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Study of the corrosion behaviour of Cu–10Sn bronze in aerated Na_2SO_4 aqueous solution

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Abstract

Investigation of the electrochemical behaviour of Cu–10Sn (wt.%) alloy has been conducted in aerated aqueous sulphate solution and compared to that of pure Cu and Sn. *Eoc* versus time and cathodic and anodic polarizations have been performed as a function of the initial sulphate concentration, the rotation speed of the electrode and the immersion time. The surface layer have been characterized by scanning electron microscopy (SEM) and analyzed by energy dispersive spectrometry (EDS) and Fourier transform infrared spectroscopy (FTIR). The anodic behaviour evidences a Cu dissolution phenomenon on the corrosion layer limited by migration process rather than diffusion. The corrosion process conducts to preserve the original surface of the electrode and conducts to an internal growth at the layer/alloy interface, from the initial surface towards the unaltered substrate. The interphase behaviour is governed by the layer formed at *Eoc* under the experimental conditions and its evolution during the time. Hydroxyl-oxy and sulphate Cu and Sn compounds recover the surface and confer to the interface a blocking behaviour mainly due to the presence of the tin compounds in the layer. The global interphase behaviour matches the Type-I model of blocking adherent layer with decuprification phenomenon evidenced on archaeological bronzes.

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1. Introduction

Until recently, the current low industrial potential of bronze (Cu–Sn alloys) has generated little interest for characterizing the bronze corrosion outside the field of conservation and archaeometry. The dedicated goals of these sciences have resulted in many case-studies [1–3], which mainly led to an extensive knowledge of the diverse specific corrosion products composing the bronze 'patinas' [4]. Since the majority of the corrosion products were identified as copper products, it has often been assumed that the mechanisms of corrosion layer formation were similar to that of pure copper [4–6], sometimes involving a selective tin de-alloying [7,8].

However, several fundamental studies [9–12] have demonstrated the systematic presence of tin compounds within naturally formed patinas on single-phase or diphase tin bronzes in atmospheric, soil and aqueous environments. Tin compounds, which may be amorphous, yield almost to no exploitable X-ray diffraction signals compared to Cu(II) products but are always clearly evidenced by others analytical methods (EDS [9–15], XPS [16–18], LIBS [19], Raman [20,21]).

A generic model of the corrosion layers found on Cu–Sn alloys identifies two typical structures [10] taking also into account the composition of bronze patina layers. Type I mainly occurs in corrosive conditions of lower aggressiveness. It is defined by a relatively thin (several micrometer) tin-enriched layer, grown under and preserving the original surface of the alloy. Above this layer, an external crust of deposited products of copper(II) cations and anions of the environment is often observed. A mechanism of formation of the tin-enriched corrosion layer has therefore been proposed, involving a decuprification process through the layer, and the migration of environmental anions through it [10]. Type-II structure is commonly observed in the case of 'bronze disease', and occurs in local or general conditions of acute aggressiveness, often in presence of chloride anions. It is characterized in a distinctive three-layer thick structure, growing at the expense of the bulk alloy, possibly until its complete alteration.

This model allowed us to describe the formation of bronze patinas according to migration processes of cationic or anionic species throughout the corrosion layer. Recent electrochemical investigations have successfully demonstrated on synthetic Cu–Sn alloys the formation of Type-I corrosion structures, in an aerated, moderately aggressive sulphate electrolyte [9,12]. Other studies conducted in chloride medium or others electrolytes [15,18,21] or even in acetate vapour solution [22] have evidenced tin species in the corrosion layers but without clear conclusion on the type of corrosion. Recently, a preliminary study conducted [23] on an archaeological bronze (9.8 wt.% Sn) in different electrolytes revealed that the alloy dissolution was also depending on the pH and on the nature of the corrosive electrolyte and was stronger for pH below 8 obtained in sulphate or chloride solutions.

The purpose of this work is to investigate the corrosion behaviour of synthetic Cu–Sn alloys, in aerated aqueous electrolytes to explore the growth process of a Type-I structure conducting to the formation of tin enriched patina layer. For that purpose, sulphate electrolytes were used to electrochemically investigate the corrosion behaviour of Cu–Sn