



Integrated analytical methodologies for the study of corrosion processes in archaeological bronzes

Maria Francesca Alberghina, Rosita Barraco, Maria Brai, Tiziano Schillaci*, Luigi Tranchina

Dipartimento di Fisica e Tecnologie Relative, Laboratorio di Tecniche Fisiche per studio e caratterizzazione dei beni culturali (UniNetLab), Università di Palermo, Viale delle Scienze Ed. 18, 90128, Palermo, Italy

ARTICLE INFO

Article history:

Received 21 May 2010

Accepted 20 December 2010

Available online 28 December 2010

Keywords:

Corrosion patina

Bronze alloy

Integrated spectroscopy technique

Laser-induced breakdown spectroscopy (LIBS)

Archaeometry

ABSTRACT

The investigations on structure and micro-chemical composition of archaeological metal alloys are needed in archaeometry. The aim of this study is devoted both to acquire information about their provenance and production technology, and to improve our understanding about the corrosion processes. In this paper we present the study of the corrosion phenomena of bronze samples, laboratory-made according to binary, ternary and quaternary alloys typical of Roman archaeometallurgical production through an integrated methodology based on the use of non or micro invasive physical techniques. Among the analysed samples, two were artificially aged through burial in the archaeological site of Tharros, along the west coast of Sardinia (Italy). The corrosion products, typical of the bronzes in archaeological sites near the sea, have been characterized by non invasive and micro-destructive measurements. In particular, the corrosion patinas were examined through optical microscopy, scanning electron microscopy and microanalysis, X-ray fluorescence and laser ablation spectroscopy. The use of integrated technologies allowed us to determine both the elemental composition and surface morphology of the patina, highlighting the correlation between patina nature and chemical composition of the burial context. Moreover, data obtained by the laser-induced breakdown spectroscopy along the depth profile on the samples, have yielded information about the stratigraphic layers of corrosion products and their growth. Finally, the depth profiles allowed us to verify both the chemical elements constituting the patina, the metal ions constituting the alloy and the occurrence of migration phenomena from bulk to the surface.

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1. Introduction

The study of the chemical degradation phenomena of the ancient metallic objects is a very complex task. These processes depend not only on many factors, such as: the chemical composition, the production techniques, but also on the environment and the type of soil in which the metal artefacts have been buried. The corrosion of metallic materials is a redox process that causes the deterioration and degradation of the physical–chemical properties of the material. In particular, the archaeological bronze artefacts present a corrosion patina that generally appears as a brownish-green or greenish-blue patina, especially when they are kept in corrosive environments. Various investigations have shown that the main constituents of the surface layer of the patina are green-coloured copper (II) compounds covering a red cuprous oxide layer in contact with the metal core of the alloy [1–4]. The environmental factors affect the formation of the copper (II) salts, in fact they could be malachite $\text{Cu}_2(\text{CO}_3)(\text{OH})_2$

formed in soil, brochantite $\text{CuSO}_4 \cdot 3\text{Cu}(\text{OH})_3$ in the atmosphere and atacamite $\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$ in the seawater. Mechanism of corrosion of bronze was often connected to copper chemistry, although lately it is increasingly emphasized in the role of alloying, which can significantly affect the corrosion behaviour of bronze [2–4].

The presence of lead plays a crucial role in the corrosion mechanism because during the solidification process of the alloy it tends to form intergranular *insulae* that become the place where the processes of corrosion are baited [1,5,6]. On the other hand, tin improves the resistance of the alloy to the growth of the corrosion patinas. In corrosion patinas, lead reach values up to four times higher than the content in the bulk [3]. Tin enrichment instead, due to the solubility and high stability of tin species, is strictly connected to the decuprification process [7]. The migration processes of the elements or ions along the analysed thickness of the alloy create a concentration gradient through the corrosion layer. Hence, the corrosion phenomena in archaeological bronzes can be understood with a multidisciplinary approach to characterize the chemistry and metallurgy of the corrosion patinas. Many analytical methods can be used to characterize the bronze corrosion product compositions. Moreover, the multi-analytical investigation can be useful to find a possible correlation between causes and effects aimed to highlight the

* Corresponding author. Tel.: +39 091 23899149; fax: +39 091 6615069.

E-mail address: tschillaci@unipa.it (T. Schillaci).

occurring processes. The nature of corrosion patina (inhomogeneous and not uniformly distributed on metallic surface) and preservation of the integrity of the archaeological samples, require non or micro-destructive analytical methods [3,8–10].

Many of the used analytical techniques are able to yield also the stratigraphic data but they need a hand-made cross-section and sophisticated, expensive, and complex sampling that compromises the integrity of the sample [11]. In this context, the laser-induced breakdown spectroscopy (LIBS), in the past ten years has been extensively tested as an advanced tool for the characterization of objects of cultural interest and especially the metal ones [11]. It can provide depth-profiling information by successive laser pulses on the same point and sequentially acquired with a minimal damage [9,12–16].

The used techniques were X-ray fluorescence (XRF), optical microscopy (OM), electron microscopy with microanalysis (SEM-EDX) and laser induced breakdown spectroscopy (LIBS).

The comparison between XRF and LIBS techniques, here used, is particularly useful in the study of cultural heritage since their results are complementary in terms of both thickness and composition of the investigated surfaces [17,18]. According to this integrated investigative approach, bronze samples, that simulate the ancient Roman alloys [5,6,19,20] and whose corrosion has been induced by burial in the Roman archaeological site of Tharros along the west coast of Sardinia (Italy) [5], were analysed. In particular, the aim of this work is to follow (from the bulk up to surface) the chemical degradation evolution, analysing and characterizing the macroscopically distinguishable brownish or greenish patinas. Moreover, the contribution of the alloying elements to the growth of corrosion layers has been evaluated.

2. Experimental

Seven laboratory-made bronze samples of binary, ternary and quaternary alloys that reproduce the typical Roman metallurgical production were analysed. Chemical composition of samples, expressed as weight percentage, is reported in Table 1. Sulfur is also present as a consequence of the melting process. THT 128 and THT 129 samples have the same composition of CNR 128 and CNR 129, and were aged for one year by burial in the archaeological site of Tharros. The measurements were performed on each side of the samples, respectively A and B. XRF and LIBS spectrometers have been calibrated by analysing the bronze samples not affected by corrosion (CNR 8, CNR 9, CNR 20, CNR 128, and CNR 129) used as reference materials.

Measurements on THT 128 and THT 129 samples allowed us to study the corrosion products typical of bronzes in a site near the sea. In order to study the genesis and evolution of the corrosion patina, we chose to analyse both the typology of the patina: brownish and greenish patinas, so measurements were performed on many areas along the sample surface. Patinas were examined with the OM, XRF and LIBS spectrometers, SEM-EDX instrument. The integrated approach has provided information useful for the interpretation of the compositional and morphological data related to patina surfaces. The OM images (magnification 30×) were acquired by an OPTECH

microscope equipped with a digital camera. With the aim to study both the surface morphology and the elemental composition, the corroded samples were examined by SEM and analysed by micro-analysis X-ray system (EDS). The experimental set-up values used for SEM-EDX measurements were: 20 kV (voltage), 240 μ A (current), and 4.97×10^{-1} mbar (vacuum). XRF analyses were performed by using a portable X-ray fluorescence (XRF) instrument ArtTAX 200 (Bruker AXS). The ArtTAX is equipped with a low-power X-ray tube that is enclosed by a radiation shield, that guarantees the maximum safety when high voltage is on. An anode of molybdenum is used as a target. A filter disk system, put before the X-ray beam, was used in order to attenuate the Bremsstrahlung radiation and to reduce the diffracted component of X-ray beam. A pinhole system, in the X-ray source, provides collimated beam in the sample making available the instrument to perform spatially resolved multi-elemental analysis on three-dimensional structures. The X-ray fluorescence is detected by a XFlash detector (silicon drift detector) with high speed and low noise electronics with an energy resolution <145 eV at 5.9 keV. ArtTAX is equipped with a helium flux system for detection of light elements, since helium flux reduces the photoelectric absorption of characteristic X-rays emitted by the sample due to air molecules. For statistical reasons, five measures were acquired for each analysed point. It is important to note that, since the lead content is not uniformly distributed in bronze samples, its measurement varies significantly depending on the area selected for analysis. This shortcoming is avoided by averaging the measurements on different areas in the sample. The experimental set-up values used for XRF measurements were: for the molybdenum anode voltage and current, of 40 kV and of 600 μ A respectively; an acquisition time of 300 s, and a helium flow rate of 1.6 l/min. The set-up parameters were selected in order to have a good spectral signal and to optimize the Signal to Noise Ratio (SNR). LIBS measurements were performed on the samples located inside a closed experimental chamber, equipped with a motorized table for exact positioning of the sample at the focus of the laser beams. LIBS instrument integrates a dual-pulse laser. Laser beam emits two collinear laser pulses at 1064 nm with an energy of 50–120 mJ per pulse with a maximum repetition rate of 10 Hz and a reciprocal delay adjustable from 0 to 60 μ s. LIBS signal, either produced inside the experimental chamber or directly on the object, is collected through an optical fiber and sent to a compact Echelle spectrometer coupled to an intensified CCD camera for spectral acquisition. The instrument is controlled via an integrated personal computer which manages sample visualization and positioning, the experimental settings of the laser (energy of the beams, delay between the pulses, and repetition rate) and spectral acquisition parameters (number of spectra averaged, acquisition delay, CCD measurement gate and gain). Spectral resolution of the spectrometer is $\lambda/\Delta\lambda < 5000$. LIBS spectra, after acquisition and storage, can be qualitatively and quantitatively analysed using proprietary software (LIBS++) which implements the calibration free-method, that it is useful to overcome the problem of the matrix effect [21]. In this work the calibration free-method was not used. Measurements of the peak intensity, for each spectral line characterizing the elements in the LIBS spectra, were performed. With the aim to characterize the profile distribution of the elements in the corroded samples, fifteen consecutive acquisitions were carried out on the brownish and on the greenish patinas in each side of the sample. Spectrum related to first shot was not included in the data-set, since it was not reproducible. The experimental set-up values used for the laser source and for the Echelle spectrometer were chosen with the aim to enhance the SNR. The instrumental set-up values were settled, for the laser source as the following: lamp laser energy of 16.5 J corresponding to an output laser energy of 60–70 mJ, repetition rate of 1 Hz, delay of the first laser pulse of 135 ms and the delay of the second laser pulse of 1 μ s. For the CCD camera the set-up values were: number of accumulations of 5 spectra. The gain of multi channel plate

Table 1
Nominal composition of the bronze samples.

Sample label	Cu (%)	Sn (%)	Pb (%)	Zn (%)	S
CNR 8	95.0	5.0	–	–	–
CNR 9	85.0	15.0	–	–	–
CNR 20	97.0	3.0	–	–	–
CNR 128	92.3	7.5	0.2	–	Inclusions
CNR 129	82.3	3.0	0.5	14	Inclusions
THT 128	92.3	7.5	0.2	–	Inclusions
THT 129	82.3	3.0	0.5	14.0	Inclusions

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