords: cerium; corrosion; electrodeposition; EIS; polarization measurements

1. Introduction

For years, different coating deposition techniques, i.e., electrophoretic deposition, chemical vapour deposition, sol-gel, dip coating, spray coating, and various materials, carbon-based nanomaterials, organic coatings (or paints), etc., were investigated and recommended for protecting metal substrates from corrosion (Naghdi, Jevremović, et al., 2016; Naghdi & Miskovic-Stankovic, 2022; Naghdi et al., 2018; Naghdi et al., 2020; Naghdi et al., 2017). Using an organic coating is the most common way to protect metals (Mg alloys, aluminium alloys, steel, etc.) against corrosion. The effectiveness of such coatings is to ensure the best possible adhesion to the base material and prevent the coating adhesion loss under the environmental influence.

Among the various protective coating, chemical conversion coatings are presented as the most effective pre-treatments, with the facile operation and low-cost coating technique. The reaction of an active solution with a metal substrate provides the ions needed to form a conversion coating that improves the adhesion of organic coatings and enhances the corrosion protection of the underlying metal. Immersion of metals in a bath containing chromate ions was the most effective and popular procedure for producing a chromate conversion coating (CCC) as the protective layer on the metal surface. Due to its outstanding corrosion resistance, favourable adhesion with top organic coatings, and simplicity in production, this coating was the most conventional industrial surface treatment of metal materials(Hagans & Haas, 1994). The self-repairing effect of CCC is one of the reasons for its superior corrosion resistance than other coatings. When CCC covers the metal substrate, it releases chromate, which can migrate and repair corrosion (Zhao et al., 2001). CCC presented an excellent corrosion protection ability of pure aluminium, aluminium alloys, zinc alloys, Mg alloys, etc., that widely used in automotive, aerospace, and electronics industries for many years (Gigandet et al., 1997; Ilevbare & Scully, 2001; Lunder et al., 2005; Piao et al., 2019).

However, over the last decades, the high toxicity of the hexavalent chromium compounds in CCC was recognized and imposed restrictions on their use in industry and food applications. Therefore, due to the environmental and health hazard in their use and disposal, a great deal of research efforts has been done to develop a new environmentally friendly alternative for CCC. Among the numerous materials, which presented a good anti-corrosion behaviour, a high benefit/cost relation, and mainly, low environmental impacts, the conversion coatings based on phosphate, cerium, zirconium, titanium salts, titanium zirconium salt, cobalt salts, molybdate, etc. have been developed and widely studied.

2. Conversion coating

As an alternative to CCC, phosphate conversion coating (PCC) could replace CCC as surface pre-treatment in various industrial applications, such as the automotive and appliance industries. Moreover, due to their low toxicity and high chemical stability, PCC received extensive attention in the field of medical metal surface modification. Cost-effectiveness, low coating formation time, simple operation, suitability for irregular surfaces, and low impact on the mechanical properties of metal substrates are some of the unique advantages of PCC. Various factors can impact the anti-corrosion performance of PCC, i.e., pH, phosphating temperature, bath ingredient, and the surface characters of the metal substrate, including compositions, microstructure, and its electrochemical activity. Altering the surface morphology of the metal substrate using laser surface texturing (LST) was presented as an effective strategy to improve the corrosion resistance of magnesium alloy (H. Liu et al., 2021). The high specific area and surface roughness produced by LST accelerated the deposition of PCC, increased the adhesion of the coating, and enhanced the adhesion of the coating to the substrate. The electrochemical tests presented a better long-term corrosion resistance of PCC coating on the metal substrate modified by LST. Using PCC as a coating on titanium (Ti) implants is also presented as an effective method for simultaneously regulating the elemental compositions and crystallographic morphological of Ti implant surfaces (Zhao et al., 2021). The PCC-coated Ti implants showed good biocompatibility that can prevent a prolonged healing period and even implantation failure. Furthermore, doping PCC coating with Zinc (Zn) that has strong antibacterial properties showed inhibition of biofilm formation on the PCC-coated Ti implant after continuous incubation up to 24 h (Zuo et al., 2022). Application of PCC on sand-cast and die-cast Mg alloys showed the effect of the production method of the substrate on the characteristics of the coating (Zhou et al., 2021). The PCC was more compact on the die-cast substrate, exhibited lower electrical contact resistance (ECR), and had better corrosion resistance (due to the intensified micro-galvanic effect through the grain refinement of the die-cast alloy) compared to the PCC on sand cast Mg alloy.

Zr-based conversion coating is another type of chromate-free pre-treatments technique that, due to its potential to lower operational cost in the area of energy, maintenance, and reducing the environmental impacts, has gained acceptance. During Zr-based conversion coating, the bath may contain various additives, i.e., organic polymers, metal ions, etc., to improve corrosion protection and adhesion properties and establish a base for subsequent painting. Liu et al. showed that adding Cu^{2+} and PAMAM positively impacted on the kinetics of the coating growth and enhanced the adhesion of the subsequent organic coating (X. Liu et al., 2021). The combination of Zr and Ti as a conversion coating (Zr-Ti conversion coating) as an alternative for toxic CCC has been studied in the automobile industry (Kolesnikova et al.). The studies showed that the application of Zr-Ti conversion coating on aluminium alloy 5556 enhanced its corrosion resistance to pitting corrosion. Adding Mo to the Zr-Ti conversion coating was investigated to further improve the corrosion resistance of LY12 aluminium alloy (Qian et al., 2021). The electrochemical tests showed that the continuous dense Mo-Zr-Ti conversion coating significantly reduced the I_{corr}, increased the film resistance R_f in the temperature range from 0 to 60 ºC, and reduced the corrosion rate. Hoang et al. investigated the impact of adding (3-aminopropyl)triethoxysilane (APTES) to Zr conversion coating on steel (Hoang et al., 2022). The results showed that Zr conversion coating containing APTES improved the corrosion protection of the bare steel and reduced the adhesion loss.

As a viable alternative to CCC, Ti conversion coating (TiCC) presented a proper anti-corrosion performance on different substrates such as Mg alloys, Al alloys, steel, and galvanized steel (Wang & Xu, 2021). Combination of such coating with cerium (Ti-CeCC) and cobalt (Ti-CoCC) was investigated as anti-corrosion resistance coatings for enhancing the adhesion property of the organic coating applied on Al-2024 substrate (Roshan & Sarabi, 2021). Results suggest that Ce and Co additives changed the morphology of the TiCC and increased the surface energy of the coating, and compared to the bare sample, Ti-CeCC and Ti-CoCC improved the anti-corrosion resistance of the sample.

Another promising candidate for replacing CCC is Ce-based chemical conversion coatings (CeCC). To obtain the best results from CeCC, pre-treatment methods, i.e., cleaning or etching to remove inorganic contamination or eliminate the native oxide layer, are required (Deng et al., 2021; Sainis & Zanella, 2022; Sun et al., 2021). Using solutions containing $CeCl_3$ and H_2O_2 was studied as a pre-treatment method for depositing CeCC on AA2024-T3 and AA7075-T6 substrates (Alba-Galvín et al., 2021). The results showed that the formation of CeCC over AA7075 was faster than over AA2024. CeCC in all samples offered cathodic protection, and the anti-corrosion properties of CeCC coating were enhanced due to the pre-treatment technique. Moreover, HF pre-treatment of Zn–5% Al alloy was revealed an increased growth rate of CeCC, and CeCC was preferentially deposited on the surface of the Al-rich phase. Furthermore, due to the uniform and thick coating formation, the HF pre-treatment exhibited a positive effect on the corrosion resistance of the coated samples (Sun et al., 2021).

The impact of bath temperature and the heating process on the formation of the CeCC on Fe50Mn30Co10Cr10 (at.%) dual-phase high-entropy alloy (DP-HEA) was investigated by Chen et al.(Chen et al., 2021). The electrochemical tests showed a decrease in both anodic current densities and corrosion current densities of the CeCC coated specimens compared to the untreated DP-HEA. Furthermore, the bath-heating process was introduced to increase the coating thickness and the superior anti-corrosion properties of the coating. In addition to the pre-treatment techniques and the coating condition, additives, i.e., Cu and manganese (Mn), were reported as a positive factor in improving the corrosion resistance of CeCC coated galvanized steel in 3.5 wt% NaCl solution (Khast et al., 2021). Kamde et al. reported deposition of a few microns' thick CeCC on the surface of Mg-4 wt%Y(Kamde et al., 2021). Increasing the deposition duration from 30 to 1800 s negatively affected the coating. Due to hydrogen bubble formation on the substrate surface, the CeCC delaminated at a few places. Moreover, due to dehydration while drying, the CeCC was deposited at a short duration (30 s, 60 s), cracks formed all over the coating. Altogether, the presence of the CeCC on Mg-4 wt%Y exhibited a better corrosion resistance than the bare substrate. The impact of Mo additive on the CeCC on Al alloy 6063 (AA6063) was investigated by Lu et al. (Lu et al., 2020). CeCC and Ce-Mo conversion coating (CeMCC) were deposited on AA6063 by immersion in alkaline conversion baths. CeMCC presented a more uniform and smoother structure than CeCC. Both coatings presented a better corrosion resistance than bare AA6063, while the CeMCC had lower corrosion current density and higher corrosion resistance than CeCC in a 3.5 wt% NaCl solution.

In addition to the conversion coatings named above, there are other types of conversion coatings, i.e., boehmite and silica conversion coatings (Braga et al., 2020), molybdate conversion coating (MCC) (Yang et al., 2021), rare earth elements (lanthanum, neodymium and yttrium) (Shih & Mansfeld, 1992), that was introduced as an alternative for replacing CCC.

3. Cerium-based conversion coatings deposition

Investigations on cerium-based conversion coatings focus on appropriate processes of their depositions. The coatings can be applied by spraying, immersion processes (M. Bethencourt et al., 1998; Fedel et al., 2014; Jegdić et al., 2013; Johansen et al., 2012; Mansfeld et al., 1991; Mansfeld et al., 1992; Onofre-Bustamante et al., 2009; Živković et al., 2013), or electrodeposition (Exbrayat et al., 2014; Stoychev, 2013; Živković et al., 2015; Živković et al., 2014). The most used method is immersing aluminium or its alloys into hot aqueous cerium solutions for a long time. The applied ceria coating has caused a multifold increase in corrosion resistance of Al. In order to reduce the deposition time of oxide/hydroxide film onto aluminium and improve the corrosion resistance, hydrogen peroxide is usually added to the solution of cerium ions (Dabala et al., 2001; Hughes et al., 1995; Yu et al., 2001; Živković et al., 2015). Besides the time of immersion, the parameters such as the temperature, pH of the conversion solution, the concentration of cerium ions, time, and potential of electrodeposition, etc., were also examined (Dabala et al., 2004; Živković et al., 2015; Živković et al., 2014). Since it was found that ceria coating morphology has the main role in corrosion protection of aluminium (Živković et al., 2014), either as a sole protecting coating or as a conversion one in combination with protectors based on metals (Exbrayat et al., 2014; Nemes et al., 2013) and organic (Živković et al., 2015; Živković et al., 2013) or silane(Zand et al., 2013) compounds, it is essential to obtain the coating with uniform fine-grained structure. This structure is expected to dry rapidly with a low tendency to crack. The sol-gel process is now well accepted as a technology for preparing such thin films and coatings (Hamdy, 2006; Schem et al., 2009), with a promising impact on corrosion protection of aluminium and its alloys (Hollamby et al., 2012; Zuo et al., 2015).

3.1. Sol-gel method

The ceria sol is obtained by forced hydrolysis according to the following procedure (Gulicovski et al., 2014; Gulicovski et al., 2009). The appropriate amount of $Ce(NO_3)_4$ solution in 0.2 M HNO_3 is added drop-wise to the boiling HNO_3 solution being vigorously stirred by a mechanic stirrer. During the ageing for 20 h, the oxide solid-phase nucleates and grows continuously, creating particles of defined shape and size. The CeO_2 coatings are formed onto aluminium panels by the dripping method. Upon application of CeO_2 coating, a smooth surface appears, with the in-place generation of narrow cracks around the pits on Al substrate beneath (Fig. 1b, d and f) (Gulicovski et al., 2016), which is the usual appearance of sol-gel-prepared ceria coatings on Al-based materials (Zuo et al., 2015). It is important to note that the size of islands between the cracks is similar to the size of the pits of the Al surface beneath the ceria coating (Fig. 1a, c and e). EIS data showed greater corrosion resistance of CeO_2-coated aluminium in comparison to bare Al during a long exposure time (Fig. 2) due to the formation of a uniform protective CeO_2 coating/Al interphase, cross-linked by AlO(OH) fibre-like structures (Gulicovski et al., 2016).

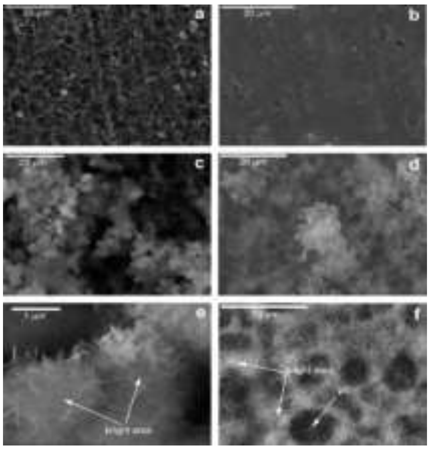


Figure 1. Surface morphology of aluminium (a) and cerium oxide coating before (b) and after exposure to 3 wt.% NaCl solution (c and e - Al after 384 h of exposure; d and f - Al/CeO_2 after 552 h of exposure) (Reprinted from (Gulicovski et al., 2016) with permission from Springer, Copyright 2016).

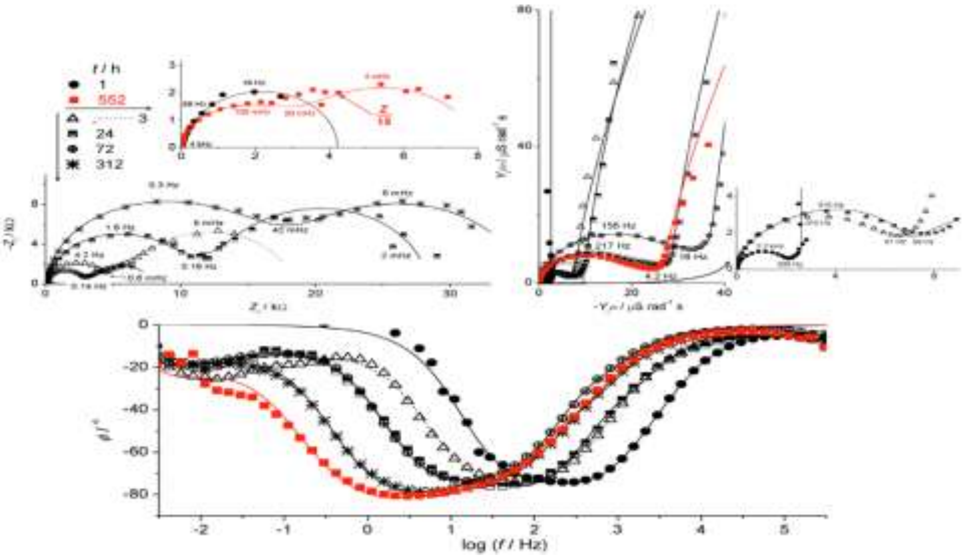


Figure 2. Experimental (symbols) and fitting (lines) data of Al/CeO_2 registered at open circuit potential after different times of exposure to NaCl solution presented as impedance and capacitance complex plane spectra and Bode phase angle plots (Reprinted from (Gulicovski et al., 2016) with permission from Springer, Copyright 2016).

3.2. Dip inmersion method

The deposition mechanism involves both anodic oxidation of Al, Eq. (1) and cathodic reduction of soluble oxygen and/or H_2O_2 added, Eqs. (2) and (3), respectively (Creus et al., 2006; Decroly & Petitjean, 2005; Pinc et al., 2009; Stoffer et al., 2006; Tang et al., 2011) as follows:

$$Al \rightarrow Al^{3+} + 3e^- \quad (1)$$

$$2H_2O + O_2 + 4e^- \rightarrow 4OH^- \quad (2)$$

$$H_2O_2 + 2e^- \rightarrow 2OH^- \quad (3)$$

$$Ce^{3+} + 3OH^- \rightarrow Ce(OH)_3 \quad (4)$$

The generation of hydroxide ions at cathodicsites leads to a strong local increase in pH near the alloy surface, which promotes the formation of $Ce(OH)_3$ precipitate or/and soluble ionic complexes such as $7e(OH)_2^+$. When H_2O_2 is added, the deposition of Ce(IV) is more favourable than Ce(III) (Creus et al., 2006; Tang et al., 2011), Eqs. (4)-(7).

$$2Ce^{3+} + 3OH^- + H_2O_2 \rightarrow 2Ce\,(OH)_2^+ \quad (5)$$

$$2Ce\,(OH)_2^+ + 2OH^- \rightarrow Ce(OH)_4 \quad (6)$$

$$Ce(OH)_4 \rightarrow CeO_2 \cdot 2H_2O \quad (7)$$

The inhibition effect is achieved by the insoluble Ce oxide/hydroxide layer formed at cathodic sites, which suppresses the oxygen reduction reaction (Eq. 2), thereby providing a cathodic inhibition (Hill et al., 2011). The number of variables that influence the rate of CeCC deposition is extensive and includes solution chemistry (cerium salt used chloride or nitrate, additives such as gelatine, glycerol to reduce cracking), concentrations of cerium and H_2O_2, 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.

A variety of conversion solutions, heated or at room temperature, has been proposed to prepare CeCCs by dip immersion or spray processes. The most commonly used is the cerium chloride solution (Allachi et al., 2010; Aziz et al., 2011; Campestrini et al., 2004; Conde et al., 2008; Hughes et al., 2009; Stoffer et al., 2006), followed by the cerium nitrate one (Bethencourt et al., 2002, 2004; Bethencourt et al., 2008; Dabala, 2001; De Frutos et al., 2008; Fahrenholtz et al., 2002; Rangel et al., 2008; Zhang & Zuo, 2008), with or without H_2O_2 as an oxidizing agent. Although components, concentration, temperature, or immersion time (number of spray processes) are somewhat different, the processing steps are similar, including substrate pre-treatment (acid or alkaline), (De Frutos et al., 2008; Fahrenholtz et al., 2002; Johnson et al., 2005; Joshi et al., 2011; Pinc et al., 2009; Rangel et al., 2008) deposition and subsequent post-treatment (Heller et al., 2009, 2010; Pinc et al., 2009).

In order to investigate the effect of deposition time and post-treatment (Jegdić et al., 2013), the CeCCs were deposited on aluminium alloy AA6060 by 5 and 20 min immersion into chloride solution, 0.05 M $CeCl_3$ and subsequent post-treated in the 2.5 % Na_3PO_4, pH4.5, at 85 ^{o}C.EIS results indicated that CeCCs prepared at longer deposition time and post-treated exhibited better corrosion protection than those prepared at short deposition time and without post-treatment (Fig. 3).

Similarly, smaller cathodic currents were measured for CeCCs than bare AA6060 since the CeCCs decreased cathodic current density of oxygen reduction (Fig. 4a) (Jegdić et al., 2013).

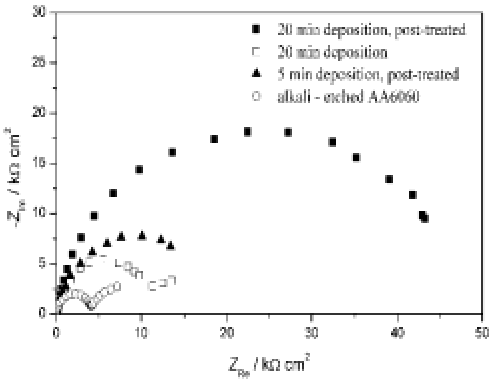
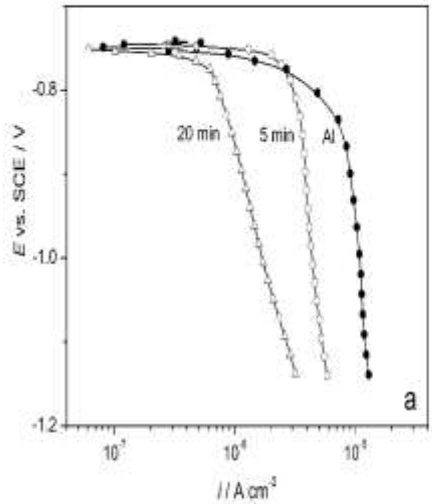


Figure 3. Nyquist plots for CeCCs: 20 min deposition without and with post-treatment, and 5 min deposition from 0.05 M $CeCl_3$ with post-treatment, after 1 h of exposure to 0.5 mol·dm^{-3} NaCl solution (Reprinted from (Jegdić et al., 2013) with permission from Serbian Chemical Society, Copyright 2013).

The CeCC deposited for 20 min reduced the current more than the one deposited for 5 min due to the diminution of cathodic sites (Bethencourt et al., 1998; Pepe et al., 2004). The anodic polarization curves (Fig. 4b) clearly indicated a reduced anodic activity of CeCCs on AA6060, especially pronounced for the sample deposited for 20 min and post-treated.



Although the CeCCs increased corrosion resistance of AA6060, slowing down the anodic and cathodic reaction rates with respect to the bare AA6060, the EIS study indicated the low pore resistance values and consequently low corrosion protection in 0.5 mol·dm^{-3} NaCl solution (Fig. 5).

In order to investigate the effect of counter ion, chloride or nitrate anion used as cerium precursor salts, CeCCs have been deposited on AA 6060 by immersion in 0.05 M $CeCl_3$ and 0.05 M $Ce(NO_3)_3$ aqueous solutions (Živković et al., 2013). Nonhomogeneous layers with visible cracks and lower impedance values were deposited from nitrate solution, while CeCCs from the chloride solution were more homogenous and crack-free, with greater impedance (Fig. 6). A subsequent post-treatment in the 2.5 % Na_3PO_4, pH 4.5, at 85 °C improved the quality of coatings in both cases.

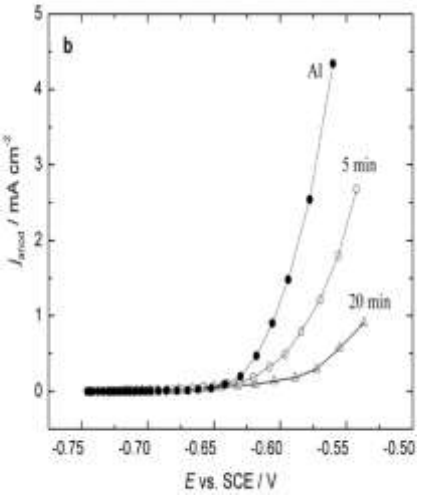


Figure 4. Cathodic (a) and anodic (b) polarization curves for CeCCs deposited for 5 and 20 min from 0.05 M $CeCl_3$ and post-treated, and alkali-etched AA6060 in 0.5 mol·dm^{-3} NaCl solution (Reprinted from (Jegdić et al., 2013) with permission from Serbian Chemical Society, Copyright 2013).

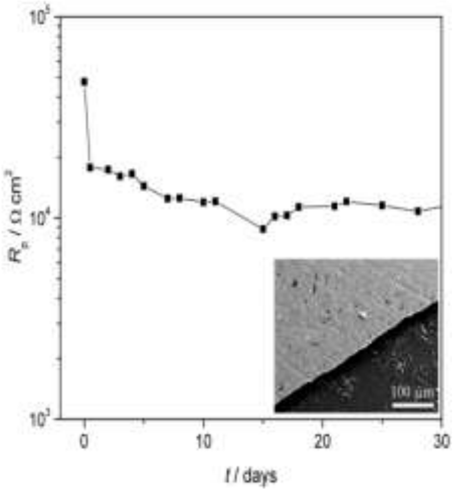


Figure 5. The time dependences of pore resistance, R_p, for CeCC deposited for 20 min from 0.05 M $CeCl_3$ and post-treated, during exposure to 0.5 mol·dm^{-3}NaCl solution (inset shows cross-sectional SEM micrograph of CeCC) (Reprinted from (Jegdić et al., 2013) with permission from Serbian Chemical Society, Copyright 2013).

On the contrary, in combination with a top polyester coating, the protective system with CeCC deposited from nitrate solution exhibited greater pore resistance during exposure to 0.5 mol·dm^{-3} NaCl solution compared to the CeCC from chloride solution (Fig. 7) due to better adhesion as a consequence of greater contact area between the cracked surface of CeCC from nitrate solution and top polyester coating. The similar values of pore resistance with polyester coating on chromate conversion coating proved the successful replacement of toxic chromate coating with “green” CeCC.

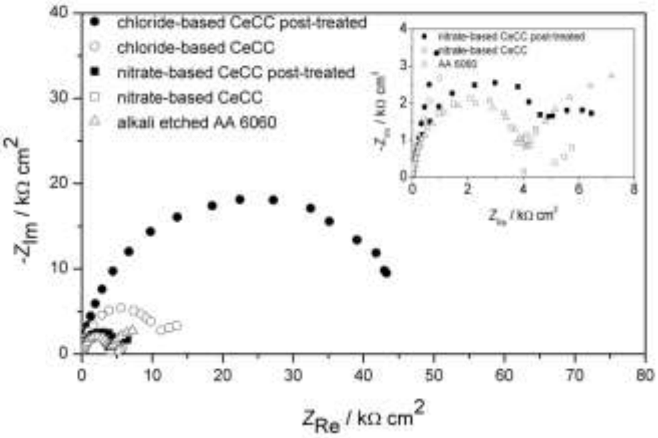


Figure 6. Nyquist plots for bare alkali-etched AA6060 and CeCCs deposited from nitrate and chloride bath for 20 min deposition without and with post-treatment, after 1h of exposure to 0.5 mol·dm^{-3} NaCl solution (Reprinted from (Živković et al., 2013) with permission from Elsevier, Copyright 2013).

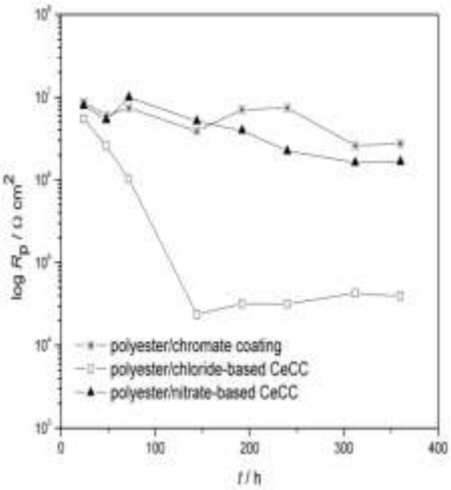


Figure 7. The time dependence of pore resistance for polyester coatings, R_p, on AA6060 with chromate conversion coating and CeCCs deposited from nitrate and chloride bath, during exposure to 0.5 mol dm^{-3}NaCl.

3.3. Electrodeposition

Electrolytic deposition (ELD) represents a powerful and cost-effective route for preparing high-quality thin oxide films on conductive substrates. It offers an easy way to vary the process parameters such as electrolyte properties (acidity level, reactant concentrations, additives), deposition current and time, temperature etc., which enables tuning of deposit characteristics (composition, morphology, thickness) (Naghdi et al., 2015; Naghdi, Jaleh, et al., 2016). Another advantage is rapid film formation. Switzer and Zhou (Zhou & Switzer, 1996) pioneered the electrochemical synthesis of ceria, followed by Zhitomirskyand Petric(Zhitomirsky, 2002; Zhitomirsky & Petric, 1999, 2001) and many other research groups. Even though ceria films have been successfully prepared by anodic deposition (Golden & Wang, 2003; Kulp et al., 2007), most authors have been using a cathodic electrolytic deposition.

The cathodic ELD method is based on reducing oxygen precursors to generate OH¯ ions, causing a local increase in pH near the electrode surface. With Ce^{3+} ions in the electrolytic solution, it is generally believed that the electrogenerated base induces the formation of colloidal particles of $Ce(OH)_3$ or hydrous oxide precipitate on the working electrode (Creus et al., 2006; Zhitomirsky, 2002; Zhitomirsky & Petric, 1999, 2001; Zhou & Switzer, 1996) and also the formation of ionic species $Ce(OH)_2^{2+}$, that hydrolyzes into ceria layer. During cathodic electrodeposition of ceria on aluminium, the OH¯ions can be produced from the reduction of dissolved O_2, reduction of NO_3^- ions, as well as from electrochemical evolution of hydrogen (Arurault et al., 2004; Hamlaoui et al., 2009). These processes occur in different ranges of cathodic potentials.

Both electrodeposition time and voltage were identified as important factors in the corrosion stability of CeCCs, along with their microstructure (Živković et al., 2014). The CeCCs were prepared from 0.05 M $Ce(NO_3)_3$ solutions, applying cathodic potentials of -1.1, -1.4 and -1.6 V *vs* SCE for different deposition times (5-20 min). The lowest potential produced thin and crack-free films. Higher potentials and/or longer time promoted cerium deposition leading to thicker layers. However, the highest potential (-1.6 V) led to highly cracked and non-adherent coatings even at the shortest deposition. The CeCCs formed at -1.4 V for 10 and 20 min exhibited the highest corrosion stability, i.e., the highest coating pore resistance, R_p and the smallest constant phase element, CPE (Table 1). It can be seen that all CeCCs deposited at -1.1 and -1.4 V for a different time, show an order of magnitude smaller corrosion current densities, j_{corr} as compared to bare aluminium (Table 2). The smallest corrosion current densities were determined for CeCCs deposited at -1.4 V for 10 and 20 min. The reason for such a finding could be a more homogeneous structure of greater thickness of the coating produced at potential -1.4 V (as compared with CeCC formed at -1.1 V). The corrosion potential, E_{corr}, values of the bare aluminium and the one coated with CeCCs are also presented in Table 2. The difference between E_{corr} and E_{pit} (pitting potential) can be used to evaluate the pitting corrosion resistance of Al ($E_{pit} \approx -775$ mV). The values of ΔE for the specimens are presented in Table 2. As can be seen, the value of 79 mV was obtained in the case of AA6060 coated with CeCC deposited at -1.1 V and over 200 mV for CeCCs at -1.4 V, indicating thatthe ceria layers markedly improved the pitting corrosion resistance of AA6060.

In order to investigate the effect of CeCC deposition voltage on the protective properties of the system CeCC/topepoxy coating, cerium-based coatings have been electrodeposited on AA6060 from 0.05 M $Ce(NO_3)_3$ aqueous solution at different deposition potentials of -0.95 V, -1.2 V and -1.4 V (Živković et al., 2015). A subsequent post-treatment of CeCCs in the 2.5 % Na_3PO_4, pH 4.5, at 85

°C formed a more uniform surface with lower roughness, as proven by AFM analysis (Table 3).

Table 1. Fitting results of EIS plots of CeCCs on AA6060 after 1h of exposure to 0.5 mol·dm^{-3} NaCl solution (Reprinted from (Živković et al., 2014) with permission from Elsevier, Copyright 2014).

***t* / min**	***E*$_{dep}$. = -1.1 V**			***E*$_{dep}$. = -1.4 V**		
	***R*$_p$/ kΩ cm^2**	**Y$_o$· 10^6/ $s^n\Omega^{-1}$ cm**	***n***	***R*$_p$ / kΩ cm^2**	**Y$_o$· 10^6/ $s^n\Omega^{-1}$ cm**	***n***
5	4.4	19.9	0.94	14.6	15.80	0.9
10	16.9	15.7	0.86	24.4	13.9	0.87
20	27.5	14.6	0.91	58.2	12.6	0.9

Table 2. Corrosion potentials and corrosion current densities of AA6060 and CeCCs, deposited at different potentials and times, in 0.5 M NaCl (Reprinted from (Živković et al., 2014) with permission from Elsevier, Copyright 2014).

Sample	***E*$_{corr}$ / mV**	***j*$_{corr}$ / µm cm^{-2}**	**Δ*E* = *E*$_{corr}$- *E*$_{pit}$ / mV**
AA6060	- 775	4.31	0
CeCC, E_{dep} = - 1.1 V, 10 min	-854	0.39	79
CeCC, E_{dep} = - 1.4 V, 5 min	-1012	0.52	237
CeCC, E_{dep} = - 1.4 V, 10 min	-995	0.28	220
CeCC, E_{dep} = - 1.4 V, 20 min	-989	0.22	214

Table 3. Surface roughness of CeCCs deposited at different potentials without and with phosphate posttreatment (Reprinted from (Živković et al., 2015) with permission from Elsevier, Copyright 2015).

Deposition potential / V	**RMS / nm**	
	without post-treatment	**with post-treatment**
-0.95	120	80
-1.2	290	150
-1.4	363	282

The EIS data recorded over a longer time exposure in 3 wt% NaCl solution confirmed a strong influence of CeCCs post-treatment on the protective properties of the CeCC/epoxy coating protective system. The CeCCs without post-treatment exhibited better corrosion resistance than post-treated CeCCs, for all deposition potentials applied. The highest impedance value (Fig. 8) and the lowest corrosion current density (Fig. 9) were provided by the protective system epoxy coating/CeCC electrodeposited at -1.2 V and without post-treatment. This homogeneous and crack-free CeCC of intermediate surface roughness enabled an efficient bonding with epoxy top coating.

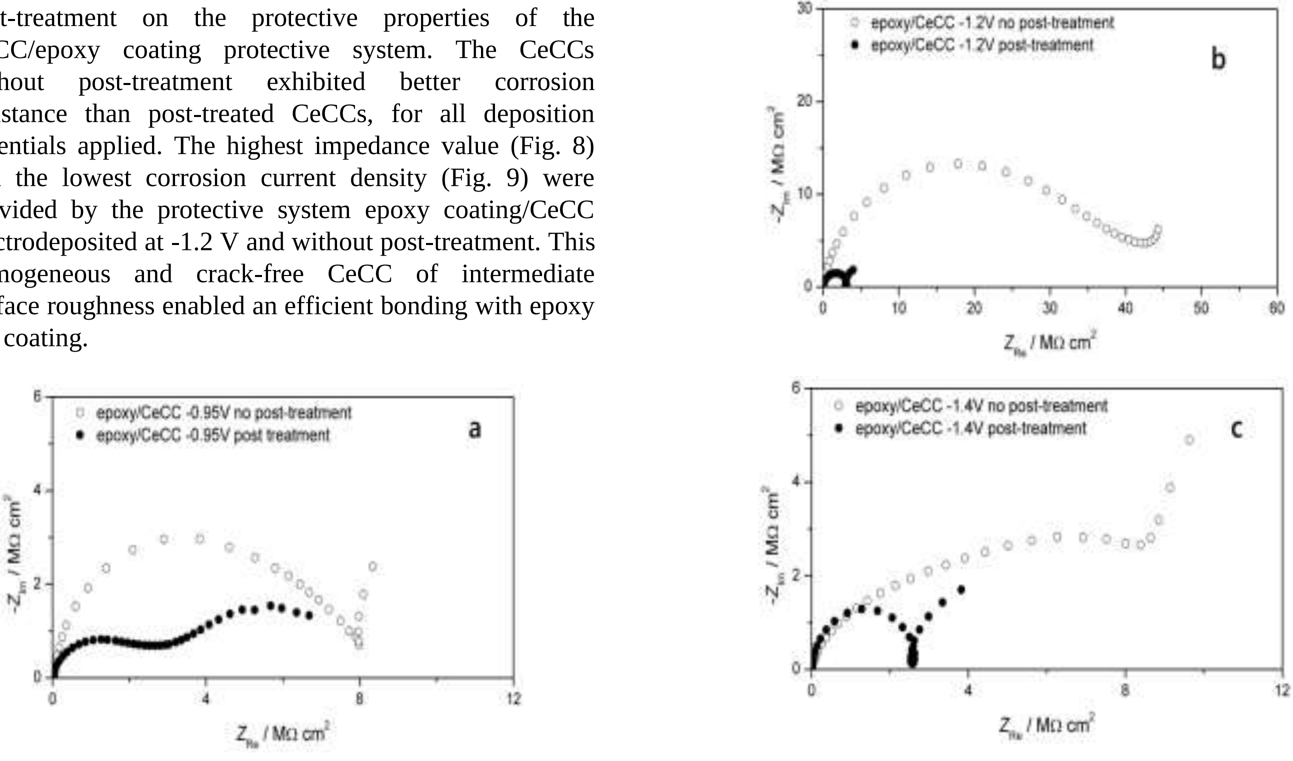


Figure 8. Nyquist plot for protective systems with epoxy coating/CeCCs

deposited at a) -0.95 V, b) -1.2 V and c) 1.4 V, without (o) and with (●) post-treatment, after 30 days of exposure to 3 wt.% NaCl solution (Reprinted from (Živković et al., 2015) with permission from Elsevier, Copyright 2015).

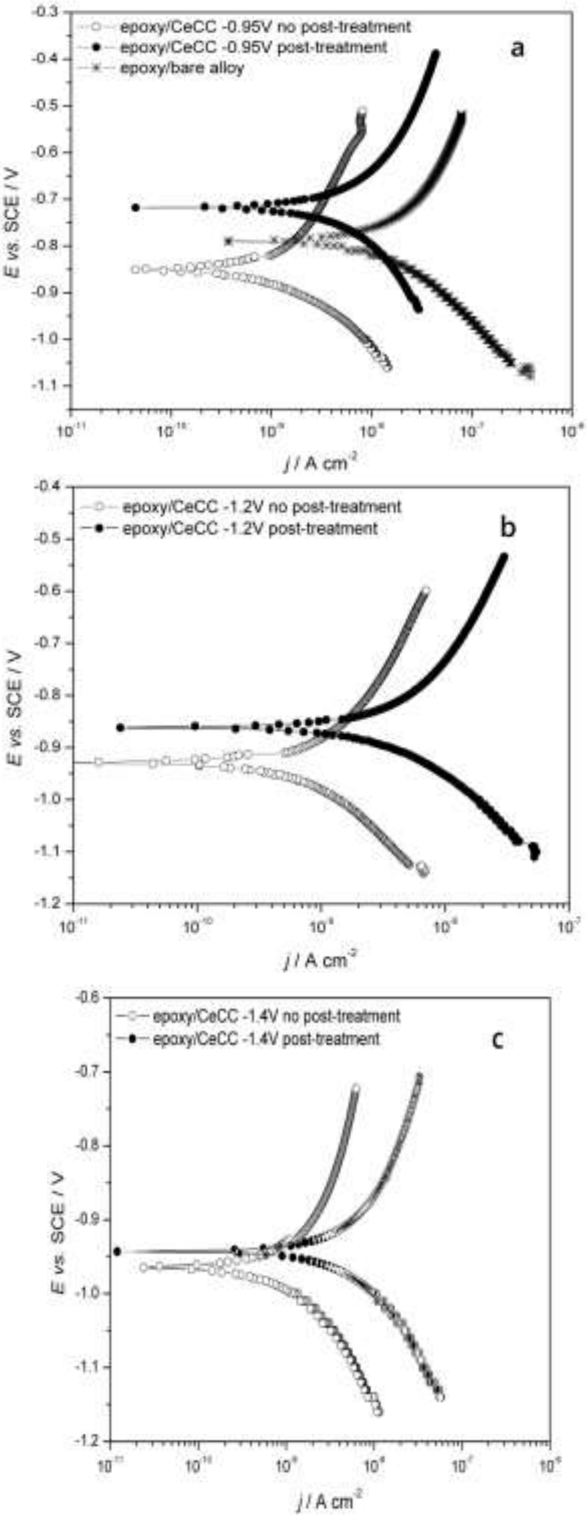


Figure 9. Polarization diagrams for protective systems epoxy coating/CeCCs deposited at (a) -0.95 V, (b) -1.2 V and (c) 1.4 V, without (o) and with (●) post-treatment, after 30 days exposure to 3 wt. NaCl solution (Reprinted from (Živković et al., 2015) with permission from Elsevier, Copyright 2015).

Figures 10-12 represent the images of microstructures of some electrodeposited CeCCs, while Table 4 summarizes the main findings of our study on CeCCs on aluminium, regarding the effect of deposition parameters on the characteristics of the deposited CeCCs alone and with top organic coating, with the aim to improve corrosion protection of aluminium substrate.

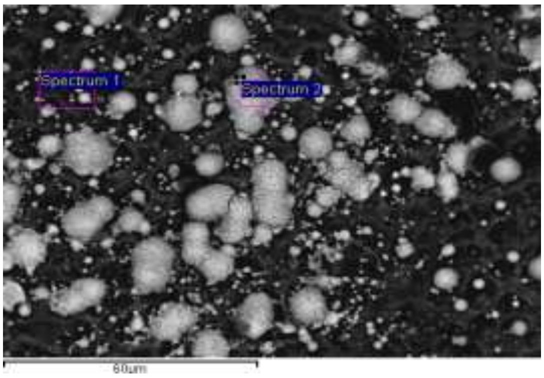


Figure 10. SEM microphotograph of CeCC electrodeposited at the potential *E* = -1.1 V for 10 min.

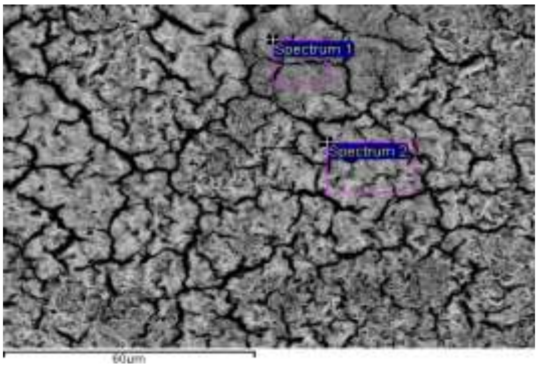


Figure 11. SEM microphotograph of CeCC electrodeposited at the potential *E* = -1.4 V for 10 min.

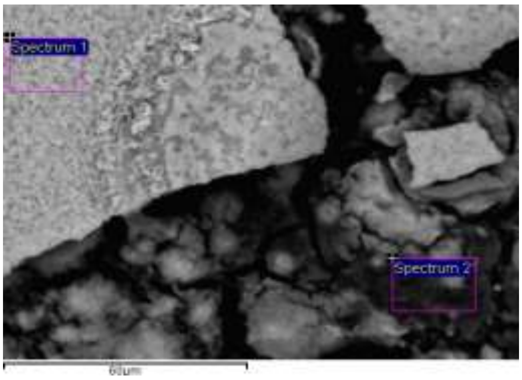


Figure 12. SEM microphotograph of CeCC electrodeposited at potential *E* = - 1.6 V for 10 min.

Table 4. Various pre-treatment and post-treatment techniques for depositing CeCCs on Al and Al alloy substrates, and the obtained results.

Substrate	Substrate pre-treatment	Coating process/bath composition	Post-treatment	Results/drawbacks	Ref.
Aluminium	Polishing, degreasing in alkaline solution and rinsing with distilled water	Sol-gel/Ce(NO_3)$_4$ solution in 0.2 M HNO_3	Drying in air at 35 °C 30 min	Increased corrosion resistance of CeO_2-coated Al in comparison to bare Al at long exposure times. The Al beneath CeO_2 coating was subjected to intrinsic formation of a uniform protective coating/Al interphase, cross-linked by AlO(OH) fibre-like structures	(Gulicovski et al., 2016)
Al alloy AA6060	Polishing, degreasing in alkaline solution and rinsing with distilled water	Dip-immersion/0.05 M $CeCl_3$, acidified to pH 2 with the addition of 30 % H_2O_2	Post-treatment in phosphate solution (2.5 % Na_3PO_4, pH 4.5) at 85 °C, 5 min. The post-treated coatings were rinsed in deionized water and dried in air.	The CeCCs prepared at longer deposition times and post-treated showed better corrosion protection than those prepared at shorter deposition times. However, due to their small thickness, even CeCCs prepared at longer deposition times and post-treated provided short term protection in the aggressive environment	(Jegdić et al., 2013)
Al alloy AA6060	Polishing, degreasing in alkaline solution and rinsing with distilled water	Dip immersion/0.05 M $CeCl_3$ and 0.05 M Ce(NO)$_3$, the pH was adjusted to 2 by small additions of HCl or HNO_3, respectively.	Post-treatment in phosphate solution (2.5 % Na_3PO_4, pH 4.5) at 85 °C, 5 min. The post-treated samples were rinsed with distilled water and dried in air.	Better corrosion protection of post-treated chloride-based CeCC compared to crack-free thin nitrate-based CeCC.	(Živković et al., 2013)
Al alloy AA6060	Polishing, degreasing in alkaline solution and rinsing with distilled water	Electrodeposition/ 0.05 M Ce(NO_3)$_{3,}$ deposition potentials -1.1, -1.4 and -1.6 V, deposition time 5-20 min	CeCCs were rinsed with distilled water	The highest Rp and the smallest CPE values exhibited CeCC deposited at −1.4 V for 20 min deposition time. This CeCC improved pitting corrosion resistance owing to homogeneous microstructure and sufficient thickness.	(Živković et al., 2014)
Al alloy AA6060	Polishing, degreasing in alkaline solution and rinsing with distilled water	Electrodeposition/ 0.05 M Ce(NO_3)$_3$, deposition potentials –0.95, -1.2 and -1.4 V, deposition time 10 min, top epoxy coating.	CeCCs were rinsed with distilled water and subjected to a post-treatment in phosphate solution (2.5% Na_3PO_4, pH 4.5) at 85 °C, 5 min	The greatest impedance and the lowest corrosion current density were provided by the protective system epoxy coating/CeCC deposited at −1.2 V and without post-treatment.	(Živković et al., 2015)

4. Conclusion

This review discussed the ability of cerium-based conversion coatings (CeCCs) as the alternative for the toxic chromate conversion coating (CCC) to protect the aluminium substrate during exposure to corrosive environments, alone or with top organic coating. These coatings overcame the health hazard regarding CCC and appear favourable under certain conditions, because they provide the similar protective properties as CCC in corrosive environments. Moreover, various parameters that influence the quality of CeCCs, like deposition techniques, solution composition, concentration, pH, temperature, pre-treatment and post-treatment, must be investigated carefully in order to fill out specific requirements. Furthermore, the most critical challenge for the long-term application is their impact on the environment and health.

Since the new alternatives based on phosphate, cerium, zirconium, titanium salts, titanium zirconium salt, cobalt salts, molybdate, etc. are recently developed, the effect of prolonging exposure time to such coatings are not apparent yet and can take decades to develop and be recognized. Therefore, since CCC is replaced due to its toxic and cariogenic effect, it is crucial to find an alternative material that does not impose the same threat on human health and environmental wellbeing.

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Conflict of interest

Authors declare that there is no conflict of interest.

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Konverzione prevlake na bazi cerijuma na površinama aluminijuma

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Abstrakt: Konverzione prevlake koje sadrže heksavalentni hrom (hromati) su decenijama masovno korišćene kao deo sistema za zaštitu legura aluminijuma od korozije. Ipak, hromati su zabranjeni zbog njihove toksičnosti i zato se moraju zameniti “zelenim” alternativnim ekološkim sistemima zaštite koji nisu štetni za životnu sredinu. Konverzione prevlake na bazi cerijuma (CeCCs) predstavljaju jednu od najperspektivnijih alternativa zato što pružaju efikasnu zaštitu od korozije, bezopasne su za životnu sredinu i ekonomične su jer imaju nisku cenu. Ovaj pregledni rad je fokusiran na zaštitna svojstva konverzionih prevlaka na bazi cerijuma (CeCCs) na aluminijumu i to kada se one koristi kao samostalne prevlake ili kao prevlaka u kombinaciji sa pokrivnom organskom prevalakom.

Ključne reči: cerijum, korozija, elektrodepozicija, EIS, polarizaciona merenja.
