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ISSN 0543-5846
METABK 54(1) 217-220 (2015)
UDC – UDK 669.3:620.193:669:620.18=111

METALLOGRAPHIC AND CORROSION RESEARCH OF COPPER FROM ARCHAEOLOGICAL SITES

Received – Prispjelo: 2014-04-29
Accepted – Prihvaćeno: 2014-09-10
Preliminary Note – Prethodno priopćenje

In this study, copper slabs - ingots, from both Gdańsk and Kraków were examined. Besides metallographic examinations, attention was focused on analyses of corrosion products. The following techniques were applied: scanning electron microscopy with fluorescent X-ray microanalysis and X-ray diffraction. The conducted investigations enabled determination of the causes of corrosion in the old copper slabs, due mainly to the mediaeval alloying techniques and copper processing technologies.

Keywords: copper, corrosion, archaeometallurgy, microstructure

INTRODUCTION

As raw materials, copper, lead and tin are found at many archaeological sites, among which the most interesting are wrecks of the sunken merchant ships, such as the Copper Ship (Miedziowiec) from Gdańsk (Poland), Kopparvraket near Trelleborg, Skafto wreck (Sweden), Helgoland (Germany) or Stavanger wreck (Norway). Copper as raw material was also found at the Main Market Square in Krakow (Poland), which proves that this town participated in European copper trade.

The biggest medieval raw materials find in Poland, two tons of copper in the form of 213 ingots of different size and weight, comes from the bottom of the Bay of Gdańsk. The wreck of a sunken ship called Copper Ship (Miedziowiec) is a unique object in the Baltic and the North Sea, where such a well-preserved and varied cargo was found.Copper played an important role in the European trade as early as in the Middle Ages, and economical progress was significantly connected with ore excavation and trading. In the Middle Ages, the city of Krakow played a very important part in the far-reaching metal trade. Krakow obtained a monopoly on trade and transit via Gdańsk to Flanders and England. As the consequence, Krakow became a member of the Hansa – the most powerful medieval trade organisation – where it was named the Copper House. In Krakow, copper trade was conducted on the Main Market Square, in the building of the Great Weigh together with the smelting houses. The remnants of the old activity of the Scales, i.e. of weighing and partitioning of the large lumps of copper, are, among others, copper–saturated archaeological layers and large amounts of copper chips coated with corrosion products. There are also larger fragments of copper – a quarter of a slab, or an irregular copper slab. One must think here of an analogy between these copper slabs and the slabs recovered from the ship that sunk in the Bay of Gdańsk probably in 1408 and, on account of its cargo, was called the Copper Ship (Miedziowiec) [1 - 3].

In this context some issues regarding the process of copper manufacturing are also worth noticing. The work of medieval miners and metallurgists was studied and disseminated by an eminent scientist, Georgius Agricola (1556) [2 - 3].

To produce copper from ore, Agricola recommended performing a number of operations, which included mining and enrichment of ore, preparation of fuels and fluxes, metal smelting and refining, and separation of noble admixtures. Studying the history of metallurgy is also significant for the comparison of technological processes of different metal materials [2 - 3].

MATERIALS AND METHODS

From a rich variety of archaeological material, for the present studies the following metal items were selected: one copper slab from the Great Weigh in Krakow and copper slabs from Gdańsk. Analyses were made of copper slabs fragments, obtained from the Copper Ship wreck (Miedziowiec), which left Gdańsk filled with a heavy copper cargo and sank shortly afterwards [1].

Studies of copper from archeological sites provided the data about microstructure, chemical composition and corrosion destruction of the old raw material [4 - 7]. The analysis provided information about the level of old copper metallurgy, as well as destruction degree of

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Table 1 **The results of chemical analysis XRF of the archeological copper specimens examined for the presence of trace elements Specimens 1 - 8 from Gdańsk slabs, specimen 9 from Krakow slab / wt. %**

	Type I				Type II				Type III
	1/hz/966	2/w5/100	3/hz/805	4/hz-831	5/hz-810	6/hz-69-8	7/hz-69-5	8/hz-69-3	9/Kr P1
Pb	0,48	1,10	0,13	0,38	2,44	1,89	1,71	2,98	0,41
As	0,89	0,91	1,06	0,64	0,54	0,67	0,28	0,61	0,1
Sb	0,13	0,14	0,58	0,0	0,0	0,28	0,26	0,11	0,09
Zn	0,0	0,0	0,0	0,0	0,22	0,0	0,0	0,0	0,14
Fe	0,11	0,15	0,13	0,32	0,98	1,31	1,14	1,59	1,29
Ni	0,0	0,17	0,12	0,12	0,04	0,03	0,03	0,03	0,0
Ag	0,11	0,0	0,18	0,0	0,0	0,19	0,15	0,20	0,02
Sn	0,0	0,0	0,0	0,0	2,14	2,46	2,89	2,61	0,05
Cu	98,3	95,7	97,9	96,7	93,6	92,8	92,2	91,4	97,83

the artefacts, by establishing the kind and extend of their corrosion [8 - 9]. Understanding the corrosion processes is significant for conservation of metal artefacts as well as maintenance of industrial equipment working in specific conditions. Researching oxide layers of copper is common nowadays, because of widespread application of copper, especially in electronics and construction sector [10 - 15].

RESULTS AND DISCUSSION

The investigations of copper slabs tell us that the metal was of an relatively high purity and the copper content sometimes reached even 99%. As a consequence of studying the Copper Ship cargo, two types of raw copper, differing in chemical content, were distinguished (Table 1).

Type I is characterised by relatively high concentration of Cu 95,7 ÷ 98,3 %, with an insignificant content of impurities 0,1 ÷ 1,1 % Pb, 0,6 ÷ 1,1 % As, 0 ÷ 0,6 % Sb and trace amounts of Ag, Fe, Sn. Type II: 91,4 ÷ 93,6 % Cu, 1,7 ÷ 3,0 % Pb, 0,3 ÷ 0,7 % As, 0 ÷ 0,3 % Sb, 1,0 ÷ 1,6 % Fe, 0 ÷ 0,2 % Ag and 2,1 ÷ 2,9 % Sn, the content of which changes the character of the raw material examined. The differences between chemical contents of Type I and Type II copper are presented in Figure 1.

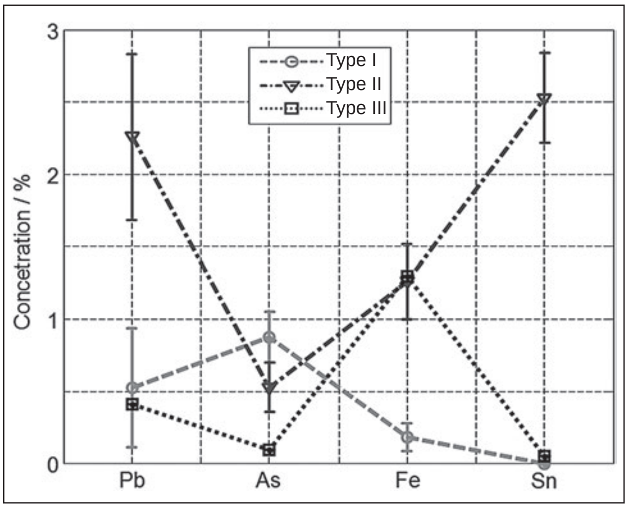


Figure 1 The results of chemical analysis of the archaeological copper specimens examined for the presence of trace elements - types I, II, III

The results are similar for the slabs from Krakow and Gdańsk (type I only). The greatest differences occur in the content of iron, which in the specimen from Krakow amounts to 1,29 % of Fe, 0,4 % of Pb and 0,1 % of Zn (type III).

In the chart (Figure1), the concentration of the chosen, characteristic elements for the three researched copper slabs (Pb, As, Fe, Sn). The mean values of elements concentration together with standard deviation are shown in the chart as well. A significant difference

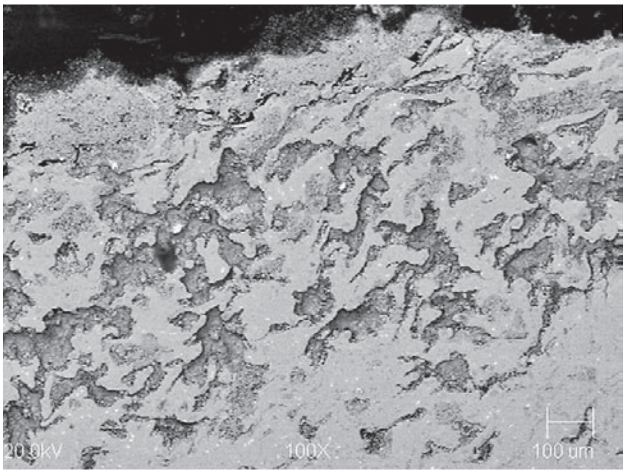


Figure 2 SEM images of corrosion products on a copper slab found under the Main Market Square in Krakow

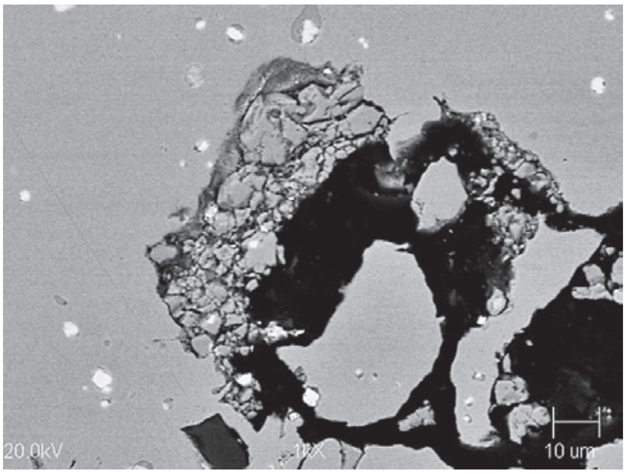


Figure 3 SEM images of corrosion products on copper slabs from "Miedziowiec"

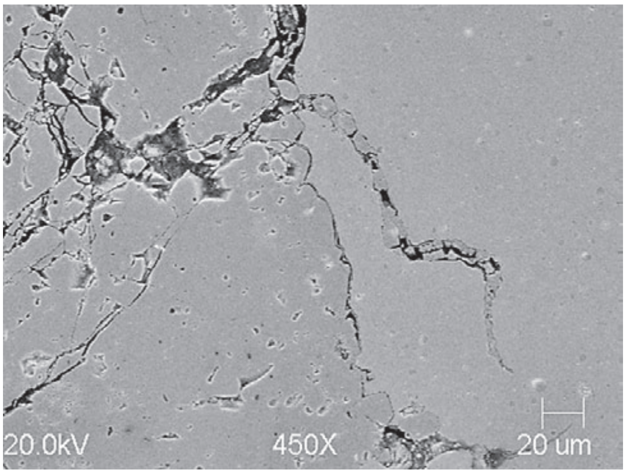


Figure 4 SEM image of corrosion of the copper slabs from "Miedziowiec"

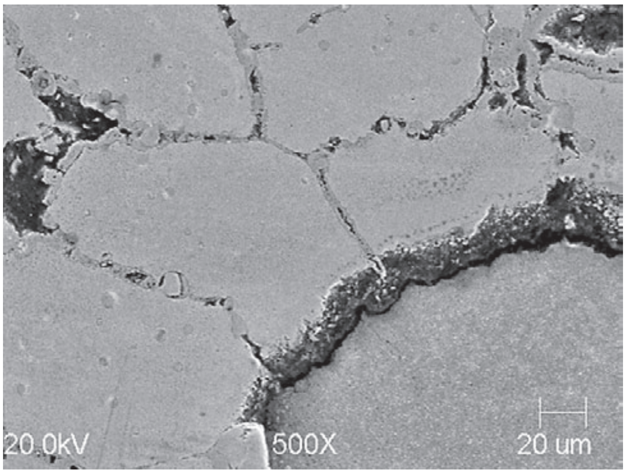


Figure 5 SEM image of corrosion of the copper slab from "Miedziowiec"

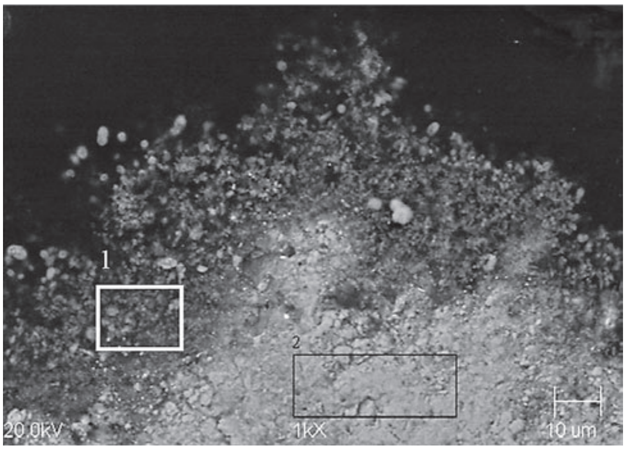
in the content of these elements is visible (mean values) as well as a significant difference in the materials homogeneity, expressed as the standard deviation value. The greatest inhomogeneity is shown by the copper form Gdańsk (type II).

SEM examinations revealed changes in boundary layers that took place due to the long-lasting effect of corrosive agents (Figures 2 and 3). In the case of Krakow slab it was the atmosphere and wet soil; in the case of slabs from Gdańsk – seawater. The investigations carried out by SEM/EDS method identified typical products of copper corrosion. These are mainly oxides, chlorides and sulphates of aluminium, iron and copper. X-ray diffraction tests established the presence of copper oxide(I) Cu_2O, copper oxide(II) CuO and copper chloride(I) CuCl on the surface of the sample. The cases mentioned below refer to the corrosion taking place in seawater and in soil.

Moreover, the slabs from Gdańsk show serious losses in the form of numerous pittings, which were certainly caused by falling out of the whole metal grains due to the corrosion of impurities present on the grain boundaries (Figures 4 and 5). The thickness of corrosion layers is different in both cases and it changes according to the area examined. In Krakow slab it occasionally exceeds 60 μm.

A SEM image (Figure 6) and a fluorescent analysis in micro-areas (Table 6) confirmed the earlier microscopy observations. Because of its inhomogeneity, the boundary layer was in this case much more porous than the centre of the specimen and coated with corrosion products, among which oxides and chlorides are present. This proves the presence of chlorine in the corrosive medium, which in this case was soil and seawater. The thickness of the changed boundary layer varies within the range of 25 - 60 μm.

The medium of seawater had a very aggressive effect on the slabs from Gdańsk, which were, however, partly protected by an insulating fossil shell composed of various matter, like pitch, wood tar, etc. While the objects collected in Krakow were subjected firstly to a destructive influence of the atmosphere and next - humid soil. Without any doubt, the atmosphere increased the degradation, as it contained some impurities originating from the waste gasses formed during the casting processes conducted in the nearby metal smelting plant.



Analysed area	Cu	O	Cl	Fe	S	Pb
1	40,7	29,0	19,2	5,6	3,1	0,7

Figure 6 SEM image and chemical composition examinations (at. %) of corrosion of the copper slabs from the Main Market Square in Krakow

Additionally. the objects were systematically coated with solid particles. like dust. dirt and soot. making moisture and salt stick to them more easily. Corrosion in soil can proceed at a high rate. and in some cases it can assume similar values to the seawater corrosion. The determining factor in this case is the electrical resistance related to the presence of soluble salts and high moisture content in the soil. We know very well that both these conditions did occur in the case of the soil in the Main Market Square. though the corrosion rate was slowed down by a large distance from the surface of the soil and the resulting weak access of oxygen. Yet. it should be remembered that the most corrosive kinds of soils are. so called. 'cultural layers' processed for a long time by man and they are mainly encountered in urban areas.

CONCLUSIONS

Copper is characterised by good corrosion resistance. Nevertheless, staying for a long time in corrosive medium, it suffered the process of significant degradation, which was of electrochemical nature, of both local and general range. Both the presence of continuous layers slowing down the progress in corrosion as well as changes of more local character in the form of pittings and crevices were observed. The research confirmed that the susceptibility to corrosion of archeological objects made from metal depends to a great extent on the structure of metals and alloys. The source of intensive corrosion are the grain boundaries as the places of increased chemical activity. The higher activity of the grain boundaries is related to technological processes, i.e., with segregation of alloying constituents and impurities, and with crystallographic defects.

The fact that the metal finds suffered from different types of corrosion deserves some attention. It should be stressed that the type of corrosive medium is very important for the run of the corrosion process in items of archeological value. In the seawater, mainly pitting and intercrystalline corrosion was observed while in the atmosphere and soil, the corrosion was of both of general and local character, but still resembling the pitting, intercrystalline and deposit types. The conducted analyses allowed to assess the similarities and differences observed in the corrosion processes.

The analysis of old metallic material with respect to its history, physical metallurgy and corrosion processes is an important contribution to broaden our knowledge of the ancient objects. Further studies are expected to bring more information about the history of old objects and the related technological processes and corrosion effects.

The collected data can help us with proper classification of artefacts and the choice of best conservation means and techniques, including the removal of corrosion products, stabilising the chemical reactions, protection from the destructive effect of environment and preparation for their exhibition.

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Note: The responsible translator for English language are D. Pedrak and A. Hardek, Krakow, Poland