



Coupling of electrochemical techniques to study copper corrosion inhibition in 0.5 mol L⁻¹ NaCl by 1-pyrrolidine dithiocarbamate

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ABSTRACT

In this work, as for the preliminary step to the protection of Al 2xxx alloys, the anticorrosion effect of environmentally friendly 1-pyrrolidine dithiocarbamate (PDTC) on Cu was investigated by combining various electrochemical methods in addition to SEM-EDS analyses and gravimetric measurements. The Cu/PDTC system was used as a model to simulate the inhibition of Cu-rich particles contained in Al 2xxx alloys. The corrosion test solution was 0.5 mol L⁻¹ NaCl in the presence of 10⁻⁴, 10⁻³, or 10⁻² mol L⁻¹ PDTC. The immersion time of the copper electrode was extended generally up to 24 h. By EQCM measurements, a marked protective effect of PDTC was observed for the highest PDTC used, and corroborated by voltammetry and EIS measurements. The cathodic reduction under constant current allowed determining the corrosion products remaining on the copper surface in terms of electrical charge. The protective effect of PDTC was explained by the formation of highly stable compounds on the copper surface, which decreases the rate of both anodic dissolution and oxygen reduction reaction.

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1. Introduction

The 2xxx series of aluminium alloys obtained by addition of large quantities of copper to pure aluminium exhibit excellent mechanical properties. This copper addition leads to a heterogeneous microstructure constituted by copper rich precipitates. However, although the high strength acquired, these alloys suffer corrosion damages due to the formation of galvanic cells between the aluminium matrix and copper rich-particles, particularly in chloride-containing medium [1,2]. These precipitates provide surfaces where oxygen can readily be reduced; therefore they constitute the cathodic area. Treatments involving the use of chromates and dichromates provide a highly efficient corrosion protection for aluminium alloys, particularly those containing copper [3]. However, chromate solutions cause health and environment risks because hexavalent chromium compounds have an important toxic effect and are carcinogenic. Efforts are then made to replace Cr(VI) by non-toxic compounds able to specifically protect Cu-rich particles. Current attention of researchers is focused

on the inhibition of electrochemical processes, especially the oxygen reduction reaction (ORR), on copper rich-particles to reach an action quite similar to that of Cr(VI). Corrosion inhibitors for copper, such as organic molecules, could then be considered as alternatives [4,5].

Corrosion protection of metals by organic compounds depends mainly on the chemical structure of the inhibitor and its adsorption mode. Several groups of heterocyclic organic compounds have been reported to exert inhibitive effect on copper corrosion in different media [6–9]. Benzotriazole (BTAH) is one of the most famous inhibitors for copper and copper alloys [10–14]. In previous works [4,5], we showed that BTAH and 3-amino 1,2,4-triazole (ATA) inhibit the dissolution associated with Cu-rich particles by the formation of protective complexes upon the particles. In the same way, Williams et al. [15] showed that organic and inorganic anions inhibit pitting corrosion of Al 2024 T3 alloy in 5% NaCl, by film formation on Cu-rich particles and/or precipitation of copper cations. However, these compounds that act efficiently on Cu-rich particles are more or less toxic or noxious. In line with environmental protection requirements, toxic inhibitors that are widely used in industrial processes should be replaced with new environmentally friendly inhibitors.

Certain dithiols as 1-pyrrolidine dithiocarbamate (PDTC) inhibit ORR on Cu electrodes [16–18]. PDTC is a non-toxic product widely used in agricultural and medical applications [19] and may therefore provide an alternative to chromate-based inhibitors. PDTC

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was shown to inhibit corrosion of steel water pipes in different corrosion media [20]. Recent works on copper corrosion inhibition in 0.5 mol L^{-1} HCl by PDTC [21] showed that this compound is able to interact with copper to form a self-assembled monolayer allowing a high inhibition efficiency to be obtained (up to 95.3%). Moreover, the authors showed that the sulphur atoms in the PDTC are the main active sites for the adsorption on the copper surface.

Our previous works [22] with PDTC showed, besides inhibition of ORR, the formation of a highly barrier film on copper in 0.2 g L^{-1} NaCl. This film constitutes a partially blocking surface to diffusion-limited reactions. Preliminary tests on 2024-T3 aluminium alloy [23] showed that PDTC decreases considerably anodic and cathodic current densities of the alloy in 0.2 g L^{-1} NaCl and shifts the open circuit potential towards cathodic values. However, PDTC has no inhibitive effect on pure Al in the same medium suggesting that PDTC interacts solely with the Cu-rich particles. To understand this interaction in more detail, it seemed important to estimate its action on copper in chloride media.

It is clear that the main objective of this work is to study Cu/PDTC system to understand the inhibitive behaviour of PDTC on Al 2xxx alloys in chloride media. However, this work is in itself relevant to inhibition of pure copper since corrosion inhibition of Cu by PDTC is scarcely reported in the literature. By selecting PDTC, the major aim of the present work focuses on its influence on general corrosion of copper in 0.5 mol L^{-1} NaCl solution. Electrochemical experiments were carried out to study the behaviour of the copper/solution interface in the presence of different concentrations of PDTC.

2. Experimental

2.1. Electrodes

The disk electrodes were made of copper cylinder rod (Good-fellow) of 5 mm in diameter. First, the lateral part of the cylinder was covered with cathaphoretic paint (PGG W975 + G323) to avoid the electrolyte infiltration. The copper rod was then embedded into allylic resin or thermal shrinking sheath. 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 vapour deposited on both the free faces of the quartz crystal blade to impose electrical field for oscillation. One of the faces was used as working electrode and, for this purpose copper was electro-deposited on the gold electrode from 0.5 mol L^{-1} $\text{CuSO}_4 + 0.5 \text{ mol L}^{-1}$ H_2SO_4 solution by a cathodic current of 30 mA cm^{-2} for 6 min. In these conditions, the mass of deposited copper was about 3.5 mg cm^{-2} or $4 \mu\text{m}$ thick. The deposit thus obtained was polycrystalline and compact. The nominal resonant oscillation frequency of quartz blade was 6 or 9 MHz. For 6 MHz quartz crystals, experimental calibration measurements gave $1 \mu\text{g cm}^{-2}$ of the mass loss corresponding to the increase of oscillation frequency of 164 Hz [24–26]. Measurements were carried out with a lab-made device and monitoring program.

The working electrode was set close to the centre of the electrolysing 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 liquid junction potential. No correction for the ohmic drop was made since its effect is negligible for analyses of polarization curves. The counter electrode was a platinum grid of large surface area set close to the cell wall.

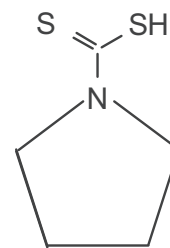


Fig. 1. 1-Pyrrolidine dithiocarbamate ($M = 147.26 \text{ g mol}^{-1}$).

2.2. Electrolytes

The blank corrosion test solution was 0.5 mol L^{-1} NaCl to which 10^{-4} , 10^{-3} , or $10^{-2} \text{ mol L}^{-1}$ of PDTC 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 . The molecular structure of PDTC is presented in Fig. 1. This molecule has three heteroatoms: one nitrogen and two sulphur atoms, thus possesses high possibilities of adsorption on metal surface conferring a good candidate for the corrosion inhibitor. This substance is considered an irritant but is otherwise innocuous [27].

2.3. Surface analysis

The surface morphology of copper electrode was investigated with a LEICA STEREOSCAN 440 scanning electron microscope (SEM) and element analyses were performed with an energy dispersive X-ray analyser (EDX; Princeton Gamma-Tech[®]).

2.4. Electrochemical measurements

For coulometric experiments to evaluate the amount of copper corrosion products accumulated at the electrode surface, the specimen was first immersed in the corrosion test solution without or with PDTC during 1 or 24 h at the open circuit conditions. Then, the copper electrode was immediately rinsed with deionized water and transferred to a borate buffer solution; $10^{-2} \text{ mol L}^{-1}$ $\text{H}_3\text{BO}_3 + 10^{-2} \text{ mol L}^{-1}$ $\text{Na}_2\text{B}_4\text{O}_7$ (pH 9). In this solution, corrosion products were reduced at the current density equal to $-50 \mu\text{A cm}^{-2}$. The solution was purged of oxygen by Ar bubbling before the experiments and then Ar was flowed over the electrolyte surface [28].

Polarization measurements were carried out in a conventional three-electrode cell. The disk working electrode was stationary and faced towards the cell bottom. Electrochemical measurements were performed after 1 or 24 h immersion (if not specified differently) in the test solution with or without the inhibitor.

The voltammetric and impedance measurements were carried out using a Gamry potentiostat/galvanostat Model FAS-1 or 300C. Polarization curves were plotted from two independent measurements in a new test solution for each run: one from the open circuit potential towards about -1.5 V after 1 or 24 h immersion period, and another from the open circuit potential to about $+1.5 \text{ V}$ at the potential scan rate of 1 mV s^{-1} . 5–10 replica experiments were carried out for each experimental condition. In spite of careful experimental manipulations, the open circuit corrosion potentials were not as reproducible as expected, and changed by about $\pm 50 \text{ mV}$. Therefore, instead of the mean value, the most representative one was presented in this paper.

The impedance measurements were performed with $10 \text{ mV}_{\text{rms}}$ from 100 kHz to 10 mHz by 10 points per decade during 48 h. For parameter regression calculation procedure, sometimes high frequency data (for instance beyond 40 kHz) were deleted since some instrumental and systematic error was observed, especially when

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