



# Study of the air-formed oxide layer at the copper surface and its impact on the copper corrosion in an aggressive chloride medium

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## ABSTRACT

The electrochemical behaviour of pre-oxidized copper surfaces prepared by heating in air at 90 °C was studied to evaluate the impact of the air-formed oxide layer at the copper surface on the corrosion in an aggressive chloride medium. In a first part, the evolution of the chemical composition and the structure of the air-formed oxide layer with the heating time were investigated by cyclic voltammetry in an alkaline medium in which the different oxide species can be discriminated, X-ray photoelectrons spectroscopy experiments (XPS) and water contact angle measurements. It was demonstrated that short heating times produce Cu<sub>2</sub>O-rich films, while CuO-rich films were obtained after long heating-time periods. Furthermore, cyclic voltammetric data strongly support a stratification of the corrosion products in the mature oxide layer. In a second part, the protection efficiency of air-formed films, aged from 1 to 22 days, against the copper corrosion was studied using a potentiodynamic technique and the electrochemical impedance spectroscopy (EIS) in an aerated 0.2 M NaCl aqueous electrolyte. Results demonstrate that the chemical composition of the air-formed oxide layer has an important impact in the overall corrosion process. Results are tentatively explained in terms of composition and structure of the oxide layer.

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## 1. Introduction

Copper is the preferred metal for electronic applications due to its high electrical conductivity. Unfortunately, copper is a poor corrosion resistant material and extensive research on the anodic dissolution of copper have been achieved to prevent its corrosion, especially in moist atmosphere and in sodium chloride solutions roughly equivalent to that of seawater [1]. Except at very low and very high pH values, copper in solution is rapidly under its passivate state and an increase of potential is accompanied by the formation of different oxide surface species, depending on the experimental conditions [2]. Although a thin layer of surface oxide species is expected to slow notably the kinetic of the corrosion process, it is well-known that the structure, thickness and chemical composition of the surface oxide film, have a profound impact on both the mechanism and the kinetic of the overall corrosion process of copper, including anodic and cathodic steps [3]. The anodic reaction consists in the copper electro-dissolution, while mainly the reduction of oxygen allows to

evacuate the electrons lost by the metal during the corrosion process in aerated media. The chemical impact of the oxide-layer on the copper corrosion process has been the subject of many studies and merits to be further pursued because copper is only viable as corrosion resistant material under its passive state [4].

Especially, the impact of surface-oxide species produced during storage in the open air is of concern to academic and industrial communities. To mimic the effects of a long-time period storage, a series of copper samples were pre-oxidized by heating in air at 90 °C for periods of time comprise between 1 and 22 days. The pre-oxidized specimens were systematically investigated by potentiodynamic polarization Tafel analysis and EIS in a 0.2 M NaCl aqueous electrolyte. Changes in surface chemistry were examined by XPS, cyclic voltammetry in an alkaline medium capable of distinguishing the different surface-oxide formed and water contact angle experiments. The main objective of this study is to investigate the influence of air-formed oxide films on the corrosion rate of copper.

## 2. Experimental section

Electrochemical measurements were achieved with a three-electrode cell configuration. All experiments were conducted at

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20 °C ± 0.1 °C. The counter electrode consists in a platinum wire and working electrodes consist in polycrystalline copper flat discs (99.99% pure) of 0.28 cm<sup>2</sup> geometric area freshly polished or pre-oxidized. Copper electrodes were first freshly polished with emery paper up to grade 800 and were thoroughly washed by sonication for 10 min in distilled water. Copper surfaces were further placed in an oven (from Memmert GmbH, model 300) at 90 °C ± 0.3 for time periods ranging from 1 to 22 days. The thermal treatment was conducted in air (under atmospheric oxygen pressure) and with a humidity less than 3%. All potential values are referred to a saturated calomel electrode (SCE). A potentiostat/galvanostat model VSP (from Bio-Logic) monitored by ECLab software was used. For the determination of the different surface oxides by cyclic voltammetry, an aqueous electrolyte containing 6 M KOH + 1 m LiOH was used and the scan rate of potential was 10 mV s<sup>-1</sup>. Polarization curves were recorded by linear sweep voltammetry (LSV) in 0.2 M NaCl, pH 6.5, at 1 mV s<sup>-1</sup>, starting at -0.5 V and stopping the anodic scan at 0.1 V, when the current density approach the value of 1 × 10<sup>-3</sup> A cm<sup>-2</sup>. The electrochemical impedance spectroscopy (EIS) were performed at the corrosion potential in the same aqueous chloride medium in the frequency range between 0.1 Hz and 100 kHz with a sinusoidal potential perturbation of 5 mV. EIS data were analysed using ZSimpWin 3.50 software (from PAR, USA). XPS measurements were performed with a Kratos Axis Ultra spectrometer using a Al K $\alpha$  monochromatic beam working at 1486.6 eV. Data were collected at room temperature and the operating pressure in the analysis chamber was kept below 5 × 10<sup>-9</sup> torr. All spectra were recorded in the CEA (constant analyser energy) mode with an analyser pass energy of 40 eV and XPS data treatment was performed with CasaXPS software. Contact angles were measured at room temperature using a GBX Digidrop MCAT instrument. A water droplet of 2  $\mu$ L were formed at the end of a syringe and deposited on the substrate.

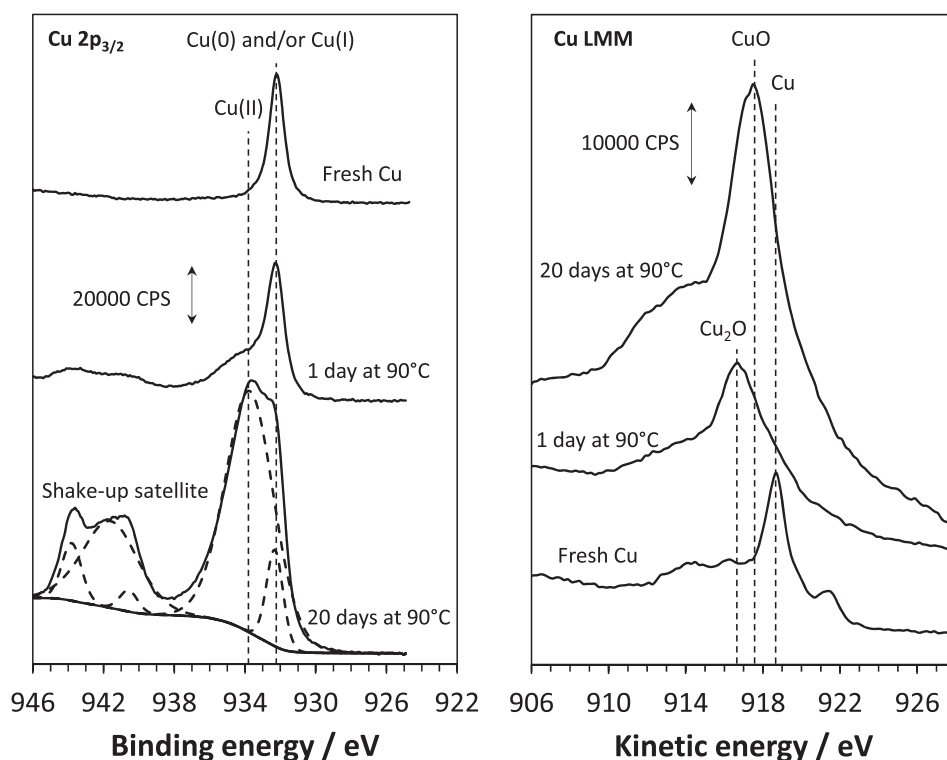
### 3. Results and discussion

#### (i) Characterization of air-formed oxide films at the copper surface.

Copper oxidation mechanism and composition of surface oxide films produced during thermal treatments under various atmospheres or storage in the open air, has been extensively studied [5,6]. When copper is heated under low or ambient oxygen pressure in dry environments, it is generally accepted that only a single Cu<sub>2</sub>O layer is formed, the growth of which increases with time exposure and temperature [7]. At higher oxygen pressures, duplex oxide films are obtained, consisting in an inner Cu<sub>2</sub>O and an outer CuO layers [8]. Beside oxygen pressure and temperature, the relative humidity (RH) is also considered as one of the most important parameters of copper corrosion in air, especially for atmospheric copper corrosion at low temperatures [9,10]. If the existence of Cu<sub>2</sub>O predominates under oxidation in air in the temperature range from 100 °C to 200 °C, water vapor is needed for the formation of CuO below 100 °C and has a similar effect to the temperature, accelerating the formation kinetic of the passive layer [11,12].

In this study, air-formed oxide layers produced in an oven at 90 °C for different times, were characterized by XPS, in order to follow the evolution of their chemical composition. After different time exposures, the copper specimens were immediately placed on an argon-filled petri dish right out of the oven, in order to minimize further atmospheric corrosion before XPS experiments. Fig. 1 shows the XPS spectra of the Cu2p<sub>3/2</sub> core level and the Auger spectra of Cu L<sub>3</sub>M<sub>4,5</sub>M<sub>4,5</sub> transition for freshly polished copper sample and for copper surfaces air-oxidized during 1 day and 20 days.

After a long heating time, the Cu2p<sub>3/2</sub> XPS spectrum shows clearly the presence of CuO with an intense XPS contribution at



**Fig. 1.** XPS spectra of the Cu 2p<sub>3/2</sub> region and Auger spectra of Cu L<sub>3</sub>M<sub>4,5</sub>M<sub>4,5</sub> transition for pure copper metallic surface and pre-oxidized specimens prepared by heating during 1 and 20 days.

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