STUDY TROUGH METALLOGRAPHICAL METHOD AND X-RAY FLUORESCENCE TECHNIQUE, ON THE SOME ROMAN BROOCHES DISCOVERED AT TOMIS-CONSTANTA

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***Abstract**: XRF method was used at the same time with a metallographic study in order to determine the concentration of the main compounds of raw materials and, in the same time, of the alloy types used in the ancient period. It was also tried a quality classification of these alloy types in the attempt of watching a development of processing and implicitly, of these objects making techniques.*
Keywords: XRF, metallographic, brooches

1. Introduction

This paper is dealing with a combined through XRF technique and metallographic method study of nine samples of different brooches discovered in the antique metropolis of Tomis area, now Constanta city – Romania. The brooches are some small accessories of clothes and decorative objects very much used in the Roman antiquity. The use spectrum goes from an object similar to the safety pin to real art objects manufactured for military or religious medals awarding. As clothes products, the brooches represents a category of accessories, which was very popular in antiquity, in a large area of using, being part of different cultures from Mediteranean basin. Even if they have their have their origins in old Egyptean civilisation, the antique brooches are evaluated through different uses and shapes, especially as a result of the Roman Empire technology development. The importance of those objects is revealed by the permanent process of manufacturing, through Middle Age to our days, even if they lost the religious symbolist cal value [1],[2]. Among the non-destructive analysis techniques, very much used in the archaeological field today is the XRF technique, too, which proves to be one of the most accurate and direct technique due to its rapid and relatively simple way of good quality results obtaining. The XRF method is usually used at material basic compounds concentration measuring.

In the same time, through the microscopic analyse, the metallographic study has the advantage of direct observation of the samples parts made of different fundamental elements, making easier both zone and global watching of the interaction between them and even of the used manufacturing technologies possibilities, their sequence in the working stages as well as the processing accuracy degree. As regards the XRF, using a radioisotope as exciting source, the emitted radiation strikes the sample and can either be absorbed by the atoms or can be diffused through the material. During this process, if the excitation radiation has enough energy the electrons are thrown out from the inner levels, vacancies being created this way. An unsteadiness stage for atom is thus produced. When it returns to the steadiness conditions, the electrons from the outer levels are transferred on the inner levels and the specific X- rays is emitted as a result of this process. This is the X-ray fluorescence [3].

2. Experimental

In this study we try to present the result of same samples measurement, (from nine different brooches), in order to investigate varieties and similarities between indigenous and abroad-techniques. The samples were initially cleaned of the superficial stratum consisting of corrosion elements. The sample surface needs to be as smooth as possible, in order to avoid the incidental radiation reflection from the source. The samples were ranged in 2π-irradiation geometry, namely the source in front of the sample, the radiation spreading in all directions. The samples were placed at 5 cm from the source. The ^{241}Am radioisotope that emits gamma photons of 59.5 keV energy was used as a source. This ^{241}Am ring shaped source has a 10 mCi activity and provides the energy very near the absorption highest point in the target. When it is desexciting, the element emits the specific X spectrum. The spectrum has been obtained by the detecting system in 1000 seconds and it has put into value all samples elements. The detector for Si(Li) catches the radiations and then the elements can be recognized. The attached soft to the detecting chain works out the spectrum processing and calculates automatically every element concentration trough the interstandartisation method. The standards are composed of: 99.7% Cu, 0.005% Fe, 0.005%Zn, and 0.005% Sn (of MERK production). The concentrations were determined by the detection of the characteristic X-rays for the elements, using formula:

$$\rho = \frac{RR \cdot CF(RL) \cdot CF(AT)}{K} \qquad (1)$$

where: ρ is the element concentration, RR is the perturbation rate in X- ray detection, CF(RL) is correcting factor for losses, CF(AT) is correcting factor for attenuating and K is the calibration constant. During the second stage of this study, samples 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

The structural composition of the manufactured materials for different types of brooches represents an information source concerning the confirmation of the technological proceedings used in the ancient times, as well as the comparative localizing of the manufacturing centers. Because Cu is the major element in all samples, we were interested of Zn and Fe measurements. The following results were determined through X-ray fluorescence:

Table 1. Concentration of Zn and Fe in samples

Sample	Zn [%]	Fe [%]
S1	17,84 ± 0,107	0,018 ± 0,0016
S2	26,15 ± 0,156	0,150 ± 0,0013
S3	24,34 ± 0,146	0,006 ± 0,0005
S4	0,852 ± 0,007	0,009 ± 0,0008
S5	28,11 ± 0,141	0,340 ± 0,0031
S6	13,57 ± 0,081	2,760 ± 0,0221
S7	19,33 ± 0,115	0,120 ± 0,0011
S8	28,35 ± 0,141	0,007 ± 0,0006
S9	0,121 ± 0,001	0,004 ± 0,0003

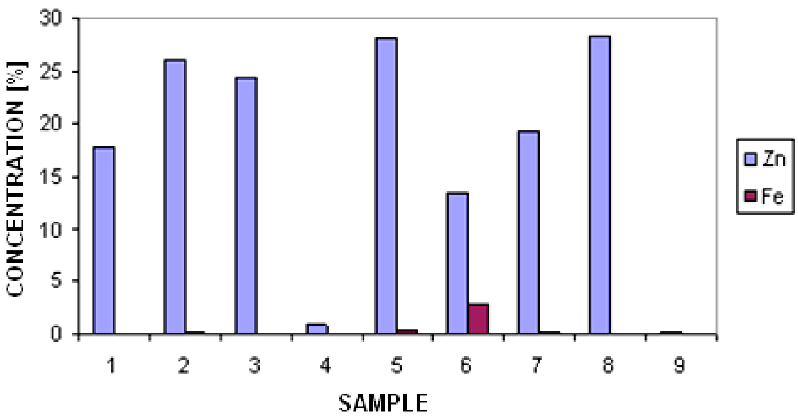

Fig. 1. Zinc and iron content of brooches

The metallographic study confirms the XRF results and offers us whole and detailed perspective regarding the each examined sample.

1st Sample is a monophasic brass (with 30%Zn) in an α-solution from with a CFC network (cube with centred faces). This type of brass has a great plasticity a mechanical resistance of about $20daN/mm^2$ and a relative lengthening of about 35%. It has a segregation that means a chemical no sameness, due to the long interval in which it crystallizes: 900-1000°C. We can conclude that the homogenizing rebacking proceeding wasn't known in that time.

2nd Sample is a monophasic brass with a very great plasticity with the same characteristics noticed in the first test. Moreover, the working out is more neglected. Many inclusions are noticed, this impurities being mainly, composed of copper oxide (Cu_2O) and copper pitch ore (CuO) that due to them a great fragility, a low mechanical resistance at breaking, as well as a relative low lengthening.

3rd Sample is very much the same the former tests, moreover a greater concentration of Cu and a lower one of Zn are noticed and the impurities are lined on the plastic deforming direction (in cold condition).

4th Sample contains a lot of Sn (8-10%). It has a moulding structure (α stage). A slow cooling at solidifying is noticed. At the granulating limit a eutectic alloy is separated (bronze – Sn). The eutectoid from the α-solid solution is a CFC with a $Cu_{31}Sn_8$ chemical compound. The complex cubic network determines a specific increasing of its hardness and mechanical resistance. Such a structure can be found at the fighting weapons (daggers). A plastically cold distortion is applied after moulding through hammer striking, so that a great increasing of hardness and resistance at breaking is obtained through inside cold- hammering.

5th Sample has a moulding without cold-hammering typical structure. It is a brass and an elaborate working out is noticed. It has a dendritic structure. The sample comes from a zone in which the cooling was made slowly, with some uniform warmth evolving.

6th Sample has the former sample features but it has a less elaborate working out. It contains less Zn and more Cu. A less spreading of oxides, especially of copper ones, is noticed. Both grains have dendrites and polygonal grains, which are delivered of recrystallisation. We can say thus, that after solidifying, the piece was rewarmed for a warm education.

7th Sample is a α-solid solution (brass). It partly presents oxides gatherings (closed zones) and segregations. The disoxidation operation for eliminating the oxides producing these segregations through agglomeration, hence a material fragility increasing wasn't used.

8th Sample is structural similar to first sample. Some dress inclusions appearing are seen by the side of a solution. Oxides in significant quantities don't appear. The explanation could be the use of a presage operation, which consists of a charcoal stratum adding at the fusion surface and of some green birch pieces with a diameter of 3-4 cm within. The oxides are thus emitted towards the superficial stratum and, in the end this can be collected and then removed.

9th Sample contains more Sn and less Fe. As in the 2nd, 5th, 6th samples, besides oxides some iron compounds very much similar in shape and colour to the oxides appear. The iron compounds also become fragile and reduce the material mechanical resistance. The iron could come from ores with a high content of iron (pyrites) or by using tools with a high content of iron. All samples have in general typical moulding structures for brooches manufacturing knowing the thick moulding techniques very well, even those with a complex geometry, thing that certifies quite advanced knowledge in the field.

4. Conclusions

Through concentrations determinations by XRF analysing and also through structures metallographic interpreting it is seen that the discovered brooches can be divided into two distinct groups, according to their localizing in time. The brooches manufactured in a single part belong to the Iron Age, hence to the Pre-Roman period, unlike those polyshaped ornamental that come from the Roman period. The models appeared in the Roman period are more complex, requiring a highest technology [4],[5]. As concerning the used material it is noticed from the very beginning that the Cu and Zn alloys with varying Sn percentages mainly with lead and Fe adding in order to confer some superior mechanical properties, especially upon the active parts. Thus 1^{st}, 2^{nd}, 3^{rd}, 8^{th} samples are of brass with 30% Zn and a great plasticity, mechanical resistance of about $20daN/mm^2$ and a relative stretching of 35%. They present chemical nonconformities due to a large crystallizing interval: 900-1000°C. The inclusions induce a high fragility, at some samples being noticed an alignment on the plastic distortion direction, from where we can come to the conclusion that cold forging after moulding was already known [6]. As for 4^{th}, 5^{th}, 6^{th}, 7^{th}, and 9^{th} samples, a superior elaboration from both technological point of view and ornamental processing methods is seen. These samples are initially moulded, too, the Romans having discovered the thick moulding technique, as well as the moulding in fusible shapes, moulded in wax. The material used is based especially on Sn-bronze alloys, with relative high Zn concentrations [7], [8]. A considerable improving of manufacturing proceedings, consisting of a collecting proceeding of oxides from the melted metal before being moulded, thus being eliminated the risk of the material becoming fragile, is seen. Also, after moulding the warm forging is applied for cold-hammering at least on the semi-finished product superficial stratum [9]. It is also seen the more and more frequent use of processing through ornamental cutting of surfaces for general mechanic resistance increasing, without neglecting the aesthetic side seen in its evolution in clothes specialized directions, in art, as well as in the military and religious field.

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