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Effect of 1-pyrrolidine dithiocarbamate on the galvanic coupling resistance of intermetallics – Aluminum matrix during corrosion of AA 2024-T3 in a dilute NaCl

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ABSTRACT

1-pyrrolidine dithiocarbamate (PDTC) effect on galvanic coupling resistance of AA 2024-T3 alloy in 0.2 g L^{-1} NaCl was evaluated by different electrochemical/gravimetric methods and surface analysis. The results obtained from polarization curves and electrochemical quartz crystal microbalance measurements showed that PDTC forms an adsorbed film on the Cu-rich particles, likely through a Cu^{I}–PDTC complex. At high concentrations, PDTC significantly decreases the alloy reactivity thereby providing a marked corrosion protection. SEM–EDX analysis showed that PDTC adsorbs preferentially on the Al–Cu–Mg particles. Electrochemical impedance spectroscopy measurements corroborate these results and show furthermore that PDTC addition increases the galvanic coupling resistance.

1. Introduction

Despite the susceptibility of 2XXX series of aluminum alloys to galvanic corrosion in chloride media [1,2], they continue to be the material of choice in different industries, particularly for several applications in the aerospace domain, due especially to their lightness and their advantageous mechanical properties. 2XXX series are obtained by addition of alloying elements, mainly copper, to confer high mechanical strength to the alloys thus formed. However, Cu addition produces a heterogeneous microstructure containing intermetallic inclusions, mainly Al–Cu–Mg (S-phase), Al–Cu–Mn–Fe, and other Cu-rich minor phases in the case of AA 2024-T3 alloy. In chloride media, all types of coarse intermetallic particles strongly affect the corrosion behavior of the AA 2024-T3 alloy but in different ways and extent. The common theory concerning the corrosion mechanism of this alloy [1,3–9] states that Al–Cu–Mg particles are initially active with respect to the matrix and are partially dissolved by dealloying resulting in a copper-rich remnant, which then behaves as a cathodic site and induces peripherical matrix corrosion near the particle due to pH increase [10]. Concerning the Al–Cu–Mn–Fe coarse intermetallics, they are always considered as cathodic sites and promote the matrix dissolution around them. This dissolution continues as long as the intermetallics retain electrical contact with the matrix, and is cathodically controlled due to the smaller area of these particles. In addition, the cathodic nature of the Al–Cu–Mn–Fe particles leads to rapid reduction of oxygen with consequent increase of the pH in their proximity which in turn causes alkaline attack of the matrix adjacent to these particles. Besides, a secondary effect of their cathodic nature is the reduction at their location of copper ions dissolved in solution, which leads to nodular Cu deposits [3].

In chloride solutions and in chloride-containing sulfate solutions, the poor resistance to corrosion of AA 2024-T3 alloy was attributed to the aggressiveness of chloride and sulfate ions to copper [11–14]. This suggests that the protection of AA 2024-T3 alloy against localized corrosion in such environments could be mitigated by the protection of Cu-rich particles. Hence, the use of compounds that generally inhibit the corrosion of Cu appears to be a promising approach for corrosion inhibition of the alloy. Several compounds have been identified as potential inhibitors for the alloy by extensive studies on the corrosion inhibition of copper [15–18].

In a previous study [19], a statistical analysis of pit nucleation times of AA 2024-T3 alloy in chloride media has shown that 1,2,3 benzotriazole (BTAH), one of the most studied inhibitors for

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copper [20–22], modifies the pit nucleation rate. In a wide range of applied potentials, the pit nucleation rate was decreased by a factor greater than five in the presence of BTAH. This compound prevents pitting corrosion of the alloy by interacting with Cu-rich particles. From electrochemical noise measurements [23], we showed that BTAH inhibits both localized and generalized corrosion of AA 2024-T3 in sulfate-containing chloride solutions. An insoluble polymeric complex of Cu^{I}–BTA forms on the Cu-rich particles, and lowers the rate of oxygen reduction reaction (ORR), which in turn prevents the dissolution of the Al matrix. We showed also [24] that electro-polymerization of 3-amino-1,2,3-triazole (ATA) on AA 2024-T3 alloy surface leads to the formation of a polymeric film on Cu-rich particles. This film protects the alloy against localized corrosion by reducing the rate of the ORR.

Several studies were undertaken to reduce the reactivity of AA 2024-T3 particles. For example, Ianuzzi and Frankel [25] suggest that metavanadates inhibit corrosion of AA 2024-T3 by blocking the ORR at intermetallic sites. Zhu et al. showed that the silicates block a number of cathodic sites on the AA 2024-T3 surface by forming covalent bonds of Al–O–Si at the interface [26]. Aldykewicz et al. reported that Ce inhibits the corrosion of AA 2024 through blocking the intermetallics to ORR with a Ce oxide film [27]. Ferreira et al showed that rare earth ions, such as Ce^{3+} and La^{3+}, lead to the formation of hydroxide deposits on S-phase particles buffering the local increase of pH and acting as a diffusion barrier depleting corrosion in active sites [7]. Yan et al. suggest that incorporation of oxyanions as inhibiting dopants into the polypyrrole Al flake composite coatings leads to efficient corrosion protection of the AA 2024-T3 alloy. The composite coating functions as both a reservoir for corrosion inhibitors and an oxygen scavenger [28]. Gupta et al. reported that polyaniline–lignosulfonate epoxy coating on AA 2024-T3 alloy improves the corrosion resistance of the alloy in 0.6 M NaCl due to the release of dopant at the defect site by formation of aluminum–sulfonate complex [29]. These studies investigating inhibitors of localized corrosion of AA 2024, in a variety of environments, have multiplied in recent years with the goal of replacing chromates, since chromates provide excellent protection for aluminum alloys [30] but are carcinogenic and quite toxic.

For several years, our interest has focused on dithiols modified molecules, particularly the 1-pyrrolidine dithiocarbamate (PDTC) which is a non-toxic product found in different applications in the areas of agriculture and medicine [31]. Previously, this compound showed to inhibit the corrosion of steel in water pipes [32]. Elsewhere, Liao et al. [33] demonstrated that PDTC forms a self-assembling membrane on Cu through the interaction of its two S atoms with the Cu surface then inhibits corrosion when the resulting surface immersed in $0.5\ mol\ L^{-1}$ HCl. Previous experiments on AA 2024-T3 in chloride media [34] showed that PDTC considerably slows down the rate of both cathodic and anodic processes. This beneficial effect likely results from the interaction of PDTC with the Cu-rich particles since other studies [35–37] have demonstrated that the dithiols inhibit the ORR on copper in neutral chloride solutions. A more complete study of the system Cu/PDTC in a chloride solution [38] was realized to help understanding the effect of PDTC on localized corrosion inhibition of AA 2024-T3 alloy. The results obtained on copper showed that PDTC is a good mixed inhibitor for Cu in $0.5\ mol\ L^{-1}$ NaCl. It acts by stabilizing the surface products that form on copper surface i.e. CuCl and Cu_2O, which consequently reduces the surface of Cu exposed to the aggressive medium thereby lowering the reactivity of the electrode.

In the light of the results obtained from Cu/PDTC system, this work describes the role of PDTC in the inhibition of localized corrosion of AA 2024-T3 in $0.2\ g\ L^{-1}$ NaCl, the solution representing a weakly aggressive natural water.

2. Experimental methods

2.1. Electrodes

The disk electrodes were made of pure copper and pure aluminum cylinder rods (Goodfellow, 99.999% of quality) of 5 mm in diameter, and AA 2024-T3 aluminum alloy rod of 1.3 mm in diameter, the composition of which is given in Table 1. Fig. 1 shows a SEM micrograph of AA 2024-T3 alloy on which coarse intermetallic particles are clearly evidenced. First, the lateral part of the cylinders was covered with a cataphoretic paint (PGG W975 + G323) to avoid the electrolyte infiltration in the lateral part of the cylinder rod. The rods were then embedded into an allylic resin or a thermal shrinking sheath. For each material, the electrode surface was abraded, just before experiments by rotating emery paper up to 1200 grade under water flow, and then rinsed abundantly with deionized water.

For EQCM (Electrochemical Quartz Crystal Microbalance) experiments, two $0.2\ cm^2$ gold electrodes were vapor deposited on both faces of the quartz crystal blade to impose an electrical field for oscillation. One of the faces was used as a working electrode, and for this purpose thin layers of test materials were vapor deposited onto the gold electrode by radio frequency plasma assisted sputtering from targets of either pure aluminum or AA 2024-T3 aluminum alloy purchased from Goodfellow. Sputtering, carried out at 2 Pa of argon gas, lasted 20 min producing sputter-deposited aluminum or aluminum alloy of about 1 μm thick. Fig. 2 shows the surface morphology of the alloy deposit. Its chemical composition is shown in Table 2. Note that the Cu-containing alloy appeared homogeneous without secondary phases observed for the AA 2024-T3 alloy. Nevertheless, this material provides a surface of a homogeneous Al alloy containing Cu. Clearly, composition and microstructure of the layer vapor deposited are different from those of the solid alloy: alloying elements do not form coarse intermetallic particles but are homogenously dispersed throughout the layer. It is, indeed, quite difficult to approach the complex microstructure of the alloy [39–43]. Thus, EQCM results of the vapor deposited layer may be quite different from those that may be obtained with the target. However it is interesting to study if PDTC interacts with Cu uniformly dispersed in such layer.

The nominal resonant oscillation frequency of the quartz blade was 6 MHz. Measurements were carried out with a lab-made device and monitoring program.

The working electrode was set close to the center of the electrolyzing cell, and under stationary conditions, i.e. without any electrolyte stirring.

The reference electrode was a calomel electrode in saturated KCl (SCE). All potentials are referred as measured without any correction of neither liquid junction potential nor ohmic drop. The counter electrode was a platinum grid of large surface area set close to the cell wall.

2.2. Electrolytes

The blank corrosion test solution was $0.2\ g\ L^{-1}$ NaCl to which 10^{-4}, 10^{-3}, or $10^{-2}\ mol\ L^{-1}$ of PDTC ($C_5H_9NS_2$, $M = 147.26\ g\ mol^{-1}$, supplied by Sigma®) was added as inhibitor. 100 mL of electrolyte was used for each experiment. The corrosion test was carried out without purging of dissolved oxygen and maintained at 20 °C.

Table 1
Composition of AA 2024-T3 alloy.

Al	Cu	Mg	Mn	Fe	Zn	Si	Cr	Ga	Ni
Base (wt%)	4.75	1.61	0.56	0.15	0.18	0.065	0.009	0.007	0.002