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Slavic production of iron in light of slag analysis

Introduction

One of the main driving forces of development of Slav tribes after settling in the Carpathians region during Migration period, was production of iron from ores. It is well - known that Slavs developed their basis knowledge of smelting and working of iron in original settlements prior to Migration period. It was not fully recognized, how beginnings of Slav iron metallurgy after inhabitation of new territories were influenced by experience of previous inhabitants. Metallographic analysis of iron objects of both Slav and Avaric origin showed many similar features (Mihok, Soláriková, Holly, 1991, p.103-107; Mihok, Pribulová, Mačala, 1995, p.145-188) suggesting important influence of new neighbour, Avar Kaganate. Level of Slav iron metallurgy culminated in the Great Morava period, when iron smelting was performed in three kinds of small reduction furnaces, characteristic for this region.

This paper presents study of smelting remnants found in four archaeologic sites in Spiš, north-east Slovakia and in Central Slovakia site Sliač - Horné zeme (fig.1). All sites are dated to pre-Great Morava and Great Morava periods.

Slags found in Slav sites at Spiš. Spiš region in North-East Slovakia, owing to its favourable position on trading path from Mediterranean to Baltic, was dense populated in protohistoric and early Medieval times. It is the reason, why whole territory of Spiš is full of archaeologic sites and finds. Many of them are related to smelting and working of iron. Members of archaeometallurgic group at Faculty of Metallurgy did the research of many finds from numerous sites in Spiš that enabled them to describe developments of iron metallurgy from La Tene period up to the 19th century in this region.

Results of chemical analysis of slags from four Slav sites are in Tab.I.

Four pieces of slags, designated SN2, SN7, SN13A, SN13B, represented pre-Great Morava site Spišské Tomášovce - Pod Hradiskom. First three ones were characterized as bowl shaped or fragments of bowls, containing many charcoai prints on their surfaces. Sample 13B had glassy character on some places, it was not characterized as slag.

Sample 13B represented very rich hematite iron ore, as was clear from chemical analysis. Microscopic analysis of samples SN2, SN7 and SN13A showed, they represented smithy slag. They contained two component silicate matrix, remnants of scales, corrosions products, remnants of silica sand and charcoal (fig.2). This finding was also confirmed by chemical analysis of these samples, namely ratio Fe_{ox}/Fe^{2+}

Multiphased inhabitation (Bronze Age, Late Roman Era, Great Morava period) was found in site Poprad-Stráže, Na rázcestí. The slag, represented by sample SN21, belongs probably to Great Morava horizont. Analyzed piece was characterized as dark-grey lump of porous slag. Microscopic analysis showed typical analysis of slag

from smelting process in small reduction furnace. It contained wiistite dendrites in two component silicate matrix (fig.3). Shape of slag piece and structure features don't allow to decide, if slag was tapped from the furnace or not.

Inhabitation dated to the Great Morava period (8th - 9th centuries A.D.) was found in site Zehra, Hlinky I. Here Slav pottery, slag and parts of clay walls of smelting furnace were found. Sample SN8 contained three pieces of slag. All three pieces had smooth, melted surface, two of them had rope-like shape. Structure of all three samples confirmed analysed slag was waste of iron smelting in small reduction furnace. The structure was typical by wustite dendrites (smaller or bigger) in two - component silicate matrix (fig.4). The structure of all three pieces was relatively homogeneous. This fact together with shape and appearance of slag pieces suggested high liquid state of slag in furnace that probably enabled to tap it. Pieces of broken slag cakes of tapped slag were not found at the site. Analyzed set of samples from site Zehra, Hlinky I contained also the fourth piece. Its analysis showed it was very rich hematite ore, sample SN18 (Table I).

Large settlement, dated to the 9th and 10th centuries A.D., was found at site Helenin dvor, cadastre Veľká Lomnica. Two slag pieces, designated as SN5, were selected for analysis. One of them, SN5A, had shape of flat bowl and contained charcoal prints. The second one, SN5B, had irregular shape with melted, smooth surface and many cracks. The sample SN5A was typical smithy slag, its structure had all typical features of smithy slag. The sample SNB had structure, that was dominated by two component silicate and contained a lot of metallic iron particles and a lot of corrosion products (fig.5). It was probably also smithy slag, though its shape was not typical for such kind of slag, but possibility, that slag represented spoiled heat in small reduction furnace, could not be excluded.

Slags found in Slav sites Sliač - Horné Zeme. Slav sites in locality Sliač - Horné Zeme belong to Slav inhabitation of Zvolen basin in the Central Slovakia. Two Slav settlements separated by branch of the river Hron were excavated. The settlements, dated to the 8th – 9th centuries A.D., had agricultural and craftsmen character. Besides other finds also many pieces of slag, iron ore and fragment of tuyere were found. Two of the excavated objects were described by archaeologist as smelting furnace and smithy workshop. Also finds of iron objects were frequent.

21 pieces of slag and four pieces of iron ore were submitted for chemical and microscopic analysis. Samples of iron ore had iron contents from 43 to 54 wt %. Samples of slag were divided into two groups according to their shape. Most of the slag in the first group were described as dark grey small pieces with smooth, melted surface. Most of them had rope-like shape. Big slag pieces of indefinite shape, that remained in furnace hearth together with bloom, missed. All pieces of slags in the first group were fragments of big slag cakes, that resulted from tapping of slag from the furnace. This fact suggested better temperature conditions in the hearth, resulting in liquid slag of low viscosity.

Microscopic analysis of these slags pointed to another decisive factor. Only three

of slags from the first group had higher content of wüstite in their structure. Most of the slag had very similar structure, composed of two or three silicate components with very little (fig.6) or none particles of wüstite (fig.7). This fact proved better reduction conditions in the furnace and better yield of iron. Resulting silicate slag with low contents of wüstite had lower melting point which resulted in its lower viscosity under temperature conditions in furnace hearth.

The slag in the second group was smithy slag, the slag that was collected at the bottom of the smithy hearth. It possessed all typical features of smithy slag: two-phased silicate, remnants of scales, remnants of silica sand, corroded pieces of metallic iron. Example of such structure is in fig.8.

Smelting activity at the site was supported by finds of iron ore pieces. Chemical, microscopic and X-ray diffraction stmcturat analysis showed all four analyzed pieces represented bog ore. One of analyzed pieces is in fig.9. As can be seen from the figure, the piece is composed of distinctly separated layers formed in process of sedimentation of iron salts dissolved in water. Author of the paper studied structure of bog ore from excavations of Hallstat settlement in Cečejovce (Mihok, 1994, p.69-90) but no macrostructure of bog ore with separated layers was found. X-ray diffraction structural analysis of bog ore from site Sliač - Horné Zeme determined two main iron-bearing components: limonite $FeO(OH)$ and $Fe_2Si_2O_5(OH)_4$.

Discussion of analysis results. Very little is known what was development of iron metallurgy from the beginnings of Slav inhabitation of the present Slovakia up to culmination of Slav era in Great Morava Empire. Three main types of iron smelting furnaces in Great Morava period were described: free standing shaft furnaces with shallow or deep sunken hearth, Imola type furnaces built in intentionally prepared terraine steps, and Zeiechovice type furnaces. Very little is known what was the development leading to those furnaces. Many questions were put by leading archaeometallurgist related to slag tapped or not tapped iron smelting furnaces in Roman Era and Early Medieval (Tylecote, 1992).

At last three types of furnaces were recognized in LaTene and Roman Era on the territory of Slovakia: free standing small shaft furnaces, slag pit shaft furnaces and in one site also cupola type furnaces (Cengel, Mihok, Javorský, 1982, p.522-525; Mihok, Fröhlichová, Balážˇ, 1995, p.51-63; Mihok, Pribulova, Pieta, 1999, p.9-14). Slag pit shaft furnaces were by their construction designed for slag tapping, slag was tapped also from cupola-like furnace. Concerning Great Morava furnaces, Zeiechovice type and Imola type were not designed for slag tapping. Free standing small shaft furnaces could be slag tapped but experimental smelting of Czech archaeologists found tapping of slag with high viscosity difficult.

Author of presented work analyzed a lot of metallurgy finds from Roman sites at Spiš. At least at one site, Spišské Vlachy, Pod lazík, iron smelting furnaces were slag tapped. It was very difficult to recognize from analysis if slag from iron smelting furnaces found in Slav sites at Spiš, were tapped from furnace or not, but tapping of slag in site Zehra, Hlinky I was very probable. Unlikely those finds, slags from Central

Slovakia Slav sites Sliač - Horné Zeme were tapped from the furnace. Striking difference between Spiš and Central Slovakia slags is in their structure. Slags with purely silicate structure with no or very small contents of wüstite fully prevailed among slags from Sliač - Horné Zeme site. Such structure indicated high liquidity of slag in the furnace hearth, ready to be tapped. No such structural features were found in Spiš smelting slags.

It is typical that either rich hematite iron ores or easy reducible bog ores were used as charge components for reduction furnaces. No siderite iron ores or products of their roasting treatment, were found.

Preparation of iron semiproducts or iron objects in smithy hearth for next smithy operation didn't change for centuries. Smithy slags, described in this contribution, had the same structural features as the ones from La Téne or Roman times or as the ones from culminating Medieval many centuries later. The authors studied also manufacturing methods of Slav blacksmiths, the results are published in other papers. High skills of blacksmiths, very sophisticated and purposeful techniques were recognized.

Conclusions

The paper deals with slags from iron smelting and working, found in excavation of some Slav settlements in Spiš and in Zvolen basin in Slovakia. Chemical and microscopic analysis of slags revealed:

1. It was impossible to recognize on the basis of slag analysis, what types of iron smelting furnaces were employed at the sites. The furnaces, used in Spiš sites, were probably slag tapped, furnaces in Central Slovakia site were slag tapped.
2. The fact, that the latter ones were tapped, was supported by slag structure, composed solely from silicate components.
3. Rich hematite iron ores were used as iron smelting charge in Spiš sites, bog iron ore was used in site Sliač - Horné Zeme in Zvolen basin.
4. The finds from both regions contained a lot of smithy slag pieces. Standard smithy technique of iron semiproducts and iron objects preparation in smithy hearth prior to smithy manufacturing techniques was found.

Literature

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Resumé

The contribution presents evaluation of slag finds from four Slav sites in Spiš and from one Slav site in Central Slovakia. The slags both from iron smelting process in small reduction furnaces and from smithy process of iron objects manufacturing were analyzed. Problems of slag tapping from smelting furnace were extensively discussed. At least smelting slags from Central Slovakia site Sliač-Horné zeme were tapped from the furnace. Analyzed sets of finds contained also pieces of hematite iron ore and bog ore that were used in charges for smelting furnaces.

Table I. Chemical analysis of slaga from sites in Spiš, wt %

Sample no.	SiO_2	Fe_{celk}	CaO	AgO	Al_2O_3	MnO	FeO
SN2	13.08	56.96	1.68	1.20	1.42	2.16	54.17
SN7	26.58	42.44	2.80	0.80	0.40	6.67	34.48
SN13A	12.94	59.76	2.83	0.40	0.61	0.15	60.50
SN13B	3.66	60.80	2.80	0.40	0.20	0.37	1.43
SN21	2.30	56.90	1.6	0.80	1.80	1.40	60.49
SN8A	25.08	48.58	1.12	1.20	1.02	4.81	56.04
SN8B	16.52	57.52	1.12	0.80	0.81	3.26	63.37
SN8C	21.22	50.26	4.48	0.40	1.43	3.63	59.92
SN18	4.26	62.50	3.92	0	0.20	4.29	2.06
SN5A	8.50	59.20	2.24	0.40	0.20	1.55	45.55
SN5B	14.72	59.20	2.80	0.80	1.02	0.32	49.00

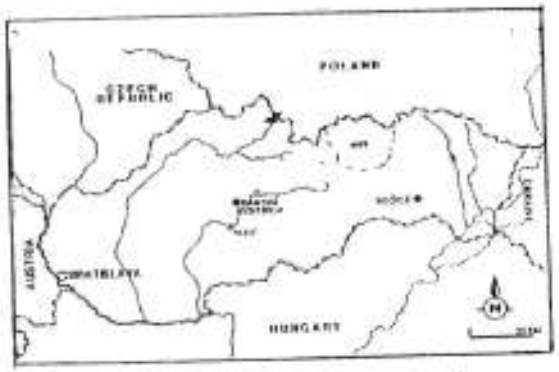

Fig.1-Location of Slav sites described in the paper.

Fig.2-Corrosion products, remnants of charcoal and silica sand in structure of slag SN2.

Fig.3-Structure of furnace slag, sample SN 21.

Fig.4-Structure of furnace slag, sample SN 8

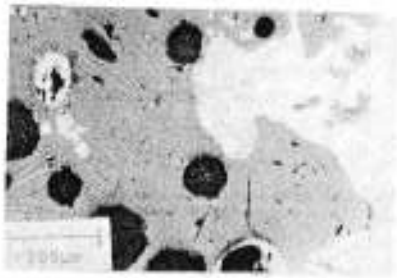

Fig.5-Two component silicate, metallic iron particles and corrosion product in structure of sample SN 5ft

Fig.6-Structure of slag from iron smelting, site Sliač – Horné zeme

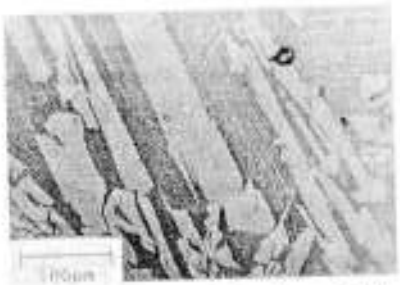

Fig.7-Structure of slag from iron smelting, site Sliač – Horné zeme

Fig.8- Structure of smithy slag, site Sliač – Horné zeme

Fig.9-Piece of bog ore, site Sliač – Horné zeme