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## Heterogeneity of glass components in slag after nickel acquisition process from Kola Peninsula (Russia)

Niejednorodność składników zeszkłonego żużla  
pochodzącego z procesu hutniczego rud niklu  
z Półwyspu Kolskiego (Rosja)

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### **Abstract**

The problem of the disposal of metallurgical slags in the copper-nickel industry also remains open in the Kola Peninsula area, where this kind of exploitation and processing of sulphide Cu-Ni deposits is conducted. The urgent need is to reuse the waste slag heaps through the effective manner of their use based on our available technologies. The slag obtained after processing sulphide copper-nickel ores in the Kola Peninsula contains about 4 wt.% of the ore. The chemical and mineral composition of the slag plays a key role when considering the possibility of its re-use in the context of environmental nuisance. The line of processing Cu-Ni sulfide deposits from the slag proposed by the authors is based on the ability to change the slag phase composition by its oxidation and reduction processes for the enrichment of ore mineralization for reuse.

**Keywords:** metallic glass, slags, nickel metallurgy, de-sulphating

### **Streszczenie**

Kwestia utylizacji żużli hutniczych przemysłu miedziowo-niklowego pozostaje otwarta również na Półwyspie Kolskim, gdzie jest prowadzona eksploatacja i obróbka siarczkowych złóż Cu-Ni. Pilną potrzebą jest ponowne wykorzystanie hałd. W tym celu, przy zastosowaniu dostępnych technologii, poddaje się je efektywnemu przetworzeniu. Podczas przetwarzania siarczkowych rud miedzi z niklem w żużlu pozostaje około 4% wag. minerałów rudy. O ponownym wykorzystaniu żużla decyduje jego chemiczny i mineralny skład, który nie może zagrażać naturalnemu

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środowisku. Zaproponowany przez autorów projekt linii przetwarzania osadów siarczków Cu-Ni z żużla zakłada uzyskanie zmiany składu fazowego żużla w wyniku utleniania i redukcji w trakcie obróbki cieplnej, koniecznej do wzbogacenia mineralizacji rudnej, a tym samym do jej ponownego użycia.

**Słowa kluczowe:** metaliczne szkło, żużel, metalurgia niklowa, odsiarczenie

## 1. Introduction

The problem of disposing metallurgical slags in the copper-nickel industry remains open, as long as this type of exploitation and processing of Cu-Ni sulphide deposits is conducted in the Kola Peninsula region. The urgent need is the reuse of the growing heaps of waste slag by the effective way of their use based on the available technologies. During the processing of copper-nickel sulphide ores in the Kola Peninsula, slags are left with an ore concentration at a level of approximately 4%. The chemical and mineral composition of the slag evokes concern in the case of considering the possibilities of its reuse in the context of environmental nuisance [1–3]. One of the directions of research on the slag derived from processing the Cu-Ni sulphide deposits is focused on the possibility of changing its phase composition by oxidation and reduction during heat treatment to increase the contrast of properties of the individual phases for their effective separation with the enrichment method [4].

## 2. Methodology

Separated samples of the metallurgical slags were subjected to thermal annealing and chemical etching. Specimens in the form of thin platelets and polished sections were made from the slags at different stages of processing using the processes described below. The specimens were observed using a POLAM P-312 reflected light polarizing microscope, an Ultraphot-3 Opton reflected light metallographic microscope, and a Leica DM2500P reflected and transmitted light polarizing microscope. The POLAM P-312 microscope was located at the Geological Institute of the Kola Scientific Center RAN, the Ultraphot-3 Opton microscope at the Institute of chemistry of the Kola Scientific Centre RAN, and the Leica DM2500P microscope at the Department of Geology and Lithosphere Protection UMCS. These samples were then examined in micro-areas using SEM LEO-1450 and Cameca MS-46 MPSA scanning electron microscopes (located at the Geological Institute of the Kola Scientific Center, RAN) as well as a Hitachi Su6600 (at the Department of Geology and Lithosphere Protection, UMCS). Thermal and chemical analyses were performed in accordance with the method patented by the authors [4].

Thermal treatment of the sulphide slags was performed at the Institute of Chemistry of the Kola Scientific Centre RAS in Apatity in a TK.5,6-1750.N.1F laboratory high-temperature furnace manufactured by AOA "Termokeramika" (Moscow, Russia).

In reducing conditions, a mixture of the slag was enriched with 10 wt.% of C (reducer) and 15 wt.% of  $\text{Na}_2\text{CO}_3$ . The slag mixture was then placed in a cold furnace. The heating time was between 3 to 6 hours depending on the required heating temperature (from  $500^\circ$  to  $1200^\circ\text{C}$ ) with the possibility of exposing the sample to the maximum temperature (from 0 to 3 hours). Under oxidizing conditions, the slag mixture was enriched with 15 wt.% of  $\text{Na}_2\text{CO}_3$  and then placed in a furnace chamber. The samples were heated to temperatures in a range of  $800^\circ$  to  $1100^\circ\text{C}$ , which were maintained for 30 minutes.

### 3. Results

The discussed slag samples derived from metallurgical heaps located in the Kola Peninsula have the form of fine granules of vitrified grains of silicate melt with an amorphous structure containing olivine and pyrrhotite crystallites. The primary component of the slag was tempered silicate glass, which constituted 75% of its volume.

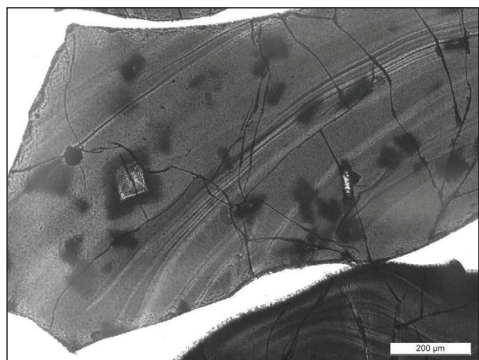
The minor components of the glass, apart from its main components (i.e., Si, Mg, K, Na, and Al), are also dissolved elements such as Fe, S, Ni, and Cu. According to the research in the micro-areas carried out using the Cameca MS-46 microprobe, chemical composition of the glass is as follows: FeO – 29.69; CaO – 3.36; MgO – 9.72;  $\text{SiO}_2$  – 40.97;  $\text{Al}_2\text{O}_3$  – 7.87;  $\text{TiO}_2$  – 1.03; MnO – 0.42;  $\text{Na}_2\text{O}$  – 1.67;  $\text{K}_2\text{O}$  – 1.10; S – 3.92; NiO – 0.10; CuO – 0.11 [wt.%].

Studies of the glass using the technique of optical and electron microscopy allowed us to demonstrate the micro-heterogeneity of the glass structure correlated with the location of the olivine crystals and droplets of metallic alloys. In the transmitted light, glass has a non-uniform mottled and band structure (Fig. 1). Also, quite-well visible is the inhomogeneous structure of the glass, manifesting itself by a shifting of layers of different density. This form corresponds to an over-cooled solution of a silicate alloy, which in a liquid phase was subjected to complex turbulent flow during phase dissection (displacement) under the influence of different current speeds for separate parts of the mixed-out alloy [5–7]. It was experimentally confirmed by the authors that the boundaries of the alloy differentiation showed low reactivity.

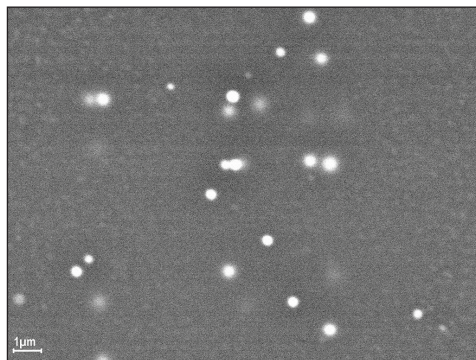
It has been shown that the areas of phase transition have a “cluster” nature of heterogeneity in which the glass is saturated with Fe-S particle inclusions. Passive areas have a mottled structure in which the glass contains inclusions of alloy drops (Fig. 2). Glass in layers with the alloy droplets is cleaner and more chemically passive. A chemical analysis of the glass from the area of phase transition has shown that it is more ferruginous, but it does not contain any additions of ferrous metals. Glass from the chemically passive areas is more stable, but it contains additional Ni, Cu, and Co [1].

The experimental results proved that the distribution of iron and sulphur in the glass takes on two forms: 1) “cluster”; and 2) ordinary inclusions. Clusters are inclusions without clear boundaries that become visible in the glass structure as a result of analyses

of the backscattered electrons (BSE) as well as changes in the Fe and S content against the silicate matrix. The size of the clusters is within a range of 0.1 to 0.5 microns. The cluster structure proves the mostly complete dissolution of iron and sulphur in the molten silicate. This type of gray glass constitutes a significant part of the slag. The second form of the presence of iron and sulphur in the form of inclusions proves the incomplete dissolution of sulphide components in the silicate alloy. There are alloy droplets; the sizes of these droplets can fluctuate within a range of 0.1 to 0.5 microns and can even reach 50 or more microns in some cases. These are the droplets of an alloy that did not dissolve in the glass or were not separated during the ore recovery in the metallurgical processing, being located in a bottom area of the tank. Glass with the alloy droplets forms the border between the layers of the cluster glass, and it likely has cooled down earlier.



*Fig. 1. Inhomogeneous of glass structure, shown in transmitted light at parallel nickels. Photograph illustrates scattered olivine crystals in background of glass and strips of differing densities due to uneven distribution of Fe-S compounds and alloy droplets*



*Fig. 2. Mottled glass structure (visible in BSE micro-photograph): bright spots – undissolved particles of iron alloy in substrate*

We should also see a specific nature of glass heterogeneity in the areas of olivine and pyrrhotite crystallization in the vicinity where alloy droplets also occur. In these areas, the content of magnesium and silicon decreases while iron increases; this is a result of the migration of  $MgO$  and  $SiO_2$  from glass to olivine. However, because of its high sulphur content, iron reacts with it – creating pyrrhotite.

The micro-heterogeneity of glass plays an important role in the process of forming new phases under the influence of sulphides during firing. Thanks to the cluster structure, iron and sulphur are poorly connected with the structure of glass, creating dispersed admixtures of a maladjusted nature, and they easily react with C and  $O_2$  in reducing or oxidizing conditions during firing.

### 3.1. Behavior of iron in glass subjected to desulphating in reducing conditions

It has been found experimentally that, during the firing of the slag in reducing conditions at temperatures from 500° to 1000°C in slag particles, iron sulphides – pyrrhotite ( $\text{Fe}_{1-x}\text{S}$ ) – as well as metallic iron (Fe) are formed [8]. Both phases form irregular oval globules, which are randomly distributed in the entire volume of the glass particles (Fig. 3). The amount of metallic iron and pyrrhotite in different glass particles corresponds to its ferruginous nature. At 1000°C, pyrrhotite has already been separated; and in the place of particles of glass beads, the iron globules were observed. This way, iron and sulphur are reduced at the same time in the reducing conditions, wherein a portion of the iron bonds with sulphur, creating pyrrhotite, and the other part forms globules of metallic iron. As a result of the reaction with carbon, a decrease in the content of iron and sulphur occurs in the clusters. BSE microphotographs show the “porous” glass structure that is formed after heating in the reducing conditions; these are the dark areas (“pores”) in which are no atoms of heavy elements. The light areas indicate where iron atoms are concentrated (Figs. 4, 6).

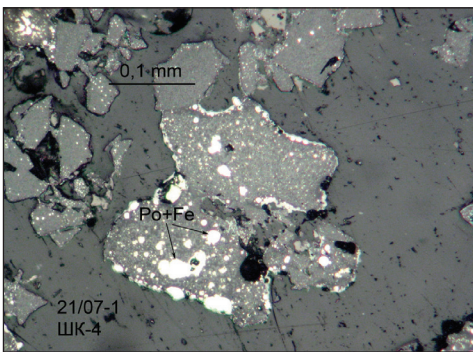


Fig. 3. BSE microphotograph of emulsion structure of pyrrhotite and iron distribution in glass in reducing conditions

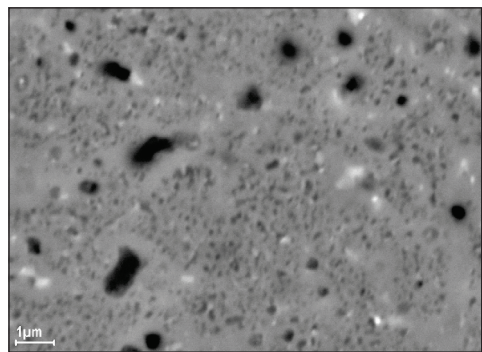
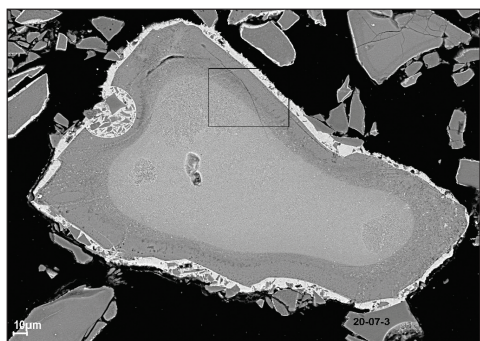


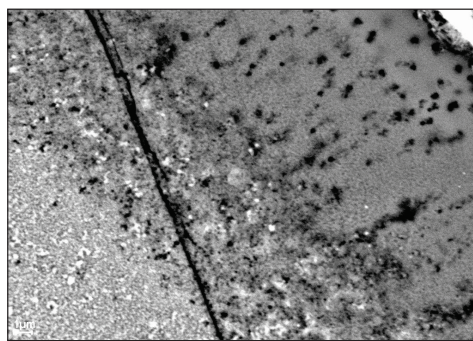
Fig. 4. Zone structure of glass particles shaped in conditions of slow oxidation process

### 3.2. Behavior of iron in glass subjected to desulphuring in oxidizing conditions

Studies of the glass during firing under oxidizing conditions have shown that, at temperatures of 500° to 700°C, oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  occurs, and hematite ( $4\text{Fe} + 3\text{O}_2 = 2\text{Fe}_2\text{O}_3$ ) forms. Oxidation starts from the surface of the glass particles. During the slow oxidation process diffusion in the glass, maintaining original forms without processing core parts of the glass, causing maintenance of the original sulphide inclusions (Fig. 4). In more-dynamic conditions, a total destruction of the glass structure occurs, along with the evaporation of the sulphide inclusions and formation of hematite.



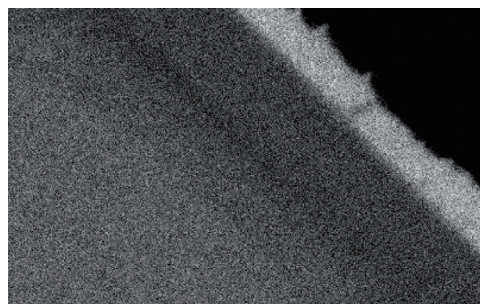
*Fig. 5. Zone structure of glass associated with migration of iron towards surface and creation of hematite shells (BSE microphotograph)*



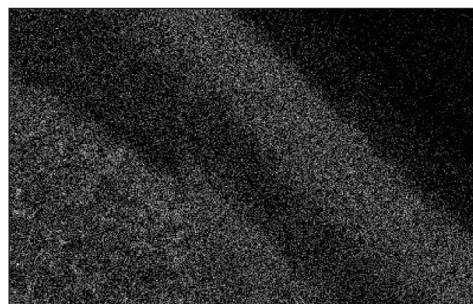
*Fig. 6. Structure of iron migration zones: in intermediate zone, we see chaotic arrangement of light and dark spots, indicating uneven distribution of iron in diffusion area. Visible dark spots and stripes of most-effective iron migration areas from glass (enlargement of fragment from Fig. 5)*

Iron migrates from deeper parts to the glass surface, where it reacts with oxygen and forms hematite (Figs. 5, 6). During the removal of iron from the glass, two depleted zones are formed in relation to the original content of iron. The first zone (inner) is located directly inside the glass particles, while the second (diffusion) is located on their boundary with separated hematite. In the first zone, the regrouping of iron atoms occurs; in the second – intense migration to the oxidation zone occurs, where the formation of iron atom migration channels are observed (Fig. 6).

a)



b)



*Fig. 7. Zone arrangement of iron (a) and sulphur (b) in subsurface layer of glass particle. Photographs of characteristic X-ray beams obtained by means of microprobe*

Sulphide inclusions in the glass in the conditions of the conducted experiments were passive in all cases, so there is no reason to assume that the iron used in forming the hematite was extracted from the Fe-S clusters. This is consistent with the structure

of zones, and in dynamic oxidation conditions together with hematite, a pyrrhotite can be formed.

Sulphur dissolves in the glass and also participates in the oxidation process; it migrates from the inner zone to the surface along with iron. Sulphides are not created at that time, but the sulphur undergoes oxidation or remains in the boundary zone with hematite. Because sulphur has a small atomic number in contrast to iron, its distribution in glass is easy to detect with X-ray observation (Fig. 7). Under the conditions of the conducted experiments, no compounds of sulphur were observed; this means that the sulphur transformed into gas [SO<sub>2</sub>].

## 4. Conclusions

Glass from the metallurgical processing of nickel ores shows the heterogeneity of the microstructure; this is caused by the uneven distribution of iron and sulphur in the form of atom admixtures and alloy droppings in slags formed in converters.

With the method of glass heating, it is possible to transfer the iron dissolved in the glass into metal (reduction conditions) or oxide – hematite (oxidizing conditions) – and recover it in the form of mono-mineral phases.

The process of iron release from the glass has a diffusion nature, but the reaction direction is different; in iron-reducing conditions, iron reacts with carbon in the whole volume of particles (which means that metal is formed); under oxidizing conditions, an oxidized phase is formed on the surface of the glass particles.

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