Microchemical study of the corrosion products on ancient bronzes by means of glow discharge optical emission spectrometry

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Glow discharge optical emission spectrometry (GDOES) has been used for studying the corrosion product layers, i.e. the *patinae*, on Punic bronze artefacts found at Tharros (western Sardinia, Italy) during an archaeological excavation. For all these materials, the results show that via GDOES it is possible to obtain reliable and reproducible quantitative chemical composition for the bulk alloys by taking into account that bronze artefacts are quite inhomogeneous. Some examples of the GDOES analytical capability as elemental depth-concentration profiles through thick bronze *patinae* are shown and briefly discussed in combination with the microchemical features obtained via scanning electron microscopy/energy dispersive spectrometry (SEM+EDS) and x-ray diffraction (XRD). These results show that GDOES, with its ability for routine and rapid analysis of layers of thickness up to 120 μ m, has significant potential in studies of the corrosion products and for the restoration and conservation of ancient bronzes. Copyright © 2000 John Wiley & Sons, Ltd.

KEYWORDS: bronze; Punic ancient artefacts; glow discharge optical emission spectrometry; concentration-depth profiles

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.¹⁻¹¹ Indeed, GDOES analysis has been applied successfully to the bulk and depth profile analysis of a large number of industrial products such as steels, white cast iron, zinc-aluminium and zinc-nickel alloys and hot-dip zinc-coated steels. Recently, this method has been used also for analysing different reference materials that include bronzes, brasses and copper and a group of bronze Punic coins.² 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 atomic absorption spectroscopy (ICPAAS), can be obtained for evaluating the contents of the main alloying elements Cu and Sn, as well as some minor elements such as Fe, Ag, Zn and Pb.

In this work, GDOES elemental concentration-depth profiles have been obtained for thick corrosion layers, i.e. the *patinae*, on ancient Punic bronze artefacts (5th to 3rd century BC) found at Tharros (western Sardinia, Italy) during an archaeological excavation. Even though the surface roughness could be of dimensions quite similar to the

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thickness of the oxide films, and this can lead to the degradation of the elemental concentration–depth profile,¹² this chemical information, combined with scanning electron microscopy (SEM) results, could be useful for understanding the surface chemical composition of the *patina*, the corrosion mechanisms, the interaction between the *patina* and the soil constituents and therefore for selecting the cleaning, the restoration and the conservation procedures to be used for small and flat ancient bronze artefacts.

EXPERIMENTAL

The reference materials used for the 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 and CSM S4, S 11, S 12, S 13 and S 14. The contents of Cu, Sn, As, Ag, Fe, Zn, Sb and Pb in the reference materials used for calibration are reported elsewhere.² The GDOES analysis was carried out with a LECO GDS-750A instrument that comprises a Grimm-style glow discharge lamp and by selecting constant discharge conditions (voltage 700 V and current 20 mA) in order to kept the sputtering rate constant. The internal diameter of the tubular anode was \sim 4 mm and the analysed area was therefore \sim 0.14 cm². It is worth noting that in this instrument it is possible to use also other commercially provided tubular anodes or a laboratory-made smaller anode that results in a slight loss of sensibility. The Grimm-type atomization/excitation source was evacuated by a rotary pump to a pressure of <1 Pa. After evacuation, flowing argon as 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 have been acquired and handled using the LECO data handling system.^{10,11} Prior to the GDOES measurements, the bronze artifacts have been first gently washed with distilled water and a brush and then with ethanol in order to remove the surface contamination. The crater depths used for evaluation 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 saw, embedded in a resin and metallographically polished with carborundum papers and diamond pastes up to 0.25 µm. Both SEM and energy-dispersive spectroscopy (EDS) characterization were carried out by using a Cambridge 360 scanning electron microscope equipped with an LaB₆ filament and an EDS apparatus. X-ray diffraction patterns were recorded directly on the ancient bronzes by multiple scanning using an automated Seifert XRD-3000 diffractometer. The identification of the species was carried out by using a Seifert XDAL 3000 Software Index I.

RESULTS AND DISCUSSION

In Table 1 are reported the chemical compositions for the Punic bronze alloys used for performing the GDOES study of the surface corrosion layers. The chemical compositions have been obtained via inductively coupled palsma mass spectrometry (ICPMS). The bronzes are classic copper-tin alloys¹²⁻¹⁸ with minor or trace constituents such as As, Ag, Sb, Fe and Zn and a highly variable content of lead. With regard to lead, it is worth noting that the data reported in Table 1, are comparable with those of the Etruscan, Greek and Italic objects^{13,14,18} and with the few literature data concerning the lead content of the Phoenician and Punic artefacts from Spain.¹⁵ Because lead has substantially no solid solubility in copper and copper-based alloys, if the percentage of lead in bronze is higher than a few weight per cent (wt.%), lead occurs as a dispersion of fine particles throughout the bronze and the number of the lead particles, as globules, increases with increasing lead amount. Furthermore, the distribution and size of the lead globules from the external surface to the centre of the bronze artefact are remarkedly affected by the cooling process of the alloy.¹⁶ As a consequence, a leaded bronze object will not be homogeneous at a microscale level and the resulting corrosion products will be characterized by a very complex microchemical structure. Furthermore, as pointed out by several authors,^{12,17} the identification of the long-term corrosion products formed over 2000

| Table 1. | Content | of Cu | Sn, | As, | Zn, | Pb | and | Fe | (w | t.% |
|----------|---------|----------|-------|-------|-------|------|-------|------|-----|-----|
| | present | in the a | ncier | nt br | onze | allo | ys us | ed i | for | per |
| | forming | the GD | OES | mea | surei | nent | s | | | |

| Ancient bronze alloys | Cu (wt.%) | Sn | Zn | As | Pb | Fe |
|-----------------------|-----------|------|------|-------|-------|------|
| 1 | 69.03 | 9.16 | 0.72 | 0.023 | 21.75 | 0.28 |
| 2 | 93.20 | 2.52 | 3.25 | 0.18 | 0.82 | 0.31 |
| 7 | 66.35 | 5.76 | 0.15 | 0.32 | 26.27 | 0.18 |
| 8 | 78.87 | 4.71 | 0.38 | 0.45 | 14.40 | 0.17 |
| | | | | | | |

The Ag and Sb contents are <0.1%. The contents have been measured via inductively coupled plasma mass spectrometry (ICPMS).

years or even more is more difficult than expected, owing to the complexity of the microstructure of the Cu–Sn alloy. Indeed, the bronze artefacts are generally produced first via a casting process and then are subjected to cold and/or hot hammering and heating cycles for obtaining the final shape. Their microstructures can be characterized by a dendrite structure and also twinning, slip lines and deformed crystals, with inclusions and copper sulphide particles at grain boundaries, can be present. Of course, this complex microstructure plays a determining role in the formation of the corrosion products.

In Fig. 1, the GDOES elemental concentration-depth profiles for samples 7 and 8 are shown. The distribution of the main alloying or added elements (Cu, Sn and Pb) and of the silicon and phosphorus coming from the soil and introduced into the *patina* during the weathering process has been considered for determining the nature of the corrosion products. The presence of silicon and phosphorus is clearly revealed with a broad interface between the external *patina* layer and the inner parts. This finding demonstrates that corrosion products reacted with soil and air components to form silicates and phosphates whose presence has been revealed by XRD results (not shown). Indeed, XRD patterns have disclosed for these samples the occurrence of tenorite (CuO), cuprite



Figure 1. The GDOES elemental concentration–depth profiles for the *patina* grown on samples 7 and 8.

(Cu₂O), lead oxide (PbO₂) and cassiterite (SnO₂) produced from the alloy corrosion process and also leadhillite (PbSO₄·2PbCO₃·Pb(OH)₂), lead silicate (PbSiO₄), quartz (SiO₂), cerussite (PbCO₃), malachite (CuCO₃·Cu(OH)₂) and atacamite (CuCl₂·3Cu(OH)₂) coming from the soil or produced via interaction between the soil and air constituents and the corrosion products. We point out that in some cases XRD has shown the presence of both Cu(I) and Cu(II) oxides. The occurrence of these copper species is strictly related to the soil nature,¹² where the *patina* has been formed during long-term corrosion, and in particular, to the pH value of the soil, and the presence of both cuprite and tenorite on the same bronze could reflect a variation of the soil nature or of the weathering conditions.

In order to gain further insight, the microchemical structure of the *patina* obtained via GDOES technique, has been compared to the results obtained by means of SEM/EDS. With this aim in mind, backscattered electron images and some EDS spectra for the *patina* of samples 7 and 8 are reported in Fig. 2. These results indicate that the thickness of the corrosion layer varies between 100 and 150 μ m and in some cases, the *patina* can be separated into two or more zones. For better comparison of the results, it is worth considering that GDOES elemental



Figure 2. Backscattered electron images and EDS spectra for the patina grown on samples 7 and 8.

concentration-depth profiles have been obtained from an area of ~ 0.14 cm² and therefore describe the average presence of the considered elements on a large area where a very complex microchemical structure can be present. On the contrary, the SEM/EDS micrographs shown in Fig. 2 are obtained from a smaller area of $\sim 0.02 \times 0.015$ cm $(0.30 \times 10^{-3} \text{ cm}^2)$ and therefore can give only a local microchemical description of the patina structure. However, the comparison between GDOES and SEM/EDS results confirms the occurrence of a discrete layer enriched in silicon and phosphorus for both samples 7 and 8, owing to the interaction between the patina and soil constituents. Furthermore, the surface tin enrichment on the patina for these samples, evidenced by the GDOES results, is clearly shown by the SEM/EDS results reported in Fig. 2 (spectrum A), thus demonstrating the occurrence of tin-selective oxidation and redeposition phenomena. The study of the tin long-term corrosion behaviour and the location of its presence in the *patina* are important for selecting the conservation and restoring procedures because tin plays a sacrificial role in preventing the oxidation and hydration of copper.¹⁸ However, the tin content in ancient bronzes^{13–15} can vary from 2 wt.% to 18 wt.%, because tin has the ability to improve the final mechanical properties of bronzes as a function of its content, and therefore was added in variable amounts as a function of the required final properties.

The GDOES tin elemental concentration-depth profile confirms that the long-term corrosion of bronzes generally proceeds with the growth of the tin oxide film on the alloy surface. Furthermore, the GDOES and SEM/EDS results converge to reveal that, as a function of the corrosion conditions, tin oxide can remain at the patina/metal interface, being chemically stable as cassiterite, can participate in the formation of the patina and can be dissolved or redeposited instead of remaining in situ after the reaction with soil or atmospheric components to form new compounds. With regard to lead in the patina of sample 7, the Pb concentration-depth profile shows an increasing presence of this element from the external surface toward the bulk of the *patina*, thus demonstrating selective depletion of this element. On the contrary, the copper concentration-depth profile shows a different behaviour, its content being increased in the *patina* with respect to the bulk. Also for copper, the GDOES results indicate selective corrosion and redeposition phenomena.

Copper and lead elemental concentration-depth profiles for sample 8 show a different behaviour with respect to sample 7. Indeed, after GDOES erosion of the external part of the patina, copper and lead contents are quite steady and constant throughout the analysis of the corrosion products layers. We point out that the difference between samples 7 and 8 could not be due to the nature of the environment or the soil because these samples were found close to each other during the archaeological excavation of the metallurgical and industrial areas of Tharros (western Sardinia, Italy). The difference in the chemical composition and structure of the patina for samples 7 and 8 is likely to be due to the difference in the chemical composition and structure of the alloys. The role played by the metallurgical and chemical features in determining the nature of the *patina* is confirmed by the GDOES results for samples 1 and 2, as shown in Fig. 3. Also, these flat bronze objects have been found during the archaeological excavation at Tharros and therefore they have



Figure 3. The GDOES elemental concentration-depth profiles for the *patina* grown on samples 1 and 2.

probably suffered the same weathering and corrosion conditions of samples 7 and 8 but are characterized by a different microchemical structure. Indeed, also for these samples, the GDOES technique combined with SEM/EDS and XRD results (not shown) allows the chemical nature of the long-term corrosion products to be described and the presence of a layered structure to be dissolved. The GDOES results for sample 1 indicate a surface copper, silicon and tin enrichment and a lead depletion, whereas in the inner layers at an increasing amount of lead there is a noticeable decrease and then an increase in the amount of copper. For sample 2, whose bulk alloy is characterized by a small amount of lead, the elemental concentration-depth profiles for the thin corrosion product layers show a copper surface enrichment, then a silicon- and tin-enriched zone and finally a copper oxide layer that XRD diffraction indicates to be cuprite (Cu_2O) .

Finally, from an analytical point of view, we point out that the GDOES results for the bulk chemical composition of the alloys are in good agreement with those found via ICPMS, as reported in Table 1.

CONCLUSIONS

This work has been aimed at exploring the potential of the combined use of GDOES, SEM/EDS and XRD in the surface and bulk analysis of the long-term corrosion products of ancient bronzes of different chemical and microstructural compositions. The results provide good insight into the microchemical structure of the *patinae*, evidencing selective corrosion and depletion phenomena leading to the formation of thick layers and, further, showing clearly the interaction between the soil and air constituents with the corrosion products. From an analytical point of view, these results show that GDOES, with its ability for routine and rapid analysis, has significant potential in studies of the bronze corrosion phenomena for the restoration and conservation of ancient artefacts.

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REFERENCES

- Harrison WW, Barshik CM, Klinger JA, Ratliff PH, Meil Y. Anal. Chem. 1990; 62: 943A.
- Ingo GM, Bultrini G, Manfredi L-I. Archaeometry 1997; 39: 59.
- Bengtson A, Lundholm M. J. Anal. At. Spectrom. 1988; 5: 879.
- Bengtson A, Eklund A. Software for Quantitative Evaluation and Graphical Presentation of GDOES Depth Profiles—Users Manual. Swedish Institute for Metals Research: Stockholm, Sweden, 1993.
- Bengtson A, Mundholm M. J. Anal. At. Spectrom. 1985; 3: 631.
- 6. Payling R, Jones DG. Surf. Interface Anal. 1993; 20: 787.
- 7. Payling R, Jones DJ, Gower SA. *Surf. Interface Anal.* 1993; **20**: 959.
- Payling R, Jones DJ, Gower SA. Surf. Interface Anal. 1995; 23: 1.

- 9. Payling R. Surf. Interface Anal. 1995; 23: 12.
- 10. Weiss Z. J. Anal. At. Spectrom. 1994; 9: 351.
- 11. Weiss Z. J. Anal. At. Spectrom. 1997; 12: 159.
- Schweitzer F. In Proc. Symp. organized by the Paul Getty Museum, Scott DA, Podany J, Considine BB (eds). The Getty Cons. Inst.: Malibu, CA, 1994; 1–20.
- 13. Craddock PT. J. Archaeol. Sci. 1976; 3: 93.
- 14. Craddock PT. J. Archaeol. Sci. 1977; 4: 103.
- 15. Giumlia-Mair AR. Archaeometry 1992; 34: 107.
- Butts A. Copper, The Science and Technology of the Metal, its Alloys and Compounds, Am. Chem. Soc. Monogr. Ser. 12. American Chemical Society: New York, 1954; 702–705.
- Fabrizi M, Scott DA. In *Recent Advances in the Conservation* and Analysis of Artifacts, Black J (ed). Summer School Press: London, 1987; 131.
- Paparazzo E, Moretto L, Northover JP, D'amato C, Palmieri A. J. Vac. Sci. Technol. A 1995; 13: 1229.