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Full Length Article

Artificial patina formation onto copper-based alloys: Chloride and sulphate induced corrosion processes

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ABSTRACT

Naturally grown patinas are typically detected onto the surface of modern copper-based artefacts and strictly affect their surface reactivity and appearance. The production of representative patinas is a key issues in order to obtain model systems which can be used for the development and validation of appropriate conservation materials and methods. In this study, we have prepared different artificial representative patinas by using a quaternary Cu-Sn-Zn-Pb alloy with chemical composition and metallurgical features similar to those of valuable modern works of art. In order to produce degradation products usually observed onto their surface, chloride and sulphate species were used to induce corrosion processes. Different patinas were produced by changing the nature of corrosive species and the set-up for the accelerated degradation. The composition and structural properties of the patinas were investigated by attenuated total reflectance Fourier transform infrared spectroscopy, X-ray diffraction, optical microscopy and scanning electron microscopy combined with energy dispersive X-ray spectroscopy. The results allow to identify degradation products and to distinguish copper hydroxychloride polymorphs and copper hydroxysulphates with similar structure. Our findings show that patina composition can be tailored by modifying the degradation procedure and patinas representative of modern artefacts made of quaternary Cu-Sn-Zn-Pb alloy can be obtained.

1. Introduction

Modern copper-based artefacts are typically characterized by the presence of naturally grown surface patinas, whose composition can be complex and depends on several parameters, such as alloy composition, metallurgical features and environmental conditions [1–10]. The growth of surface patinas is induced by degradation processes occurring on the metal surface and leading to the formation of alteration products and reactive compounds, such as oxides, carbonates, chlorides, hydroxychlorides, nitrates, sulphides and sulphates [1–4]. Among these species, particular attention has to be payed to chlorides, which in the presence of moisture and oxygen, are extremely harmful since are responsible for the “bronze disease”, based on an inexorable cyclic copper corrosion process. This degradation process can significantly compromise the conservation status of valuable works of art and modify the object surface appearance transforming it in a greenish powder. However, stable degradation products can be also formed on the metal substrate thus creating a passive protective layer, known as “noble” patina. Therefore, it is important to identify the chemical composition of surface patinas since they can strictly affect both surface reactivity and appearance of the metal artefacts, which have to be considered in the identification of the most appropriate conservation materials and methods.

The conservation of modern copper-based works of art needs the development of novel corrosion inhibitors that can fulfil the always most demanding protective, aesthetic and safety requirements. For the assessment and optimization of corrosion inhibiting materials, the viability of reference Cu-based alloys that can be sacrificed represents a key issue. Different studies have been performed on different artificially achieved chemical patinations mainly with the aim to obtain protective layers or to investigate degradation mechanisms and the attention has been focused

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especially on archaeological artefacts [9–14]. In this frame, the production of reference Cu-based alloys with chemical composition and metallurgical features similar to modern works of art is still an important challenge. To this aim, it is first necessary to select a representative alloy and then to induce the formation of artificial patinas with composition comparable to those grown on modern works of art. According to the literature [1–3], valuable modern artefacts (as from Rodin, Epstein, Herbert, Giacometti, etc.) have been truly characterized to get information about the composition of the metal alloy and surface patina. The results have shown that the investigated copper-based alloys contain different amounts of alloying elements, mainly Sn, Zn and Pb.

Concerning the surface patinas, they have been formed spontaneously due to corrosion processes or could have been created by the artist for aesthetic reasons [15,16]. The naturally grown patinas confer to the copper-based alloy different colours depending on the nature of degradation products. For example, a greenish patina can be obtained due to the formation of atacamite and its polymorphs $Cu_2(OH)_3Cl$, nantokite CuCl, antlerite $Cu_3(OH)_4SO_4$, malachite $Cu_2(OH)_2CO_3$, and it can be lightened by lead carbonate $PbCO_3$ or tin oxide SnO_2 [2,11]. The metal surface can be reddened by an underlayer of cuprite Cu_2O, whereas a blueish colour is typically due to some copper hydroxysulphates, as posnjakite $Cu_4SO_4(OH)_6{\cdot}(H_2O)$ and brochantite $Cu_4SO_4(OH)_6$, and to azurite $Cu_3(OH)_2(CO_3)_2$ [2,11].

The most frequently identified compounds in the patina of modern indoor and outdoor bronze sculptures are $Cu_2(OH)_3Cl$ polymorphs and cuprite. Since chloride species are the most dangerous for copper-based artefacts, great attention is payed to their characterization and in particular to the identification of $Cu_2(OH)_3Cl$ polymorphs. The phases typically found in the patinas are the orthorhombic atacamite, the monoclinic clinoatacamite, the monoclinic botallackite and the recently discovered triclinic anatacamite [17,18]. Other aggressive degradation products are copper hydroxysulphate compounds produced in the presence of sulphate species. The most common phases are the orthorhombic antlerite, the monoclinic brochantite and the hydrated monoclinic posnjakite [11,19,20].

The present work is aimed to the production of representative artificial patinas on copper-based alloys with chemical composition and metallurgical features similar to modern copper-based works of art, which can be used as model systems for the optimization and validation of protective materials and methods.

To this purpose, we have prepared different artificial patinas by using a quaternary copper-based alloy (Cu-Sn-Zn-Pb) as metal substrate and by inducing the formation of degradation products with chloride and sulphate species. The patina composition was modified by changing the nature of corrosive species (i.e. HCl, $CuCl_2$, $CuCl_2$/HCl and $CuSO_4$, in the presence of H_2O/O_2) and the set-up used for the accelerated corrosion procedures (i.e. interaction with acidic vapours, soaking or wetting with corrosive solutions). The composition and structural properties of the patinas were investigated by attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), X-ray diffraction (XRD), optical microscopy and scanning electron microscopy combined with energy dispersive X-ray spectroscopy (SEM-EDS).

2. Experimental

2.1. Copper-based alloy

A commercial bronze alloy, labelled 555, with nominal composition of 85% Cu, 5% Sn, 5% Pb, 5% Zn and produced by casting, was used as representative Cu-based alloy. The 555 alloy disks have been polished by using SiC papers at 1200 grit and diamond pastes up to 1/4 μm in order to obtain a flat and smooth surface with a mirror-like finish. After polishing, the Cu-based alloys have been cleaned with ethanol.

2.2. Production of artificial patinas

In the case of chloride-induced patina, artificially corroded samples have been prepared by accelerated corrosion treatments induced by chloridric acid and/or $CuCl_2$ in the presence of water.

The patinated alloy A, labelled as PA-A, was prepared by treating the bare 555 alloy with acidic water vapours (HCl 5 wt%/H_2O) in a closed vessel for 3 days.

The patinated alloy B, labelled as PA-B, was obtained by immersion of the bare 555 alloy disk into a $CuCl_2$ 1 M aqueous solution for 24 h and subsequent exposure to water vapours for 24 h by using a procedure similar to the one reported in the literature by Faltermeier [21].

The patinated alloy C, labelled as PA-C, was prepared by treating the bare 555 alloy with a cotton swab embedded with an aqueous solution containing $CuCl_2$ 0.5 M and HCl 0.1 M and subsequent exposure to water vapours for 3 days.

In the case of sulphate-induced patina, a patinated alloy D, labelled as PA-D, was prepared by immersion of the bare 555 alloy disk into a $CuSO_4$ 17 mM aqueous solution at 200 °C for 2 h and subsequent immersion into a $CuSO_4$ 50 mM aqueous solution at room temperature for 15 days.

2.3. Micro-chemical, morphological and structural analysis by SEM-EDS, OM, ATR-FTIR and XRD

Micro-chemical and morphological characterisations were performed by means of a scanning electron microscope (SEM) Cambridge 360 equipped with a LaB6 filament equipped with an energy dispersive X-ray spectrometer (EDS) INCA 250, and a four sectors back-scattered electron (BSE) and secondary electron (SEI) detectors.

Optical microscopy (OM) investigations were performed by using a Leica MZFLIII microscope equipped with a digital camera (Leica DFC 320).

Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy was used for the surface characterization of patinas. The infrared spectra were collected using a Nicolet iS50 spectrometer (Thermo Fisher) equipped with an ATR accessory. The measurements were recorded using a diamond crystal cell ATR using typically 32 scans at a resolution of 4 cm^{-1}. The samples were all measured under the same mechanical force pushing the samples in contact with the diamond crystal. No ATR correction has been applied to the data.

XRD patterns were recorded by Siemens 5000 X-ray powder diffractometer using a Ni-filtered CuKα radiation (λ = 1.5418 Å). Angular values with a step size of 0.05° and a sampling time of 2 s were the experimental parameters used for data acquisition. In order to identify the crystalline phases, the analysis of X-ray diffraction patterns was carried out by using electronic databases.

3. Results and discussion

Within this study, we have selected a quaternary copper-based alloy (Cu-Sn-Zn-Pb, 555 alloy) as representative of modern copper-based works of art on the basis of literature data obtained from the analysis of several modern bronze sculptures [1–3]. The metallurgical structure and chemical composition of the selected 555 alloy were investigated by SEM-EDS. A representative SEM image in Fig. 1 confirms that the selected alloy has a dendritic structure which is typical of cast bronze artefacts. The results of EDS analysis reported in Table 1 indicate that the surface chemical composition