



## Mathematical model of copper corrosion



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### ABSTRACT

A new partial differential model for monitoring and detecting copper corrosion products (mainly brochantite and cuprite) is proposed to provide predictive tools suitable for describing the evolution of damage induced on bronze specimens by sulfur dioxide (SO<sub>2</sub>) pollution. This model is characterized by the movement of a double free boundary. Numerical simulations show a nice agreement with experimental result.

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## 1. Introduction

Deterioration of copper and bronze artifacts is one of the main concerns for people working in cultural heritage [1]. More specifically, bronze, a copper-tin alloy, has been widely employed for daily-use and artistic purposes from the Bronze Age up to present. Conservation studies are based on a knowledge of the environmental conditions to which copper and copper alloys may be exposed and include all the information on the material technologies and the nature of the corrosion films or patina, which cover their surfaces. In particular a significant effort has been devoted to study the corrosion due to environmental conditions, such as temperature, moisture and the concentration of pollutants [2–4]. Although in recent years air pollution in European urban areas has decreased considerably, there still remain concentrations of pollutants such as sulfur dioxide (SO<sub>2</sub>) from combustion of fossil fuels, being one of the most important factors in the deterioration of bronze. Indeed SO<sub>2</sub>, mixed with water vapor, reacts to produce sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), which causes corrosion phenomena on copper surfaces and produces several corrosion products as basic copper sulphates, such as antlerite, posnjakite, brochantite [5]. The latter is the final product of several reaction steps, which can be approximated by two main chemical reactions: cuprite formation, which occurs after a few weeks of exposure to atmospheric conditions, and brochantite formation, which is the final reaction step (for more details on chemical background see Section 2.1) [6].

The complexity of corrosion processes creates the necessity for a quantitative model approach to develop predictive tools, which simultaneously provide both quantitative information as well as simulations of the various processes involved. These methods, similar to those introduced in [7], are useful for the monitoring and detection of surface alterations even before they are visible, making it possible to determine optimal intervention strategies. In this paper we introduce a new partial

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differential model, which is used to describe the evolution of damage induced on a bronze specimen by atmospheric pollution. It is based on fluid dynamical and chemical relations and it is characterized by a double free boundary: one between copper and cuprite, the other between cuprite and brochantite. A similar approach was first proposed in the seminal paper [8], and then explored in many other works, see for instance [9–11]. In our paper we apply this approach to metal corrosion, and we validate it by calibrating the model according to the experimental results in [12]. The paper is organized as follows: in Section 2.1 we analyze the main chemical corrosion phenomena and in Section 2.2 we review the main mathematical models already proposed in literature. The Section 3 is entirely focused on the description of the model's equations and the numerical schemes used, meanwhile in Section 4 we describe the experimental setting and the calibration of the model. Finally, in Section 5, we present the main results related to the simulations produced by our model and in Section 6 the related conclusions.

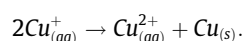
## 2. Modeling backgrounds

### 2.1. Chemical backgrounds

Most of the oxidation processes occurring on bronze metal artifacts, when exposed to environmental conditions, are electrochemical and involve interactions between the metal surface, the adsorbed moisture and various atmospheric gases (SO<sub>2</sub>, CO<sub>2</sub>, NO<sub>x</sub>, hydrocarbons) [13]. Electrochemical corrosion processes in electrolyte and condensed moisture layers have been the subject of extensive studies, based on numerous and different approaches [14–16]. When exposed to the atmosphere, copper and its alloys form a thin layer of corrosion, from brownish-green up to greenish-blue colors, which is designated as patina. In the case of copper in a low pollutant levels atmosphere, a native cuprite (copper (I) oxide or Cu<sub>2</sub>O) film of approximately a few nanometers thick, protects the metal surface from further oxidation. The general reaction is well described in literature, where, in aerated solution, copper can dissolve electrochemically forming copper (I) oxide formation, due to the reaction of copper with oxygen. It is represented by the following schematic reaction [17]:



However, in an aggressive environment, like urban atmosphere, the protective nature of this oxide layer is altered and there is the formation of a non-protective, multi-component, tarnish layer. When the copper is exposed to humidity and sulfur dioxide, three kinds of basic copper sulfate hydroxide are mainly produced: Brochantite Cu<sub>4</sub>SO<sub>4</sub>(OH)<sub>6</sub>, which is a well-known patina constituent, or other similar products like Antlerite or Posnjakite. In the following we focus our attention to the formation of Brochantite, which is the main observed product. Gaseous sulfur dioxide and sulfate particles are deposited on the electrolyte on the cuprite. Their deposition reduces the pH of the adsorbed water, and this promotes the dissolution of cuprous ion (Cu<sup>+</sup>) and its oxidation, thus forming cupric ions (Cu<sup>2+</sup>). In detail, copper (I) ions in solution disproportionate to give copper (II) ions and a precipitate of copper



When the cupric and sulfate ion concentrations in the electrolyte are high enough to form brochantite, this phase starts to precipitate on the cuprite [18,19]. In [20] it is indicated that, in the initial oxidation process, cuprite formation is followed by posnjakite, as a precursor phase to brochantite, see also [21], but we are going to neglect this intermediate transformations, due to the elevated speed of the reaction with respect to the time scale of the mathematical model which we are going to present.

### 2.2. Existing mathematical models

Graedel and his collaborators [22,23] have studied atmospheric copper sulfidation at AT&T Bell Laboratories in both experimental investigation and physical or mechanistic model development; furthermore a systematic investigation of copper sulfidation kinetics has been performed. In the paper [23] Tidblad and Graedel developed a model able to describe the SO<sub>2</sub> copper corrosion. Their work is based on aqueous chemistry and without considering spatial dimensions. In the paper [24], they introduce a model which describes the corrosion of copper exposed to moist air with a low SO<sub>2</sub> concentration. Here, they consider four stages in the development of a corrosion patina: the metal, a non-protective oxide film which has a high ionic transport property, an outer layer of corrosion products which can permit the penetration of water and gases and an external adsorbed water layer. More recently, Larson proposed in [25] a different model that describes the atmospheric sulfidation of copper by proposing a physical copper-sulfidation model that includes four distinct phases: the substrate metal, a cohesive cuprous sulfide (Cu<sub>2</sub>S) product layer, a thin aqueous film adsorbed on the sulphide and the ambient gas. Larson postulated that transport through the sulfide layer occurs via diffusion and electromigration of copper vacancies and electron holes. Later, in the 1990s, copper sulfation by SO<sub>2</sub> was investigated by Payer et al., who focused their attention on the early stage of corrosion in moist air (75% relative humidity (RH) at 25°C) with a sulfur dioxide concentration of 0.5%. The techniques employed (SEM, AES and TEM) allowed for an analysis and characterization of the oxide film (composed of

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