



Spectroscopic analysis of corrosion products in a bronze cauldron from the Late Iberian Iron Age

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ARTICLE INFO

Article history:

Received 19 February 2018

Received in revised form 21 June 2018

Accepted 24 July 2018

Available online 25 July 2018

Keywords:

Bronze

Corrosion

Micro-Raman spectroscopy

XRF

Atacamite

Malaquite

Cuprite

ABSTRACT

Selected bronze fragments unearthed at Cerro de la Cruz (Almedinilla, southern Spain) were analyzed to determine the chemical composition of the corrosion products formed on their surface. The fragments came from a large bronze cauldron used in an Iberian village that was devastated in the mid II century BCE – possibly around 141 BCE. The fragments were analyzed by using various instrumental techniques including electron scanning microscopy coupled to energy dispersive X-ray spectroscopy (SEM-EDS), X-ray fluorescence (XRF) spectroscopy, and also by X-ray diffraction (XRD) and micro-Raman spectroscopy. Based on the results, being buried for a long time caused the main elements in the alloy to mineralize and form stratified layers consisting of various mineral phases including cuprite (Cu_2O), malaquite [$\text{Cu}_2\text{CO}_3(\text{OH})_2$] and cassiterite (Sn_2O). The fragments also contained chloride and trihydroxychloride compounds such as nantokite (CuCl) and atacamite [$\text{Cu}_2\text{Cl}(\text{OH})_3$], respectively, which make conservation of archaeological objects troublesome. These results testify to a strong interaction of the alloy elements with soil components. Also, the results obtained suggest a Type I of corrosion structure. Using the SEM-EDS, XRD and XRF and micro-Raman spectroscopies allowed corrosion products in the fragments to be successfully characterized in microchemical and structural.

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1. Introduction

Bronze is a copper tin alloy that has been one of the most widely used materials for making a variety of household utensils since ancient times [1]. Sometimes, bronze contains other elements such as lead at variable concentrations [2]. Tin is typically used for greater hardness and lead to increase porosity. In an aggressive environment (e.g., burial environment of soil environment), bronze undergoes gradual corrosion and forms a usually brownish green or greenish blue coating called a “patina”. The coating can contain various copper salts depending on where the alloy has been. For example, prolonged burial in soil causes morphologically different corrosion, from a thin corrosion layer to a completely corroded and mineralized artefact [3]. Thus, earth-buried bronze typically forms carbonates such as malaquite $\text{Cu}_2\text{CO}_3(\text{OH})_2$. The presence of chloride ions in soil may lead to formation of nantokite (CuCl). This compound, during burial or after excavation, can form copper trihydroxychlorides (atacamite or paratacamite) in the presence of oxidants conditions and moisture [4]. In the air, however, bronze forms sulphates such as brochantite [$\text{CuSO}_4 \cdot 3\text{Cu}(\text{OH})_2$], and in sea water or chloride-rich environments it forms chlorides such

as atacamite [$\text{Cu}_2\text{Cl}(\text{OH})_3$]. The patina usually coats a red layer of cuprous oxide in contact with the alloy metal core [5–7]. The presence of sulphide ions in the medium causes the formation of copper or lead sulphides [8].

The corrosion compounds formed in bronze objects can be studied by using various instrumental techniques. In recent times, vibrational (Raman and IR) spectroscopies and microspectroscopies have proved highly effective for archaeological characterization purposes [9–17]. For example, our group has successfully used Raman spectroscopy to characterize the pigments in Roman wall paintings [18] and to identify those used in statues from also Roman times [19].

Raman spectroscopy and other instrumental techniques have greatly facilitated the duty of museum restorers and curators in preventing degradation of archaeological heritage, whether exhibited or otherwise. Metal objects require special care as they can easily corroded and bronze objects abound in museum collections throughout the world as a result of the alloy being used since the dawn of mankind to make not only everyday objects but also statues, architectural elements and monuments.

In this work, the objective was study the patina on an Iberian cauldron found at Cerro de la Cruz, archaeological site in Almedinilla (southern Spain) in order to identify the corrosion products formed, so that later restoration professionals can choose the most appropriate

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procedure for its conservation. For this purpose, fragments of the cauldron were characterized by scanning electron microscopy–energy dispersive X-ray spectroscopy (SEM–EDS), X-ray diffraction (XRD) and Raman microspectroscopy.

1.1. Archaeological Context of the Cauldron

Cerro de la Cruz, located in Almedinilla (a population in the province of Cordoba, southern Spain) is an *oppidum* (i.e., a fortified town from Iberian culture, which spanned the centuries V to I BCE). The site has been known since the XIX century but was not thoroughly and scientifically excavated until fairly recently (specifically, over the periods 1985–90 [20] and 2006–2010 [21]). It spans an area of ca. 3.5 ha and is thus mid-sized among Iberian archaeological sites. The studied stage was that of the eventual destruction of the original village, which probably occurred during the campaigns of the Roman consul Servilianus in 141 BCE as told by the Greek author Appian [22]. The initially estimated date, based on local and foreign ceramics and coins, was confirmed by carbon-14 analysis.

The village houses, made of stone and mudbrick, comprised two floors plus a terrace and collapsed under fire. The skeletons of two mutilated corpses were found on the streets and various other human remains encountered among the rubble [21]. Some grain mills were working at the time the village was destroyed [23]. Fire lasted a long time and the resulting rubble was not subsequently removed; as a result, all remains (ceramics, food, tools) were sealed under mudbrick rubble.

The bronze cauldron studied was found in room III, a quadrangular space directly accessed from main street XXV. It was scrambled with many other objects including a lead cup which had melted under the heat, and many amphorae and other ceramic vessels, in the building's collapse rubble. The building's ground floor was used to store grain (particularly barley) in amphorae. As can be seen in Fig. 1, the cauldron, made of copper alloy, was severely smashed and distorted by the collapsing building (Fig. 2). It was probably hemispherical in shape and about 38.2 cm in rim diameter. The cauldron showed signs of repair with rivets (Fig. 2c); also, it contained imprinted organic material (Fig. 2b) – possibly esparto or some rough fabric [21]. It was used mainly to cook meat [22] but may also have been employed for other purposes.

2. Materials and Methods

One side of the fragments examined in this work had abundant adhered material whereas the other was virtually clean. The cauldron

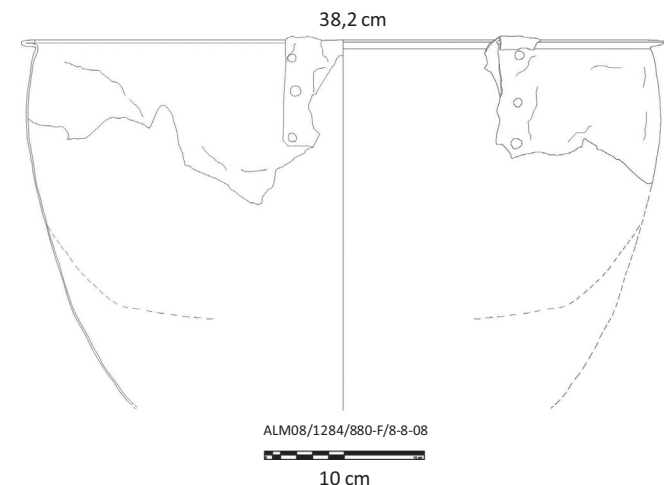


Fig. 1. Reconstructed profile and volume for the bronze cauldron.

surface was greenish on both sides but lighter on the clean side. Under a light microscope, the cross-section of each fragment was found to contain a red-coloured central layer accompanied by another consisting of a mixture of greyish, greenish and reddish hues (Fig. 3). In all cases, different fragments were analyzed, corresponding to significant parts of the cauldron.

The chemical composition and nature of the corrosion products in the fragments was determined by scanning electron microscopy–energy dispersive X-ray spectroscopy (SEM–EDS), X-ray diffraction and Raman microspectroscopy.

Scanning electron micrographs and energy-dispersive spectra were obtained with a JEOL JSM 6300 microscope interfaced to an X-act 80 semi-quantitative elemental microanalyzer.

To check the chemical composition of the cauldron, X-ray fluorescence (XRF) spectroscopy was used. Spectra were acquired with a Rigaku ZSK PrimusIV wavelength X-ray spectrometer. The system is equipped with a 3 kW Rh-target X-ray tube, ten analyzer crystal, a sealed proportional counter for light elements detection and a scintillation counter for heavy elements. For analysis of elemental distributions along a line (i.e. line scan) of the cauldron, a MAXXI 6 Coating Thickness Analyser from Hitachi High-Tech Analytical Science was used. The angle of incidence of the SR beam was 45° and the energy dispersive (Röntec) fluorescence detector was positioned normal to the beam in the horizontal plane.

X-ray diffraction patterns were obtained with a Bruker D8 Advance diffraction spectrometer equipped with a goniometer and a DACO-MP automated data acquisition system. Samples were irradiated with light from the K_{α} line of copper ($\lambda = 1.54 \text{ \AA}$). The spectrometer was furnished with a nickel filter and a graphite monochromator. The goniometer speed was 2°/min. Some samples were ground to a small enough grain size in an agate mortar prior to analysis. Then, an appropriate amount of powder was placed on a plastic slide and compressed to ensure that the light-exposed surface would be as flat and uniform as possible.

Raman spectra were recorded on a Renishaw spectrometer (InVia Raman Microscope) equipped with a Leica microscope with various lenses, monochromators, filters and a CCD detector. Spectra were recorded over the wavenumber range 150–1700 or 150–4000 cm^{-1} upon excitation with green laser light. The number of spectra recorded in each run differed with the experimental conditions. In any case, the primary aim was to maximize the signal-to-noise ratio. As for the XRD patterns, some samples were ground in an agate mortar prior to recording of their spectra.

3. Results and Discussion

3.1. SEM–EDS

The surface of the cauldron fragments consisted of corrosion layers and adhered debris from the material under which they were buried. The debris was largely on one side and covered virtually the whole fragment surface. Observation under a light microscope of the fragment cross-sections revealed the presence of a greenish–reddish–greyish layer and a reddish layer, and provided an indication of their thickness. As can be seen from the micrograph of Fig. 3, the whole object was corroded; also, it exhibited no trace of the original metal structure. The corrosion layers and their sequence were similar in all fragments.

Each of the four layers was subjected to semi-quantitative analysis by EDS to determine their elemental composition. Fig. 4 shows the four zones in the scanning electron micrograph obtained, namely: (A) a green outer layer containing abundant adhered debris, (B) a greenish–reddish–greyish inner layer, (C) a reddish inner layer and (D) a green outer layer containing less adhered debris. Table 1 summarizes the results of the analysis. Because the results for each layer were similar among fragments, the table shows the average value for each quantity. Interestingly, all layers contained silicon, most probably from

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