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The “Metallurgist's Hoard”. Silver and Lead Smelting in the Early Medieval Poland

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Abstract

During archaeological research of early medieval settlement in Dąbrowa Górnicza - Łosień, a hoard of silver coins and silver smelts was discovered, over 1000 items in total. There was also found a mining shaft and numerous furnaces in the settlement area, confirming its mining and metallurgical character. The settlement development was based on excavating and smelting rich lead ores, containing significant amount of silver. Silver was separated from lead in successive stages with the help of cupellation.
The paper presents the analyses of silver smelts and coins coming from the hoard. Optical and scanning microscopy were applied as well as the methods of chemical content analysis by X-Ray Fluorescence (XRF), Scanning Electron Microscopy and Energy Dispersive Spectroscopy in microareas (SEM-EDS), and also phase analysis with the help of X-Ray Diffraction method (XRD).
The impurities of the silver clumps testify to the fact that they are semi-products. After refining and modifying the material by adding copper, denars were minted from it. The silver coins belonging the hoard are made from relatively pure material, including a small lead. An insignificant amount of other metallic elements testifies to the good quality of the raw material and efficiency of silver production in the early Middle Ages.

Keywords: Non-Destructive Testing, Silver, Lead, Archaeometallurgy, X-Ray Fluorescence, Cupellation

1. Introduction

Nowadays, silver is widely used in jewellery, technology and electrotechnology. Research is conducted concerning improving the properties of silver, especially its durability and resistance to wear. Also, silver is a component of alloys and composites [1-2]. Historically, silver was an important element of the payment system and silver mines and smelting shops belonged to strategic manufacturing.

Silver played an important role during the formation period of the Polish country. Ornaments were manufactured and first coins were minted from it. Probably cut silver pieces and silver smelts (cakes) were used as currency in settling commercial transactions.

In the early days smelting lead and silver from ores took place in boles, which took advantage of natural gusts of wind. This method relied mainly on galena reaction, this is lead sulphide(II) with lead oxide(II). The reduced lead travelled down, where it solidified in the shape of flat cakes. Silver was separated from silver by the cupellation method (Fig.1). [3-6]

In Poland a more advanced method was used, namely ore smelting took place in shaft furnaces [5]. Silver that was obtained during the furnace process was subsequently separated from lead [8]. To reduce galena also iron compounds were used [8].

In the Middle Ages, at the present day boundary between Little Poland and Upper Silesia, the greatest amounts of non-ferrous metals were produced, mainly lead (including lead rich in silver). In Poland, smelting lead and obtaining silver form galena can be dated, owing to archaeological sources, already to the second half of 11^{th} century. The nearest centres of ore mining functioned in Germany [9].

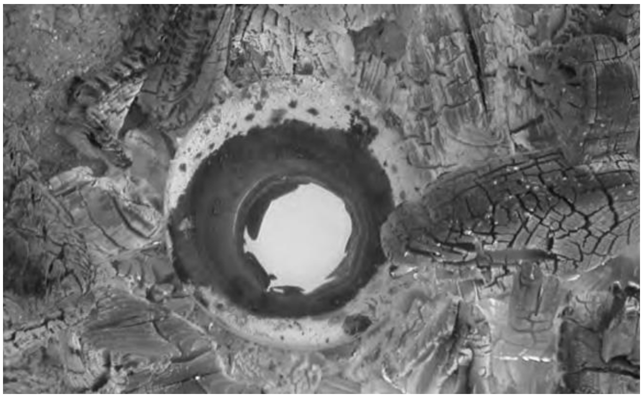

Fig. 1. Cupellation Experiment [6]

In Poland, silver and lead ores are connected with zinc-lead deposits located on the Silesian and Kraków-Częstochowa Upland. They contain about 86,6% of lead with silver additions (0,01-1%), as well as zinc, iron, copper, antimony and other.

Archaeological research was conducted of two sites in Dąbrowa Górnicza-Łosień, which were recognised as early medieval metallurgical workshops processing lead and silver. [10], in fact there are the first traces of direct lead smelting from local ores. The finds of hundreds of tuyeres, ladles, fragments of moulds and crucibles, including a cupel with traces of silver, testify to the fact that production took place here Metallurgical furnaces were also found in Sosnowiec-Zagórze and Dąbrowa Górnicza-Strzemieszyce. During the analysis of furnace stock, the reduction of lead compounds with the help of iron compounds was ascertained, which is at present the oldest example of applying this method. Metallurgist furnaces with clay walls and stone enclosures were discovered, as well as simple hearths, without additional constructions. Some of the hearths could be used for roasting galena during the process of obtaining litharge, this is lead oxide(II), being also a commercial product.

In 2006, during archaeological research of the area of metallurgist settlement in Dąbrowa Górnicza – Łosień, the - so called - Metallurgist's Hoard was discovered. The treasure consists of over 1000 silver coins and clumps; it was hidden between 1160 and 1165 AD [10,11]. At present it is exhibited in “Sztygarka” Museum in Dąbrowa Górnicza. The metal science analyses of the coins and silver smelts were conducted at the Jagiellonian University, at the *Museum* of *Archaeology* and Ethnography in Łódź, and at the Foundry Faculty of AGH [10,12].

2. Methodology and materials for research

Silver artefacts found during the archaeological research in the area of silver and lead production in the early Middle Ages were analysed. Non-destructive macro- and micro-analyses were conducted with the help of light and scanning microscopy; chemical content analysis using Energy Dispersive X-Ray Fluorescence (XRF), Scanning Electron Microscopy and Energy Dispersive Spectroscopy in microareas (SEM-EDS), and also phase analysis with the help of X-Ray Diffraction method (XRD).

3. Results of research

Chosen elements of the Metallurgist's Hoard, this is silver raw material and coins, were tested, and also, for comparison, galena (lead ore) from Silesia-Krakow deposit and the casting mould containing a drop of alloy were researched.

3.1. Lead ore analysis

There were conducted tests for galena coming from the Trzebinia mine, which belongs to the Silesia-Krakow deposit, where historically lead and silver were obtained. For the galena sample (Fig.2) the tests were performed using scanning microscopy with chemical content analysis in microareas (Table 1).

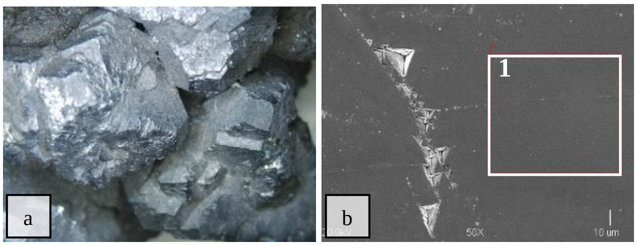

Fig. 2. Galena from the Trzebinia mine: (a) macrostructure, (b) SE picture with the microarea for analysis marked (1)

Table 1.
Chemical composition of the lead ore (wt.%)

Chemical composition (wt.%)					
Area	Pb	S	Fe	Ag	Zn
1	91,4	4,5	-	1,0	0,9

The observation of the sample microstructure showed crystal structure of the sulfides. Together with the lead content (91,4%) a small proportion of silver was also noted (1%).

3.2. Silver raw material analysis

Silver raw material was subjected to macro- and microscopic observations (Fig.3-4).

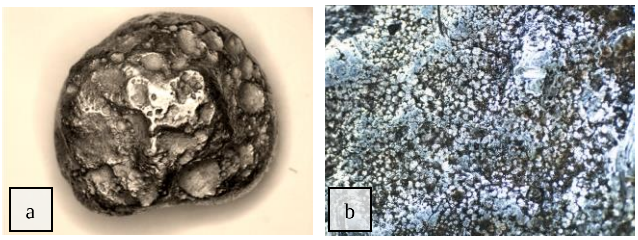

Fig. 3. Silver raw material: a) silver smelt, b) macrostructure 20x

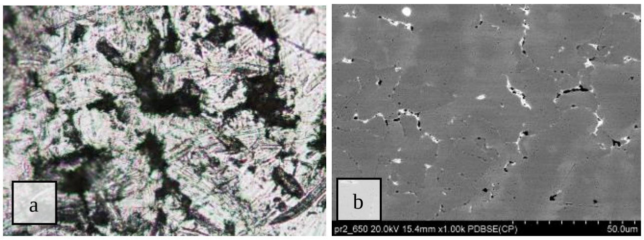

Fig. 4. Silver raw material: (a) microstructure, 200x; (b) SE picture, 1000x.

The observations showed that the surface is not uniform, which reflects the coarse-grained structure of the material, showing features of dendritic structure (Fig. 3b). On the surface of the silver material there is reflected the shape and coarse-grained surface quality of the mould or crucible where it solidified. Also the plane of free solidification was registered, showing the presence of crystallites.

During scanning microscopy the coarse-grained dendritic microstructure was observed. A small volume of another phase was noted in the interdendritic spaces (Fig. 4b). Diphase build of the microstructure was confirmed when researching the phase content by X-Ray Diffraction method. The diffractogram shows silver and lead, without other phases present (Fig. 5).

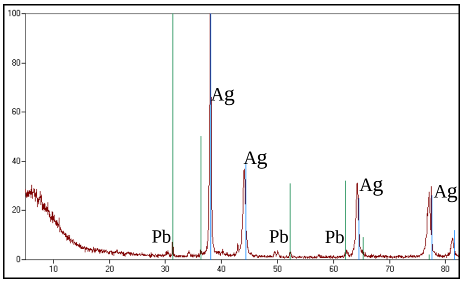

Fig. 5. Diffractogram of the silver raw material, Ag and Pb were identified

Chemical composition of the raw material was assessed with the help of X-Ray Fluorescence in macro- (XRF) and microarea (SEM-EDS). The series of chemical content tests were analyzed statistically, and the results are shown in Table 2.

Table 2.
Chemical composition of the silver raw material (wt.%)

Chemical composition (wt.%)			
No.	**Ag**	**Pb**	other
1	93,2	6,4	0,4
2	94,0	5,7	0,3
3	92,6	7,1	0,3
4	93,6	6,0	0,4
5	94,7	5,0	0,3
average	**93,6**	**6,0**	0,4

Chemical content analysis confirmed the inhomogeneity of the raw material with reference to its chemical content and structure. To picture the layout of the microstructure content, the layout map was done for silver (Fig. 6a) and lead (Fig. 6b). These maps confirmed the inhomogeneity of chemical content within the sample volume. They show that the silver is located mainly in the solid solution and the lead in the interdendritic spaces.

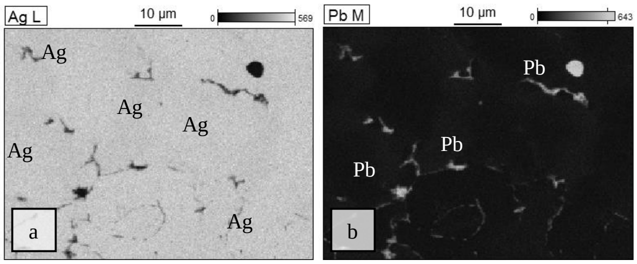

Fig. 6. SE picture, the elements layout map: silver a) and lead b)

3.3. Silver coins analysis

The surface observation and chemical content analysis were conducted for 19 coins from the hoard. The chosen results are presented in the pictures (Fig.7) and in Table 3.

Fig. 7. Silver coins belonging to the Metallurgist's Hoard, reverses, Władysław II the Exile, type IV, 12th century, a D-31, b)D-37

Table 3.
Chemical composition of the silver coins (wt.%)

Chemical composition (wt.%)				
No.	**Ag**	**Pb**	**Cu**	other
D-31	92,0	1,3	6,4	0,3
D-37	95,8	0,9	2,7	0,6
D-113	93,6	1,0	4,9	0,5
D-131	94,5	0,8	4,1	0,6
D-195	97,3	0,3	1,7	0,7
average	**94,6**	**0,9**	**4,0**	0,3

The chemical content analysis showed the dominant part of silver (within the range of 92-97,3%), remaining amount of lead (0,3-1,3%) and the alloying addition of copper (1,7-6,4%).

3.4. Ceramic mould analysis

Additionally, chemical content of the ceramic mould was investigated, because of the metallic drop found in it (Fig. 8).

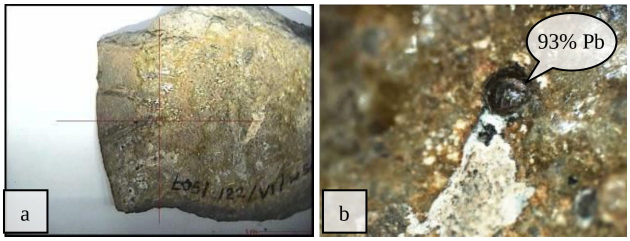

Fig. 8 Casting mould from Dąbrowa Górnicza – Łosień: a) spectrometer camera picture, b) macrostructure with the lead drop visible

The presence of the lead in this mould confirms the knowledge of foundry technology.

4. Discussion of results

The results of chemical content analysis of silver raw material and coins are collated in the chart (Fig.9). To show the correlation, the content of silver and lead is shown in logarithmic scale.

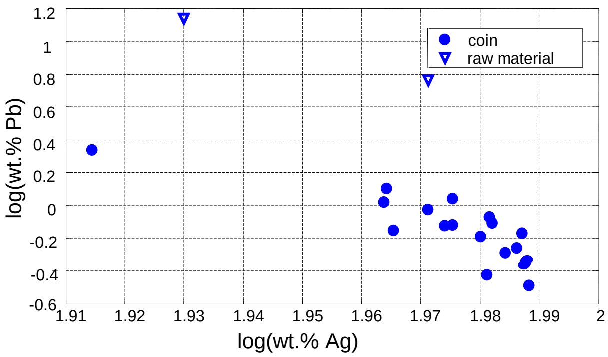

Fig.9. The chart showing relation of Pb and Ag (wt%) in the raw material and coins

The analysis shows that in most cases of the coins tested the relation of Pb and Ag is similar, which is attested by clear points concentration in the chart. The raw silver material is distanced in relation to other points, which is connected with lower silver content in comparison to lead.

5. Conclusions

The research conducted for galena, the raw silver material, coins and the casting mould from the region where the existence of medieval production has been proved, has allowed to assess the technological aspects of lead and silver smelting as well as production of silver coins.

Silver cakes are traces of the old silver production in Dąbrowa Górnicza – Łosień. Hightened lead concentration in the silver alloy and unevenly spread lead concentrations attest to silver and lead production by galena roasting. Pb-Ag alloy consists of two solutions of low solubility: silver solid solution in lead and lead solution in silver. During the cupellation process gradual and effective separation of the lead and silver phases took place.

The impurities of the silver cakes are the evidence that they are a semi-product. After refining and modifying their content with copper addition, denars were minted from them. The silver coins belonging to the hoard show the material of relatively high purity, including low lead content. Slight addition of other metallic elements testifies to the good quality of raw material and the effectiveness of its production method in the early Middle Ages.

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