



Ce(III) corrosion inhibitor release from silica and boehmite nanocontainers

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ABSTRACT

Electrochemical impedance spectroscopy clearly appeared as a suitable technique to investigate the releasing properties of cerium (III) loaded on silica and boehmite nanocontainers. In this way the electrochemical behavior of the AA2024-T3 was evaluated by electrochemical impedance spectroscopy in a 0.045 mol L⁻¹ NaCl solution with nanocontainers containing the inhibitor. Results show that the inhibitor release is influenced by both the chemical nature and the morphology of the nanocontainers. The lower loading and release phenomena were observed for the mesoporous silica nanocontainers, whereas the inhibitor is liberated until 168 h from dense silica nanocontainers. Boehmite nanocontainers combine a good loading ratio with a longer release until the second week of immersion.

1. Introduction

The AA2024-T3 aluminum alloy is widely used in aircraft manufacture because of its optimal weight to strength ratio, however this alloy is one of the most susceptible towards localized corrosion. For many decades, chromates conversion technology has been widely used for the corrosion protection of this alloy to very good effect [1,2]. Unfortunately, hexavalent chromium is extremely toxic, carcinogenic, and environmentally harmful, so this technology is now unsustainable. An interesting alternative route lies in the hybrid sol-gel coatings, which provide a good adhesion to the substrate and enhanced compatibility with additional organic top coatings [3]. Organic-inorganic hybrid sol-gel coatings exhibit good barrier properties that hinder the progression of the aggressive species [4–6]. Moreover, self-healing properties can be brought to coating thanks to the addition of organic [7,8] or inorganic [7–9] corrosion inhibitors. Among alternative inhibitors, rare earth elements and more especially the cerium (III) cation provide an effective corrosion protection to the AA2024-T3 [7,10–16]. It was reported that a cerium content in the coating ranging from 0.2 to 0.6 wt% is an optimum because higher concentrations lead to defects in the coating backbone [17,18]. Introduction in the hybrid coatings of corrosion inhibitors trapped in host containers allows minimizing this detrimental effect [19,20]. In this way, corrosion inhibitors can be released to compensate coating defects like scratches by providing excellent self-healing functionality. Nanosized inorganic oxides are very often introduced as nanocontainers in sol-gel based films, including

silica the morphology of which allows to form hollow spheres [21], mesoporous nanospheres [22,23] or nanotubes [24]. Zirconia and titanium dioxide hollow mesoporous nanospheres as other smart nanocontainers for organic corrosion inhibitor are reported by Wang [25] and Chenan [26] and by Balaskas [27] and Tang [28] respectively. Other containers are the Mg-Al and Zn-Al layered-double-hydroxides (LDH) [29–31] or nanoclays such as halloysite nanotubes [32–34], which can be loaded by anionic organic or vanadate inhibitors. Among the organic corrosion inhibitors, benzotriazole (BTA) [24,32,34,35], hydroxyquinoline (8-HQ) [27,34,36] and mercaptobenzothiazole (MBT) [23,26,29,33] are the most reported. Surprisingly few studies relate to inorganic inhibitors such as vanadate [30,31], molybdate [36] and cerium nitrate [36,37,38] despite the well-known efficiency of the latter. Tavandashti and al [38] described the improvement of self-healing performances when cerium loaded boehmite nanocontainers are incorporated in sol-gel epoxy coatings.

Because nanocontainers embedded into coatings also act as fillers which improve the barrier property and in order to assess the inhibitor release property of the nanocontainers, the present work focuses on the study of the Ce(III) release in a corrosive solution. Most of the reported studies involve organic inhibitors whose release from nanocontainers is easily quantified by spectrophotometry [8,39] but few studies dealt with inorganic inhibitors such as lanthanide cations which require other methods such as ICP titration which involves multiple separation steps [40]. Moreover in the case of very small nanoparticles (under 20 nm), the separation of loaded nanoparticles remains a difficult task,

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preventing the use of this analytical technique. The indirect method chosen in this work is based on electrochemical impedance spectroscopy measurements (EIS) which is largely used to evaluate the influence of the addition of Ce(III) to the NaCl solution on the electrochemical response of aluminum alloys when corrosion occurs. Cerium cation acts as a cathodic inhibitor, blocking the areas occupied by the cathodic intermetallics through the precipitation of a cerium oxide or hydroxide. The inhibition effect is reflected in the electrical response of the system by the minimisation of the values of the elements of the electrical loop related to the response of the cathodic intermetallics. Using EIS, circuits can therefore be proposed to model the electrochemical behavior of the system when Ce(III) is added to the medium. It has been established that the film produced over the metal surface can be characterized by the values of the resistance R and capacitance C in each loop. [12–16,41] Thus, the increase observed in the values of R when the cerium salt is added to the solution could be related to the formation of a more compact film, as a consequence of the precipitation of cerium in the cathodic zones. In a solution containing Ce(III) and nanoparticles, if interaction between inhibitor and nanoparticle is established, the free Ce(III) concentration will decrease and as a consequence the corrosion of the aluminum substrate will intensify. The electrical response of the system is therefore an indirect method to prove the cerium loading on nanoparticles. In the same way an increase on the protection of the substrate could be related to the inhibitor release phenomenon.

Based on this improved method to characterize the inhibiting properties of cerium in solution towards aluminum alloys, this study involves EIS to evidence the inhibitor loading of nanocontainers and its release to protect AA2024-T3 in 0.045 mol L^{-1} NaCl solution.

Taking into account the chemical compatibility between the nanocontainers and the hybrid aluminosilicate sol-gel coatings which are known for their effective barrier properties [18,42], silica and boehmite nanocontainers have been considered in this work. Comparisons between these nanocontainers have been made, bearing in mind their different chemical natures and surface properties, given that the silica surface is negatively charged whereas the boehmite surface is positive, at the considered pH [43]. Their morphology was also modulated using dense or mesoporous nanospheres for silica and boehmite nanoneedles. Different nanocontainers could thereby be discriminated according to the nature of the matrix and/or its morphology.

2. Experimental part

2.1. Materials

2.1.1. Starting nanomaterials

An initial boehmite sol was obtained from commercial Disperal P2 dispersible powder purchased by Sasol. A second boehmite starting material was prepared according to Yoldas method [44] by hydrolysis of aluminum tri-*sec*-butoxide (ASB) in hot water, followed by a peptisation step using nitric acid (69%) and the solution was kept at 85°C during 24 h for maturation. These materials, prepared with an aluminum concentration of 0.5 mol L^{-1} , will henceforth be referred to respectively as C-ALOOH and Y-ALOOH.

For the silica matrix, Ludox TMA (34 wt%) sol was used as received from Aldrich, 3.6 mL was added to 46.4 mL of deionized water to obtain a 0.5 mol L^{-1} silicon concentration. A second silica starting material was synthesized using a microemulsion method described by A.B.D. Nandiyanto [45] with styrene as porogen reagent. After calcination

(500°C , 5 h) to remove the template, 0.3 g of the powder was dispersed in 50 mL of deionized water by mechanical attrition at 0.1 mol L^{-1} silicon concentration. These materials will henceforth be referred to respectively as C-SiO₂ and M-SiO₂.

2.1.2. Cerium loaded nanocontainers

In order to consider an exposed surface of 220 m^2 in each experiment and taking into account the different specific areas of the nanomaterials, different volumes of the boehmite (C-ALOOH and Y-ALOOH) and silica (C-SiO₂ and M-SiO₂) solutions described in 2.1.1 have been used. 50 mL of boehmite solution was prepared using 22 mL of C-ALOOH or Y-ALOOH added to 28 mL of deionized water, whereas for the silica solution, 50 mL of C-SiO₂ or M-SiO₂ solutions were directly used. The corrosion inhibitor, Ce(NO₃)₃·6H₂O, in powder form was added to the corresponding nanocontainers solutions (50 mL) and was stirred constantly for 12 h at room temperature. The total cerium concentration was fixed at $10^{-3} \text{ mol L}^{-1}$ for all the experiments. These Ce(III) modified sols will henceforth be referred to respectively as C-ALOOH-Ce, Y-ALOOH-Ce, C-SiO₂-Ce and M-SiO₂-Ce.

In order to study the effect of the C-ALOOH nanocontainer concentration a second sol of C-ALOOH-Ce was prepared using directly 50 mL of the as-prepared solution (see 2.1.1) to have an exposed surface of 500 m^2 , the total cerium concentration was kept at $10^{-3} \text{ mol L}^{-1}$.

2.1.3. Aluminum alloy substrate

The 2024-T3 aluminum alloy samples, the dimensions of which were $80 \times 53 \times 1 \text{ mm}^3$ were used after a surface preparation. The sample was cleaned according the following protocol: immersion in alkaline aqueous solution (pH = 9) for 20 min at 60°C followed by immersion sulfo-nitro-ferric pickling for 5 min at room temperature. The sample was finally washed with acetone and air-dried. For the electrochemical experiments, a 7.06 cm^2 circular work area was delimited using Teflon adhesive. The chemical composition of AA2024-T3 alloy (UNS A92024/EN-AW 2024) is given in Table 1.

2.2. Experimental techniques

The size and the morphology of the nanomaterials were examined by TEM microscopy using a high definition JEOL JEM-1400 at 120 kV. The powders were diluted in ethanol and then deposited on copper grid. For Cryo-TEM of the boehmite samples, 3 μL of sample were deposited onto a glow-discharged 200 mesh lacey carbon grid and loaded into the thermostatic chamber of a Leica EM-GP automatic plunge Freezer, set at 20°C with 95% humidity. The grid was immediately flash frozen in liquid ethane cooled at -185°C . Specimens were then transferred into a Gatan 626 cryo-holder, and Cryo TEM was carried out on a Jeol 2100 microscope, equipped with a LaB₆ cathode and operating at 200 kV, under low dose conditions. The specific surface area, measured by BET method and adsorption-desorption isotherms were carried out with a Micromeritics Tristar 3020, using pure dinitrogen gaz. Prior to this, samples were degassed under vacuum at 200°C during 12 h. Solid state NMR experiments were carried out with a Bruker Avance III 400 MHz (9,4 T). Decompositions of the CP MAS NMR spectra to extract the proportion of the corresponding species were performed with the DMfit software [46]. The Dynamic Light Scattering measurements (DLS) of aqueous dispersion of nanocontainers were taken using a Malvern Nanosizer ZS 90. The Electrochemical Impedance Spectroscopy (EIS) measurements were carried out, at room temperature with a corrosion cell (flat cell by Metrohm) in a Faraday cage, using a Biologic SP-150

Table 1
Composition specification (wt%) of the AA2024-T3.

Alloys	Al	Cu	Mg	Mn	Si	Fe	Zn	Cr	Ti	Others
2024-T3	90.7–94.7	3.8–4.9	1.2–1.8	0.3–0.9	0.5	0.5	0.25	0.1	0.1	0.15

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