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MICROSTRUCTURES OF METALLURGICAL SLAGS

Abstract: The article characterizes microstructures of metallurgic slag of varying age remaining from the production of iron and steel and the Zn-Pb ore processing in relation to magmatic rocks and ores. Based on microscopic observations – among others – hypocrystalline, hyaline and felsite (characteristic for magmatic rocks) microstructures were observed in the slag. Also microstructures related to ores, including framework and dendritic, colomorphic and corrosive structures were noted. The diversity of the microstructures presented in the article is a result of the differentiation in the formations of individual components of the slags, which depends, inter alia, on the method and the rate of cooling of the alloys.

Keywords: metallurgical slag, microstructure, phase composition

1. Introduction

The mineralogical study of slags provides a lot of significant information concerning their phase composition, including the resistance of the respective components to weathering processes, heavy metals substitution possibilities in their structures as well as information concerning the crystallization processes of phases from the alloy. It is also significant to determine the shape and size of individual phases and the ratio of their sizes. In relation to natural rocks, the issues referred to above regarding minerals are described by microstructure [9].

In case of artificial non-organic materials, the notion of polycrystalline aggregate microstructure is introduced, denoting the sizes, numbers and relative distribution of crystalline phases and, if need be, amorphic components. Moreover, it is assumed that the microstructure is influenced by the genesis of the material, related to e.g. a correct temperature [2, 3, 7, 12]. The above substantiates the analysis of artificially produced non-organic materials in a manner similar to the analysis of natural rocks. The study and the control of microstructures are extremely significant, especially regarding the application of artificial materials in various branches of the economy. The type of microstructure often impacts the technical properties of the materials – this concerns e.g. steel or cast iron [2, 3, 7, 10, 11], but also applies to waste materials.

Considering the fact that the processes occurring as a result of high temperatures in the furnace are often identified with natural magmatic processes, this article undertakes to relate the magmatic rock microstructures to the slags from metallurgic processes, especially that there is no separate microstructure classification for slags.

In magmatic rocks, the microstructure is defined by such traits of a rock as the crystallinity level, size of mineral components, mutual relations between components of various sizes and the formation mode of these components. On the other side, it has to be considered that slags are formed as a result of metal ore sintering or by remelting of scrap. Thus, it seems reasonable to apply the names of the ore microstructures in case of slags. In relation to ores, this term relates to a set of characteristics providing information on shapes, mineral grain sizes and mutual relations (types of intergrowths) and the crystallinity level [8, 13]

2. Material and methods

The research was conducted for slags of different ages, remaining after the production of iron and steel. The slags were formed as a side-product as a result of various metallurgic processes:

- slag from the electric arc furnace (current production) (Fig. 1a),
- slag from the ladle furnace (current production) (Fig. 1b),
- blast furnace slag (current production) (Fig. 1c),
- open-hearth slag (slag gathered on the dump) (Fig. 1d).

In addition to the studies, highly weathered and transformed slag after zinc and lead production was used (Fig. 1e).

a)

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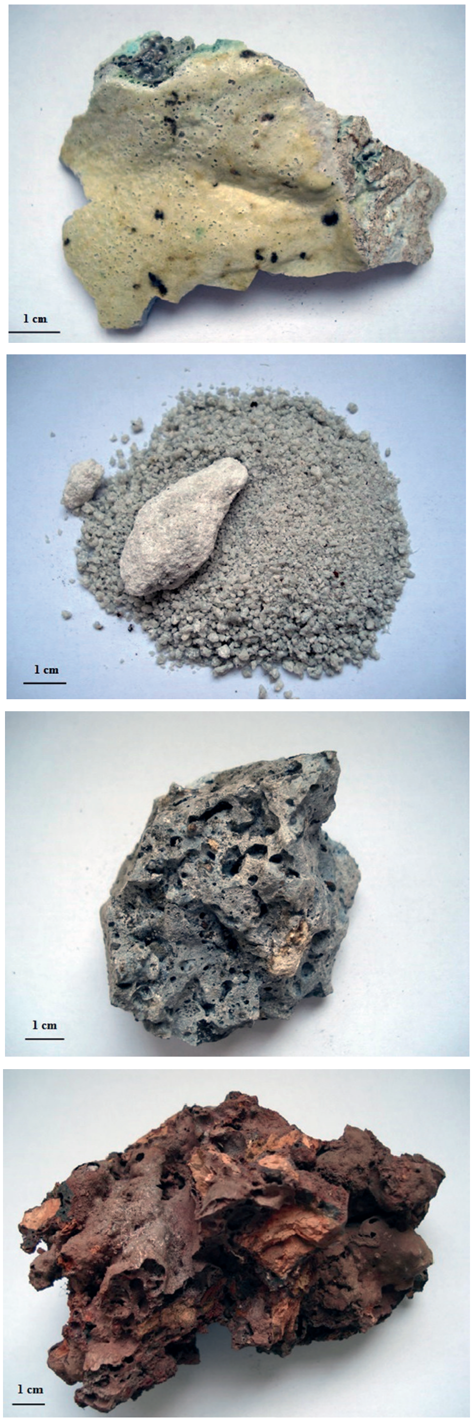

b)
c)
d)
e)

Fig. 1. Metallurgical slags: a) slag from the electric arc furnace; b) slag from the ladle furnace; c) blast furnace slag; d) open-hearth slag; e) slag after zinc and lead production

The samples for testing were obtained from several metallurgic plants and dumping grounds localized in Upper Silesia.

The slags were subject to macroscopic observation regarding their color, compactness and crumbling tendency as well as porosity. The microscopic study was performed in transmitted and reflected light with the application of polarizing microscopes manufactured by Zeiss. Moreover, samples of the slags were subject to tests using electron scanning microscopy and X-ray spectral microanalysis. The presence of certain phases occurring in the slags was additionally confirmed using the method X-ray diffraction.

3. Results

The phase components in metallurgic slags exhibit a highly variable level of crystallization, which is largely dependent on the time of alloy cooling [1, 5]. As a result of rapid drop in temperature during the pouring of the alloy from a ladle to prepared pits or directly to the dumping sites, the crystallization of phase components may be rapidly interrupted, which results in the presence of large amounts of glaze in the slags.

In relation to the above and due to the crystallinity level in the slags, hypocrystalline microstructures may be found in slags in which a part of the components crystallized and the rest of the alloy set as glaze and glaze-hyaline microstructures (Fig. 2, 3; Tab. 1). As in the volcanic glaze, in metallurgic glaze fine crystallites which are unrecognizable in microscopic observations, that is crystalline nuclei of mineral phases or fragments of non-melted input material covered in glaze may be found.

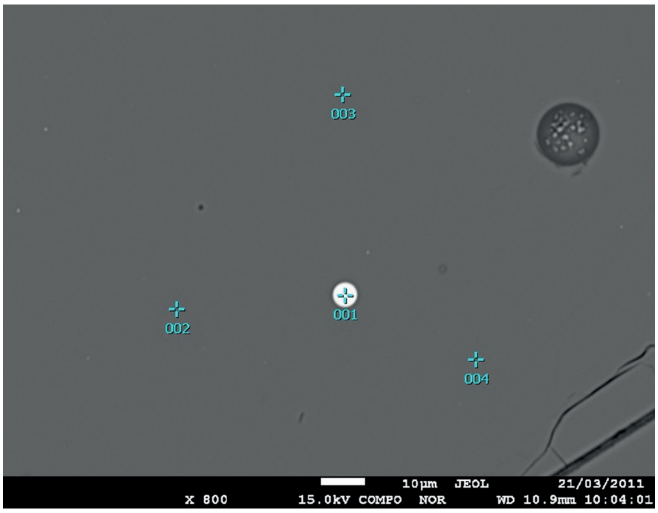

Fig. 2. Hyaline microstructure; microphotography from X-ray spectral microanalysis, blast furnace slag

TABLE 1

Chemical composition of metallic precipitation and galze according Fig. 2

Point of analysis	Elements [Mass %]													
	O	Al	Si	Mg	Ca	Fe	Mn	Ti	V	Ni	Cr	Zn	Pb	S	P
1	0.14	-	0.06	-	1.02	94.50	0.08	-	0.07	-	0.01	0.11	0.09	0.02	3.91
2	38.84	4.35	18.48	3.51	33.61	0.06	0.12	0.20	-	-	-	-	0.05	0.80	-
3	38.79	4.39	18.64	3.45	33.51	0.03	0.06	0.20	0.02	0.03	-	0.02	0.03	0.84	-
4	38.67	4.35	18.61	3.52	33.67	0.06	0.07	0.16	0.01	0.01	0.02	0.01	0.01	0.82	0.02

Explanations: point 1 – metallic precipitation; points 2-4 – glaze

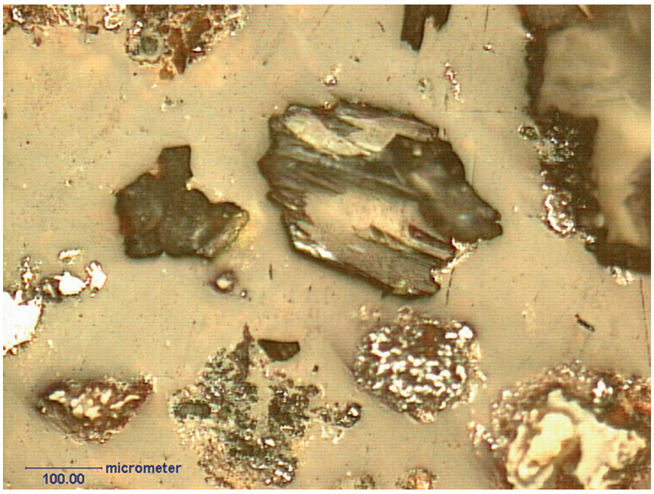

Fig. 3. Hyaline microstructure; reflected light, magnification 100x, one nicol, Zn-Pb slag

From the point of view of the mutual ratio of crystal sizes, vari-crystalline and equi-crystalline microstructures can be generally distinguished in magmatic rocks. In the metallurgic slag, the vari-crystalline structure is predominant, especially one of its forms – the porphyrytic microstructure, in which one of the components forms larger crystals while being surrounded by fine and medium-grained structures. An example of it are dicalcium silicate crystals covered in fine-crystalline mass found in open-hearth slag, which allows to draw conclusions that their crystallization occurred earlier, in a higher temperature of the alloy (Fig. 4).

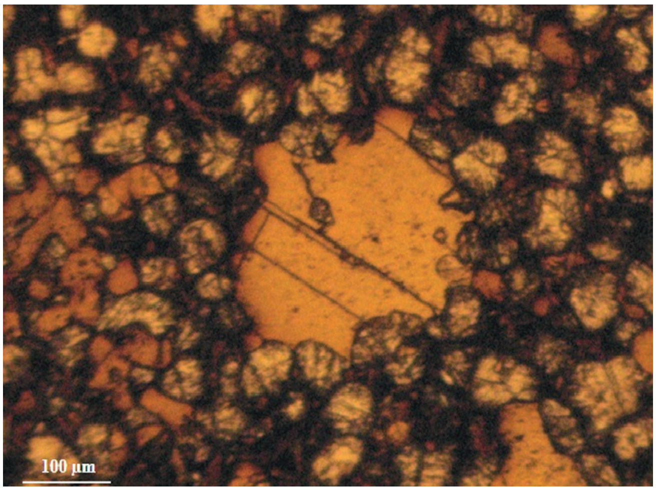

Fig. 4. Porphyritic microstructure; calcium silicates against a fine-crystalline background; transmitted light, magnification 100x, one nicol, open-hearth slag

While examining the level of phase formation in mineral assemblages, both idiomorphic (maintaining their own shape) and xenomorphic (adjusting to free spaces) components may be noted in slags. Due to their presence in slags, a hipidiomorphic microstructure has been distinguished (Fig. 5) in which both components exist along with hipidiomorphic crystals (with not entirely regular shapes) as well as panxenomorphic microstructure in which the components do not exhibit tendencies to create their own forms.

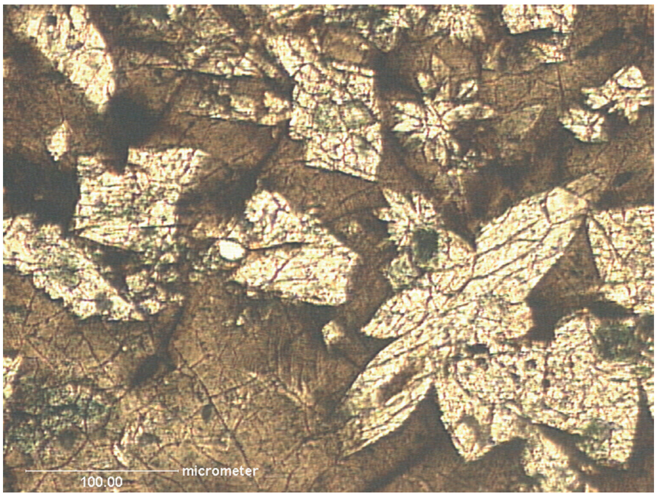

Fig. 5. Hipidiomorphic microstructure; idiomorphic and hipidiomorphic phases of pyroxenes against a glaze background, transmitted light, magnification 200x, one nicol, Zn-Pb slag

The presence of idiomorphic components in slags is usually related to the occurrence of melilite phases: akermanite $Ca_2Mg[Si_2O_7]$ and gehlenite $Ca_2Al[(Si,Al)_2O_7]$, monticellite $CaMg[SiO_4]$, and wollastonite $Ca_3[Si_3O_9]$, as well as pyroxenes – mostly augite $(Ca,Mg,Fe^{2+},Fe^{3+},Ti,Al)_2[(Si,Al)_2O_6]$ and jadeite $NaAl[Si_2O_6]$, which may also be characterized by hipidiomorphic morphology [4].

In slags characterized by hypocrystalline or holocrystalline microstructure, a diversified behavior of the crystalline phases was noted. It is influenced by the age of the waste and the time of their deposition. Among the slags in concern, the processes of crystalline phases weathering were most evident in slags resulting from Zn-Pb metallurgy, which come from a hundred years old dumping site. The surface of the phases was cracked and covered in blooms and pyroxene pseudomorphs were present –filled with an amorphous substance. The weathering processes were also highly visible in slags of hyaline structure, where the dominant component is glaze [4]. This especially concerned the Zn-Pb slag glaze; its surface was cracked, opaque, covered with a bloom of precipitating iron compounds. In the studied slags from iron and steel metallurgy, signs of weathering were found in open-hearth slags which were deposited at a dumping site. The glaze of the iron slag coming from current production was of a completely different character. The glaze was well preserved, smooth-surfaced, free of cracks and isotropic. Slags are often characterized by a microgranular microstructure which renders the identification of individual components impossible. Batches of material were observed in which the main mass was constituted by fine grains of silicate or oxide phases and an amorphous substance. By analogy with magmatic rocks, it may be assumed, that it is a felsitic microstructure.

Among magmatic rocks there is also an entire series of microstructures characteristic to specific types of magmatic rocks. Due to that only the most important and common types were included in the presented comparison. In comparison to ores, the microstructures of slags also exhibit a high variation. Among the microstructures that are the most characteristic and typical for ores the following may be distinguished:

equigranular, non-equigranular (e.g. porphyritic, framework and dendritic), colomorphic, spherolytic, corrosive (e.g. etched, reticulated, framework, veiny) and cataclastic (deformative). A separate type is constituted by microstructures resulting from the decay of solid solution which result from its cooling. Among them, platy, lenticular, reticulated structures and structures exhibiting asterism may be distinguished.

In the analyzed metallurgic slags, the presence of non-equigranular microstructures was noted – including the dendrite and framework structure. Fig. 6 presents a clear increase of the dendrite phase. The chemical composition tests have exhibited that it was a solid solution of Fe_2O_3 and CaO oxide phases with numerous impurities. It is characteristic that the increase in dendrites occurs in a radial pattern – from the central part, rich in iron oxide. In slags, dendrites may also be linked to the crystallization of other phases, e.g. olivines, referred to by Vernon [13].

Also microstructures related to the presence of colloids are present in slags, that is the colomorphic and spherolytic structure – as well as a large group of microstructures resulting from the decay of solid solution.

In case of the colomorphic microstructure (Fig. 7), mineral areas may be observed which are distributed in a concentric manner, depending on their subsequent build-up. In several spots, round, spherolytic forms are visible, which comprise of several concentric layers. Such form is characteristic of goethite found in open-hearth slags.

Another type are corrosive (metasomatic) microstructures, especially the etching microstructure. In the natural environment, it is characteristic of silicate ores [6], the processes of mineral corrosion are, however, known to occur in magmatic environment. In case of slags, these processes were noted in oxide phases. Fig. 8 presents the phases with clearly distinguished corrosive cavities (light fields) containing FeO wustite. The grey background denotes glaze.

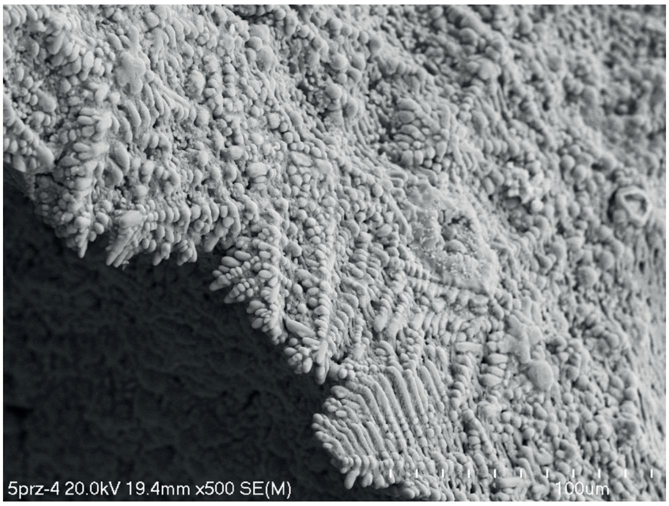

Fig. 6. Dendritic microstructure; SEM microphotography, slag from the electric arc furnace

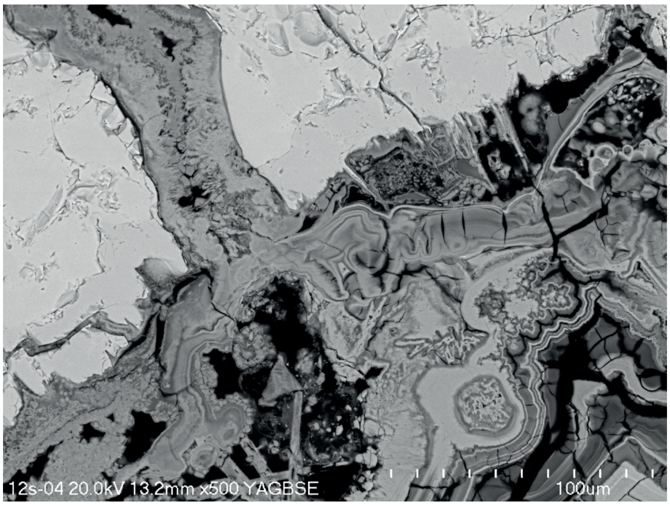

Fig. 7. Colomorphic microstructure; BSE microphotography, open-hearth slag

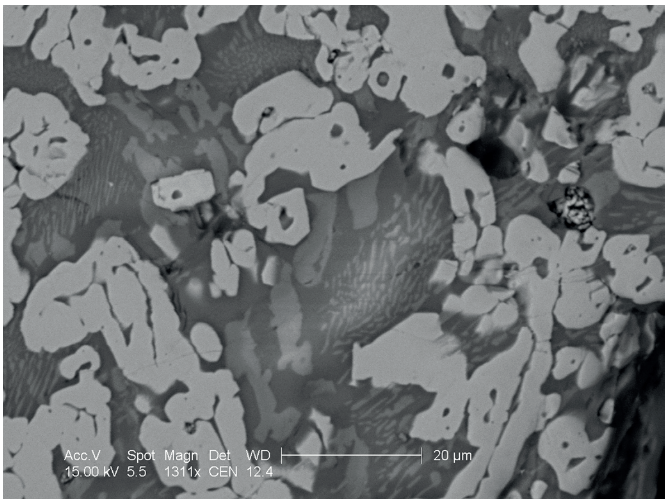

Fig. 8. Etched microstructure; BSE microphotography, Zn-Pb slag

Microstructures resulting from the decay of solid solution were also distinguished in slags. These are a result of its cooling. Depending on the rate of the cooling of the alloy, microstructures differing regarding the form of crystals and their orientation may be identified. The presence of reticulated (Fig. 9), droplet and emulsion microstructures (Fig 10) and microstructures exhibiting asterism (Fig. 11) was noticed.

The reticulated microstructure is linked to the precipitation of dicalcium silicate in form of elongated crystals at a background of calcium aluminate. In the droplet and emulsion structure, fine white fields may be noted – these are related to the precipitation of the FeO-MnO-MgO solid solution. The asterisk microstructure is characterized by calcium ferrite precipitates ($CaO \cdot 2Fe_2O_3$) in form of fine crosses or asterisks.

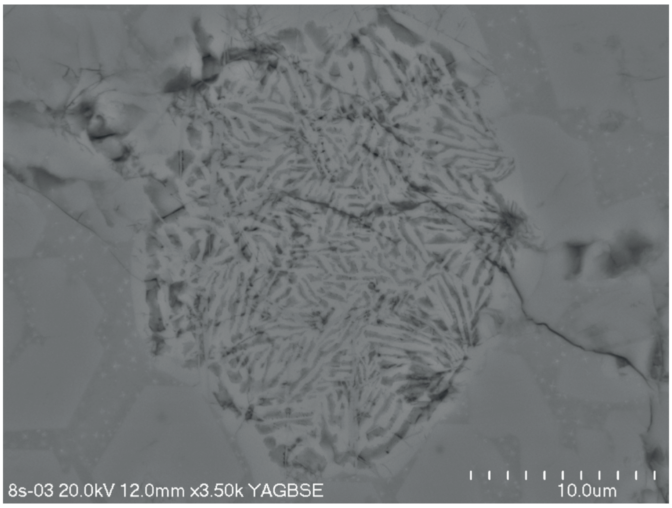

Fig. 9. Reticulated microstructure; BSE microphotography, slag from the ladle furnace

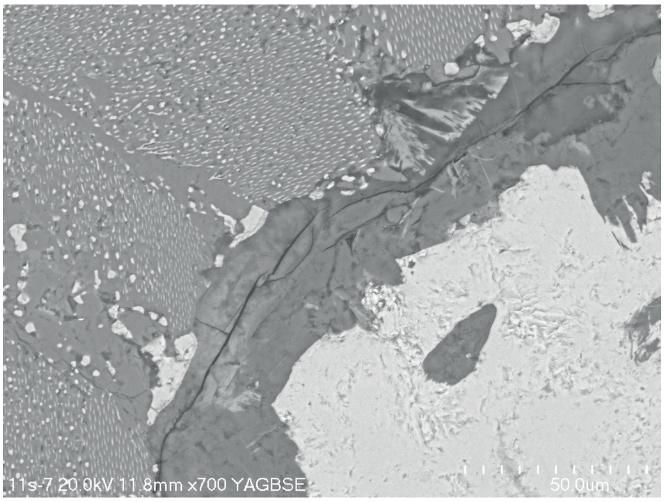

Fig. 10. Droplet microstructure; BSE microphotography, open-hearth slag

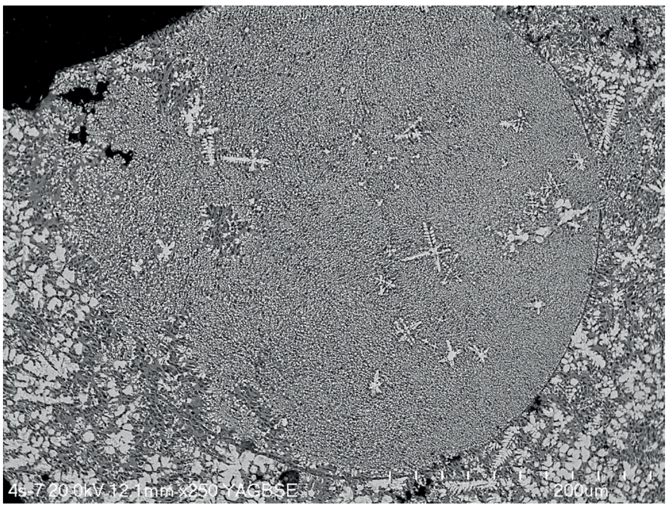

Fig. 11. Asterisks microstructures; BSE microphotography, slag from the electric arc furnace

4. Conclusions

Metallurgic slags may be examined in categories specified for magmatic rocks by analogy of their genesis. Both in the underground processes and in the furnace – the temperature plays a key role and the crystallization conditions of individual phases are determined by the location and rate of the alloy setting. Moreover, considering the phase composition of slags, their microstructure may be analyzed in comparison to ores.

Due to the crystallinity level, mostly hypocrystalline and hyaline microstructures were distinguished, the holocrystalline microstructure constituting a smaller part. This is related to the intensity of the alloy cooling process – a rapid drop in temperature favors the formation of glaze microstructures.

Due to the size of the components in slags resulting from iron and steel metallurgy, porphyritic microstructure may often be observed while the non-equigranular mictrostructure dominates in Zn-Pb slags – without a clear size domination of one of the components. In both examined types of slags, a microstructure characterized by the presence of very fine grains which form a quite compact mass was present. Such microstructure is called felsitic in case of magmatic rocks.

The microstructures related to ores are equally interesting and diverse. Among these, e.g. the dendrite-framework microstructure may be distinguished, which depicts the growth of mineral phases. Iron compounds, mainly Fe_2O_3, iron hydroxides and its colloidal forms often occur as a build-up of mineral strips. This is a colomorphic microstructure which has only been noted in highly-weathered slags that were deposited for a longer time. In both types of slags the presence of corrosive structures was confirmed.

In the slags resulting from the current iron and steel metallurgy, a series of microstructures caused by the decay of the solid solution was recognized: reticulated, droplet and emulsion microstructures and microstructures exhibiting asterism. These types of microstructures have not been noted in the analyzed slags from Zn-Pb metallurgy.

The number of microstructures of metallurgic slags presented in this article proves their diversification: in relation to the way of formation of the respective components, their shape, size and the sequence of crystallization. Moreover, the type of slag microstructure is influenced by the method and rate of alloy cooling, the age of the slags and the conditions of their deposition.

All of the above indicates the high complexity of the question of determination of the phase composition of metallurgic slags and forms a basis for further mineralogical and chemical research which is necessary for further commercial use of metallurgical slags.

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