

## **SURFACE PHENOMENA AND THE RESULTS OF CHEMICAL ANALYSIS OF BRONZE ARTEFACTS**

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The preferred method in natural scientific examination of Bronze-Age metallic artefacts is non-destructive surface analysis. One of the scopes of this type of investigations is the chemical analysis of the alloys. But the chemical composition of the surface is modified by surface phenomena such as micro- and macro-segregations or corrosion. The chemical analysis alone can show a different picture about the metal. This study collects and introduces some examples from a detailed research where the metallography of the objects shows different results and reveals the origin of the differences in bulk and surface analysis.

**Keywords:** metallography, artefacts, chemical analysis, surface, bronze

### **INTRODUCTION**

Segregation phenomena take place in metals during the processing, mainly at crystallization and corrosion processes [1], [2]. Both processes have a great effect on the microstructure and chemical composition of artefacts from Bronze Age [3]. This early stage of metallurgy and processing technology could produce inhomogeneous materials [4]. The long-term corrosion processes have a great effect on the surface of the artefacts [5]. Therefore, every time the method of examination is a great question. The metallographic observations and descriptions provide the detailed information about the objects related to the microstructure and chemical composition [6]. Based on this data it is possible to describe the most probable production method. Some information could be uncovered on the smelting of ores and alloying by the analysis of inclusions and composition. Through the detailed testing of the corrosion layer, additional information appears from the utilization of the objects or the burial

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customs [7]. The metallography of Bronze Age objects gives detailed data and a lot of estimation could be made to excess the archeologic research based on them [8]. The only problem with metallography is that it is a destructive material testing method, so the sampling of the objects is necessary. Additionally, to obtain the largest amount of data the position of the sample is determined by the assumed processing technique. The function, the shape and sometimes the surface defects show the possible sequence of production steps [9]. Generally, the position of the samples needs a large area to be destructed [10]. When the principles of heritage protection are required to be taken into consideration, taking these kinds of samples is not allowed. Sampling can also be prohibited in cases of special or unique objects.

Modern analytical methods give the possibility to analyze the surface region without sampling or without destructing the objects. Therefore, this method is currently preferred by the archaeometric studies. Based on these studies average composition is defined, and using this as the raw material composition, hierarchical data clustering and analysis is performed. Another way to research the origin of the material is the Sn or Pb isotope analysis and clustering [11]. The data from these studies are sometimes confusing. Szabó [12] made a collection of analyzed data and shows that the tin content of the Bronze Age artefacts is dramatically increasing when the analyzed volume is decreased. These tests are made at the surface or close to the surface and Szabó clearly shows that the cause of this phenomena is tin segregation at the surface. Szabó estimates there are some technological specialties where this can be reached artificially, however as presented in this study, the corrosion processes are enough to cause it.

Another problem with these techniques and methods is that generally only the chemical composition is revealed without any information on the microstructure. The smelting, alloying and processing has a strong effect to the microstructure of the forming phases. Without analyzing the phases, estimating the chemical composition of the raw material, in this case the copper, is impossible. The local chemical analysis is just a part of the necessary information. Due to heritage protection usually this is the only possibility, but in this case, it is necessary to take this into consideration during the interpretation of the data.

This study introduces this problem through the analysis of three objects from the cemetery of Vértesszőlős, excavated and studied by Julianna Cseh – Museum of Tatabánya.

Metallographic sample was prepared from one object. This object is unique, but it has great importance from an archeologic point of view. Therefore, the interest overwrites the heritage protection. The samples were taken from a part of the objects in a way that allows the full restoration of the objects. Sampling of other samples was prohibited. In case of one sample it was possible to remove enough material to study the composition of the bulk material and the surface together. The third sample was examined with minimal preparation. The chemical composition of the samples is compared in this article.

## 1. MATERIALS AND METHODS

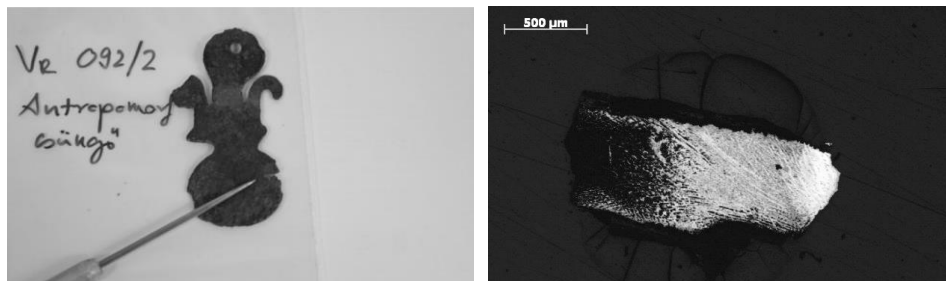
Three different artefacts from Vértesszőlös cemetery were chosen: an anthropomorphic pendant, a wheel-like pendant and a disc headed pin. All of them are bronze artefacts. A sample was taken from the anthropomorphic pendant for metallographic examination. The cut surface of the sample was grinded and polished mechanically, than immersion etching was made using a  $K_2CrO_4$  and water solution. The sample was examined by OM and SEM-EDS technique. Sampling of the wheel and the pin was not allowed. A small surface area was grinded on both artefacts. The grinding was made deep enough to reach the metallic material. This area was examined by SEM-EDS. The local chemical composition was measured and compared after the different sample preparation. A Zeiss AxioImager optical- and a Hitachi S4300 CFE electron microscope was used for the observation and analysis.

## 2. RESULTS AND DISCUSSION

*Figure 1* shows the position of the sample taken from the anthropomorphic pendant and it's a low magnification optical micrograph. The estimated production technique is casting and free hammering. Therefore, the largest area of the shape was chosen for sampling where the effect of the hammering can be observed clearly. At first sight a large corrosion layer can be observed. The thickness of the layer is  $\sim 0.5$  mm. A smooth transition zone was found between the corrosion layer and the bulk metal. At larger magnification (*Figure 2*) a recrystallized microstructure appears with small grains. This suggests a heating after cold hammering, which is a typical technological method in this period. At higher magnification the composition difference caused by the microsegregation during crystallization shows the original dendritic structure, and within this structure the small recrystallized grains can be seen. Only a small extent of cold hammering is assumed based on this. Additionally, this explain the nature of the transition zone. The corrosion process was faster in the segregated zones between the dendrite arms. The hammering makes the direction of the dendrites perpendicular to the direction of hammering, so an elongated nature of the transition zone also can be seen.

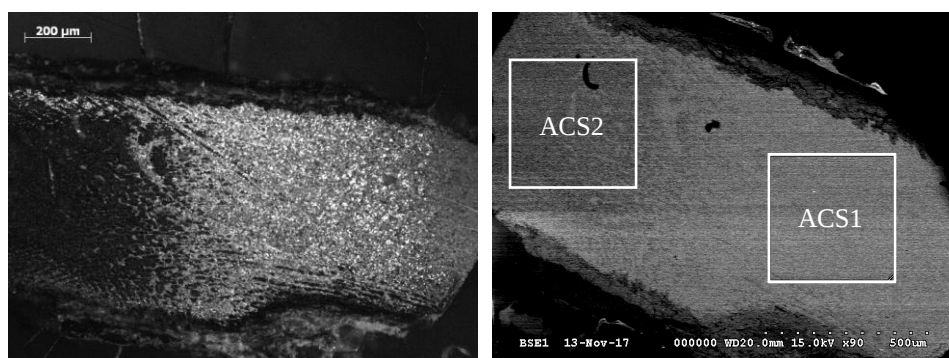
When visual examination shows metallic a surface, the measured composition is the combination of the original composition of the metal and the corrosion layer. For the accurate measurement the corrosion layer must be removed at 0.5 mm depth. This destruction is comparable to sampling.

The chemical composition of the metal is measured in ACS1 area. The tin content is 9.1 w/w%, which is normal in that case when the casting plays a significant role in the production. This composition is near to the limit where the tin bronze can plastically deform. Next to the tin a small amount of Sulphur (0.31 w/w%) and phosphorus (0.24 w/w%) content was measured which is originated to the smelting process. 0.81 w/w% silver content can also be detected. Recently the assumed source of silver is the copper ore.



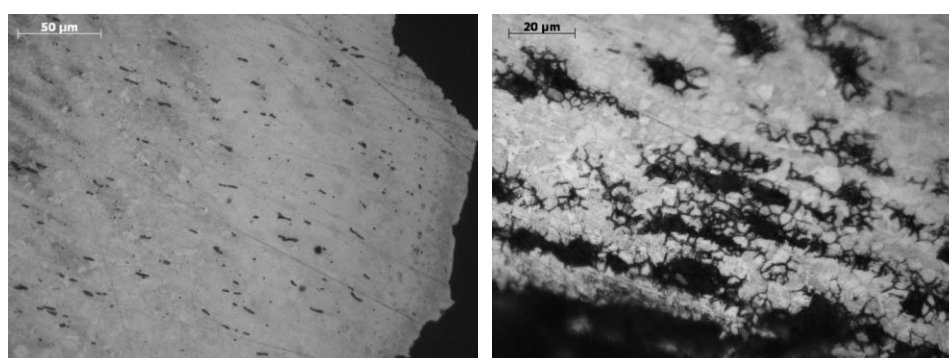
**Figure 1**

*The position and the prepared surface of the metallographic sample are taken from the anthropomorphic pendant*



**Figure 2**

*Optical and SEM micrographs from the microstructure of antropomorphie pendant. The areas of the local chemical analysis are signed of the SEM micrograph by ACS1 and ACS2*



**Figure 3**

*The microstructure of the anthropomorphic pendant in lower and higher magnification. The high magnification reveals the primary dendritic structure driven corrosion process*

The chemical composition of the corrosion layer is measured at ACS2 area. The tin content here is nearly double (15.6 w/w%). The phosphorus disappeared from the layer; the Sulphur level is nearly the same (0.23 w/w%). The silver content increased also dramatically to 2.35 w/w%. Several elements were detected and measured which are not contained in the raw metal, these originate from the soil: Mg, Al, Ti, Cr, Mn, Co. The main problem is that such elements are also measured in the corrosion layer which are used as an indicator of certain ore source. These are the Ni, Fe, Sb and As. All these elements are treated as trace, and within a small range classify the metals. But these metals are not detected in the raw metal. The surface and the bulk analysis can classify the origin to two totally different source, if the extremely high tin and silver content are not taken into consideration, because the microstructure cannot be revealed by a surface analytical method. So, the fact of hammering in this case is unknown, and the high tin content can suggest a casting process only.

In higher magnification due to the originally segregated metal, tin and silver particles can be seen in the corrosion layer. These metals segregate during the corrosion reactions in this nearly pure form. These particles are quite small ones (1–3  $\mu\text{m}$ ). But as Szabó showed, the examined volume with the development of the equipment is decreasing, therefore it is possible to measure extreme high tin and silver content in this case.

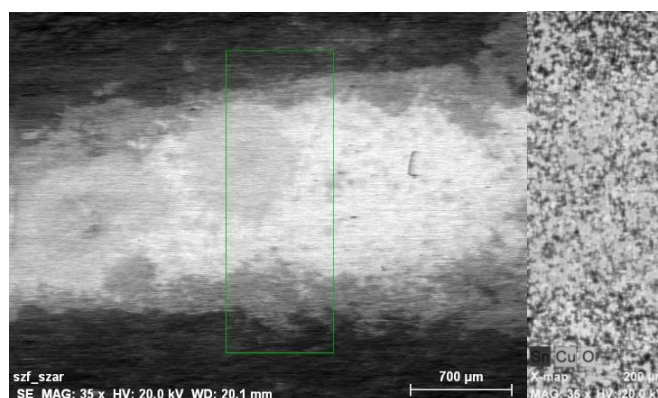
This comparison of the surface region and the bulk metal shows a lot of questions. Therefore, as a case study two other object were examined, but only at the surface of the artefacts. *Figure 4* show the wheel shaped pendant and the measurement set-up. More corrosion layer was removed by grinding while the bronze metal appears to see the previous study. Nearly a similar tin content was measured (8.3 w/w%). High As (2.2 w/w%) and Ni (1.1 w/w%) content was also detected. It is hard to decide if this is the real concentration, or the segregation increases the amount of these element.



**Figure 4**

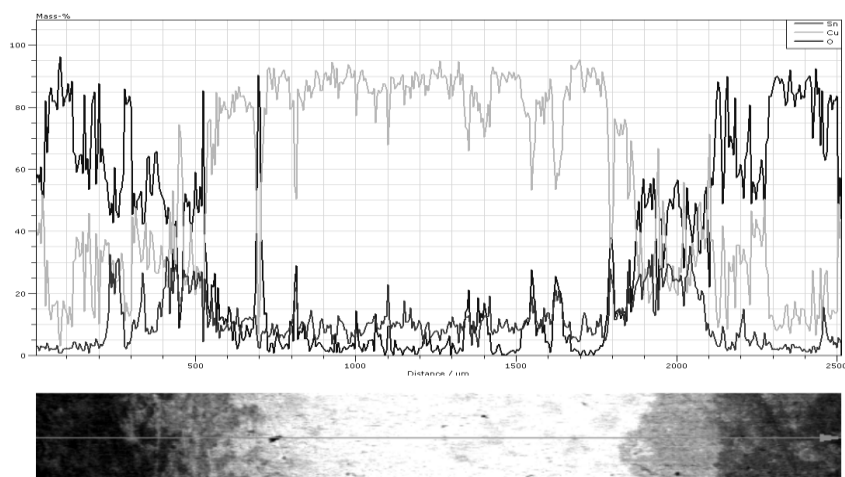
*The wheel-like pendant, and the measurement set-up at SEM chamber*

The advantage of the SEM-EDS technique is that visual information also available. A map and a line analysis were made to study the distribution of the elements. The bright area shows the metal, the dark area is the corrosion product on the surface of the object. there is a grey transition zone where the thickness of the corrosion product is smaller due to the curved surface. The map clearly shows the segregated region of tin. The line scan proves that this area is the light grey band between the metal and the corrosion product. The average copper concentration is the same as it was measured in the first analysis. Considering the copper distribution, when the copper content drops, the tin and oxygen content increase combined, so tin-oxide is assumed to be present in the metallic surface. This indicates that deeper grinding would reveal the real bulk metallic material a composition.



**Figure 5**

*Local chemical analysis of wheel-like pendant by SEM-EDS, the right image shows the element map of the signed rectangle*



**Figure 6**

*The element distribution along a line scan at the analysed area of wheel-like pendant*

A disc headed pin was measured. These kinds of objects are rare, therefore the protection is the main issue in this case. Sampling was not allowed, so the surface was grinded cautiously, and just the necessary amount of material was removed until the bronze colour became visible. Then the composition of the object was measured by SEM-EDS (*Figure 7*). Extremely high tin content was measured (27.1 w/w%). The colour of the alloy with such high tin content is white instead of the typical colour of bronze. Additionally, the alloy containing so much tin would be brittle, and it is impossible to deform plastically. Also, high arsenic (2.45 w/w%) and phosphorus (0.77 w/w%) content was measured. Iron (0.46 w/w%) and nickel (0.94 w/w%) were also detected. The origin of these metals cannot be identified in this case. These either can be contained from the metal or comes from the soil. The large aluminium (1.57 w/w%) and silicon (2.92 w/w%) content surely originates from the soil and the presence of these metals is due to the corrosion reactions. In this case the measured concentration is far from the original concentrations and does not show an acceptable picture about the object.



**Figure 7**

*The position of the local chemical analysis of the disc headed pin and the set-up of the measurement*

The current study uses EDS analysis, but the results are independent from the measuring technique, because the samples carry these composition differences themselves. This introduced problem with the concentration, and the question about the accuracy exists in all testing method where the sample was analysed from the surface region.

## CONCLUSIONS

It is well known that the corrosion processes modify the concentration of the surface region in metallic materials. It is frequently true in the case of Bronze Age objects which went through a long-term corrosion and covered by a thick corrosion layer.

The segregation processes which takes place during the manufacturing processes also can modify the status, the structure and the thickness of the corrosion layers. Therefore, without measuring the real thickness of the corrosion layer, there is no chance to avoid the modification effects of the corrosion reactions, where some elements segregate and others disappear from the corrosion layer. If the measurement of the real metallic concentration is the aim, it is necessary to remove the whole corrosion layer when sampling is prohibited. In other cases, the metallographic analysis is the best way, where microstructural information also can be seen next to the local concentrations. In current researches the concentration of the metals is used in statistical analysis and comparisons to determine groups. In these cases, same elements are used as trace, which has small concentration. This study presented examples where the measurement in the surface layer can give a totally different picture about the metal. In that cases where the heritage protection allowed the metallography is the best way to analyze the metals and collect that information which helps the statistical analysis and the work of archeologists.

#### ACKNOWLEDGEMENT

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