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Volta potential of clad AA2024 aluminium after exposure to $CeCl_3$ solution

F. Andreatta [a,*], M.-E. Druart [b], E. Marin [a], D. Cossement [c], M.-G. Olivier [b], L. Fedrizzi [a]

[a] University of Udine, Department of Chemistry, Physics and Environment, Via del Cotonificio 108, 33100 Udine, Italy
[b] University of Mons (UMONS), Materials Science Department, Place du Parc 20, 7000 Mons, Belgium
[c] Materia Nova asbl, Belgium, Avenue Copernic 1, 7000 Mons, Belgium

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ABSTRACT

AA2024 clad with AA1050 was immersed in $CeCl_3$ solution to promote deposition of cerium species. The deposition occurs on the entire sample surface for the alkaline etched substrate, while it is very limited for the degreased substrate. The surface potential (Volta potential) was investigated by scanning Kelvin probe force microscopy after different immersion times in $CeCl_3$ solution. The preferential deposition of Ce compounds at Al–Fe intermetallic sites progressively reduces their Volta potential difference relative to the matrix in the alkaline etched substrate. This reduces the susceptibility to localized attack of the intermetallics as proven by potentiodynamic polarization measurements.

1. Introduction

Lanthanide salts are amongst the most promising alternatives to the use of chromates [1] either as corrosion inhibitors [2–10] or conversion coatings [11–13] In particular, different inorganic salts of Ce like chlorides [14–17], nitrates [7,18–20] and sulphates [20] have been investigated for corrosion protection of aluminium alloys. Moreover, Ce-based organic–inorganic inhibitors including cerium dibutyl phosphate [21,22], cerium diphenyl phosphate [23–24] and cerium cinnamate [25] were investigated for corrosion inhibition of different metals and alloys. Arnot and Hinton proved for the first time in the 1980s that cerium chloride could provide cathodic inhibition to AA7075 aluminium alloy [2,11] with an inhibition mechanism related to the reduction reaction of dissolved oxygen. In the presence of anodic dissolution of the aluminium substrate, oxygen reduction occurred at the cathodic sites with a pH increase. The precipitation of cerium oxides–hydroxides on the cathodic intermetallic compounds is promoted by the local pH increase at the cathodic sites. Moreover, it was proved that the cerium layer consisted of a crystalline film of CeO_2 and an amorphous hydrated layer containing Ce^{3+} and Ce^{4+} ions for rather long immersion times (5–20 days) [26–27] An Al–Ce–O complex was detected on the aluminium surface suggesting that the cerium oxide progressively replaces the native alumina on the metal surface. A multistep process was suggested for the deposition of Ce compounds. The first step is the precipitation of cerium oxide on the cathodic zones and the formation of cerium islands. After the nucleation, complete coverage of the aluminium surface is achieved through an island growth mechanism of the Ce compounds. The Ce compounds establish a physical barrier between the metal and the environment inhibiting the oxygen reduction and consequently decreasing the corrosion rate of the metal [28–30]. Recently, Yasakau et al. described the inhibition mechanism of cerium and lanthanide salts for AA2024-T3 focusing on the behaviour of S-phase particles, which are preferential sites for the initiation of localized corrosion [7]. According to the proposed mechanism, cerium is present in the form of Ce^{3+} in neutral solution. The local increase of pH due to the cathodic behaviour of the S-phase particles leads to the initial formation of hydroxo complexes followed by the formation of cerium hydroxide compounds at the sites of S-phase particles when the pH becomes 10 due to the oxygen reduction reaction. Moreover, it was reported that trivalent cerium could be oxidized to the tetravalent state forming highly insoluble hydroxides that provide additional inhibition of corrosion processes taking place at the locations of the S-phase particles.

The mechanism of deposition of Ce compounds on aluminium alloys is strongly affected by the immersion conditions. Indeed, inhibition by Ce species is affected by the aggressiveness and oxidizing ability of the solutions containing Ce [8,31,32]. In particular, Mansfeld et al. reported that a high concentration of cerium chloride might induce localized attack of the substrate due to

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[*] Corresponding author. Tel.: +39 0432 558838; fax: +39 0432 558803.
E-mail address: francesco.andreatta@uniud.it (F. Andreatta).

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competition between the deposition of Ce compounds and the attack of the substrate due to the presence of chloride ions. On the other hand, oxygen saturation of a Ce-containing solution could promote the precipitation of cerium compounds on galvanised steel according to the work of Olivier et al. [32]. However, the precipitation of rather large amount of Ce compounds on the substrate could not guarantee a good inhibition of the localized corrosion of the substrate [8].

The role of intermetallic particles in the initiation of localized corrosion of aluminium alloys is well known [33–34]. In particular, Fe-rich particles are sites for oxygen reaction and promote the nucleation of pitting corrosion [35–37]. Cathodic reactions at the intermetallic sites lead to local alkalinization that can induce local dissolution of the surrounding aluminium matrix. The pH due to local alkalinization could be as high as 11 near the Fe-rich particles [35,38]. Nisancioglu reported that dealloying of aluminium in Al_3Fe intermetallics leads to iron-rich remnants that are catalytically active for oxygen reduction [36]. Since localized corrosion phenomena take place at the micrometer or sub-micrometer scale, local techniques have been considered for the investigation of the localized behaviour of intermetallic particles. Localized corrosion of aluminium alloys has been extensively investigated by means of local techniques in order to highlight the role of intermetallic compounds on the initiation of pitting corrosion. Amongst the local techniques, the scanning Kelvin probe force microscopy (SKPFM) [39–47], the scanning vibrating technique (SVET) [7,48] and the electrochemical micro-cell [34,49–54] are the most employed methods for the study of the electrochemical behaviour of the intermetallic compounds due to their lateral resolution in the micrometer or sub-micrometer range. Moreover, local techniques have been recently used for the study of corrosion inhibition in different aluminium alloys. The SKPFM has been used for the study of corrosion inhibitors including triazole and thiazole derivatives [55], salicylaldoxime, 8-hydroxyquinoline and quinaldic acid [47,56] and rare earth compounds [7,15,57]. Moreover, the SKPFM was employed for the investigation of different conversion coatings on aluminium alloys [12,58–62]. The SVET has proved to be very useful for the study of different inhibitors [48,63], primers [64,65] and coatings containing corrosion inhibitors [66–72] The use of the electrochemical micro-cell for the study of inhibition processes in aluminium alloys is a rather new approach initially introduced by Ralston et al. and Birbilis et al., who investigated the behaviour of intermetallics in AA2024-T3 exposed to aqueous vanadate solutions [73,74]. Paussa et al. recently employed the micro-cell for the in situ investigation of intermetallics in AA2024-T3 after exposure to aqueous solutions containing Ce salts [9] and to highlight the precipitation mechanism of cerium species [10]. Moreover, this technique was recently employed in our group in order to investigate the effect of Ce species on the electrochemical behaviour of Fe-rich intermetallic particles in clad AA2024 [8].

Although the SKPFM is a very useful method for understanding local corrosion phenomena of aluminium surfaces, the interpretation of measured Volta potential differences is not straightforward and should be supported by information on composition, corrosion morphology and other local electrochemical data [62]. In particular, the major limit of the SKPFM is that Volta potential measurements are carried out in air and not directly in solution. Hence, it is rather difficult to relate the Volta potential differences to the corrosion behaviour in aggressive electrolyte. Moreover, the Volta potential can be affected by several parameters like adsorbed species on the sample surface, trapped charges, changes in humidity and reorientation of water dipoles, plastic deformation of the sample, oxide layers on the sample surface and sample topography [41,75–79].

This work considers inhibition of clad AA2024 by Ce compounds, which was previously targeted by means of electrochemical micro-cell technique [8]. In particular, this paper investigates the effect of surface preparation (degreasing or alkaline etching) on the deposition of Ce species since it was found that Ce species improved the electrochemical behaviour only in the case of the alkaline etched substrate [8]. The experimental approach of this paper is based on the use of SKPFM in order to obtain information about the effect of the microstructure of the clad layer (alloy AA1050) on the deposition of Ce species for different conditions of the substrate. In particular, the topography and Volta potential difference measured after immersion in $CeCl_3$ solution by SKPFM can provide further insight about the role of surface preparation on the deposition of Ce species on the Fe-rich intermetallic particles and the matrix.

2. Experimental procedures

2.1. Substrate, surface preparation and deposition of Ce species

The substrate for this investigation was AA2024 aluminium alloy clad with AA1050 (clad AA2024). The chemical composition of the clad layer, the AA1050 alloy, is reported in Table 1. The thickness of the clad layer is about 4% (40 μm) of the sheet thickness, which was 1 mm. Before immersion in the solution containing Ce, the samples were polished and subjected to surface preparation according to the following procedures: degreasing in acetone or alkaline etching in 40 g/l NaOH at 50 °C for 30 s.

After surface preparation, the substrate was immersed in a 2.5 mM $CeCl_3$ solution in order to promote the deposition of cerium species. The content of O_2 dissolved in the $CeCl_3$ solution was 8 ppm (aerated condition). The oxygen concentration was evaluated by means of a Consort Z621 oximeter. The immersion times were 1 h, 3 h, 6 h or 24 h for degreased or alkaline etched samples. All the experimental parameters are reported in Table 2.

2.2. Microstructure characterization

The morphology of the samples was investigated by scanning electron microscopy (SEM). Energy dispersive X-ray spectroscopy (EDXS) was employed to acquire elemental spectra at different locations of the sample surface in order to evaluate the deposition of Ce species. In particular, the EDXS analysis was carried out mainly at the location of Fe-rich intermetallics. In addition, the deposition of the Ce species was investigated by means of time of flight-secondary ion mass spectroscopy (TOF-SIMS). Surface imaging was carried out using a TOF-SIMS IV from ION-TOF GmbH. A pulsed Ga^+ 25 keV ion beam at a current of 0.60 pA was used for the analysis. The detection was made in the positive ion mode. Prior to every experiment, surface sputtering by a 3 keV Ar beam at a current of 20 nA over an area of $300 \times 300\ \mu m^2$ was performed in order to remove the carbon contamination. The spectra were acquired on areas ranging from $5 \times 5\ \mu m^2$ to $200 \times 200\ \mu m^2$. TOF-SIMS was employed in this work in order to acquire information about the precipitation of Ce compounds on the substrate since this technique is sensitive to small amounts deposited on the surface. However, it was decided to avoid quantification of

Table 1
wt% composition of the cladding alloy (AA1050).

	wt% composition							
Element	Si + Fe	Cu	Mn	Mg	Zn	Ti	Other	Al
Min.	–	–	–	–	–	–	–	Base
Max.	0.7	0.1	0.05	0.05	0.1	0.03	0.03	

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