JOURNAL OF SCIENCE AND ARTS

OPTICAL EMISSION SPECTROMETRY AND METALLOGRAPHIC EXAMINATION OF ROMAN MIRRORS FROM DOBRUDJA, ROMANIA

I. V. POPESCU[1, 2] , V. GHIŞA[3], M. BELC[3] , M.BAHRIM[4]
[1]Physics Department, Valahia University of Târgovişte, 0200, Târgovişte, Romania
[2]Academy of Romanian Scientists,Romania
[3]Physics Department, Ovidius University of Constanța, Constanța, 8700, Romania
[4]High School Ovidius, Constanta, Romania

Abstract. *The miscellaneous population of Roman Empire, their diverse cultural tradition, their ability to assimilate the roman civilization spirits, had determinate a permanent reassessment on roman contribution. the object of this work is the study of some roman-source mirrors, discovered recently in Dobrudja zone, Romania. Analysis was undertaken using optical emission spectrometry and of optic microscopy aiming at identifying the constituents and the type of structure we are dealing with. All of the roman metal-mirrors analysed have been found as made of speculum, with one exception. Although chemically the samples are alike, structurally they differ a lot, due to the various modalities of processing these.*

Keywords: optical emission spectrometry, optic microscopy

1. Introduction

Hand-mirrors date from prehistoric times, when it is likely that discs of polished slate were used. The earliest known metal mirrors belong to the Egyptian 1st dynasty (c. 3100 BC), and during the Old Kingdom, which lasted about 700 years, the characteristic shape still exists today was first introduced. The Egyptian mirrors were originally made of cooper, but this was later superseded by bronze. The faces were highly polished and ornamental ivory, glazed or painted handles were provided.

Roman art history has to refer to not only the creations from the italic land, but also to those achieved on the Roman Empire.

The aim of this work consist in determination of the differences between the smaller (sample no. 2 and 3) and the larger (sample no. 1 and 4) mirror modalities of processing.

The Roman mirrors analysed during this research had found to be made of speculum (a high tin bronze). A tin content of 15% or higher can give a silvery-white alloy, which can be polished to give a reflective surface [1]. The Roman mirrors that we analysed had tin content of 16.5 %, with one exception of 4.5 %. In addition, all of the mirrors had only trace levels of zinc and some a relatively high lead content (1.13 %) [2], [3].

2. Experimental

The samples that this paper suggests paying attention to for further analysis represent roman mirrors – bronze (plaque) boards, well polished, and designed particularly to this aim. The samples proceed from the period when Pontic-Dacia was occupied by the Romans (today’s Dobrudja) – fact stated by the location of their discovery, besides a multitude of other metallic or ceramics objects also from that period of time (approximately II – III centuries BC).

These objects have been restored to their initial shape, by gluing together with a special resin the separate fragments of the same whole.

First of all the samples chosen for the study have been chemically analysed through the Optical Emission Spectrometry.

Optical Emission Spectrometry is a quantitative comparative analysis technique, used to determine materials chemical composition. The principle is based on fact that excitable atoms (when they acquire sufficient energy to emit their characteristic radiation through inelastic collision with other atom, molecules or ions, for this, the atoms have to be in a gaseous state) emitting this radiation energy in a discrete wavelengths that is selected and measured.

Spark and arc excitation sources use a current pulse (spark) or a continuous electrical discharge (arc) between two electrodes to vaporize and excite analyse atoms. The electrodes are either metal or graphite. If the sample to be analysed is a metal, it can be used as one electrode.

For our purpose we used the mobile optical emission analyser ARC-MET 900. The versatile ARC-MET 900-analyser combine's easy of use with high performance features, to give reliable and accurate on-site analyses of different metal samples.

ARC-MET's measurement is based on vaporizing a small amount of sample and analysing sample's elemental components from the vapour.

The excitation chamber is made of a special ceramics and contains a tungsten electrode. An electrical arc is ignited between the electrode and the sample to produce light, which is then measured to give analytical results of the sample.

The chamber is flushed with argon, which takes the metal fumes produced by sparking to the exhaust fumes filter.

To ensure best possible results we have to take appropriate care of sample surface as analytical results depend on the sample surface condition. We put the sample into a sample holder and grind the surface (approximately 3 cm/4 cm) with grad 40 - 60 sandpaper. After this we transfer it in the excitation chamber. We must not touch the sample surface after grinding. Fingerprints on the sample surface will affect the analysis. Any contamination on the sample surface will spoil the representatively of the sample.

The measurement began by filling up the excitation chamber with argon to prevent sample oxidation. A high-frequency excitation (1-30 seconds) is used to prepare the sample surface for analysis, follow by a 10 seconds burn, the phase when the line intensities of the elements are measured. At the end argon after flow is used to cool the electrode.

During the second stage of this study two samples (no. 1 and 2) have been submitted to an analysis of optic microscopy aiming at identifying the constituents and the type of structure we are dealing with.

3. Results and discussion

According to the results of the chemical analysis and to the images of optic microscopy provided we are in position to draw the following conclusions referring to the compositional and structural nature of the present facts.

The data obtain this way are put together in Table 1 as follows:

Table 1. Results of the chemical analysis performed on the samples corresponding to the Roman mirrors.

Inv.	1621	12859	15544	4548
Sample	1 [%]	2 [%]	3 [%]	4 [%]
Cu	64.82 ± 3.645	69.43 ± 3.872	67.44 ± 3.794	56.42 ± 3. 106
Sn	> 16.50 ± 2.191	> 16.50 ± 2.697	> 16.50 ± 2.381	> 16.50 ± 2.511
Pb	< 0.004 ± 0.639	> 1.132 ± 0.042	> 1.13 ± 0.067	0.066 ± 0.385
Fe	0.373 ± 0.444	0.046 ± 0.073	0.048 ± 0.081	> 0.73 ± 0.729
Ni	0.099 ± 0.019	0.078 ± 0.014	0.024 ± 0.010	0.147 ± 0.083
Mn	0.002 ± 0.007	< 0.009 ± 0.006	0.009 ± 0.002	0.314 ± 0.398
Al	0.019 ± 0.025	0.013 ± 0.012	0.005 ± 0.028	0.075 ± 0.102
Zn	0.004 ± 0.027	< 0.004 ± 0.007	0.004 ± 0.027	< 0.004 ±0.005
P	0.014 ± 0.003	> 0.114 ± 0.017	0.017 ± 0.003	0.013 ± 0.003
Sb	0.006 ± 0.324	0.24 ± 0.856	0.093 ± 0.561	0.073 ± 0.513

Sample no. 1 confirms by means of images of optic microscopy a monophasic structure of α - solid solution of Sn in Cu, characterized by polyhedral grains which are macled and which come in different shades.

The granulation is relatively uniform of approximately 50 μm whose polyhedral shape certifies the fact that the mirror was obtained by a process of plastic deformation at warmth. The 16.5 % percentage of Sn goes way beyond the percentage of maximal solubility of Sn in Cu (of ≈ 6 %) there for it should invalidate the α monophasic structure of the α solid solution. Such a percentage of Sn in Cu guarantees that the respective bronze has a moulded structure made up of α - solid solution and (α + δ) eutectoid – a hard and fragile phase which separates when reaching the stage of grain. The lack of any eutectoid in the structure presented by figure no. 1 and no. 2 through optic microscopy, corroborated with the polyhedral aspect of the grains of α - solid solution, demonstrates the fact that the mirror, following the moulding, suffered a process of plastic deformation, probably through hammering at temperatures of 3000 – 4000 C, then a rapid cooling, practically a tempering in cold water. This cooling obviously prevented the eutectoid from forming, the structure thus obtained remaining monophasic and supersaturated.

Sample no. 2, compared to sample no. 1 was not submitted to a plastic deformation. From the chemical analysis performed we notice that sample no. 2 has a percentage of ≈ 1.13 % Pb, a chemical element non-soluble in Cu, which separates when it comes to grains (see the interdendritic dark Pb from the images of optic microscopy no. 3 and 4) making plastic deformation difficult, but fluidising the fusion, in the facilitating the moulding mirrors of certain desired dimensions.

Figures no. 3 and 4 clearly indicate a dendritic structure with obvious separations of Pb and Cu_2O compounds.

As far as the presence of Cu_2O in concerned, as a general characteristic of structural nature of both samples corresponding to the roman mirrors we have to mention the status of advanced corrosion, accountable for all the objects. In a humid atmosphere copper, when having such small thickness as the mirrors have, suffers in time an obvious structural degradation, in conformity with the following chemical reactions:

$$2Cu + O_2 + H_2O \rightarrow 2Cu(OH)_2 \qquad (1)$$

$$Cu(OH)_2 + Cu \rightarrow Cu_2O + H_2O. \qquad (2)$$

Both the fissure net in figures 1 and 2, and the status of highly advanced interdendritic corrosion in figures 3 and 4 fully certify the chemical reactions described above.

Both samples drawn from the two roman mirrors have shown from a chemical point of view approximately the same chemical composition, except the Pb found in a higher percentage (of ≈ 1.13 %) in sample no. 2.

Although chemically the samples are alike, structurally they differ a lot, due to the various modalities of processing these. Mirror no. 1 was obtain by moulding and hammering at warmth, followed by cooling the product whereas mirror no. 2 was obtain directly by moulding the specific desired dimensions (a process which is made easier by the presence of Pb in the structure that allowed it by fluidising the fusion) [4,5]. In the same time due to the instant cooling in water there appeared some fissions in the intercrystallin structure, in togetherness with relative movement and the distortion of intercrystallin planes.

As a matter of fact, mirror no. 2 is dimensionally much smaller that mirror no. 1 (Φ2 ≈ 10 cm and Φ1 ≈ 20 cm).

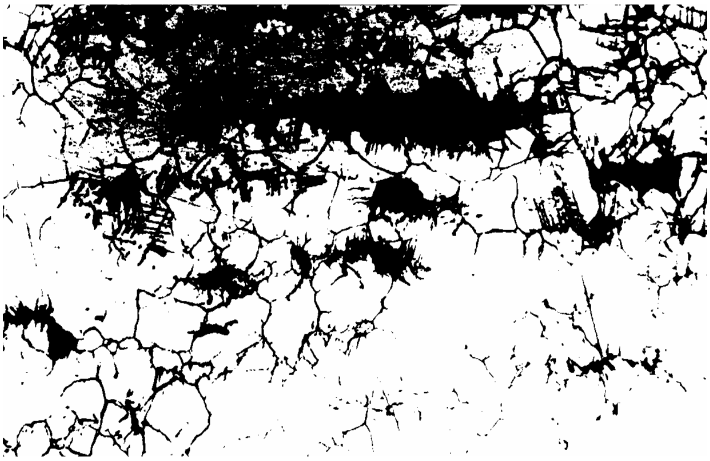

Figure 1. Image of optic microscopy (× 200) of a sample from the roman mirror no. 1 – alloy of Cu-Sn; unattached sample; an advanced status of intercrystallin corrosion is to be noticed.

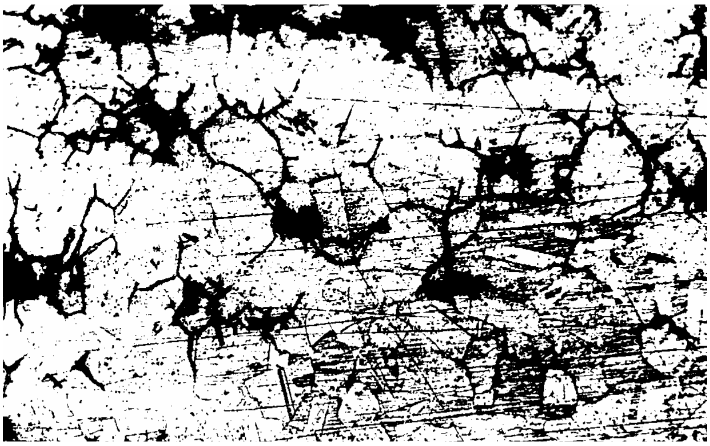

Figure 2. Image of optic microscopy (× 200) of a sample from the roman mirror no. 1 – alloy of Cu-Sn; ferric chloride attack; macled polyhedral grains presenting an advanced status of intercrystallin corrosion; α monophasic structure.

Figure 3. Image of optic microscopy (× 200) of a sample from the roman mirror no. 2 – alloy of Cu-Sn; unattached sample; a dendritic moulding structure is to be noticed presenting an advanced status of interdendritic corrosion and a multitude of globular components of Cu2O, light grey.

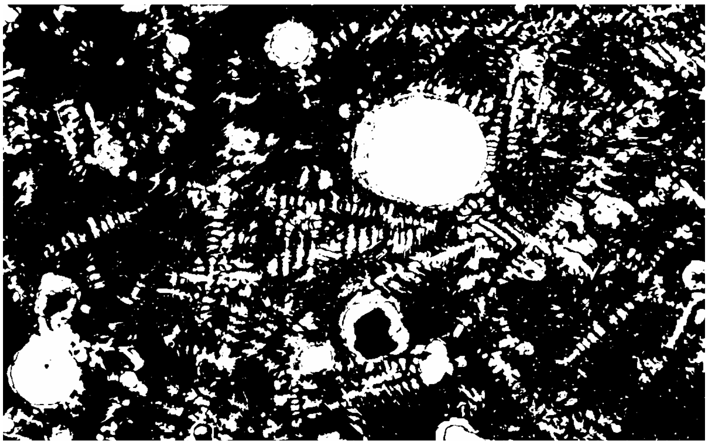

Figure 4. Image of optic microscopy (× 200) of a sample from the roman mirror no. 2 – alloy of Cu-Sn; ferric chloride attack; dendritic moulding structure and globular components of Cu_2O.

4. Conclusions

The conclusion reached is that for smaller mirrors a simple moulding of reached of the alloy will do (with a supplement of Pb), whereas for larger mirrors process of supplementary plastic deformation is compulsory. The plastic distortion in warming conditions offered to those pieces a better homogeneity of internal fiber and an increase of mechanical resistance and plasticity. In all our observation, the presence of the Cu_2O oxides goes to a bigger fragility of the raw material, too. On the other hand it is possible that on the starting level of moulding, after obtaining of the molten alloy, to set out a desoxidation process and a collecting of them, of course through some rudimentary techniques especially from the surface layer (the most accessible). The polishing of the mirrors surfaces shows us a prove of already existence of specialised workshops for the manufacturing of those object types. So, in the certain way, more than the imports from the Empire, there exist some local workshops which were well-developed, this fact being shown by the finding in the observed site some special places for keeping of objects with use of ornamental clothing and housing devices.

References

[1] D. B. Dungworth, *Iron Age and Roman Copper Alloys from Northern Britain*, http://intarch.ac.uk/journal.issue2/dungworth/index.html.

[2] J. A. Smythe, *Roman objects of copper and iron from the north of England*, Proceedings of the University of Durham Philosophical Society 9 (1936).

[3] P. T. Craddock, *The composition of the Copper Alloys used by the Greek, Etruscan and Roman Civilizations* 3: The origins and early use of brass, Journal of Archaeological Science 5 (1978).

[4] J. Christian, *Phase transformation, Physical Metallurgy*, North-Holland, Amsterdam (1965), p. 443-540.

[5] H. G. Bachmann, *Schlacken-Indikatoren archäomtallurgischer prozesse*, ed.: H.W. Heinniche, Mineraliche Rohstoffe als kulturische Informationsquelle,Hagen (1978), p.66-108.

[6] D.L. Massart, B.G.M. Vandeginste, L.M.C. Buydens, S. De Jong, P.J. Lewi, and J. Smeyers-Verbeke, *Handbook of Chemometrics and Qualimetrics : Part A* (Elsevier, Amsterdam, 1997), chapter 6.

[7] P.W.J.M. Boumans, *Spectrochim. Acta* 46B, 431 (1991).

[8] J.M. Mermet, A. Cosnier, Y. Danthez, C. Dubuisson, E. Fretel, O. Rogérieux, and S. Vélasquez, *Spectroscopy* 20(2), 60–68 (2005).

[9] Y. Danthez, C. Dubuisson, E. Fretel, J.M. Mermet, and O. Rogérieux, Spectroscopy, Applications of ICP and ICP-MS Techniques for Today's Spectroscopist, 14–19 (2005).

[10] S. Willie, Z. Mester, and R.E. Sturgeon, J. Anal. At. Spectrom. JAAS 20, 1358–1364 (2005).

[11] G. Ertas and J.A. Holcombe, J. Anal. At. Spectrom. JAAS 20, 687–695 (2005).

[12] L. Yang, S. Willie, and R.E. Sturgeon, J. Anal. At. Spectrom. JAAS 20, 1226–1231 (2005).