Corrosion Science 101 (2015) 66–74

Contents lists available at ScienceDirect

Corrosion Science

journal homepage: www.elsevier.com/locate/corsci

Synergistic effect between 8-hydroxyquinoline and benzotriazole for the corrosion protection of 2024 aluminium alloy: A local electrochemical impedance approach

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A R T I C L E I N F O

Article history:
Received 4 June 2015
Received in revised form 1 September 2015
Accepted 2 September 2015
Available online 8 September 2015

Keywords:
A. Aluminium
B. EIS
B. SEM
C. Neutral inhibition
C. Passive films

A B S T R A C T

This work is devoted to the corrosion inhibition of the 2024 aluminium alloy (AA2024) in neutral aqueous solution by 8-hydroxyquinoline (8-HQ) and benzotriazole (BTA). First, current-voltage curves and global electrochemical impedance measurements confirmed that 8-HQ and BTA are two effective corrosion inhibitors for AA2024. Mixing the two compounds led to a synergistic effect for the corrosion protection of the alloy. From the impedance data analysis, it was shown that 8-HQ acted mainly on the aluminium matrix with an additional action of the BTA on the intermetallic particles. Then, to analyse the role of the inhibitors on the galvanic coupling between the aluminium matrix and the particles, local electrochemical impedance measurements were performed on a model system (Al/Cu couple). It was shown that in the presence of 8-HQ or BTA alone, the galvanic coupling between copper and aluminium was little reduced while in the presence of both compounds together it was strongly limited. The local impedance results confirmed the specific inhibition of the 8-HQ and of the BTA on Al and Cu respectively.

1. Introduction

Among the numerous studies concerning the replacement of Cr(VI) for the corrosion protection of structural alloys, such as the 2XXX series, some compounds, such as rare earth salts (mostly cerium) [1–9] or organic compounds, such as triazole, thiazole derivatives and more recently carbamate derivatives [10–16], have presented interesting corrosion protection activity. It was shown that this type of inhibitor acts on the copper-rich particles decreasing their cathodic activity. Despite their promising performance, these compounds do not achieve the same level of protection as chromates. To increase corrosion protection, the use of mixtures of inhibitors could be a good strategy. Recently, multifunctional inhibitors, offering both anodic and cathodic inhibition, were investigated: inorganic cations (rare earths) acting on the cathodic sites and organic anions, acting on the anodic sites [17–20].

Among the organic compounds, 8-hydroxyquinoline (8-HQ) and benzotriazole (BTA) were studied as corrosion inhibitors in aqueous solution [10–12] or encapsulated in reservoirs and added to organic or sol–gel coatings for the corrosion protection of AA2024 [21,22]. 8-HQ is known for its chelating properties on different metals [10–12,23,24] and BTA is well known as a corrosion inhibitor for copper [25]. These compounds are generally studied separately.

The aim of the present work is to investigate the 8-HQ + BTA mixture for the corrosion protection of 2024 aluminium alloy and more particularly to obtain a clearer picture of the inhibitive effect of each compound. The final goal of this study is to develop a methodology which could be used to evaluate and compare the efficiency of different compounds or inhibitive mixtures. The methodology chosen is based on the use of both conventional and local electrochemical impedance spectroscopy (EIS). It is important to keep in mind that the degradation of the AA2024 is mainly due to local galvanic coupling between the intermetallic particles and the surrounding matrix [26–33]. To investigate the action of the inhibitor molecules on the particles, an Al/Cu model couple was used. In a previous study, this model couple was designed to understand the corrosion phenomena associated with copper-rich intermetallics in aluminium alloys [34] and was recently used to study the corrosion inhibition of AA2024 by sodium decanoate [14].

2. Experimental procedure

The materials and the electrochemical techniques used are presented in this section. The AA2024 electrode surface was examined

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http://dx.doi.org/10.1016/j.corsci.2015.09.002

Table 1
Chemical composition (wt.%) of 2024 T351 aluminium alloy.

Cu	Mg	Mn	Si	Fe	Zn	Ti	Al
4.50	1.44	0.60	0.06	0.13	0.02	0.03	Bal.

by optical and scanning electron microscopy after being immersed in the solution containing the inhibitors.

2.1. Materials

8-hydroxyquinoline (8-HQ) and benzotriazole (BTA) were analytical grade reagents (purity = 99%) from Alfa Aesar and Sigma–Aldrich respectively, and were used as received. The concentrations of 8-HQ (3×10^{-3} M) or for BTA (10^{-2} M) were chosen near their solubility limits in neutral solution. These concentrations allowed the highest efficiency of the compounds tested alone to be obtained.

For the conventional electrochemical measurements, the corrosive medium was prepared from deionised water by adding 0.1 M Na_2SO_4 and a small concentration of chloride (0.05 M NaCl) (reagent grade). Sodium sulphate was chosen to increase the conductivity of the solution and for its low corrosiveness toward aluminium alloys. For the local impedance experiments (Al/Cu model couple), dilute solutions were used: 10^{-3} M NaCl, 10^{-2} M BTA, 3×10^{-3} M 8-HQ or 10^{-2} M BTA + 3×10^{-3} M 8-HQ. The inhibitors were tested without NaCl in the deionised water to keep a solution with a low conductivity [34]. The electrolytes were in contact with air at room temperature (20 °C ± 2 °C).

Aluminium alloy 2024 T351 was used for the investigations. The average chemical composition of the alloy is given in Table 1. Electrochemical experiments were carried out on an AA2024 T351 rod of 1 cm^2 cross-sectional area machined from a rolled plate (cylinder surface parallel to the plane of rolling). For comparison, some electrochemical tests were performed on pure aluminium (99.9999 wt.%), kindly provided by Praxair or on pure copper (99.9 wt.%) purchased from Alfa Aesar. The body of the rods (1 cm^2 cross-sectional area) was covered with a heat-shrinkable sheath, leaving only the tip of the rod in contact with the solution. The samples were abraded with successive SiC papers and diamond pastes (grade 1200–1 μm), cleaned in ethanol in an ultrasonic bath and finally dried in warm air.

In order to study the interactions between the inhibitors and the matrix and/or the intermetallic particles, a simple system consisting of a pure aluminium/pure copper (Al/Cu) couple was used [34]. The electrode was prepared as follows: a cylinder of pure aluminium (99.9999 wt.%) was drilled in its centre and a cylinder of pure copper (99.9 wt.%) was introduced by force into the hole (Fig. 1). The radii were 1 and 0.315 cm for the aluminium and copper bars, respectively. The assembly of the two materials gave a perfectly joined interface, avoiding crevice corrosion due to surface defects. The electrical resistance between Cu and Al was lower than 0.5 Ω. The electrode was then embedded in an epoxy resin. Before immersion in the electrolyte, the Al/Cu disk electrode was prepared in the same way as the AA2024 or pure Al and Cu rods.

2.2. Electrochemical measurements

For the conventional experiments, a three-electrode cell was used with a platinum grid auxiliary electrode, a saturated calomel reference electrode (SCE) and the rod of AA2024 or the pure Al rod as rotating disk electrode. The rotation rate was fixed at 500 rpm. Polarisation curves and electrochemical impedance measurements were obtained using a Biologic VSP apparatus. The anodic and the cathodic parts were obtained independently from the corrosion potential at a potential sweep rate of 0.6 V/h. Impedance diagrams were obtained at the corrosion potential over a frequency range of 65 kHz to a few mHz with eight points per decade using a 20 mV peak-to-peak sinusoidal potential. The electrochemical results were obtained from at least three experiments to ensure reproducibility.

The corrosion behaviour of the model couple with and without inhibitor was studied by local electrochemical impedance spectroscopy (LEIS). The measurements were carried out with a Solartron 1287 Electrochemical Interface, a Solartron 1250 frequency response analyser and a Scanning Electrochemical Workstation Model 370 (Uniscan Instruments). This method used a five-electrode configuration. Details are provided elsewhere [35–39]. The probe (i.e., a bi-electrode allowing local current density measurement) was stepped across a selected area of the sample. The analysed part had an area of 14 mm × 14 mm and the step size was 400 μm in the X and Y directions. Maps were obtained at a fixed frequency, chosen in the present case at 10 Hz, and admittance was plotted rather than impedance to improve the visualization of the result. Local impedance diagrams were recorded over a frequency range of 3 kHz–300 mHz with ten points per decade. The time to record all the local diagrams (from the centre to the edge) was lower than 60 min. The local impedance measurements were carried out in a low conductivity medium to optimize resolution. The measured conductivities of the different media are reported in Table 2. With the experimental set up used, only the normal component of the current was measured.

2.3. Surface characterization

The AA2024 surface was observed after 20 h of immersion in the solution (0.1 M Na_2SO_4 + 0.05 M NaCl) containing the inhibitors by a scanning electron microscope with a Leo 435VP apparatus to obtain a better description of the corrosion morphology, particularly on the intermetallic particles. Observations of the Al/Cu interface of the model couple were also performed by optical microscopy with a Nikon Eclipse MA200 microscope after 20 h of immersion in the solution containing the inhibitors.

3. Results and discussion

Fig. 2 illustrates the variation of the free corrosion potential (E_{corr}) of the AA2024 in a 0.1 M Na_2SO_4 + 0.05 M NaCl solution without inhibitor or in the presence of inhibitors: 8-HQ, BTA or a mixture of the two compounds. Without inhibitor, E_{corr} stabilizes rapidly whereas in the presence of the inhibitors E_{corr} increases with time

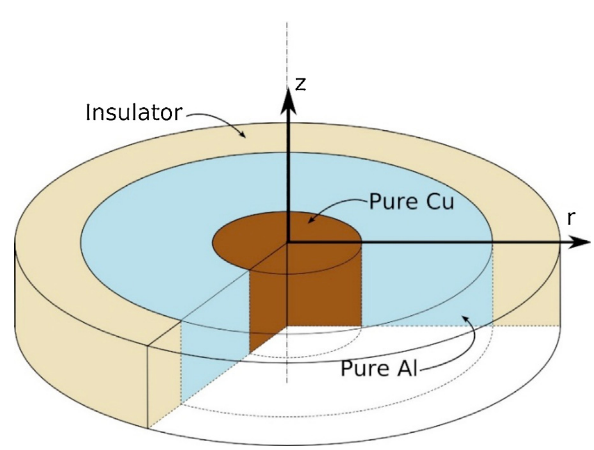

Fig. 1. Schematic representation of the pure aluminium/pure copper model couple. The radii of the two cylinders were equal to 1 and 0.315 cm for aluminium and copper bars, respectively. The electrode was then embedded in an epoxy resin so that a disk electrode was obtained at the extremity.