

Study of long-term corrosion layers grown on high-tin leaded bronzes by means of the combined use of GDOES and SEM + EDS

G. M. Ingo,^{1*} E. Angelini,² G. Bultrini,³ I. Calliari,⁴ M. Dabala⁴ and T. De Caro¹

¹ Istituto di Chimica dei Materiali del CNR, CP 10, 00016 Monterotondo Stazione, Roma, Italy

² Dipartimento SCIMAT, Politecnico di Torino, c.so Duca degli Abruzzi, Torino, Italy

³ Dipartimento di Chimica, Università di Catania, v.le A. Doria 6, 95125 Catania, Italy

⁴ Dipartimento DIMEG, Università di Padova, via Marzolo 9, 35131 Padova, Italy

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Glow discharge optical emission spectrometry (GDOES) and scanning electron microscopy + energy-dispersive spectrometry (SEM + EDS) are used for studying the microchemistry of the long-term corrosion products, i.e. the *patina*, on archaeological high-tin leaded bronzes used by Romans, most likely as mirrors. The results show that via GDOES it is possible to obtain reliable and detailed elemental composition–depth profiles for the corrosion products of the *patina* and for the bulk chemical composition of the bronzes that are in good agreement with the microchemical features obtained via SEM + EDS. The results provide good insight into the corrosion layers, showing copper and lead selective corrosion and depletion phenomena leading to the formation of a complex microchemical structure and, further, showing clearly the interaction between the inorganic and organic constituents of the soil, such as iron, silicon and phosphorus, in contact with the corrosion products grown on the bronzes. Finally, the results show that GDOES, with its ability of routine and rapid analysis of layers of thickness up to 150 μm , in combination with SEM + EDS, has significant potential in studies of the corrosion products for the restoration and conservation of ancient high-tin leaded bronzes. Copyright © 2002 John Wiley & Sons, Ltd.

KEYWORDS: high-tin bronze alloys; elemental concentration–depth profile; corrosion; glow discharge optical emission spectrometry; SEM + EDS; Roman mirrors

INTRODUCTION

Glow discharge optical emission spectrometry (GDOES) is an important and versatile analytical technique for bulk and depth profiling analysis of thin films and coatings with a total analysed depth ranging between a few nanometres and tens of micrometres.^{1–8}

Recently, this method has been used successfully also for analysing archaeological low-tin bronzes such as Roman and Punic coins and common-use objects.^{2,8} The results have shown that quantification of GDOES data can be accomplished in a simple and straightforward manner and linear calibration curves of GDOES vs. chemical composition obtained via inductively coupled plasma mass spectrometry (ICP-MS) can be obtained for evaluating the contents of the main alloying elements, Cu and Sn, as well for many minor elements such as Fe, Zn, Pb and Ag.^{2,8}

In this work, the use of GDOES has been extended to the analysis of thick corrosion layers, i.e. the *patina*, on archaeological (I–III AD) high-tin leaded bronze fragmented

and flat objects whose original use was likely to be as mirrors.⁹ Indeed, as pointed out by Scott, ancient tin–copper alloys can be divided conveniently in to two classes.⁹ The first class includes the low-tin–copper alloys that were used for producing common-use objects and in which the tin content is <17 wt.%. For the materials, the addition of the rare and expensive tin to the copper was made with in variable amounts as a function of the required final properties of the objects because tin has the ability to improve the final mechanical properties of bronzes as a function of its content. However, the usual higher amount of tin for common-use objects is ~14 wt.% and it is rare to find a bronze with a higher amount of tin in the α -solid solution. The second class includes the high-tin–copper alloys containing an amount of tin ranging from 17 to 35 wt.%. These alloys with the addition of lead were very scarcely produced in pre-Roman and Roman times and they have been used only to manufacture luxurious and precious works of art, such as bells and mirrors, having a silver-like highly reflecting surface when polished. The production and working of these alloys was troublesome in antiquity because they are characterized by poor mechanical properties owing to the presence of different tin–copper brittle intermetallic phases.

*Correspondence to: G. M. Ingo, Istituto di Chimica dei Materiali del CNR, CP 10, 00016 Monterotondo Stazione, Roma, Italy.
E-mail: ingo@milib.cnr.it
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We point out that, to our best knowledge, this is the first time that the microchemical structure of the *patinae* on high-tin leaded copper alloys has been studied by means of the combined use of GDOES and scanning electron microscopy + energy-dispersive spectroscopy (SEM + EDS) for gaining information about the microchemical composition of the corroded layers. This information could be very useful for understanding the ancient manufacturing method and for selecting cleaning, restoration and conservation procedures for these bronzes. Indeed, on the basis of the microchemical nature of the *patina* and of the typology of corrosion, different and tailored methods for cleaning and restoring could be proposed for ensuring the chemical and physical stability of the *patina* and a long life to the objects.

EXPERIMENTAL

Prior to the GDOES measurements, the high-tin bronzes were first gently washed with a brush and distilled water and then with ethanol to remove the surface contamination.

The reference materials used for the GDOES calibration include the following materials: NIST 1174 A, NBS 1175, NBS 1175A, NBS 1144 A, NBS 1177, NBS 1104, NBS 1108, NBS 1256 A, BCS 197f, Centro Sviluppo Materiali S 4, S 11, S 12, S 13, S 14 and CNR internal standards Sn 10, Sn 15, Sn 20, Sn 24, Sn 32 and Sn 40.

The GDOES analysis was carried out with a LECO GDS-750A instrument that comprises a Grimm-style glow discharge lamp and the selection of constant discharge conditions (voltage = 700 V and current = 20 mA) in order to maintain a constant sputtering rate. The internal diameter of the tubular anode was ~4 mm and the analysed area was therefore ~0.14 cm². The Grimm-type atomization/excitation source was evacuated by a rotary pump to a pressure of <1 Pa. After evacuation, flowing argon as a working gas (99.995% purity) was introduced to a constant pressure of 18 Pa. The pressure was measured on the low-pressure side of the lamp. The GDOES results were acquired and handled using the LECO data-handling system.^{10,11} The crater depths used for valuation of the sputtering rates were measured by SEM on the cross-sectioned samples after the GDOES measurements. To analyse the sectioned microchemical structure of the *patina*, a sample was removed with a jeweller's diamond saw, embedded in a resin and metallographically polished with carborundum papers and diamond pastes up to 0.25 µm.

Both SEM and EDS characterization were carried out by using a Cambridge 360 scanning electron microscope equipped with an LaB₆ filament and a backscattered electron detector.

X-ray diffraction patterns were recorded directly on the ancient bronzes by multiple scanning using an automated Seifert XRD-3000 diffractometer. Identification of the species was carried out by using a Seifert XDAL 3000 Software Index I.

RESULTS AND DISCUSSIONS

In Table 1 are reported the bulk chemical compositions for the archaeological high-tin leaded bronze artefacts whose

Table 1. Content of Cu, Sn, As, Zn, Pb and Fe (wt.%) present in some ancient high-tin leaded bronzes (Ag and Sb contents are <0.1%)

Bronzes	Cu	Sn	Zn	As	Pb	Fe
4	62.66	28.31	0.32	0.023	8.31	0.15
11	61.83	30.05	0.61	0.042	7.12	0.08
6	63.18	29.52	0.53	0.170	6.15	0.28
7	64.42	27.32	0.46	0.063	7.42	0.23

The chemical composition has been obtained via ICP-MS.

patina has been studied by means of the combined use of GDOES and SEM + EDS. The chemical composition was obtained via ICP-MS. These alloys are classic bronzes used by Romans^{9,10} for manufacturing luxurious mirrors and are characterized by a high content of tin and a slightly variable content of lead. The other method used by Romans for manufacturing mirrors was based on the deliberate tinning of low-tin bronzes or copper to produce low-cost and easy-to-work artefacts characterized by a silvering appearance.

With regard to the microchemical structure of the surface tinned copper or of the high-tin leaded bronzes, a detailed full description of the copper–tin phase diagram is not appropriate here and is well described in the metallurgical literature.^{9–11} The possible phases present on ancient mirrors may be the three following intermetallic compounds whose chemical composition could vary by ±0.25%: η -Cu₆Sn₅ containing 61.0 wt.% tin; ε -Cu₃Sn containing 38.2 wt.% tin; and δ -Cu₃₁Sn₈ containing 32.6 wt.% tin. These latter phases and the $\alpha + \delta$ eutectoid could be present when deliberate tinning of low-tin bronzes or copper was carried out.

The mirrors produced by using high-tin leaded bronzes are characterized by a more complex microstructure and this is especially true if the alloy was quenched.^{10,11} As a consequence, a leaded high-tin bronze will not be homogeneous at a microscale level and the resulting corrosion products will be characterized by a complex microchemical structure as shown in Fig. 1, where a backscattered electron image of the cross-section of the *patina* and the subsurface region of mirror 4 is reported with EDS spectra.

These SEM + EDS results show the presence of small rounded lead globules dispersed in a very fine homogeneous $\alpha + \delta$ eutectoid cast structure. No other intermetallics such as η -Cu₆Sn₅ and ε -Cu₃Sn phases are present, indicating that a deliberate tinning process was not carried out for coating these alloys with a thick metal tin-enriched layer.

It is worth noting that contemporary Chinese bronze mirrors are also characterized by a similar chemical composition, structure and surface finish.^{9,10} On the basis of this observation, the possibility that the use of these alloys for producing mirrors should have been transmitted to Rome by way of trade with China has been suggested.^{9,10}

Furthermore, the SEM + EDS results indicate that corrosion of the surface $\alpha + \delta$ phases gives rise to the formation of a ghost mineralized eutectoid structure in the inner corroded layer and of a remarkable tin oxide surface enrichment with the presence of silicon and phosphorus in the external layer.

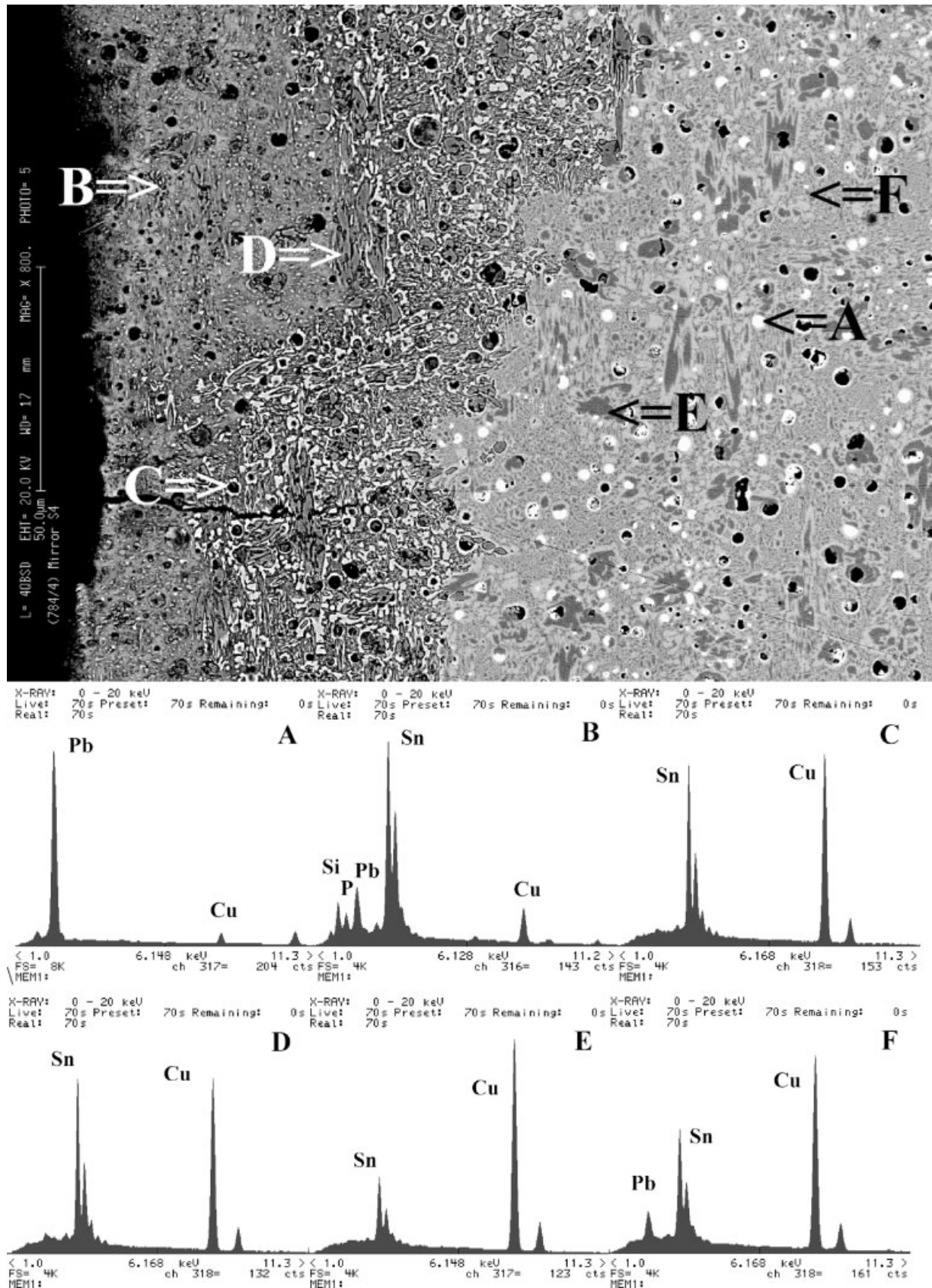


Figure 1. Backscattered electron image and EDS spectra for the cross-sectioned *patina* grown on sample 4.

The GDOES elemental chemical depth profiles for sample 4 reported in Fig. 2 confirm the severe alteration in the concentration of tin and copper compared with the bulk chemical composition. Indeed, the surface of the high-tin

lead bronze is completely oxidized with a remarkable tin surface enrichment with associated ingress of phosphorus, iron and silicon diffused from outside towards the *patina*. The occurrence of iron and silicon on the mirror surface

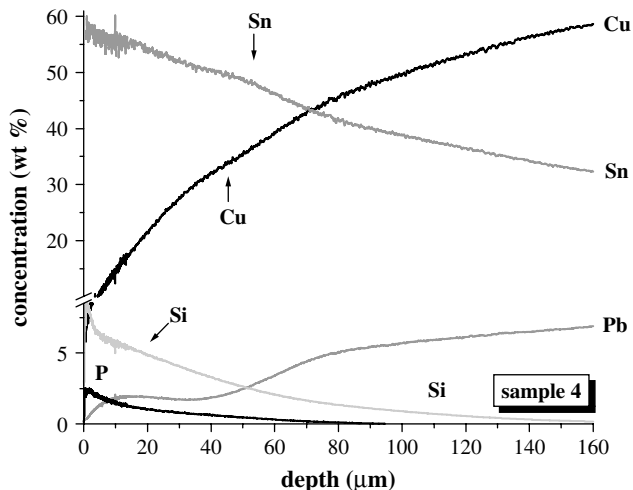


Figure 2. The GDOES elemental concentration–depth profiles for the *patina* grown on sample 4.

may be the result of soil contamination to the buried mirror and to the diffusion of ions into the *patina*. The presence of phosphorus could be related to the presence of decomposed bones that contain calcium phosphate or to other organic materials in the soil.

With regard to the variation in the amount of lead in the *patina* of sample 4, the Pb concentration–depth profile shows an increasing presence of this element from the external surface towards the *patina* and, further, towards the bulk, thus demonstrating a selective surface depletion of this element. It is worth noting that lead, having substantially no solid solubility in copper-based alloys, occurs as a dispersion of fine globules throughout the bronze.¹¹ The copper concentration–depth profile shows a similar behaviour, its content being lower on the outermost layer with respect to the bulk and progressively higher in the inner region of the *patina*.

The most important feature disclosed by the GDOES elemental chemical depth profiles is the tin surface enrichment, whose thickness is $\sim 60 \mu\text{m}$, and x-ray diffraction (XRD) analysis (not shown) has indicated that it is constituted by cassiterite (SnO_2), whose colour is black when iron oxide is present. The high concentration of tin at the surface of ancient bronzes observed via GDOES and SEM + EDS can arise via several processes.^{9,10} The first is the deliberate tinning of copper or bronze, carried out in ancient times by simple dip or wipe tinning or by tin sweat, i.e. the tin concentration on the bronze artefact due to the tin inverse segregation during cooling of cast bronzes. Another tin surface enrichment process is the copper-selective corrosion phenomena occurring during burial, by which a high-tin copper alloy suffers corrosion and loses copper near the surface, leaving behind a tin-enriched *patina*. It is worth noting that corrosion and tin sweat are natural processes but in some cases could have been induced by the ancient metallurgist to create silver-like coloured artefacts as cheaper substitutes for precious and expensive silver objects.^{9,10} All these possible processes complicate the interpretation of the mechanism by which a tin-enriched surface was formed and only a detailed microchemical and microstructural description could help to

gain detailed insight into the manufacturing techniques and the corrosion phenomena.

It is worth noting that the tin surface enrichment could be responsible for the dark-grey silvery lustrous appearance of the *patina* of this mirror, which in some smooth areas is still reflecting. This effect has been noted already by other authors,^{9,10,12,13} who have observed that high-tin leaded bronze mirrors sometimes still possess a highly lustrous dark-grey or black *patina*, thus suggesting that these alloys remain quite stable after about 2300 years of burial. What is not clear is whether in ancient times such high-tin bronzes were deliberately oxidized and leached to increase the tin surface content and then polished to smooth the mirror surface and to enhance the silvery lustrous¹⁴ or whether this microstructure results solely from a long burial corrosion effect.^{9,10}

In order to compare the microchemical structure of *patinae* with different visual appearances, in Fig. 3 are reported the GDOES elemental concentration–depth profiles for a *patina* characterized by a less lustrous dark-grey surface, and in Fig. 4 a SEM image and EDS spectra are given for this cross sectioned sample. The SEM + EDS results show that the *patina* grown on this archaeological high-tin leaded

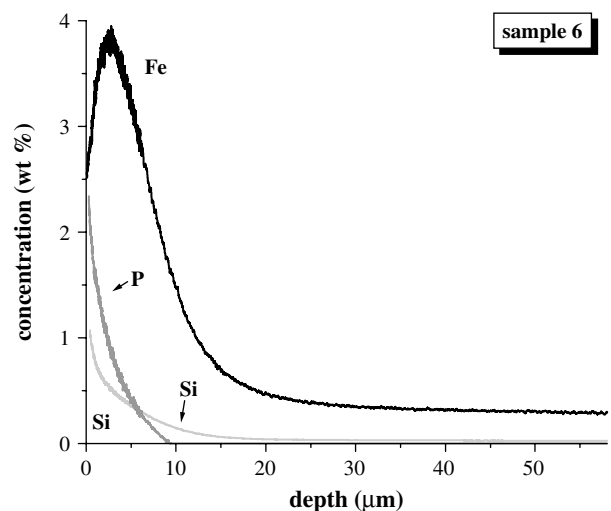
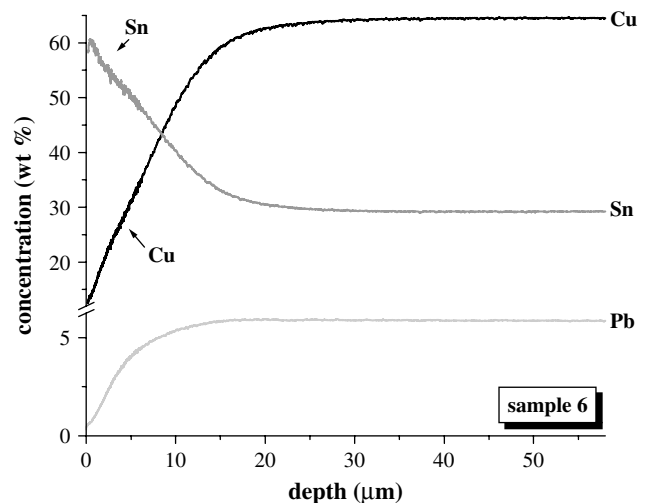


Figure 3. The GDOES elemental concentration–depth profiles for the *patina* grown on sample 6.

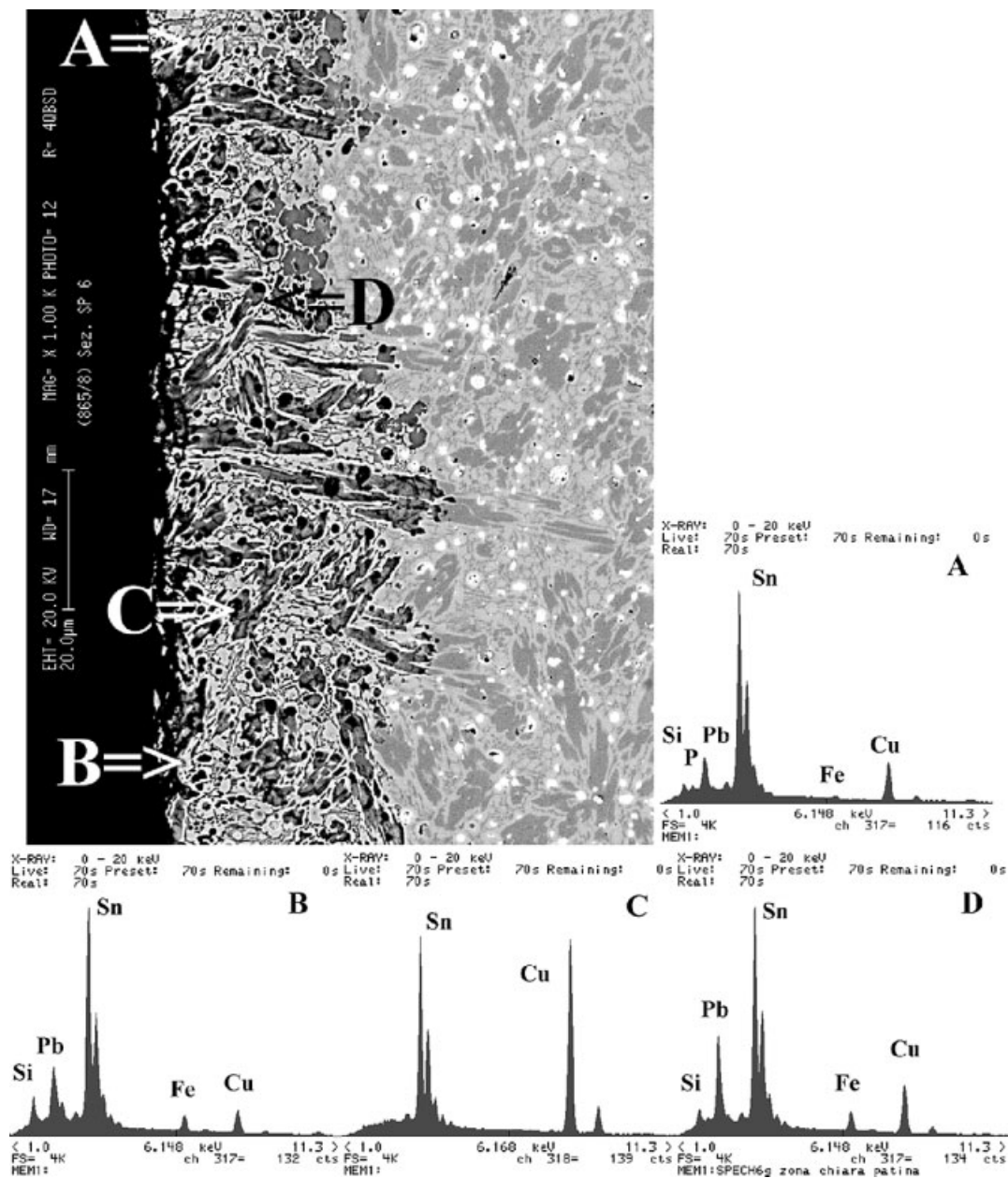


Figure 4. Backscattered electron image and EDS spectra for the cross-sectioned *patina* grown on sample 6.

bronze is characterized by a homogeneous and mineralized $\alpha + \delta$ eutectoid ghost structure throughout and that the bulk microstructure maintains its physical form in the *patina*.

The image shown in Fig. 4 indicates also the presence of a very thin surface enrichment with respect to sample 4. This presence is confirmed by the GDOES elemental concentration–depth profiles reported in Fig. 4. Furthermore, the GDOES copper and lead depth profiles show that Cu and Pb are selectively corroded on the outermost layers and removed, thus decreasing their surface content up to a few per cent.

The comparison between the above-reported results, as well as some archaeological considerations, indicates that the different microchemical structure of the *patina* for samples 4 and 6 could not be related to corrosion phenomena. Indeed, the chemical composition, the microchemical structure and the metallurgical features of these high-tin leaded copper

alloys are quite similar. Furthermore, the difference between the microchemical structure of the *patina* for samples 4 and 6 could not be induced by the nature of the environment or soil, these samples being found close to one another during the archaeological excavation. Therefore, the difference in the chemical structure of the *patinae* could be due to different ancient manufacturing techniques and polishing methods, as mentioned above.

Finally, from an analytical point of view, it is noticeable that the GDOES results for the bulk chemical composition of the bronzes are in good agreement with those found via ICP-MS and reported in Table 1.

CONCLUSIONS

This work has been aimed at exploring the potential of the combined use of GDOES and SEM + EDS in the

surface and bulk analysis of long-term corrosion products of archaeological high-tin leaded bronzes characterized by different microchemical structures of the *patina*. The results provide good insight into the corrosion layers, showing copper and lead selective corrosion and depletion phenomena leading to the formation of a complex microchemical structure and, further, showing clearly the interaction between the inorganic and organic constituents of the soil, such as iron, silicon and phosphorus, in contact with the corrosion products grown on bronzes. From an analytical point of view, these results show that GDOES combined with SEM + EDS can provide detailed information about the surface chemical nature of the archaeological bronze objects as well as helping to explain the ancient manufacturing method of bronze artefacts and their present state and leading to recommendations for restoration and preservation.

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