Surface Science 605 (2011) 121–130

Contents lists available at ScienceDirect

Surface Science

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

# Comparative AFM nanoscratching tests in air of bulk copper and electrogenerated cuprous oxide films

Lila Chaal [a,b,c], Catherine Debiemme-Chouvy [b,c], Claude Deslouis [b,c], Georges Maurin [b,c], Alain Pailleret [b,c,*], Boualem Saidani [a]

[a] Laboratoire de Technologie des Matériaux et de Génie des Procédés, Equipe Electrochimie et Corrosion, Faculté de la Technologie, Université A. Mira – Béjaia (06000), Algeria
[b] CNRS, UPR 15, Laboratoire Interfaces et Systèmes Electrochimiques, (LISE, case courrier 133), 4 Place Jussieu, F-75005, Paris, France
[c] UPMC Univ Paris 06, UPR 15, Laboratoire Interfaces et Systèmes Electrochimiques, (LISE, case courrier 133), 4 Place Jussieu, F-75005, Paris, France

ARTICLE INFO

*Article history:*
Received 4 July 2010
Accepted 2 October 2010
Available online 20 October 2010

*Keywords:*
Nanoscratching test
Atomic force microscopy (AFM)
X-ray photoelectron spectroscopy (XPS)
Cuprous oxide
Copper
Erosion–corrosion

ABSTRACT

The normal and lateral spring constants of rectangular silicon AFM cantilevers bearing pyramidal silicon tips were accurately calibrated using a procedure that takes into account their tilt compared to horizontal orientation and their trapezoidal cross section. Such systems were used to carry out nanoscratching tests in air on technical substrates presenting a moderate roughness (RMS≈40 nm) and made either from bulk copper or from cuprous oxide thin films electrogenerated on copper. The various events occurring during these nanoscratching procedures were characterized in details. In particular, the features of the scars appearing on the scratched zones and SEM observations of the AFM tips used during the nanoscratching procedures are described and exploited to establish a better understanding of the effects of the nanoscratching procedures on the targeted samples. In the case of electrodeposited $Cu_2O$ films, these effects are discussed with the help of chemical and structural characterizations using XPS and XRD studies. All this set of information is used i) to describe the history of the nanoscratching tests and ii) to compare mechanical resistance of bulk copper and electrogenerated $Cu_2O$ thin films using these nanoscratching tests carried out in air. The wear mechanism occurring during nanoscratching tests is discussed for both kinds of samples and compared with the one observed during erosion in erosion–corrosion tests.



## 1. Introduction

Erosion–corrosion phenomena are particular cases of corrosion. They result mainly from a fluid circulating at a fast flowing rate along a metallic surface. They are potentially influenced by geometrical characteristics of metallic installations. Erosion–corrosion phenomena are increasingly investigated nowadays as they potentially have a severe impact on the integrity of fluid networks in industry and pollution in environment. As an illustration, one can cite among the various installations or metallic parts exposed to such corrosion process, distribution networks of either cold or hot water, metallic structures in ports, pipelines, thermal exchangers, pumps, turbines or propellers for example. In fact, soft metals (copper and lead for example) as well as metals whose resistance to corrosion strongly depends on the stability of a superficial film (aluminum, stainless steels, other steels) are all expected, and were actually shown, to be indeed victims of erosion–corrosion phenomena. In the latter cases, turbulent flows may lead to a systematic and progressive destruction of the protective films (such as oxide films for example), which obviously results in very high corrosion rates for the bare metals. Such situation was indeed found to occur for stainless steels in artificial chlorinated media [1], carbon steels in seawater [2] as well as copper and copper alloys [3–5]. In a previous experimental investigation related to erosion–corrosion phenomena, cuprous oxide ($Cu_2O$) was chosen as an experimental model of moderately adherent protective coating of copper. It was exposed to erosion–corrosion risks produced by corrosive aqueous solutions under measurable and controlled flow conditions using a so-called rotating cage setup [6]. This choice was made on purpose so as to characterize the beneficial effect of hydrodynamic drag reducing agents, such as cationic surfactants, in erosion–corrosion situations.

Cuprous oxide is the most frequently encountered corrosion product of copper [7]. Its formation is known to depend on solution pH, potential of copper and composition of the electrolytic solution. For example, chloride traces deeply complicate and accelerate copper corrosion at the copper/aqueous solution interface. Cuprous oxide is also a well-known p-type semiconductor that presents moreover interesting optical and magnetic properties [8]. Lately, cuprous oxide received considerable attention due to its potential applications in solar energy conversion, nanoelectronics, magnetic storage devices, catalysis, biosensing and lithium ion batteries [8].

* Corresponding author. CNRS, UPR 15, Laboratoire Interfaces et Systèmes Electrochimiques, (LISE, case courrier 133), 4 Place Jussieu, F-75005, Paris, France. Tel.: +33 1 44 27 41 69; fax: +33 1 44 27 40 74.
*E-mail address:* alain.pailleret@upmc.fr (A. Pailleret).

0039-6028/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.susc.2010.10.009

Our long term objective is to correlate characteristic mechanical parameters of electrogenerated cuprous oxide films and bulk copper with the mechanical resistance they present during erosion–corrosion experiments carried out in our research group. During these latter experiments, critical shear stresses exerted by the moving fluids led to the partial removal of the cuprous oxide films electrodeposited on bulk copper.

In the frame of this contribution, our purpose was i) to show the feasibility of AFM nanoscratching tests on rather rough electrogenerated cuprous oxide films and bulk copper samples (RMS ≈ 40 nm), ii) to identify the various events occurring during these tests, and iii) to establish from these tests strategies leading to characteristic mechanical parameters of the targeted materials as well as to a better understanding of the observed wear mechanisms.

## 2. Experimental methods

Bulk copper samples were prepared from copper rods (diameter: 5 or 10 mm) purchased from Goodfellow (Purity 99.99%), which were coated with an insulating cataphoretic lacquer and subsequently embedded in an epoxy resin. The cross section of these copper rods was first polished on emery SiC paper up to 1200 grade, then on a microabrasive paper made from alumina deposited on polyester film (grain size 9 μm (MOA 9), ESCIL, Chassieu, France). The resulting copper electrodes were rinsed with demineralized water, then placed in an ultrasonic bath for 10 min, rinsed again, dried, and finally stored in a dessicator until testing. They were then used as samples for nanoscratching experiments of bulk copper or as working electrodes for the electrogeneration of cuprous oxide thin films. In this latter case, the retained electrochemical procedure implied a usual three electrode electrochemical cell including a platinum counter electrode and a mercury/mercurous sulfate saturated reference electrode (SSE). The three electrodes were connected to a SOTELEM potentiostat/galvanostat and used for the electrodeposition as well as for the electrochemical characterization of the resulting $Cu_2O$ films.

$Cu_2O$ films were electrogenerated by oxidizing anodically rotating copper disks in the galvanostatic mode in a corrosive aqueous solution containing $Na_2SO_4$ (0.1 M) and NaCl (1 mM) at pH 8. In this purpose, the copper electrode was polarized for 1 h at a current density of 1 mA/cm$^2$ while its rotation speed was kept constant at 100 rpm. These experimental conditions were close to those used in an earlier work dealing with the behaviour of copper covered with a copper oxide layer in neutral media in erosion–corrosion experiments [9]. Moreover, pH was raised to slightly alkaline values so as to promote efficiently the formation of cuprous oxide layers according to Pourbaix' diagram of copper. Little NaCl amounts were also added to the electrolytic solution in order to prevent cuprous oxide films from self-healing once they were partly pulled out during the erosion–corrosion experiments [6]. The presence of sodium chloride was thought to provoke a few morphological, and possibly mechanical, heterogeneities that were necessary to allow the resulting cuprous oxide films to offer a moderate mechanical resistance to the erosion–corrosion tests.

In a second step, these electrogenerated $Cu_2O$ films were thoroughly characterized using *ex-situ* techniques such as X-Ray Diffraction (XRD), and X-Ray Photoelectron Spectroscopy (XPS) as well as voltammetry.

XRD analyses were carried out using a horizontal goniometer (Philips) and a filtered Mo$K_\alpha$ source. The resulting diffractograms were interpreted by comparing them with JCPDS files.

XPS analyses were carried out at ITODYS laboratory (Paris, France) using a VG ESCALAB 250-iXL spectrometer. The X-ray source was monochromatic Al $K_\alpha$ radiation (1486.6 eV). Before analysis, the surface of the samples was etched with $Ar^+$ cations in order to remove the native oxide and/or the contamination layer (≈1 nm). The high-resolution spectra were recorded with a pass energy of 20 eV in the constant analyzer energy mode. The detection angle was 90° with respect to the sample plane. The photoelectron peaks were analysed after subtraction of the background calculated using Shirley's method.

AFM scratching and imaging experiments were carried out on copper working electrodes either freshly polished or coated with electrogenerated cuprous oxide thin films. For this purpose, these substrates were immobilized below the AFM tip of the Molecular Imaging AFM setup using a homemade sample holder. This setup was composed of a Pico-LE base equipped with a micro-positioning device allowing the precise positioning of the AFM tip in the x–y plane of the sample, a large zone AFM scanner (100 μm × 100 μm) bearing a photo-detector and the AFM nose adequate for tapping mode AFM (TM-AFM) experiments. A PicoScan 2100 controller connected to a computer was used to drive the scanner and to collect the data generated by the laser impact on the photo-detector. In this purpose, rectangular silicon cantilevers bearing pyramidal silicon tips were used. The resonance frequency and spring constant announced by the AFM tip provider were in the ranges of 260–365 kHz and 25–50 N m$^{-1}$ respectively. Nanoscratching and subsequent imaging experiments were carried out *ex-situ* in air using the contact and TM-AFM modes respectively. All AFM images shown hereafter underwent a tilt correction process.

The scanning electron microscopy (SEM) images were obtained with the help of an Ultra55 Zeiss field-emission gun-SEM (FEG-SEM) microscope.

## 3. Results

### 3.1. Theoretical considerations and experimental calibration of the tip/cantilever system

An accurate calibration of the cantilever/tip systems is crucial if one wants to extract quantitative and comparable information from force measurements or nanoscratching experiments carried out using an AFM equipment. The calibration procedure reported hereafter is easily applicable to most rectangular cantilevers as it does not necessitate any substrates or cantilever/tip systems elaborated especially for calibration purposes. As only rectangular cantilevers were used throughout this work, the force calibration was relatively simple. On its own, a cantilever immobilized at one end and bearing a pyramidal tip at the opposite end displays a mechanical behaviour that requires eight spring constants to be described accurately [10]. Although an analytical expression has been proposed for each of them in literature, only two of them, namely the normal spring constant, $k_N$, and the lateral spring constant, $k_L$, are systematically exploited for the quantitative determination of mechanical properties of materials using AFM [11]. They express the ability of the cantilever for simple normal bending and lateral friction (or torsion) respectively. These two major constants can be calculated for a cantilever beam with a rectangular cross section from the following expressions, respectively [10,11]:

$$k_N = \frac{3E_{Si}I}{L^3} \tag{1}$$

and

$$k_L = \frac{4G_{Si}I}{Lh^2} \tag{2}$$

$I$ is the moment of inertia of the cantilever beam. In the case of a rectangular cross section, $I$ can be calculated using the following expression:

$$I = \frac{wt^3}{12} \tag{3}$$