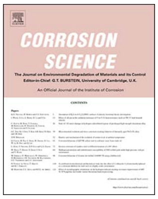
Corrosion Science xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Corrosion Science

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



Coupling of electrochemical, electrogravimetric and surface analysis techniques to study dithiocarbamate/bronze interactions in chloride media

W. Qafsaoui[a,*], A. Et Taouil[b], M.W. Kendig[c], H. Cachet[d], S. Joiret[d], H. Perrot[d], H. Takenouti[d]

[a] Laboratoire de l'Eau et de l'Environnement, Faculté des Sciences d'El Jadida, BP 20, El Jadida, 24000, Morocco
[b] Institut UTINAM, UMR 6213 CNRS, Université de Bourgogne Franche-Comté, 30 Avenue de Observatoire, 25009 Cedex, Besançon, France
[c] Kendig Research Associates LLC, 496 Hillsborough, Thousand Oaks, CA, 91361, USA
[d] Sorbonne Universits, UPMC Univ Paris 06, CNRS, Laboratoire Interfaces et Systèmes Electrochimiques, 4 place Jussieu, Paris, F-75005, France

ARTICLE INFO

Keywords:
A. Bronze
B. Polarization
B. EIS
B. Raman spectroscopy
B. XPS
C. Neutral inhibition

ABSTRACT

Interaction between ammonium pyrrolidinedithiocarbamate (PDTC) and bronze in 30 g L^{-1} NaCl was investigated at several concentrations between 0.1 and 10 mM by means of various electrochemical and spectroscopic techniques. Electrochemical measurements revealed a fast adsorption process of PDTC on Cu and Pb and the formation of a thick insulating and protective film with a high surface coverage. At high concentrations, PDTC prevents oxides formation. Surface analyses confirm PDTC adsorption on bronze mainly via interaction between sulphur atoms and Cu sites to form Cu^{I}-PDTC complex.

1. Introduction

Bronzes (Cu-Sn based alloys) are among the first alloys developed by mankind to make different tools especially sculptures, weapons and armors. Nowadays, they are still widely used in metal industry in various application area including networking sectors [1–3] or lithium battery electrode materials [4,5] thanks to their good conductivity and resistance to corrosion. Bronzes are copper alloys containing generally 1–10% of tin. They also may contain other elements such as lead, zinc, manganese, aluminium, silicon or iron depending on the variety. Mechanical properties strongly depend on the composition of bronze, especially the amount of tin which make it more resistant to wear.

In natural environments (soil, sea, atmosphere, etc.), the bronze surface undergoes corrosion and becomes overtime covered by a spontaneous degradation layer named "patina"[6–8] and exhibiting a passive behaviour. Indeed, many archeological bronze artefacts were properly conserved through formation of thick corrosion products layer formed while the object was in long contact with various media. Nevertheless, when the archeological object is extracted, sudden change of environment can accelerate corrosion process and may lead to fast complete decomposition of the object. As a consequence, methods for improving protection of bronze substrate or the reinforcement of protective property of patina layer are needed to offer less control to this phenomenon. In order to do so, the use of corrosion inhibitors has proven its efficiency and presents many advantages like easiness of application and reasonable cost.

Dermaj et al. studied the effects of an organic corrosion inhibitor: 3-phenyl-1,2,4-triazole-5-thione on corrosion behaviour of a bronze. They evidenced an inhibiting effect increasing with both inhibitor concentration and sample immersion time [9]. Other works [10,11] were devoted to the effects of organic inhibitors on copper corrosion as the corrosion of bronze is assimilated to that of copper since corrosion products are mainly copper mineral compounds [6–8]. Chemical structure and adsorption mode are important parameters in term of corrosion protection efficiency. The presence of heteroatoms like sulphur, nitrogen or phosphorus are of importance in chemical structure of inhibitor to permit binding with copper substrate [12]. Various works report the efficiency of sulphur-containing molecules for copper corrosion inhibition [13–20]. Heteroaromatic compounds have been particularly studied and proved to provide good protection. Among them, benzotriazole (BTAH) is one of the most famous [21–25]. A mechanism involving the formation of a Cu^{I}-BTA complex was proposed [26]. The formation of such Cu^{I}-organic complex was also observed for other organic inhibitors such as mercaptobenzothiazole [16] or methyl mercapto-phenyl amino butanate [27]. Among the innoxious thiadiazole derivatives, 2-amino-5-mercapto-1,3,4-thiadiazole [12,28], 2-amino-5-ethylthio-1,3,4-thiadiazole [29,30], and 2-acetamino-5-mercapto-1,3,4-thiadiazole [31] showed good corrosion inhibitive effect on copper or bronze in different aggressive media. For several years, the non-toxic ammonium pyrrolidinedithiocarbamate (PDTC), used in agriculture

---

* Corresponding author.
E-mail addresses: wqafsaoui@gmail.com (W. Qafsaoui), abdeslam.et_taouil@univ-fcomte.fr (A.E. Taouil), martin.kendig@verizon.net (M.W. Kendig), hubert.cachet@upmc.fr (H. Cachet), suzanne.joiret@upmc.fr (S. Joiret), hubert.perrot@upmc.fr (H. Perrot), hisasi.takenouti@upmc.fr (H. Takenouti).

https://doi.org/10.1016/j.corsci.2017.10.034
Received 3 July 2017; Received in revised form 22 October 2017; Accepted 31 October 2017

Please cite this article as: Qafsaoui, W., Corrosion Science (2017), http://dx.doi.org/10.1016/j.corsci.2017.10.034

and medicine [32], has risen interests as corrosion inhibitor: this compound proved to bring efficient corrosion inhibition towards steel corrosion [33]. Recent studies investigated the use of PDTC as corrosion inhibitor for copper. It was shown that PDTC forms a self-assembled layer through sulphur/copper interactions [34]. In previous works we showed that the protective effect of PDTC might be explained by the formation of a highly stable Cu^{I}-PDTC complex on copper surface that leads to decrease in rate of anodic dissolution and of oxygen reduction reaction [35,36]. Moreover, we carried out similar studies on AA 2024-T3 aluminium alloy that showed good corrosion protection by PDTC thanks to the formation of an adsorbed layer on Cu-rich particles [37].

As far as we know, no study has been dedicated to corrosion protection of bronze by PDTC. Therefore, the aim of this work is to investigate the behaviour of PDTC modified bronze samples exposed to corrosive conditions i.e. chloride medium. Different electrochemical and spectroscopic techniques were used to study the adsorption of PDTC on bronze, the chemical structure of the grafted molecule, the surface morphology and the behaviour of the bronze/solution interface in the presence of different concentrations of PDTC.

2. Experimental methods

2.1. Chemicals and materials

All chemicals (sodium chloride and ammonium pyrrolidinedithiocarbamate) were purchased form Sigma Aldrich (analytical grade) and used as received without further purification. The disk electrodes were made of 5 mm diameter cylindrical rods of pure Cu, Sn, Pb, Zn (Goodfellow, 99.999% of quality) and Bronze B3 which is an industrial bronze used in aerospace and automobile industries, containing 10.5–13 in wt% of Sn and corresponding to the AFNOR norm “CuSn12”. Its composition is given in Table 1. Fig. 1 clearly evidenced a dendritic structure and non-miscible lead (white globules in Fig. 1a). The center of the dendrite (region A) is rich in Cu and its periphery (region B) is rich in Sn (Fig. 1b). The material is thus an alpha-cored bronze. The dendrite composition, determined by EDS analysis, is reported in Table 2. Moreover, the low amounts of Zn and Ni are uniformly distributed (Fig. 1c and d) in the Cu-Sn matrix in contrast to Pb (Fig. 1e and f) which is localized in the interdentritic spaces.

The materials rods were embedded into allylic resin or a thermal shrinking sheath. Prior to this preparation, the lateral part of the cylinder rod was coated with a cataphoretic paint (PGG W975 + G323) to avoid the electrolyte infiltration. The electrode surface was then abraded under running water just before experiments, by rotating silicon carbide paper up to 1200 grade, and then rinsed thoroughly with deionized water.

2.2. Electrochemical measurements

Electrochemical measurements were carried out in aqueous solutions in a conventional three-electrode cell, using a Gamry potentiostat/galvanostat Model FAS-1 or 300C. The reference electrode was a saturated calomel electrode (SCE) and all the potentials measured were referred to SCE. The counter electrode was a platinum grid of a large surface area set close to the cell wall. The working disk electrode was faced towards the cell bottom under stationary conditions without electrolyte stirring. Test solution was $30\ g\ L^{-1}$ NaCl to which 10^{-4}, 10^{-3} or $10^{-2}\ mol\ L^{-1}$ of PDTC was added as corrosion inhibitor. For each experiment, 100 mL of electrolyte was used. The corrosion test was carried out under temperature control (20 °C) without purging dissolved oxygen. Three replica experiments were carried out for each experimental condition.

2.2.1. Electrochemical polarization

Polarization measurements were performed after one hour immersion in the test solution with or without PDTC. The curves were plotted from two independent measurements in a new test solution for each run: one from the open circuit potential towards about −2 V/SCE, and another from the open circuit potential to about +1.5 V/SCE at a potential scan rate of $1\ mV\ s^{-1}$.

2.2.2. Electrochemical impedance

The impedance measurements were performed with $10\ mV_{rms}$ from 100 kHz to 10 mHz taking 10 points per decade at different immersion times up to 24 h. Experiments were carried out at open-circuit potential. The data were fitted by Simad software, a lab-made software using a simplex regression method.

2.2.3. Electrochemical quartz crystal microbalance

For EQCM (Electrochemical Quartz Crystal Microbalance) experiments, two $0.2\ cm^2$ gold electrodes were vapour 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 bronze were vapour deposited onto the gold electrode through radio frequency plasma assisted sputtering from an industrial bronze target. Sputtering, carried out under 2 Pa of argon gas, lasted 20 min producing sputter-deposited bronze of about 1 μm thick. Fig. 2 shows the surface morphology of the alloy deposit. Note that the deposit appeared homogeneous without enriched regions in a dendritic structure. Clearly, the composition and microstructure of the vapour deposited layer differ from those of the solid alloy. However it is interesting to see how PDTC interacts with the uniformly dispersed alloying elements.

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

2.3. Surface analyses

2.3.1. Scanning electron microscopy (SEM)/Energy dispersive spectroscopy (EDS)

The surface morphology and the composition of the surface films were investigated using a field emission gun scanning microscope (FEG-SEM, Zeiss, Ultra 55) coupled with energy-dispersive X-ray spectroscopy (EDX). Element analyses were performed with a Quantax Bruker detector and data were analyzed by the Bruker Esprit software.

2.3.2. Raman micro-spectroscopy

Raman micro-spectroscopy analyses were carried out with a Labram-Jobin-Yvon spectrometer. The samples were irradiated with a He-Ne laser at λ = 632.8 nm. The laser power was varied between 0.1 and 1 mW to avoid any thermal effect on sample during the analyses. A confocal microscope was used and the investigated area was limited to $5\ \mu m^2$ using an Olympus 80× Ultra Long Working Distance (ULWD) objective lens.

Table 1
Composition of the industrial bronze.

	Cu	Sn	Zn	Pb	P	Ni	Fe	Al	Mn
at%	91.050	6.227	1.570	0.482	0.282	0.280	0.104	0.0123	0.00011
wt%	85.61	10.93	1.519	1.48	0.130	0.243	0.086	0.00491	0.00009