



Effect of *Pseudomonas fluorescens* on the electrochemical behaviour of a single-phase Cu-Sn modern bronze

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ABSTRACT

The corrosion behavior of a modern bronze (12 wt% Sn) is studied during 100 h of exposure to a *Pseudomonas fluorescens* culture. Bacteria colonization, preferentially occurring in the form of black spots, caused an ennoblement of the open circuit potential and a decrease of the pitting potential. *Eriochoalite* (CuCl₂·2H₂O) and *Nantokite* (CuCl) were found in the micro-pits detected under the biofilm, associated to a local pH decrease. Electrochemical measurements *via* impedance spectroscopy revealed a decrease of the charge transfer resistance, which is attributed to the bacteria involvement in the process of passive layer development.

1. Introduction

Bronze artifacts can be subjected to microbial corrosion to a great extent during their long life-cycle in natural environments. Nevertheless, the influence of microorganisms on the corrosion mechanism of archeological artifacts has seldom been considered and little literature on the subject is currently available [3–6]. Particularly in the case of bronze, a generalized form of corrosion is usually reported, whose specific corrosion products and morphologies are ascribed to the chemical and physical characteristics of the environment [1,2].

Microbiological corrosion is a combination of many factors, which are usually difficult to detect altogether. Indeed, bacteria influence the corrosion process releasing metabolic products and creating a biofilm that interferes in different ways with the metal surface [7–10].

Mechanisms as differential aeration, selective leaching, corrosion under deposit, cathodic depolarization, metal ion binding by extracellular polymeric substances (EPS), have been suggested, all assumed to be the cause of a development of localized forms of corrosion [12–15]. The ennoblement of corrosion potential of passive metals or alloys in presence of bacteria in any type of environment, from fresh water to estuarine or marine water, is also widely confirmed by literature data [11–14].

In natural environments, bacteria synergistically act in a consortium on conductive surfaces and not as single species, optimizing the use of resources in sustaining their aerobic or anaerobic metabolisms. Nevertheless, literature studies highlight the influence of single bacteria

species on corrosion of materials, including copper and copper alloys [10,16–19]. For instance, *Sphingomonas* spp. [16,19], *P. paucimobilis*, *Rhodotorula* spp. and *Flavobacterium* spp. [17], *Acidovorax* spp. [19], *Cytophaga johnsonae*, and *Micrococcus kristinae* [18], have been identified in biofilms that cause MIC in copper pipes. Furthermore, *Shewanella oneidensis*, many strains of *Pseudomonas* spp. (*Aeruginosa*, *Fluorescens*, *Putida*, etc.) and *Escherichia coli* become tolerant towards copper ions and survive in adverse conditions [7–9].

Many heavy metals, such as copper, iron, and zinc, are required in trace amounts for bacterial growth even if they are toxic when present in excess [20]. In particular, copper induces oxidative stresses that can damage the cell membrane through lipid peroxidation, leading to membrane permeability and cell death [21]. However, the relatively high adaptability towards copper ions of bacteria is normally attributed to a genetic transformation of the colonies [22]. Furthermore, recent studies stated the possibility that those mutant genes are also responsible for binding appreciable amounts of Cu(II) and Zn(II) ions from aqueous solutions [22–24].

Aerobic bacteria such as *Pseudomonas* spp. were detected in marine biofilms on corroding copper alloys [10] but also in other kind of biofilms, on different conductive materials [25]. In fact, they are bacteria able to attach to the surface, producing an oxygen free environment *via* respiration and creating oxygen or ion concentration cells [26,27] causing pitting [28–30]. Many other mechanisms have also been suggested, including passivity breakdown or cathodic reduction by catalase enzymes [31,32].

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In this work, the corrosion behavior of a binary Cu-Sn modern (12% wt) alloy was investigated in the presence and absence of *Pseudomonas fluorescens*, in aqueous solution containing mixed chlorides, nitrates, sulphates and carbonates, simulating a natural condition of stagnant fresh water. The alloy chosen for the investigation was subjected to a thermal treatment in order to eliminate the more anodic eutectoid $\alpha + \delta$ phase arising from the interdendritic areas of the α -phase matrix. This way, the α -phase entirely constituted the matrix, avoiding any electrochemical unbalances at the interface with the solution, causing differences in the reactivity of the bacteria with the substrate [33]. The choice of a *Pseudomonas* strain was due to the special ability of these bacteria to survive in presence of a solution rich of copper ions [34–36]. The aim of the study was to verify, using electrochemical techniques, the adaptability of those bacteria to tin-bronzes and their ability to shift corrosion equilibria. Open circuit potential (E_{oc}) measurements, polarization curves and electrochemical impedance spectroscopy (EIS) were carried out on alloys specimens, supported by post-experiment observations of the corroded surfaces.

2. Materials and methods

Pure cultures of *Pseudomonas fluorescens* strain N3 [37] were grown at 32 °C in sterile artificial fresh water (AFW) [38] amended with 0.06% peptone, under continuous shaking. The mineral base composition of AFW was: $MgSO_4 \cdot 7H_2O$ (100 mg L⁻¹); $MgCl_2 \cdot 6H_2O$ (135 mg L⁻¹); $NaHCO_3$ (185 mg L⁻¹); Na_2CO_3 (230 mg L⁻¹); KNO_3 (20 mg L⁻¹). The solution was autoclaved, and the pH was adjusted to 8.1. The conductivity of the solution was measured with a conductivity cell (AMEL 134 digital conductivity meter) and was $1020 \pm 80 \mu S cm^{-1}$. After overnight incubation the cells were washed twice with AFW and re-suspended in AFW at the final concentration of 1×10^7 CFU mL⁻¹ (colony forming unit mL⁻¹).

A commercial 12% Sn bronze (UNI-EN CC483 K) was chosen for the experimentation. $1 \times 1 \times 0.5$ cm specimens were cut from a sheet and then thermo-mechanically treated to avoid heterogeneities of the solid solution and presence of secondary phases, sources of variability of the system. Samples were heavily work-hardened (cold hammering) creating superficial and bulk defects and, following the Cu-Sn phase diagram, heated up to 600 °C for a suitable period in order to allow recrystallization. The procedure was repeated twice to have no doubt of the effectiveness of the treatment. The final microstructure was checked by metallographic etching with $FeCl_3$ for 10 s. Fig. S1 shows the differences between the initial inhomogeneity of the alloy, as displayed by the secondary phases ($\alpha + \delta$) and the effect of the homogenization treatment. Specimens were then polished with SiC paper up to 1000 grit.

Samples of the alloy were immersed, for 1 h and 100 h, in the solution with (biotic) and without bacteria (abiotic), electrochemically monitored and withdrawn at different exposure times. The experimentation was conducted at room temperature (22 ± 2 °C).

2.1. Electrochemical measurements

2.1.1. Open circuit potential monitoring

Electrochemical measurements of the E_{oc} of the tin-bronze samples exposed in biotic and abiotic solution under static conditions were performed using a 0,3 L three-electrode cell with the sample as Working Electrode (WE), Ag/AgCl (sat.KCl) as a Reference Electrode (RE), a platinum wire as a Counter Electrode (CE). RE was equipped with a Luggin capillary and positioned as close as possible to the working electrode, so that no compensation of the ohmic drops was necessary. E_{oc} was recorded for 100 h on both biotic and abiotic systems.

2.1.2. Electrochemical impedance spectroscopy

EIS measurements were carried out at E_{oc} with the amplitude of the a.c. signal of ± 20 mV in the frequency range 100 kHz–10 mHz.

Impedance spectra were analyzed using the Differential Impedance Analysis (DIA) [39–41]. Such technique, following the structural approach, is able to characterize dispersed behavior and distributed time constants. The information about the model structure obtained by DIA were used for the parametric identification, which was performed by Complex Non-linear Regression Least Squares (CNRLS) [42–45].

2.1.3. Polarization curves

Cathodic and anodic polarization curves were performed on four replicated samples, since the resulting changes in the corrosion processes could distort any consideration about their evolution over time. Once stable E_{oc} values had been assessed, measurements were carried out in quasi-stationary conditions, using a scan rate of 10 mV min⁻¹ (0.166 mV s⁻¹). Electrochemical characterization was carried out using a Ivium CompactStat (Ivium Technologies).

Corrosion current (I_{corr}) for each tested condition were estimated by Tafel extrapolation method.

2.1.4. Post experiment characterization

Post experiment characterization was carried out on specimens from both EIS and polarization curve experiments, via metallurgical, morphological and physical-chemical analyses. The effect of bacterial culture on the metallic surface was documented by Scanning Electron Microscopy and Backscattered Electron Detectors (SEM-BSE) micrograph (SEM; Zeiss Evo40; Carl Zeiss, Oberkochen, Germany). Chemical analyses of the corroded layers were performed with energy-dispersion X-ray spectroscopy (EDS; Cambridge INCA 300 with PentaFET EDXS detector; Oxford Instruments, Oxfordshire, U.K. sensitive to light elements, $Z > 5$) connected to a SEM. Also, micro Raman spectroscopy (μ RS; Renishaw Raman System 2000; Renishaw, Inc., Hoffman Estates, IL, USA), with a charge coupled device (CCD) Peltier-cooled as detector, excited using a 632.8 nm He-Ne laser at 1 cm⁻¹ was performed on the corrosion layers.

3. Results and discussion

3.1. Open circuit potential trends

Fig. 1 shows the E_{oc} of tin-bronze samples during 100 h of immersion in both biotic and abiotic systems. The E_{oc} trends were both characterized by a general ennoblement of 50–100 mV, with the biotic sample showing more pronounced instabilities. The initial decay of the E_{oc} in the biotic system can be associated to a fast oxygen consumption, being a primary source for the microorganisms' metabolism. Generally, the first step of corrosion is characterized by the formation of protective cuprous (Cu^+), stannous (Sn^{2+}) and stannic (Sn^{4+}) species, whose oxides and hydroxide precipitated at the interface in the presence of dissolved oxygen. Hence, the fluctuation trend in biotic condition can be related to the unstable formation of oxides and hydroxides layers on

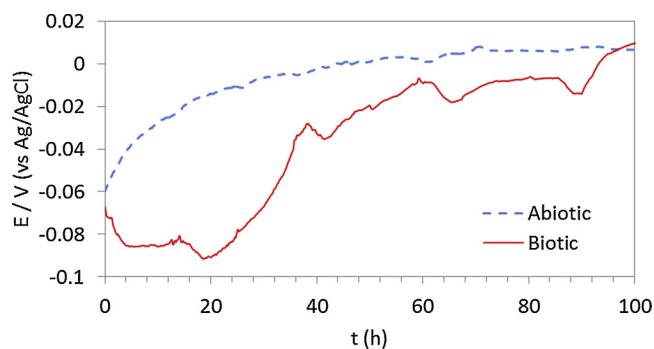


Fig. 1. Open circuit potentials (E_{oc}) trends of two samples of modern bronze during 100 h of immersion in abiotic and biotic (with *Pseudomonas fluorescens*) conditions.

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