



Contents lists available at ScienceDirect

Corrosion Science

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

Protection of copper against corrosion in simulated urban rain by the combined action of benzotriazole, 2-mercaptobenzimidazole and stearic acid

Gregor Žerjav, Ingrid Milošev*

Jožef Stefan Institute, Department of Physical and Organic Chemistry, Jamova 39, SI-1000 Ljubljana, Slovenia

ARTICLE INFO

Article history:

Received 16 October 2014

Accepted 13 May 2015

Available online xxx

Keywords:

- A. Copper
- B. Polarization
- B. Weight loss
- B. EIS
- B. SEM
- C. Acid inhibition

ABSTRACT

Inhibition of corrosion of copper in simulated urban rain was studied using the self-assembly of benzotriazole, 2-mercaptobenzimidazole and stearic acid in ethanol solution, as individual inhibitors and in combinations. The morphology of layers differed greatly. Electrochemical measurements and weight loss immersion test revealed differences in the inhibitory action of the compounds, individually and combined. The results rule out benzotriazole as a possible inhibitor, unless combined with stearic acid. In contrast, 2-mercaptobenzimidazole gave good results, and even better in combination with stearic acid. Surface roughness, 3-D topography and contact angles were deduced. The optimal procedure was established for each inhibitor.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Copper is commonly used in many fields for different applications in various environments, including those that promote corrosion attack. There are several ways of conferring protection, including the formation of anodic films and treatment with organic inhibitors [1–4]. Numerous studies have been carried out using benzotriazole, one of the most effective inhibitors for copper and copper alloys in different environments [5–12]. It is a heterocyclic organic compound consisting of benzene and triazole rings with the formula $C_6H_5N_3$. In addition to its high effectiveness, the advantages of benzotriazole are low price and low toxicity [6]. While its effectiveness as an inhibitor is good in basic and near-neutral solutions, it is rather poor in acidic solutions due to the higher solubility of benzotriazole layers at low pH [13]. One solution of this problem could be to synthesize a benzotriazole derivative that has a greater inhibitory activity under these conditions. Since the S atom has a strong affinity for Cu, heterocyclic compounds containing a mercapto group have been explored as copper corrosion inhibitors [14,15]. Given the effectiveness of imidazole inhibitors, another route could be to investigate mercapto-imidazole compounds as Cu corrosion inhibitors, e.g. 2-mercaptobenzimidazole [16–19].

2-Mercaptobenzimidazole is more effective than benzotriazole in achieving good corrosion protection of copper in aerated aqueous HCl environments [16]. 2-Mercaptobenzimidazole ($C_7H_4N_2S$) contains a sulphur atom, presumably involved in forming a thick polymeric film that is strongly adsorbed on the Cu surface [18,19].

Another way to protect a metal against corrosion is to make its surface hydrophobic and thus not wetted by aqueous liquids. Carboxylic acids ($CH_3(CH_2)_mCOOH$) have been used to generate hydrophobic surfaces on various metal substrates [20–25], including the copper-based substrates bronze and brass [26,27]. The length of the carbon chain affects the properties of the self-assembled layer on Al [20]. In our previous study it was shown that long chain carboxylic acids such as stearic acid provide the most effective barrier to corrosion of Cu and brasses in simulated urban rain [28].

The aim of the present work was to investigate whether better corrosion protection of copper in simulated rain can be achieved by using a combination of individual corrosion inhibitors. Two types of inhibitors have been explored, benzotriazole and 2-mercaptobenzimidazole, both known as effective corrosion inhibitors for copper in other media e.g. HCl, NaCl [5–11,13,15–19], and stearic acid as a carboxylic acid investigated mainly as a means of corrosion inhibition achieved through increased hydrophobicity of adsorbed layers [26–28]. In the majority of studies the 2-mercaptobenzimidazole and benzotriazole inhibitors were added to the solution in which electrochemical tests were carried out.

* Corresponding author. Tel.: +386 14773452.
E-mail address: ingrid.milosev@ijs.si (I. Milošev).

Only in a few studies was the layer formed by immersion during pre-treatment [18,19]. In the present study we assessed several procedures for pre-treating copper by self-assembling of the inhibitor in solution before testing the resistance of the modified samples to corrosion in simulated urban rain. The surface of Cu was first modified using individual inhibitors (stearic acid, benzotriazole and 2-mercaptobenzimidazole). Two different procedures were then explored, both involving combinations of inhibitors: binary layers obtained by successive immersion in solutions of organic inhibitor and SA, and immersion in a mixture of organic inhibitor and SA. The aim was to select the optimal combination of inhibitors and the best way to modify the surface in order to achieve long-lasting protection. Diverse analytical methods were used, including electrochemical performance, gravimetric testing and analyses of contact angle, surface topography and morphology.

2. Experimental

2.1. Material and chemicals

Samples in the form of discs 15 mm in diameter were cut from 2 mm thick copper foil. The foil (99.95% purity) was supplied by Goodfellow Cambridge Ltd. Stearic acid (octadecanoic acid, $C_{18}H_{36}O_2$, purity 97%) was supplied by ACROS-Organics. Benzotriazole (1 H-benzotriazole, purity > 98%, $C_6H_5N_3$) was provided by Fluka and 2-mercaptobenzimidazole (purity > 98%, $C_7H_6N_2S$) by Sigma Aldrich. Stearic acid, benzotriazole and 2-mercaptobenzimidazole were dissolved in absolute ethanol (Carlo Erba, purity 99.9%).

Electrochemical measurements were performed in simulated urban rain solution containing 0.2 g/L Na_2SO_4 (Merck, purity 99%), 0.2 g/L $NaHCO_3$ (Sigma Aldrich, purity $\geq 99.5\%$), 0.2 g/L $NaNO_3$ (ACROS-Organics, purity > 99%) and deionized water (Milli-Q water, resistivity 18.2 M Ω cm). The pH of the solution was lowered with 10% H_2SO_4 (Carlo Erba, purity 96%) to a value of 5 to simulate the acid rain found in polluted urban environments. 10% HNO_3 (ACROS-Organics, 60%) solution was used for etching the copper.

2.2. Sample preparation

Copper discs were ground using, successively, 1200, 2400 and 4000-grid SiC emery papers (provided by Struers, Ballerup, Denmark), cleaned ultrasonically in ethanol for 5 min, rinsed with deionized water and dried in a stream of N_2 . They were then etched for 30 s in 10% HNO_3 . After etching, the discs were modified by exposure to the following compounds, under the appropriate conditions:

- immersion for 20 min in an 0.05 M ethanol solution of stearic acid (denoted SA),
- immersion for 1 h in an 0.01 M ethanol solution of BTAH (denoted BTAH),
- immersion for 1 h in an 0.01 M ethanol solution of 2-MBI (denoted 2-MBI),
- immersion for 1 h in an 0.01 M ethanol solution of BTAH followed by immersion for 20 min in 0.05 M ethanol solution of stearic acid (denoted BTAH/SA),
- immersion for 1 h in an 0.01 M ethanol solution of 2-MBI followed by immersion for 20 min in 0.05 M ethanol solution of stearic acid (denoted 2-MBI/SA),
- immersion for 1 h in an ethanol solution containing 0.01 M BTAH and 0.05 M stearic acid (denoted BTAH + SA),
- immersion for 1 h in an ethanol solution containing 0.01 M 2-MBI and 0.05 M stearic acid (denoted 2-MBI + SA).

After immersion, the samples were dried with a stream of N_2 and used for further investigation.

2.3. Electrochemical and immersion measurements

Electrochemical measurements were performed in simulated urban rain solutions at room temperature. A corrosion cell K0047 with a volume 1 L was used. The working electrode was embedded in a Teflon holder with exposed area 0.95 cm². A graphite electrode served as a counter electrode with saturated calomel electrode (SCE) as the reference electrode ($E = 0.224$ V vs. a standard hydrogen electrode). All potentials in the text refer to SCE scale. Measurements were performed using a potentiostat/galvanostat Parstat 2263 controlled by PowerSuite software. After stabilization at open circuit potential (E_{oc}), potentiodynamic measurements were made from 250 mV negative to E_{oc} up to 0.4 V, with a scan rate of 1 mV/s. The time of stabilization was varied from 1 h to 24 h. Electrochemical parameters (corrosion current density, j_{corr} , corrosion potential, E_{corr} , anodic and cathodic Tafel slopes, β_a , β_c) were determined by Tafel analysis using PowerSuite software. Experiments were repeated in triplicate and representative measurements are presented in graphical or tabular form.

Impedance spectra were obtained in the frequency range from 100 kHz to 5 mHz with 10 points per decade and 10 mV amplitude of the excitation signal. They were recorded after 1 h and 24 h immersion at the E_{oc} . The electrochemical process was modelled by electrical circuit elements using EIS spectrum Analyser 1.0 software.

Corrosion was assessed by immersion of weighed samples for 14 days at 25 °C in 100 mL closed glass vials containing simulated urban rain. A Metler Toledo AB104-S scale was used. After immersion the specimens were rinsed with Milli-Q water, dried with a stream of nitrogen and again weighed. Each experiment was carried out in triplicate. Results are presented as mean weight loss \pm standard deviation. Prior and after the immersion test the morphology, topography and contact angle of the surface were examined.

2.4. Measurements of surface morphology, topography and contact angle

The morphology of modified samples was characterized by field-emission scanning electron microscopy (FEG-SEM, Jeol, JSM-7600F) at an energy of 3 kV. Prior to analysis the samples were coated with a thin layer of gold.

Surface topography was analyzed employing a profilometer, model Bruker DektakXT. The instrument has a lateral resolution of 1 μ m and vertical resolution of 5 nm. The surface profile is measured in one direction. Measurements were performed on three 1 mm² spots of each sample and averaged. Data were processed with TalyMap Gold 6.2 software to create 3-D surface topography and to calculate the mean surface roughness (S_a). Results are presented as mean surface roughness \pm standard deviation. Corrections were made to exclude general geometrical shape and possible measurement-induced misfits.

Contact angles (θ) were measured using a tensiometer Krüss DSA 20 (Krüss GmbH, Hamburg, Germany). The drop-shape analysis software enables the fitting of the image of a deionized water drop on the sample surface and allows precise determination of the contact angle. Each reported contact angle value is the mean of at least three measurements made on different locations of the same sample. Results are presented as mean contact angle \pm standard deviation.

Download English Version:

<https://daneshyari.com/en/article/7895260>

Download Persian Version:

<https://daneshyari.com/article/7895260>

[Daneshyari.com](https://daneshyari.com)