Bowl-shaped slags from post-reduction phases of an ancient smelting process in the Świętokrzyskie region (Poland)

Szymon ORZECHOWSKI(1), Ireneusz SULIGA(2)

(1) Institute of History, The Jan Kochanowski University in Kielce, Poland
(2) AGH University of Krakow, Poland

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Résumé : La sidérurgie ancienne des Montagnes Sainte-Croix est connue essentiellement grâce aux recherches faites sur les ateliers de production primaire. De nouvelles perspectives d'études ont été apportées par les recherches menées sur l'habitat à Pokrzywnica, où l'on a attiré l'attention sur un nouveau genre de scories en forme de calottes. On les trouve dans des structures interprétées comme de foyers d'épuration de masses brutes. Les analyses chimiques indiquent que ces scories en formes de calottes sont plus riches en Fe_2O_3 et FeO par rapport à celles des bas fourneaux. Cela pourrait être interprété comme l'apparition d'une phase contenant des ions Fe^{2+} et de Fe^{3+}. Cette phase pourrait être l'hématite Fe_2O_3. En phase liquide la réaction est possible entre la fayalite et l'hématite. Il est possible que ce soit un apport de l'extérieur, comme des battitures issues du travail des masses brutes durant le chauffage et martelage dans le foyer. Les scories en forme de calottes seraient alors générées par la fusion des scories et des battitures qui se formaient sur la surface du fer.

Abstract: The ancient iron metallurgy of the Holy Cross Mountains is known mainly thanks to research carried out on the production workshops. New perspectives for study have been provided by research conducted on the settlement at Pokrzywnica, where attention has been drawn to a new type of slag in the form of bowl-shaped slags. These are found in structures that are interpreted as hearths for purifying sponges. Chemical analyses indicate that the bowl-shaped slag is enriched in Fe2O3 and FeO compared to that from slag-pit furnaces. This could be interpreted as the appearance of an oxidation element of Fe^{2+} and Fe^{3+} ions. This element could well be hematite Fe_2O_3. In its liquid phase, a reaction between fayalite and hematite is possible. It is possible that this is the result of external intervention, such as slagging, which appears on iron sponges during smelting and hammering in the hearth. The bowl-shaped slags were generated by the melting of slag and slagging that formed on the surface of the iron.

Introduction – purpose and scope of the study

The ancient metallurgy of the Świętokrzyskie region, recognized as the largest iron production center in *Barbaricum*, is primarily known due to studies of production sites known as slag-pit furnace clusters. Professor K. Bielenin investigated approximately 120 such workshops, collectively comprising several thousand bloomery furnaces. In his research, he distinguished two types of production organization within the "organized and inorganized" slag-pit furnace clusters[1].

Previous studies have focused almost exclusively on the furnaces themselves, with only occasional investigations extending to the associated workshop infrastructure. As a result, our understanding of facilities related to the broader post-reduction phases remains limited. Furthermore, the survey-based nature of prior research does not allow for a definitive conclusion as to whether the characteristic structured workshops of Świętokrzyskie metallurgy, located outside settlements, engaged in iron processing or were solely dedicated to primary reduction. The present study attempts to address this issue by analysing an unknown type of slag previously undocumented in this region, referred to as *bowl slag*. According to the authors, this slag type represents evidence of activities related to the purification of iron-bearing shale before it was delivered to the main forge.

1 Type of metallurgical production at the slag-pit furnace clusters

Reconnaissance of the bloomery ironworks performed to date in the Świętokrzyskie region indicates that within the region of the "organized" slag-pit furnace clusters some unindentified activities related to the preliminary treatment of the raw iron sponge were performed. The idea may be supported by the presence of the so-called gromps occurring. They occur often in the fillings of the pits which are named in the literature as "adjacent-to-slag-pit cluster pits". The pits used to be found in close neighbourhood to the bloomery furnaces, at the peripheries of the slag-pit clusters. They operated most likely as supportive facilities and formed the 150 to 300 cm wide and 60-80 cm deep pits, in which one may find some fractions of the slags coming mainly from broken blocks, fragments of furnace shaft outer body, rocks and ceramics. The data established by K. Bielenin proves that within the investigated so far slag-pit furnace clusters investigated to date from one to a few objects identified as the so-called reheating hearths or iron sponge forge works were recorded at 17 sites (Bielenin 1992, p. 130, tabl. 1).

In principle, only the so-called gromps may indicate conclusively that within the region of the considered slag-pit furnace clusters the operations linked to the post-reduction stages of metal processing were performed. The gromps are small pieces of raw iron sponge, which due to mechanical forging, were discarded from the main body of the processed material. They are of 1 to 80 mm in size and about 500 g in weight. The metal in the gromps is mostly porous accompanied by slag. Almost all the structures of iron-carbon system, from pure ferrite through ferrite-pearlite up to the structures typical for the white and gray pig iron, were found (Nosek 1994). The presence of

[1] Bielenin 1992, p. 89-127.

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such materials in the close vicinity of the bloomery furnaces proves that the first stage of iron sponges' forging took place at the furnaces stand, probably directly after the heated sponge had been removed from the furnace and transferred to undefined processing works.

2 Bowl-shaped slags – indications of "raw" iron sponge processing

The new explorations which have been carried out at the large settlement-production complex at Pokrzywnica, dis. Pawłów, provided new research opportunities. The site is located at the heart of the Świętokrzyskie metallurgical center, near the Pokrzywianka River (Figure 1). The site at Pokrzywnica is a big complex of a few hectare area composed of a settlement and several dozen slag-pit furnace clusters situated at the settlement's peripheries (Figure 2). The up-to-now investigations have proved that, in that region, a few settlement phases may be identified dated for the period between the 1st to the 4th A.C. century linked to the Przeworsk culture.

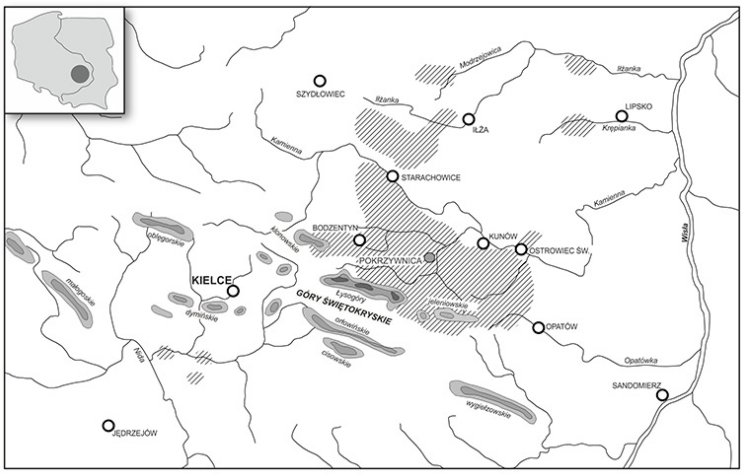


Fig. 1 : The location of the studied site within the Świętokrzyskie metallurgical center is depicted in the accompanying diagram (shaded areas indicate the extent of metallurgical sites).

A broad variety of bowl-shaped slags appearing within the considered complex are to be noted as to their shapes as well as to their sizes and structures (Figure 3). For comparison reasons the slags in question were divided into 3 groups. The main criterion were their size and their weight. Three types of the slags were distinguished : small, medium and very large. To the first group belong the elements of, as a rule, 5-10 cm in diameter and a few dozen to about 200-300 g in weight (Figure 3 : 6, 7, 8). The medium forms are over 10, but less than 25 cm in diameter achieving even 3 kg in weight (Figure 3 : 2, 3). The very large slags are even bigger than 30 cm in diameter weighing a dozen or few more kg (Figure 3 : 11, 12).

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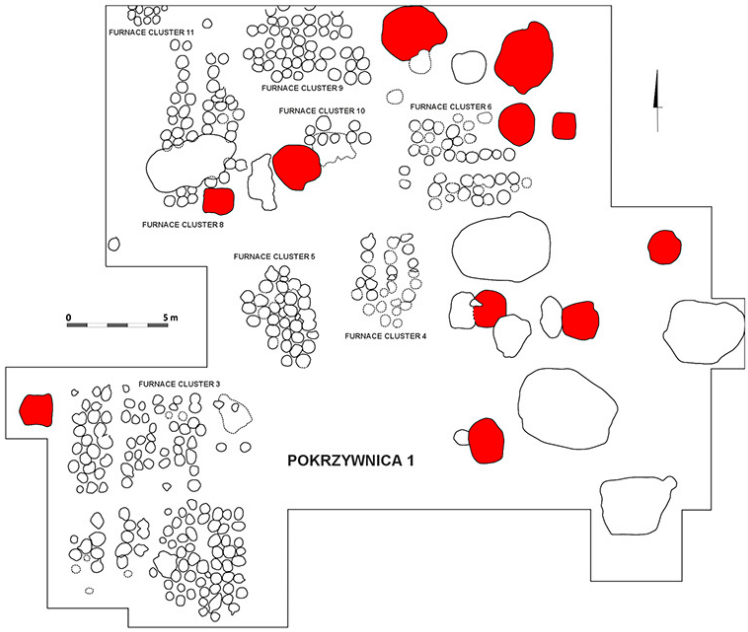


Fig. 2 : Pokrzywnica, dis. Pawłów, site 1. General layout of the settlement-production complex at the West side of the site (the hearths are marked in red).

Particular objects, within the same group as well, may differ as to their structure and shape. Most of them are round, in some cases they look like a slightly elongated ellipse with a flat or slightly concave top face and, as a rule, a regular, convex bottom face (Figure 3). Individual objects have at their bottom a typical casting as a result of the upflow of the slag by the narrow channel (Figure 3 : 10). Also evident are slags in a form of the trough channels achieving the length of a dozen or so up to about 20 cm and 5-7 cm wide (Figure 3 : 9).

Within the area of the settlement of Late Roman period (eastern part) the bowl-shaped slags found at Pokrzywnica comprised a significant component of the culture layer and of the fillings of different objects. Their presence "in situ" has been recorded for the first time in the hearths. It is worth mentioning in particular 3 shallow pits of 0,95-120 cm in diameter denoted by the numbers : 11, 12 and 27, whose setup looks like an ordered one imposed by some stipulations of some technological line. The materials were the subjects of the detailed metallographic and chemical analyses published in Dialogues d'Histoire Ancienne (Bielenin *et al.* 1998, p. 142-164). Results of those analyses will be discussed later in this paper.

In recent years the excavation works were relocated to the settlement's West periphery, where due to geophysical investigations a substantial complex of the slag-pit clusters dated to the 1st-2nd c. A.D. was found. Apart from the individual, large, organized slag-pit clusters localized outside of settlements and small unorganized works at settlements known from the literature, some complex metallurgical centers amounting to a few, a dozen or so and even a few dozens of bloomery furnaces' clusters containing

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in total up to a few thousand of castings there have also been discovered. They are accompanied by a number of support objects in the form of pits, heating stoves and furnaces containing the bowl-shaped slags mentioned above as well as other materials in a form of slag rubble and residues of shaft body of some unidentified metallurgical objects (Figure 2). The complex is situated at the periphery of an inhabited settlement and forming with it one functional entity (Orzechowski 2006, p. 43-59).

For the problem under consideration, of particular importance are due to the pits, which played a role of hearths linked probably to some as yet unknown stages of the metallurgical process aimed at purification and blacksmithing of raw iron sponge. On the site under consideration, one may distinguish at least 3 types of such objects.

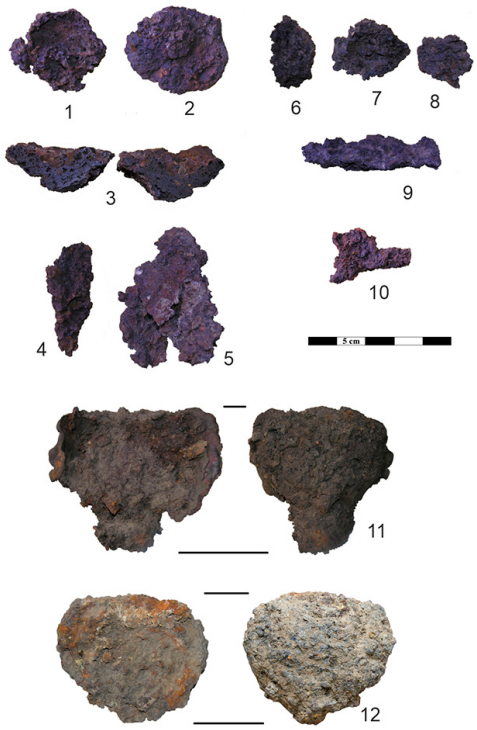


Fig. 3 : Pokrzywnica, dis Pawłów, site 1. Various forms of plano-convex slags appearing on the site and in the neighborhood of the slag-pit clusters. General view and profiles.

Only some of these hearths have *in situ* bowl-shaped slags. They are represented among the others by the objects N° 174, 187, 192, 195, 198. They occur in groups at some distance (a dozen or so to a few dozen meters) to the slag-pit clusters close to the inhabited objects (Figure 2). They are pits of 170-220 cm. in diameter and 50-70 cm in depth with almost vertical sidewalls and flat bottom (Figure 4). The sidewalls bear marks of the extensive burning reaching a depth of 2 to 7 cm. On the bottom occurs an ash layer “in situ”, in which are immersed single bowl-shaped slags. The objects contained from several dozen to over 200 kg of bowl-shaped forms

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of different size (structure N° 198 – 150 kg, structure N° 192 – 210 kg) and from several dozen up to nearly 100 kg of slagged, thin walls of the shaft over-ground body (structure N° 198 – 62 kg, structure N° 192 –92 kg). Those hearths were most likely fed by a bellow situated close to them in a shallow pit (structure N° 195).

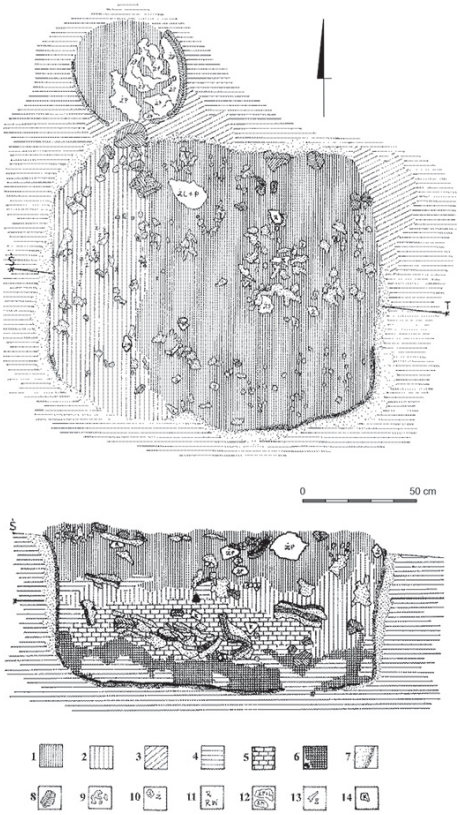


Fig. 4 : Pokrzywnica, dis. Pawłów, site 1. Hearth No 187 – general view (above), profile (down).
1. loess of brown colour containing substantial amounts of the rubble from crushed shafts' walls accompanied by fine slags of porous structure, 2. pieces of bright loess, 3. the layer analogous to the first one with more slag rubble and walls' fragments, 4. layer of ash and charcoal chippings, 5. pure loess together with loess rock-bed, 6. loess with traces of advanced burning, 7. strongly burned walls of hearth shaft body, 8. the walls, as above, but covered with slag and in part vitrified, 9. reduction porous slags, 10. iron ore, 11. rock, 12. animal bone.

Significant dimensions of the object indicate that it could be a reheating hearth in which might be simultaneously performed carburization and deslagging of the iron sponge coming from a few or over a dozen furnaces. It should be noted that the bowl-shaped slags occuring by those objects are more massive and heavier that the forms found earlier and they may be qualified for the second or the third group. Those forms achieve the sizes within 10-20 cm limits, although one could meet some specimens exceeding 25 cm in diameter and over a dozen kilograms in weight.

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3 Metallographic and chemical analysis of the bowl-shaped slags

The bowl-shaped slags from Pokrzywnica have been subjected to the chemical and structural analysis performed by a team of the French research workers. Two conceivable technologies leading to the formation of those types of slags were considered, i.e., from a smith forge or from a furnace for cleaning of the iron sponge. From the studied slags, in general there was no observation of any secondary oxidation of metallic elements which may indicate the smith forge option. There was almost a complete lack of any markers or specific indicators, but rather only the inherited markers. In the authors opinion it was proof that the analysed bowl-shaped slags originated from the stage of cleaning of the sponge which followed the reduction process (Bielenin *et al.* 1998, p. 148, 160).

In recent years this work has been continued by Polish metallurgists from the University of Mining and Metallurgy, Cracow who performed a series of analyses of the bowl-shaped slags found during the archeological explorations at the Pokrzywnica site (Suliga *et al.* 2002, p. 183-190). The presented work is a continuation of the main track of investigations mentioned above. The newest materials found at the stand at Pokrzywnica in a form of the so-called "big bowls" have also been included for analysis. The aim of those investigations was to locate the latter in the total spectrum of the slags whose origin was the ancient iron metallurgy of the Świętokrzyskie region.

4 Methods and scope of investigations

The subject of the investigations were the specimens of the slag sampled from the big bowls and their comparison to the other types of the bowl-shaped slags and the slags coming from smelting. A classical chemical analysis and X-ray diffraction (XRD) phase analysis of the slag were performed after the samples were ground into a fine powder. The mass of the analysed samples was 10g. These studies were supplemented by microstructural observations and energy-dispersive X-ray spectroscopy (EDS) microanalysis of individual structural components on polished sections of solid samples. The scope of the EDS microanalysis was dependent on the size of the individual structural components. The results of those analyses allowed to define the chemical, phase and structure composition of the samples and to refer them to the analogous earlier research made on the bloomery and bowl-shaped slags which originated from the same archeological site.

The analysed slags have been divided into 4 groups : bloomery – d, small bowl-shaped – mm, big bowl-shaped – md, very big bowl-shaped – mbd. In classifying the bowl-shaped slags, only their size was taken into account. All the slags were of the same geommetric shape, i.e., a flat top surface and a convex bottom and when top viewed a shape of an elongated ellipse. Their sizes were diversified while their size ratio was equal to mbd : md : mm = 1 : 0,5 : 0,3 referenced to the longitudinal size of the very big ones – 34.5 cm.

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5 Results of the analyses

The results of the chemical analysis of the slag samples, per oxide are presented in Table 1. They were ordered according to the slag' character and for each of the groups the mean values were computed. As to the bloomery slags the analyses refer to the specimens sampled from the top N° 12 (1) and the bottom of the slag block N° 12 (2). Analogously, the bowl shaped slag N° 190 was sampled from the places diversified macroscopically, i.e., solid structure N° 190 (l) and porous N° 190 (2) Tab. 1.

Tab. 1 : Chemical composition of slags conversed into oxides (descriptions type of slag as in Figure 5)

Slag	No	Fe	SiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	MgO	CaO	P_2O_5	S
d	12g	0,68	24,32	3,9	7,21	58,2	1,85	0,54	1,9	0	0,88
	12d	0,68	26,77	5,29	8,6	51,2	2,34	0,74	2,87	0	0,46
	average	*0,68*	*25,54*	*4,59*	*7,9*	*54,7*	*2,09*	*0,64*	*2,38*	*0*	*0,67*
mm	41	0,95	10	2,3	7,22	73,7	0,41	0,76	3,28	0,48	0,75
	102	1,09	52,2	5,02	12,5	19	0,41	0	3,28	0,42	0,23
	107	0,68	12,98	2,97	17,98	57,8	0,5	1,29	2,87	0,71	0,34
	135	0,82	17,89	2,86	14,92	54,8	1,27	1,36	2,6	1	0,38
	average	*0,88*	*23,26*	*3,29*	*13,15*	*51,3*	*1,29*	*1,14*	*3,01*	*1,3*	*0,42*
md	174s	0,35	19,8	2,91	24,44	48	0,75	0,41	1,66	0,34	0,13
	174w	0,35	11,2	1,69	41,08	38,6	0,7	0,41	4,44	0,32	0,08
	average	*0,35*	*15,5*	*2,3*	*32,79*	*43,4*	*0,73*	*0,41*	*3,05*	*0,33*	*0,1*
mbd	190p	0,25	15,1	3,48	23,19	50,9	0,79	0,82	3,88	0,32	0,06
	190l	0,51	14,7	2,99	12,11	65,4	0,5	0,2	2,22	0,23	0,05
	average	*0,38*	*14,9*	*3,23*	*17,65*	*58,1*	*0,64*	*0,51*	*3,05*	*0,27*	*0,55*

Referring to the results of the analyses before conversion to oxides a high diversification of the chemical compositions of particular specimens may be noticed, even for the same objects. The differences of the elements' contents are basically of a statistical character and only for such elements like : Fe^{3+}, Mn, Si and S one may find a systematic correlation of their contents to the slags' character. The bowl-shaped slags compared to the bloomery ones are lower as to Mn, Si and S levels. Phosphor content was low at 0,11- 0,44%, while Sulphur was at 0,05-0,88% level. The interpretation of the results of the oxide analyses presented in the table was carried out together with the presentation of the results in the composition triangle (Table 1, Figure 5). The dominant-in-slags composition phases are set in the corners of the triangle, together with the phases playing an analogous role in metallurgical process : FeO with MnO and metallic Fe, SiO_2 with Al_2O_3, CaO, P_2O_5, MgO and S as well as Fe_2O_3. This presentation of the compositions of the investigated slags was guided by a modified form of the pseudo-equilibrium system from the work of S. Holewiński, concerning bloomery slags from the Świętokrzyskie region[2]. The compositional triangle presented in this study does not represent a true ternary phase equilibrium system. Instead, it is a modification of Holewiński's pseudo-system, adapted to account for the broader chemical spectrum of the analysed samples. This approach to classical chemical analysis allowed for the identification of compositional trends in the *bowl slag* and its relationship to slag blocks from the Świętokrzyskie region, as well as the interrelations among different forms of *bowl slag*.

[2] Holewiński 1956, 269.

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All the analysed slags, analogous to Holewiński's approach, are localized in the neighbourhood of the FeO corner. The bowl-shaped slags are specific in principle in a higher Fe_2O_3 content, which is particularly distinct for the big- and very big bowl-shaped ones. There is also another trend worth noticing. By drawing lines from the compositional point of fayalite ($FeO \cdot SiO_2$, Fe_2SiO_4) to hematite (Fe_2O_3, upper boundary) and magnetite ($FeO \cdot Fe_2O_3$, Fe_3O_4, lower boundary), it can be observed that the compositions of the analysed *bowl slags* align along these trajectories. This indicates that the parent bloomery slag was admixed with hematite (Fe_2O_3) or magnetite (Fe O_4). Furthermore, the *bowl slags* exhibit a higher FeO content in the diagrams, suggesting that bloomery slag was also enriched with this component during their formation (see Figure 5).

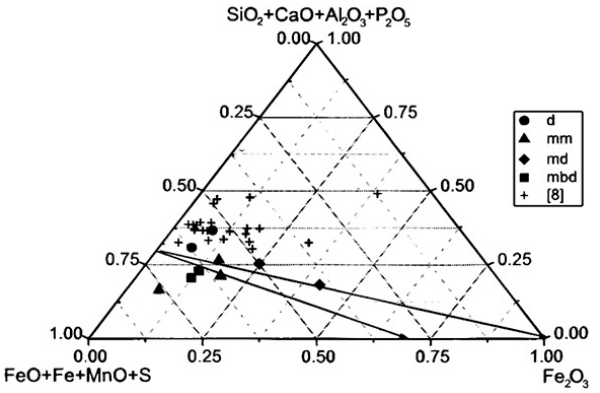


FIG. 5 : Chemical composition of analyzed slags on compositional triangles : FeO+Fe+MnO+S – SiO_2+CaO+Al_2O_3+P_2O_5 – Fe_2O_3. Slags' type according to the notations. On the triangle axes the fayalite Fe_2SiO_4 and the magnetite Fe_3O_4 are marked. (d – bloomer slag, mm – small bowl-shaped slag, md – big bowl-shaped slag, mbd – very big bowl-shaped slag, [8] – collection of typical chemical compositions of bloomer slag from the Świętokrzyskie region).

The results of chemical analysis presented above indicate, analogously to the earlier study, some enrichment of the bowl-shaped slags in Fe^{3+} ions when compared to the bloomery slags (SULIGA *et al*, 2002). Figure N° 6 presents the contents of Fe^{2+} ions (from FeO and Fe_2SiO_4) and of Fe^{3+} ions (from Fe_2O_3 and Fe_3O_4) as well as the fractions of FeO and Fe_2O_3 of the analysed slags. The ionic composition of the analysed samples was determined using classical chemical analysis methods. In general, the bowl-shaped slags are richer in Fe^{3+} ions content than the bloomery ones. The trivalent iron ions occur in hematite Fe_2O_3 and magnetite Fe_3O_4. The results of the analyses indicate enrichment of the bowl-shaped slags in those phases.

With the exception of slag N° 102, X-ray diffraction phase analysis did not prove, any presence of the hematite phase in the slags, yet it did so for the magnetite phase. The specimens were dominated by fayalite Fe_2SiO_4, yet FeO, SiO_2, mullite $Al_6Si_2O_{13}$ and a spinell phase - hercynite $FeAl_2O_4$ were also present.

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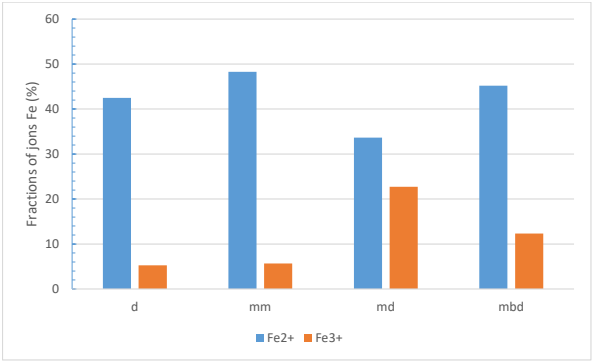


FIG. 6 : Fe^{2+} and Fe^{3+} contents in analyzed slags (descriptions type of slag as in Figure 5)

The results of the chemical and diffractional analyses confirm the thesis of the present authors on a probable admixture of the bowl-shaped slags with the products of a possible gas corrosion of the metal phase, thus they indicate that bowl-shaped slags stem from some stages of metallurgical processing of the bloomery process products, i.e., the iron sponge. Bowl-shaped slags may be considered as the bloomery slags admixtured by the gas corrosion products formed by processing of the iron sponge.

The chemical and phase composition data rather exclude any secondary oxidation of FeO by secondary heating and possibly a partial liquefaction of bloomery slags. The oxidation of the wustite follows by the scheme :

$$FeO \text{ --> } Fe_2O_3 \text{ --> } Fe_3O_4$$

By such an oxidation process some intermediate phase of Fe_2O_3 would have been formed in bowl-shaped slags, which was not the case.

Interesting data on the origin of the bowl-shaped slags is also provided also by an analysis of the slag samples microstructure (Figure 7). One may distinguish 3 structural components in the structure of the analysed samples : bright dendrites or their cross-sections crosswise to the growth forces gray prism crystals of different sizes dark-gray areas filling the interdendrites zone between prism crystals. Locally, by the latter components, one might see bright, fine dendrites or eutectics. The microanalysis performed on particular structural components made possible their phase identification possible (Table 2). The bright dendrites were the wustite FeO, the gray prism crystals were the fayalite Fe_2SiO_4, while in the interdendritic zone of the fayalite one could see a mixture of the components in a form of fine dendrites or eutectics. The mullite $Al_6Si_2O_{13}$ and the hercinyte $FeAl_2O_4$ were localized in the interdendritic zones. The structural components of the slag samples are enriched in K (mainly eutectics and interdendritic zone), Mg (locally in the fayalite) and Ti (low contents in different components).

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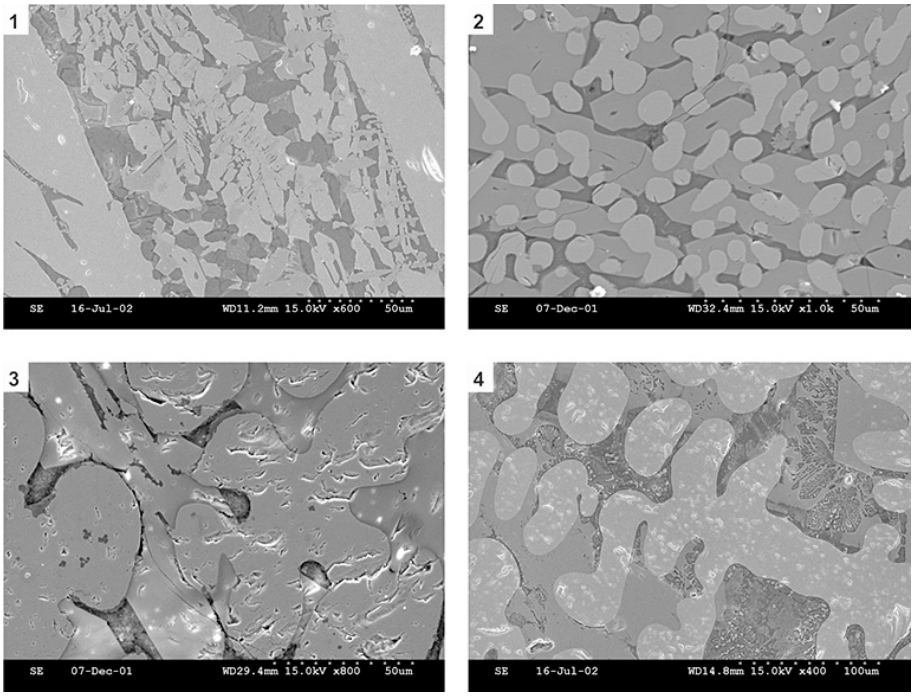


Fig. 7 : 1. Microstructure of bloomery slag sample N° 12
Fig. 7 : 2. Microstructure of small plano-convex slag's sample N° 41
Fig. 7 : 3. Microstructure of small plano-convex slag's sample N° 107
Fig. 7 : 4. Microstructure of large plano-convex slag's sample N° 190 (2)

Bloomery slags at the top part of the block are specific in coarse fayallite structure with fine dendrites of wustite on the background of fayalite and interdendritic zone. As to the samples from the bottom part of the block, almost only fayalite structure was observed with very fine FeO dendrites completely in the interdendritic zone (Figure 7 :1).

Small bowl-shaped slags exhibited a wustite-fayalite structure and coarse with a high fraction of the components crystallized in the interdendritic zone. The FeO dendrites were locally oxidized at the grain boundaries or in their inside. The material was highly porous (Figure 7 : 2, 3). The very big bowl-shaped slags were of the structure similar to the small bowl-shaped ones. They were dominated by thick fayalite needles mixed with FeO dendrites. Either FeO and Fe_2SiO_4 fayalite were strongly oxidized while the oxidation spot was free localized. Numerous areas of eutectic structure with strong oxidation of FeO and Fe_2SiO_4 fayalite phase were evident in the sample of the porous part of the slag (Figure 7 : 4).

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Tab. 2 : Chemical composition of structural components in slag sample (descriptions type of slag as in Figure 1).
Legend :
light – dendrites FeO,
gray – matrix Fe_2SiO_4,
dark – intergranular spaces of the matrix-phases eutectics from the FeO-SiO_2-Al_2O_3 system
eutectics – eutectics from the FeO-SiO_2-Al_2O_3 system

Type of slag	Structural component	Element content in % at.							
		O	Al	Si	K	Ca	Fe	Mg	Ti
d	bright	34,7	0,28	0,62	0	0,21	64,1		0,08
	gray	43	0	19,9	0	0,2	36,9		
	dark	42,4	14,6	27,2	12,6	1.07	1,93		0,2
	eutectic	42,9	7,1	22,9	4,86	7,44	14,8		0
mm	bright	29	1,56	1,03	0,09	0	68,2		0,12
	gray	37	0,75	20,7	0,05	0,5	39,2	1,8	
	dark	46,5	9,22	27,2	0.18	2,67	14,2		0,06
	eutectic	44,4	11,6	24,7	5,3	1,97	11,8		0,29
md	brght	26,5	1,3	0,73	0,13	0,2	70,8		0,34
	gray	43,5	0	19,7	0	0,2	36,6		
	dark	54,2	11,1	20,8	5,2	1,3	7,25		0.15
	eutectic	44,3	11,3	24,3	5,1	1,32	13,4		0,28

6 Summary of chemical and structural analyses

The results of the analyses prove that all the studied bowl-shaped slags have the same origin, i.e., the bloomery process and they are a modification of the bloomery slag formed probably during subsequent stages of metallurgical processing of the iron sponge. The modification consisted in admixing of the bloomery slags with the phases, which may be considered as components of the scale formed on the iron sponge during its further processing. Just at that time the slags were transformed in liquid phase and formed the alloy with the scale phases and crystallized slowly.

According to the theory of gas corrosion in iron alloys, the oxidation scale is multilayered. Dependent on the oxidation conditions, i.e., temperature, atmosphere and duration time, one obtains monophase layers of FeO, or three-phase layers FeO, Fe_3O_4, Fe_2O_3 on a pure iron sample. In the case when the scale is being detached from the substrate, there occurs intensive oxidation of the monophase layer of FeO to the multilayered one with dominating Fe_3O_4 and Fe_2O_3. Such a mechanism of scales' formation results from ion diffusion processes in which ions, vacances and electrons take part. Due to these processes a permanent dissociation of Fe occurs on the border of the matrix with internal layer of FeO, a FeO superstructure formation on the FeO–Fe_3O_4 boundary, a Fe_3O_4 superstructure formation on the Fe_3O_4–Fe_2O_3 boundary with accompanied formation of the hematite Fe_2O_3. The fractions of the particular phases present in the scale are dependent on temperature and duration time of the process. By the temperatures typical for the hearth, where the re-melting of iron sponge took place, those original fractions were approximately : 10 % Fe_2O_3, 15 % Fe_3O_4 and 75 % FeO. After delamination and off-core diffusion decay the Fe_2O_3, level and in particular Fe_3O_4 go up.

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During the preliminary processing stages, directly after the bloomery process, the sponge was strongly covered by the slag phase. Some fraction of the slag might be crushed off mechanically yet another fraction would stay in the runner extensions of the sponge. The slag protected the iron against the oxidating atmosphere of the hearth so the mass of the scale could be relatively low.

The scale could go into the slag even within the sponge or at the bottom of the pit after its detachment from the sponge by its possible transport or lifting. Consequently, at the bottom of the hearth the leaks of the bloomery slag enriched slightly in the scale could be collected. The relatively high amount of the slag may indicate that at that stage very big and big bowl-shaped slags might be produced. However, those slags have substantially higher levels of the scale than the small bowl-shaped ones. If one considers them as the products of the sponge's remelting, it is reasonable to assume that the furnaces were used repeatedly for remelting of larger quantities of the sponges.

Another stage of the iron processing might be the processing of the sponge to commercial product. It required a multiple smithing of the sponge after its preliminary heating to facilitate workable plasticity. The sponge has been in part purified of slag, consequently being more vulnerable to oxidation, yet its active-for-oxidation specific surface was decreasing all the time due to the plastic working. The particular fragments of the branched metal phase became welded and the sponge became compact.

Potentially, a small amount of the slag and the scale may have led to the formation of small bowls at the bottom of the reheating hearth. The small bowl-shaped slags thus may be considered as the material produced by the second stage of the ancient metallurgical processing, i.e., the conversion of the sponge into the half-product of commercial value.

At the current stage of investigations it is difficult to differentiate the origin of the big bowl-shaped slags and the very big ones. The big bowl-shaped slags are typical for their distinctly high content of the phases of the scale. Hence, they could stem from the same stage of processing as the very big bowl-shaped slags, but they were formed by a smaller slag-pit cluster and by a lower number of the iron sponges to be forged. It is also worth noting that all types of *bowl slag* formed in an oxidizing atmosphere, precluding the possibility of secondary iron reduction. Any iron present in the primary slag underwent oxidation.

The presented investigations have confirmed the earlier concept of the origin of the bowl-shaped slags from some stages of ancient iron metallurgy processing. They have provided the proof that the big and very big bowl-shaped slags may stem from the stage of purification of the iron sponge, while the small bowl-shaped slags, from the smith furnaces used for heating of the sponge prior to the forging performed to make the product of commercial value.

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