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A SVET study of the inhibitive effects of benzotriazole and cerium chloride solely and combined on an aluminium/copper galvanic coupling model

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ABSTRACT

An aluminium/copper galvanic coupling model suitable for Scanning Vibrating Electrode Technique (SVET) analysis was elaborated with the aim of simulating a galvanic couple characteristic of AA 2024. The inhibitive effects brought by benzotriazole (BTA) and cerium chloride ($CeCl_3$) on the Al/Cu model were evaluated, separately and combined, in neutral aerated sodium chloride solutions. A positive synergistic effect was revealed yielding permanent corrosion protection for 46 h of immersion. Complementary techniques such as UV spectrophotometry and ToF-SIMS were employed, respectively, to investigate the decomposition of BTA molecules and to confirm the chemical composition of a combined BTA-based/Cerium-based layer.

1. Introduction

The galvanic corrosion of AA 2xxx aluminium alloys in chloride-containing environments remains an important challenge in the aeronautical field. In particular, AA 2024 alloys, which are widely employed in the construction of aircrafts, are highly susceptible to localized corrosion [1,2], due to galvanic coupling formed between the Al matrix and the Mg and/or Cu based intermetallic particles [1–7]. It is well accepted that most of the AA 2024 alloys constituent phases, such as Al–Cu containing particles, have a simple cathodic behaviour relative to the matrix [4–6]. The morphological characteristic of a cathodic intermetallic particle (IMP)/anodic aluminium matrix system is the local dissolution of aluminium around an almost unattacked particle, leading to the formation of a trench [4,6,7]. Ultimately, the Cu-rich particles are detached from the matrix, becoming able to freely corrode and to be reduced over cathodic sites on the alloy surface [3,6,8]. The Cu redistribution spreads the cathodic areas, further favouring aluminium dissolution. With respect to the Al_2CuMg particles, this phase is predicted to be less noble than the Al matrix and initially undergoes anodic attack, in such a manner that aluminium and magnesium are selectively dissolved [3]. Afterwards, this Cu-enriched phase starts to behave cathodically, being able to detach from the matrix by the same trenching mechanism than the other IMPs [2,3,6].

For many decades, Cr(VI) compounds (mainly chromates) have been successfully applied as corrosion inhibitors of aluminium alloy localized corrosion in aqueous media [9–11]. Presenting an elevate efficiency/cost ratio, chromates were employed at almost every anticorrosive pretreatement/finishing procedure of aircraft aluminium alloys, including conversion coatings, anodising baths and painting primers [9,12]. Recently, however, environmental laws worldwide have imposed severe restrictions on chromate use, as they are considered highly toxic and carcinogenic [9,10,13]. Under the shadow of these environmental regulations, a huge effort has been carried out in order to develop new and Cr(VI)-free strategies of active/passive corrosion protection of AA 2024 [1,2,13–15]. Different promising approaches (sol-gel coating processes [16–19], conversion coating technology [20], multi-layered systems [21,22]) are making use of inorganic and/or organic corrosion inhibitors aiming to control localized corrosion as much as possible. Specifically, benzotriazole (BTA) [1,2,11,15] and cerium salts [23–26] have shown very promising results to inhibit corrosion reactions on AA 2024 in neutral aerated NaCl solutions.

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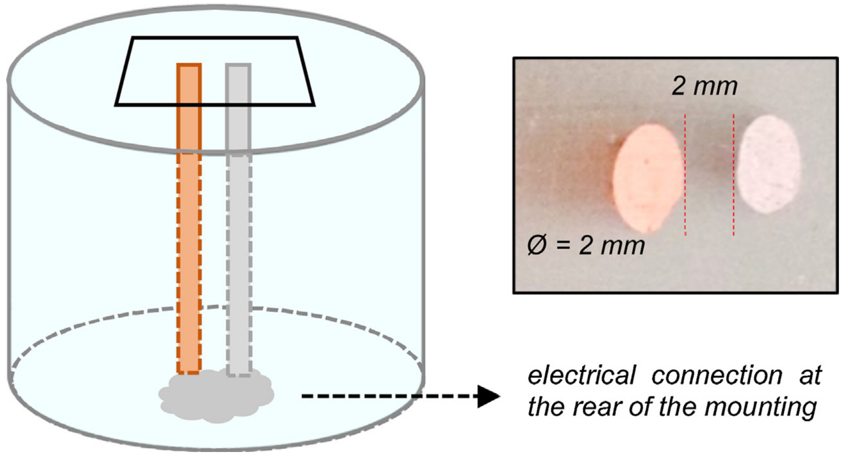

Fig. 1. Schematic representation of the Al/Cu galvanic coupling model composed of one Al rod and one Cu rod, both with 2 mm of diameter, mounted in epoxy resin respecting a 2 mm gap. At the rear of the mounting, an electrical connection was made with Sn welding.

Table 1
SVET operational parameters employed in the tests.

Probe	Pt, Ø≈50 μm, frequency = 80 Hz, vibration amplitude = 50 μm, probe-sample distance = 150 μm
Lock-in amplifier	Gain = 100, sensitivity = 4 mV, phase = 330°, time constant = 0.1 s
Scanning parameters	Area scan mode, sweep scan mode, scan velocity = 1000 μm s^{-1}, test duration≈29 min, step size≈78.8 μm

Cerium salts are film-forming cathodic inhibitors extensively employed in the protection of a variety of metals [23,24,26–29]. In near neutral solutions, these salts interfere with the oxygen reduction reaction by restricting the diffusion of dissolved oxygen to the electrode surface. In the case of AA 2024, when the pH locally increases on the top of IMPs, the Ce^{3+} species react with the produced hydroxyl ions, forming $Ce(OH)_3$ precipitates at these regions (Eq. (1)) [16,23,26]. After the blockage of the cathodic sites, $Ce(OH)_3$ can also precipitate over the Al matrix, conferring protection to the sites whose activity was initially anodic [24,30].

$$Ce^{3+} + 3OH^- \rightarrow Ce(OH)_3 \rightarrow CeO_2 + H_3O^+ + e^- \quad (1)$$

Regarding benzotriazole, it has been known as an efficient inhibitor of copper corrosion for more than 40 years [31,32] and is still the subject of numerous recent studies [1,2,15,33]. Its efficiency is attributed to the formation of a highly impermeable and resistive physical barrier layer, inhibiting both anodic and cathodic corrosion reactions on Cu [31,34]. However, the exact mechanism by which benzotriazole inhibits copper corrosion is not yet completely understood, in spite of the application of various techniques [35–46]. Recently, the use of benzotriazole as a corrosion inhibitor for AA 2024 alloys has shown favourable results [1,2,11,15]. Zheludkevich's EIS studies [1] showed that the inhibitor molecules would form a thin layer on the top of the aluminium oxide surface, hindering the corrosion activity during the first hour of immersion. Recloux's work [15] demonstrated by EIS that the low-frequency modulus related to a BTA-based film, formed on the entire aluminium surface, was one order of magnitude higher than for the bare AA 2024 and was stable until 21 days of immersion in 0.05 M NaCl + 0.03 M BTA solution. Additionally, BTA was referred to co-operate synergistically with some other corrosion inhibitors [14]. For example, Kallip et al. [47] achieved excellent results for Zn/Fe galvanic couple by combining BTA and cerium nitrate.

Considering corrosion inhibition as a complex process, where inhibitory molecules interact with local micrometric/nanometric cells formed on an active surface, comprehensive understanding of inhibition mechanisms ideally requires in situ analyses in such scales [2,33,48]. Thereby, the relatively recent local electrochemical techniques have been increasingly considered in the study of corrosion inhibition and have been greatly succeeded in extracting information at micro scales [15,49,50]. In particular, the Scanning Vibrating Electrode Technique (SVET) is presented as a monitoring approach suitable for galvanic coupling inhibition analyses and is widely reported in the literature [2,30,33,47,48,51,52].

In this work, SVET was employed in order to evaluate the inhibitive effects of benzotriazole and cerium chloride, combined and solely, on the corrosion protection of an Al/Cu galvanic coupling. So as to better highlight local anodic and cathodic processes, an Al/Cu galvanic couple characteristic of AA 2024 microstructure was simulated by separating the cell components [50,53]. In NaCl-containing solutions, the Al/Cu galvanic coupling should behave as follows: the Al electrode is preferentially corroded (Eq. (2)) while the Cu electrode is protected, being the site where the oxygen reduction reaction occurs (Eq. (3)). Theoretically, the galvanic corrosion should be limited by the cathodic reaction (oxygen reduction) which takes place on the copper surface (Eq. (3)).

$$Al \rightarrow Al^{3+} + 3e^- \quad (2)$$

$$2H_2O + O_2 + 4e^- \rightarrow 4OH^- \quad (3)$$

Making use of SVET and complementary techniques, this work aims to report the inhibitive action of combining BTA and $CeCl_3$ on the corrosion protection of an Al/Cu galvanic coupling in sodium chloride solutions. Prior to investigating the combined action of benzotriazole with the cerium salt, a SVET study on the concentration effect of BTA was carried out. Optical microscopy analysis of the electrode surfaces immerged in pH indicator containing-solutions assisted the interpretation of the SVET results. UV spectrophotometry was also employed to study the eventual decomposition of benzotriazole molecules, as a function of time, at different pH. Finally, ToF-SIMS was used to confirm the chemical identity of the BTA-based/Cerium hydroxide (oxide) protective film formed onto Cu surface.