The formation of magnetite in slag from the autogenous smelting of sulphide copper - zinc concentrates

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Abstract: Correlation dependences of magnetite and copper content in slags of products compositions (slag and matte) after autogenous smelting of sulphide copper - zinc concentrates in Vanyukov's furnace were determined by the statistic analysis method. It was defined the higher copper content in matte is, the bigger magnetite share in slag is. In addition Fe/SiO_2 and SiO_2/CaO ratios influence on magnetite formation. Phase compositions formed during slag cooling are defined by the methods of X-ray diffraction and spectral analyses. It was determined that slag consist of iron silicate phase - Fe_2SiO_4 fayalite, Fe_3O_4 magnetite, $Ca_{0.5}Fe_{1.5}Si_2O_6$ iron calcium silicate and sulphides. The data about non-ferrous metals states in slag are reported. It was defined magnetite and iron silicate phases contain zinc and copper which concentrations are up to 3.1 — 4.9% and 0.7 — 0.8% respectively. Single bulk matte inclusions up to 300 microns in size and minor sulphide crystals formed during its cooling were detected in slag. Copper and lead are dissolved into segregated sulphides and their compositions are similar to sphalerite. Achieved results has been offered to put into operation for parameters optimization of sulphide copper - zinc concentrate autogenous smelting and for losses reduction of non-ferrous metals in slags.

Key words: Slag, magnetite, autogenous smelting, sulphide copper - zinc concentrate

1. Introduction

Matte and iron silicate slags during autogenous smelting of sulphide copper - zinc concentrates are formed in Vanyukov's furnace [1, 2]. Significant quantity of non-ferrous metals is lost in slags (Cu, Zn, Pb etc.). Slags are stockpiled in dumps harming environment. It's known [3-6] that slags after oxidized smelting of sulphide copper - zinc concentrates contain magnetite. The lower temperature is, the smaller magnetite solubility is in iron silicate slags. Therefore, finely dispersed suspension Fe_3O_4 is formed during cooling in magnetite saturated slags. Besides, magnetite settling may result in an intermediate layer forming between slag and matte, and also hearth accretion (crusts in the hearth) of the furnace [7, 8]. In addition, magnetite content increase in slags leads to increasing of non-ferrous metals losses [3, 10]. Together with other factors, slag composition to be more precise silicon dioxide and calcium oxide content in it influence the magnetite formation [10-14].

Autogenous smelting technology pyrite - chalcopyrite sulphide copper - zinc concentrates (16-19% Cu, 2.5-3.5% Zn) was put into operation at Sredneuralsky Copper Smelter Plant, Joint Stock Company (Ural, Russia), in Vanyukov's furnace, and resulted in matte formation consisting of copper (40-55%) [3, 8]. The increase of copper content up to 60% in matte changes metals interphase distribution: 92-95% of copper passes into matte, but 70-80% of zinc – into slag. The aim of the work under consideration to study the influence of slag and matte composition produced by melting of sulphide copper – zinc concentrates in Vanyukov's furnace, on magnetite formation and determine phases of non-ferrous metals in slag.

2. Experimental

The data concerning slag and matte compositions produced at Sredneuralsky Copper Smelter Plant, Joint Stock Company by commercial melting of copper – zinc sulphide concentrates in Vanyukov's furnace are the basis of statistic analysis. Composition data with unstable copper content in matte in the range of 39 to 60%, and zinc in matte – from 1.96 to 5.23% were involved in calculation. Copper content in slag varied in the range of 0.75 to 1.60%, Fe_3O_4 – from 2.7 to 6.8%, SiO_2 – from 30 to 37%, CaO – from 2.0 to 3.7%.

Program Outokumpu HSC 6.12 Chemistry was used as thermodynamic modelling calculation instrument based on minimization of Gibbs energy [15]. The working body was taken as the basis of the equilibrium states in modeling, which is close to slag by composition resulting from copper - zinc concentrate melting in Vanyukov's furnace, notably (mass%): 42.3 of FeO; 4.0 Fe_3O_4; 33.2 SiO_2; 3.2 ZnO; 1.2 Cu_2S; 1.1 ZnS; 3.5 Al_2O_3; 2.9 CaO; 1.3 MgO. Activity coefficients were equal to 1. The degree of oxidation which is equal to Fe(III) : Fe(II) ratio is 0.056. The mass of the working body is 93 kg.

The forms of metal states in slag were determined for the sample with following composition, %: 1.59 Cu, 3.26 Zn, 0.60 S, 36.8 Fe, 31.1 SiO_2, 3.77 CaO, 3.35 Al_2O_3, 0.10 As, 0.06 Sb, 0.28 Pb. The sample was selected during concentrate melting on matte consisting of 61% of Cu and it was produced by molten slag cooling with the rate about 100^oC/min.

Phase composition of samples has been determined by using X-ray diffractometer (Cu – K_α–radiation). The International Centre for Diffraction Data (ICDD) 2011 had been used to interpret the results of the analysis. Determination of phase element composition (EPMA) is performed with JSM-59000LV raster electronic microscope and Oxford INCA Energy 200 dispersion X-ray spectrometer.

3. Results

By means of statistic multifactor analysis of commercial melting data it was shown that the magnetite content in slag depends on its composition and copper content in matte. The bigger Fe/SiO_2 ratio is in slag, the higher Fe_3O_4 content is in it (Fig. 1). The bend is depicted on the Figure 1 when copper content over 53% in matte. The minimum magnetite concentration in matte takes place when Fe/SiO_2 ratio is in the range of 1.05 - 1.10. The higher copper content in matte, the bigger Fe_3O_4 is share in slag. Due to high Fe/SiO_2 magnitudes concentrations of magnetite occur in matte with 55% of Cu content.

Magnetite content in slag also depends on concentrations of SiO_2 and CaO in it. In slag the quantity of Fe_3O_4 raises with SiO_2/CaO ratio increase both at low (37%) and high (60%) copper content in matte (Fig. 2). Maximum of magnetite formation has been detected within the region of copper content 46 - 50% and without taken into account the values of SiO_2/CaO ratio.

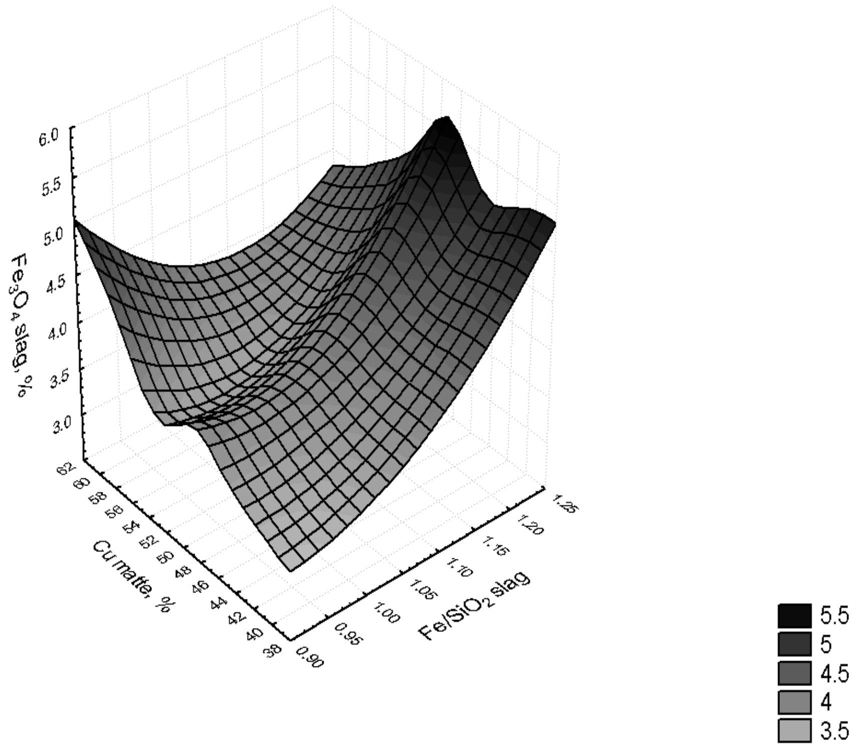

Fig. 1 The dependence of Fe_3O_4 content in slag to Fe/SiO_2 ratio and copper content in matte

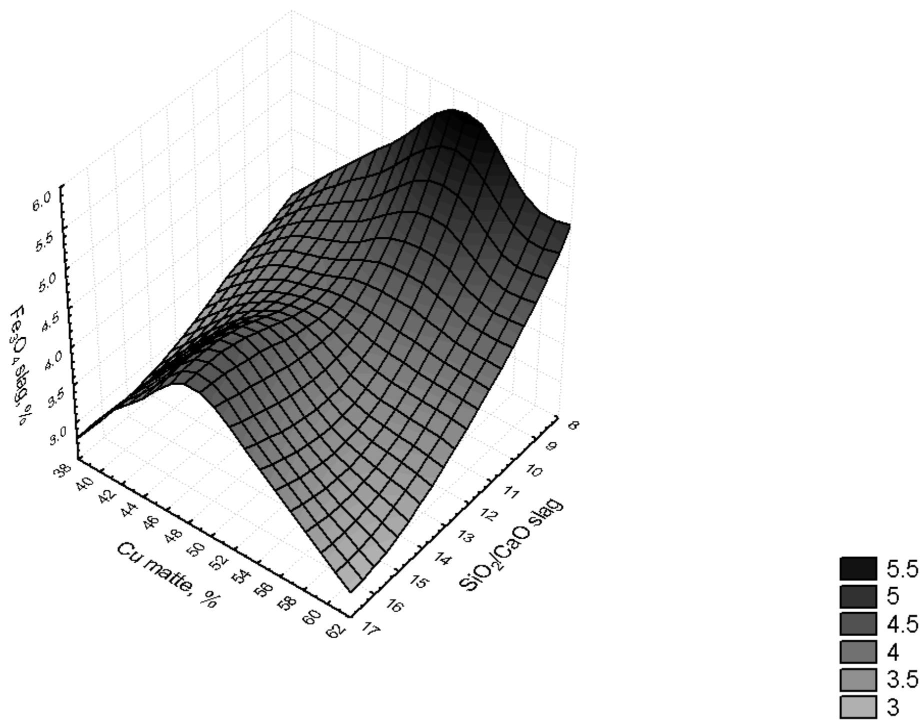

Fig. 2 The dependence of Fe_3O_4 content in slag to SiO_2/CaO ratio and copper content in matte

The magnetite influence on copper content in slag is shown in Fig. 3, 4. The growth of magnetite concentration in slag results in copper content increase in it. Especially it's vividly seen in melting matte rich in copper. Copper concentration reaches 1.6% in slag, when Fe_3O content is about 7%. The growth of Fe/SiO_2 ratio causes increase of copper losses with slag (Fig. 4). In practice magnetite content in slag doesn't influence zinc content in matte. Zinc concentration in matte goes down when copper content increases in matte and Fe/SiO_2 ratio in slag also increases (Fig. 5).

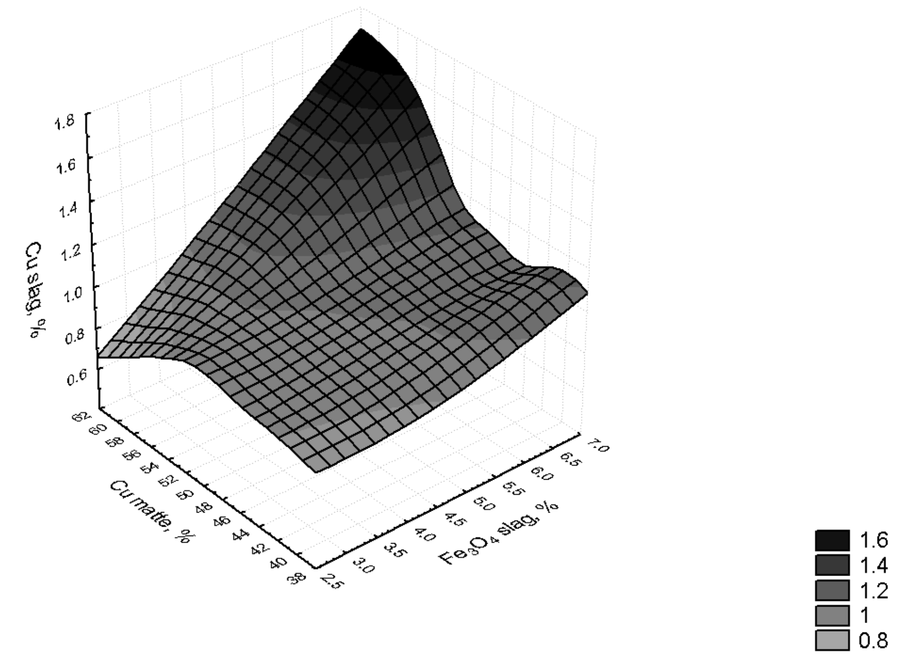

Fig. 3 The dependence of copper contents in slag to Fe_3O_4 content in slag and copper contents in matte

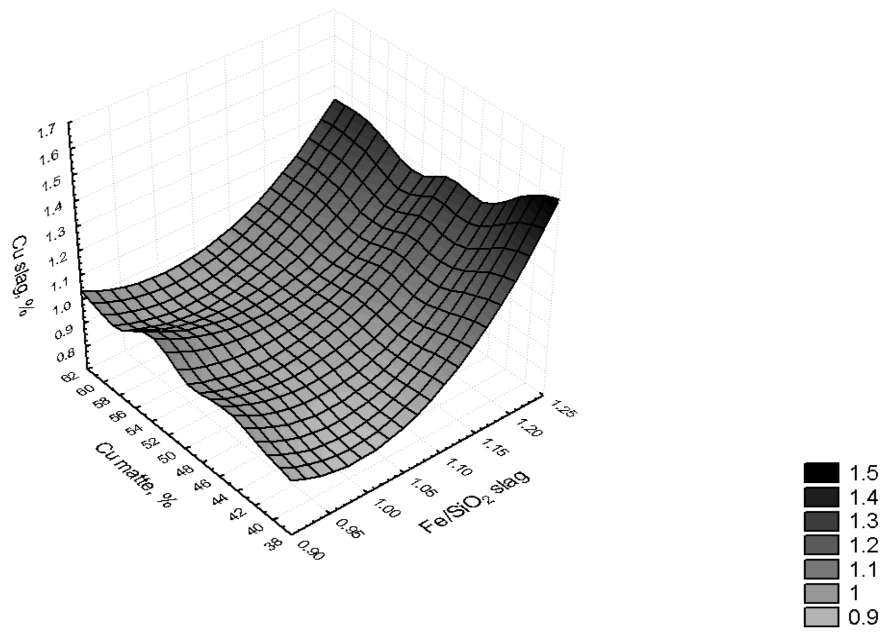

Fig. 4 The dependence of copper contents in slag to Fe/SiO_2 ratio in slag and copper contents in matte

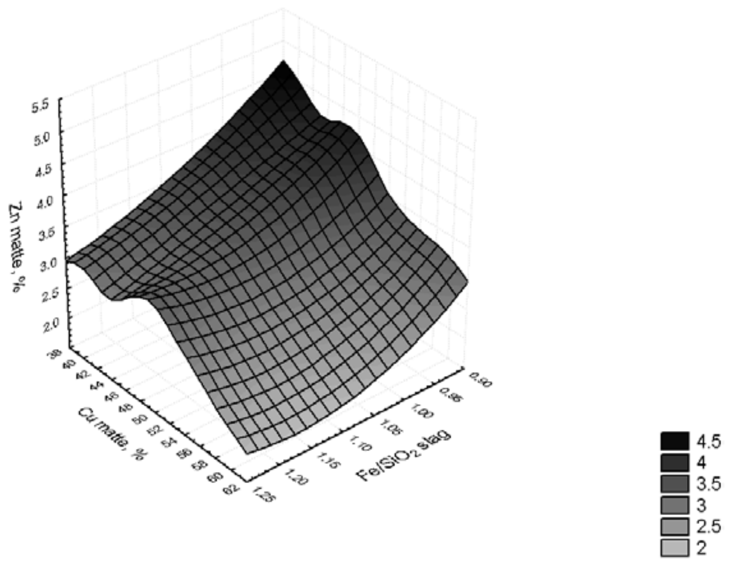

Fig. 5 The dependence of zinc content in matte to copper content in matte and Fe/SiO_2 ratio in slag

The following statistic relationships of magnetite and copper contents in the slag were determined, and relationships of zinc content and melting parameters were determined too, where [Cu], [Zn] refer to the element constituents in matte, and (Fe_3O_4), (Fe/SiO_2), (SiO_2/CaO) – in slag:

$$(Fe_3O_4) = 11.23 + 0.46[Cu] - 0.0048[Cu]^2 - 31.06(Fe/SiO_2) + 16.48(Fe/SiO_2)^2 - 0.69(SiO_2/CaO) + 0.028(SiO_2/CaO)^2 \quad (1)$$

$$(Cu) = 7.11 + 0.037[Cu] - 0.0004[Cu]^2 - 13.07(Fe/SiO_2) + 6.48(Fe/SiO_2)^2 - 0.10(SiO_2/CaO) + 0.004(SiO_2/CaO)^2 \quad (2)$$

$$[Zn] = 4.86 - 0.92(Fe_3O_4) + 0.1022(Fe_3O_4)^2 + 0.24[Cu] - 0.0032[Cu]^2 - 0.604(SiO_2/CaO) + 0.024(SiO_2/CaO)^2 \quad (3)$$

The above equations have relatively low values of correlation coefficients, r^2 values are in the range of 0.28 – 0.35. The average absolute error values of the dependent variables have been defined as 0.54, 0.086 and 0.40, as to equations (1) – (3) respectively.

The results of thermodynamic modeling of the equilibrium phases formed on cooling the working body have shown (Fig. 6), that at 25^{o}C fayalite is the basic phase and its content is close to 45%. Besides formation of $FeSiO_3$ up to 16%, $CaMgSi_2O_6$ up to 7% and other silicates up to 9% - $CaFe(SiO_3)_2$ and Zn_2SiO_4 is possible together with fayalite. Magnetite quantity is 6%, and besides the higher temperature is, the bigger its (magnetite) share is. In the sample maximum quantity of magnetite reaches 7.5% at the melting temperature nearly that of slag. According to the calculated data copper is mainly in the element state in the slag. Slag contains copper in forms of Cu_2S sulphide - $4{\cdot}10^{-5}$% and of oxide $CuFeO_2$ - $6{\cdot}10^{-7}$%. In general zinc is formed as silicate Zn_2SiO_4 - 3.78% and of ZnS sulphide - 1.95%, their share increases with temperature reduction. The ZnO quantity reduces from 2.50% to 0.02% together with this (during slag cooling).

It’s shown (Fig. 6), the phase composition of the sample is substantially modified with temperature change of working body. To justify the method of extra extraction of non-ferrous metals the data about form changes depending on temperature are very important. Thus, the changes found out in zinc sulphide share on cooling allow to suppose a possibility of its extra extraction by flotation method from crystalline sample.

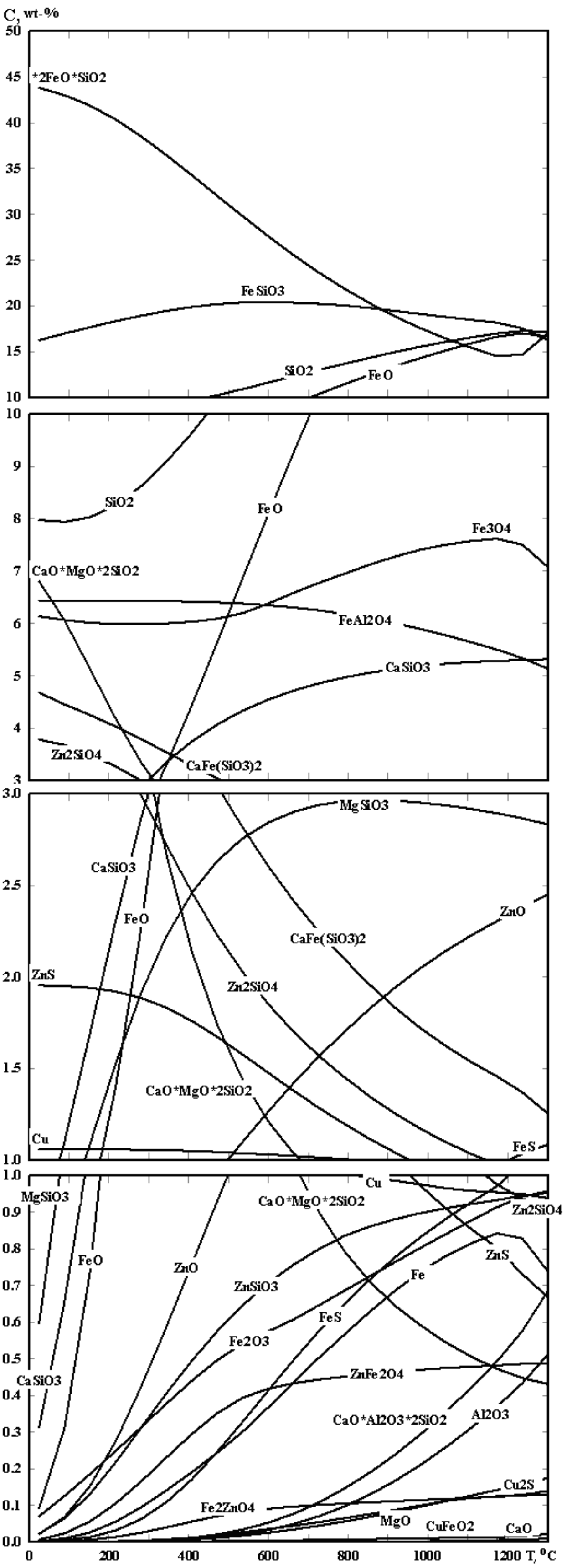

Fig. 6 The results of phase formation thermodynamic modeling during slag cooling

It was determined phase composition during investigation of slag sample from copper-zinc concentrates on matte melting (with 61% Cu content) is almost the same when melting on matte consisting 45% Cu [4]. Based on X-ray phase analysis data (Fig.7), the sample consists of following phases, namely: Fe_2SiO_4 fayalite, Fe_3O_4 magnetite, ($Ca_{0.5}Fe_{1.5}Si_2O_6$) iron calcium silicate and (Zn,Fe)S sphalerite.

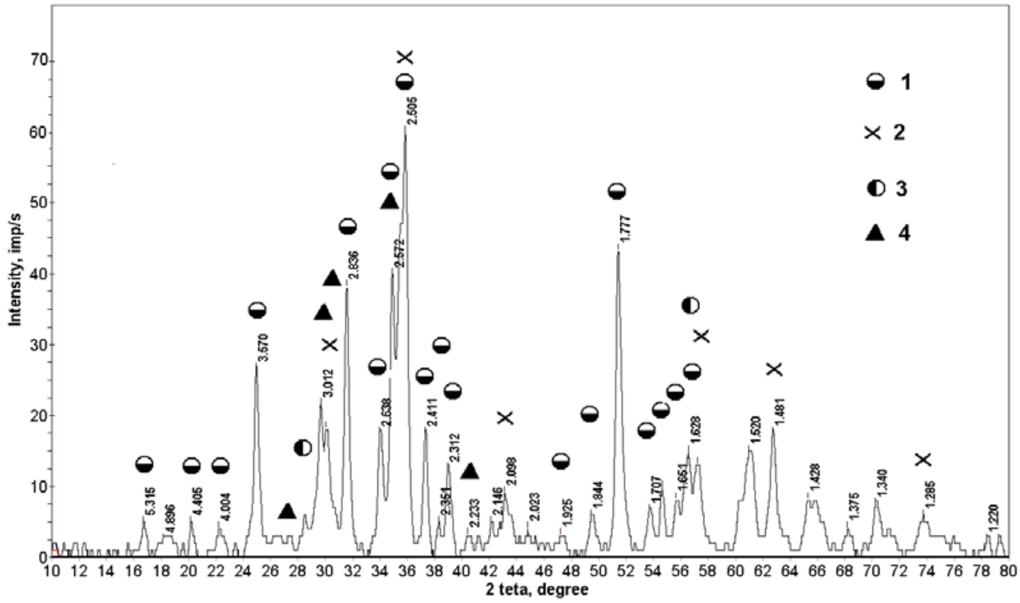

Fig. 7 Diffraction pattern of a slag sample from the concentrate smelting to matte with 61% Cu:

1 – Fe_2SiO_4, 2 - Fe_3O_4, 3 – (Zn,Fe)S, 4 - $Ca_{0.5}Fe_{1.5}Si_2O_6$

According to EPMA results, crystalline slag structure is iron silicate basis and looks like grey and dark grey bands with single bulk inclusions of matte up to 300 microns in size. Magnetite on the surface of microsection is in the form of finely dispersed dendrites. The view of the slag structure in the element characteristic radiation shows (Fig. 8), that it consists of large primary crystals which contain iron and silicon oxides, and also calcium containing iron - silicate eutectic (pyroxene). Iron and oxygen are contained in phases with dendrite structure. The main part of sulphide inclusions are copper sulphides, rarely - zinc sulphides.

The results of the spectral X-ray microanalysis of slag at the points of local probing showed that dendritic structure phases are magnetite Fe_3O_4, which contain 2.3–3.1% of Zn and up to 0.8% of Cu. Bulk fayalite crystals with the following composition $Fe_{1.72-1.77}Mg_{0.1-0.3}Zn_{0.10-0.12}Si_{1.07-1.12}O_4$ contain 3.2–3.9% of Zn and 0.5-0.6% of Cu. Pyroxene (Ca,Fe,Zn)SiO_3 with 10-12% of Ca were found out in space between fayalite crystals. Besides, 2.2% of Zn and 0.6% of Cu were deluted in slag which has pyroxene calcium containing basis. Sulphide inclusions 5 microns in size contain 9.4–31.5% of copper, 11.7-18.6% of zinc and 20.9–26.2% of iron. Sulphides have high lead content (up to 4.2%).

Iron silicate $Fe_3Si_2O_7$ formation was pointed out by analysis of smaller size phases (Fig.10 and Table 2), and there were indicated 3.7–4.9% of Zn and 0.4–0.7% of Cu. Sulphide small inclusions are similar (close by composition) to sphalerite and areas with high lead content (13.0%) were indicated in its (sulphide) particles.

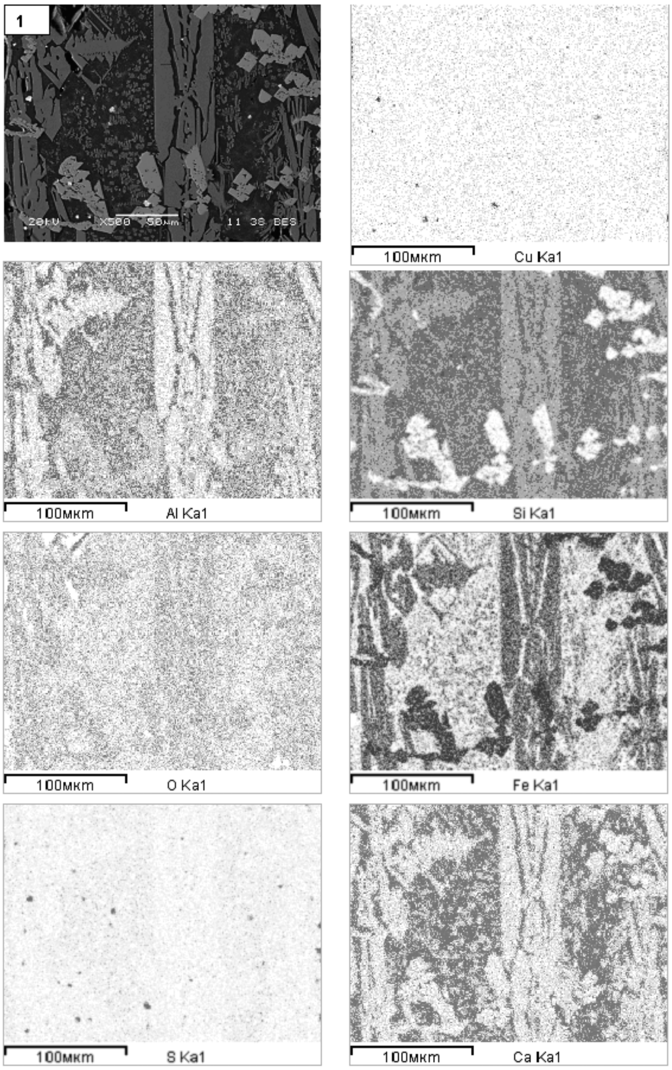

Fig. 8 Slag microstructure in element characteristic radiation

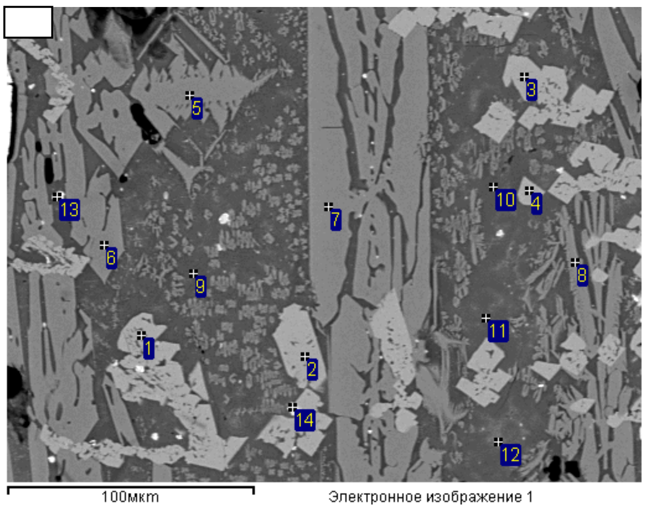

Fig. 9 Slag structure and phases local probing points

Table 1 Slag composition in local probing points (Fig. 9)

Pt. No	Content, mass.%													Phases
	O	Mg	Al	Si	S	K	Ca	Ti	Fe	Cu	Zn	As	Pb	
1	27.2	0.0	2.6	2.1	0	0	0.6	0.5	63.5	0.4	3.1	0	0	Fe_3O_4
2	26.3	0.3	2.2	0.9	0	0	0	0.5	66.5	0.8	2.5	0	0	Fe_3O_4
3	26.9	0	2.1	1.3	0	0	0.2	0.4	66.2	0.6	2.4	0	0	Fe_3O_4
4	26.9	0	2.1	0.6	0	0	0.2	0.4	67.5	0	2.3	0	0	Fe_3O_4
5	31.4	2.0	0	15.0	0	0	0.8	0	47.0	0.6	3.2	0	0	$Fe_{1.72}Mg_{0.17}Zn_{0.10}Si_{1.09}O_4$
6	30.7	2.2	0	15.0	0	0	0.7	0	47.4	0.6	3.3	0	0	$Fe_{1.77}Mg_{0.19}Zn_{0.11}Si_{1.11}O_4$
7	30.9	1.9	0	14.6	0	0	0.6	0	47.7	0.6	3.7	0	0	$Fe_{1.76}Mg_{0.16}Zn_{0.11}Si_{1.07}O_4$
8	30.7	1.5	0.3	15.0	0	0	0.9	0	47.1	0.5	3.9	0	0	$Fe_{1.75}Mg_{0.13}Zn_{0.12}Si_{1.12}O_4$
9	38.0	0	4.5	20.9	1.0	0.5	11.8	0.2	19.4	0.6	3.1	0	0	$(Ca,Fe,Al)SiO_3$
10	38.5	0	4.0	21.9	1.2	0.7	10.7	0	18.8	0.7	3.6	0	0	$(Ca,Fe,Al)SiO_3$
11	38.2	0	3.1	20.7	0.7	0.3	11.5	0	21.7	0.5	3.3	0	0	$(Ca,Fe,Al)SiO_3$
12	35.1	0	4.1	19.9	1.9	1.1	3.5	0.3	20.8	0	10.9	0.9	1.5	$(Zn,Fe,Al)SiO_3$
13	4.3	0	0.4	1.3	25.3	0.0	0.4	0	20.9	31.5	11.7	0	4.2	(Cu,Fe,Zn)S
14	6.3	0	0.3	1.5	27.4	0.0	0.3	0	26.2	19.4	18.6	0	0	(Cu,Fe,Zn)S

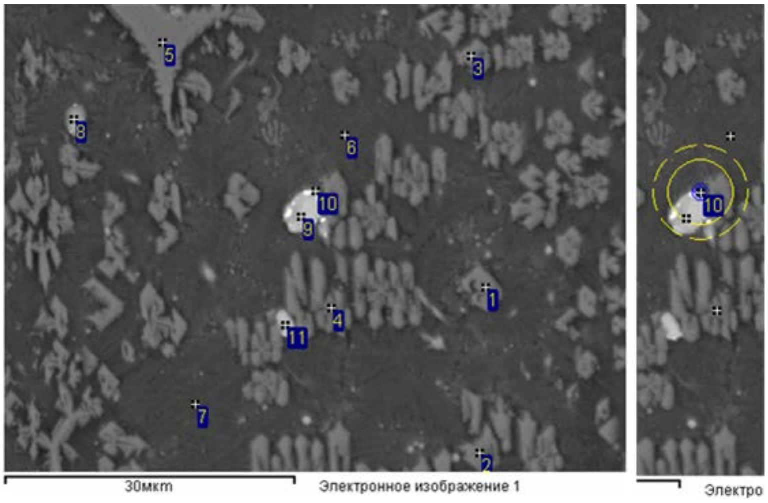

Fig. 10 Slag structure and phases local probing points

Table 2 Slag composition in local probing points (Fig. 10)

Pt. No	Content, mass.%										Phases
	O	Mg	Al	Si	S	K	Ca	Fe	Cu	Zn	Pb	
1	32.6	0.3	1.2	15.9	0.3	0.3	2.0	42.1	0.7	4.6	0	$(Fe,Zn,Ca)_3Si_2O_7$
2	32.5	0.4	1.1	16.2	0.2	0.4	2.2	41.8	0.4	4.7	0	$(Fe,Zn,Ca)_3Si_2O_7$
3	31.7	0.4	0.9	16.2	0.2	0.2	2.2	43.1	0.5	4.7	0	$(Fe,Zn,Ca)_3Si_2O_7$
4	33.3	0.3	2.0	17.3	0.3	0.5	2.2	38.6	0.6	4.9	0	$(Fe,Zn,Ca)_3Si_2O_7$
5	31.0	1.0	0	14.9	0	0	1.1	47.9	0.5	3.7	0	$(Fe,Zn,Ca)_3Si_2O_7$
6	38.9	0	4.0	21.1	0.7	0.4	12.2	19.9	0.5	2.3	0	$(Ca,Fe)SiO_3$
7	38.7	0.2	3.9	20.6	0.4	0.3	12.4	20.4	0.7	2.1	0	$(Ca,Fe)SiO_3$
8	14.8	0	2.7	12.4	17.9	0.5	6.5	26.9	5.0	13.2	0	(Cu,Fe,Zn)S
9	16.3	0	0.3	1.3	18.1	0.0	0.6	35.4	3.4	24.7	0	(Cu,Fe,Zn)S
10	23.0	0	2.3	11.4	11.0	0.8	1.7	18.8	7.0	10.9	13.0	(Cu,Fe,Zn)S
11	17.7	0	1.2	7.9	16.9	0.3	1.3	20.1	1.5	31.1	2.2	(Cu,Fe,Zn)S

Thus, the slag resulted from copper - zinc concentrate melting on matte (with 61% Cu) in Vanyukov's furnace consists of iron silicate phase crystals, pyroxenes and magnetite in form of finely dispersed dendrites. If SiO_2/CaO ratio (wt. %) is

8.2 in slag, then it is up to 2.3 in pyroxene phases. Assuming that zinc oxide in systems under consideration demonstrates properties similar to calcium oxide, then SiO_2/(CaO+ZnO) ratio is up to 2.0 in pyroxenes. Magnetite and iron silicate phases contain zinc up to 3.1 and 4.9 %, and copper – up to 0.8% and 0.7%, respectively. Single bulk matte inclusions up to 300 microns in sizes and small sulphide crystals formed during its cooling were detected in slag. Sulphides have phase size about 5 microns and their composition is similar to sphalerite. Besides, sulphides contain some quantity of copper and lead. As indicated by phase probing the most of sulphide inclusions have essential composition difference comparing with matte due to the high zinc content in general. The number of sulphide inclusions has composition similar to christophite [16] with Zn/Fe (at. %) ratio about 0.5.

4. Conclusions

Relations (Cu), (Fe_3O_4) = f{[Cu], (Fe_3O_4), (Fe/SiO_2), (SiO_2/CaO)} were discovered which allowed to evaluate copper and magnetite content in slag formed by autogenous smelting of copper - zinc concentrates. Concentrates with relatively low copper content processing with the release of 60% Cu matte is accompanied by slag formation with high magnetite content. High concentrations of magnetite can be explained by higher oxidation degree of the oxide melt during concentrate autogenous smelting.

Equilibrium phase compositions were elicited in the temperature range from 20 to 1300 ^oC by the thermodynamic analysis methods. It's shown that temperature significantly effects the non-ferrous metals state in oxide sulphur-containing working body which is similar to slag of copper - zinc concentrates autogenous smelting by composition. Due to phase and spectral x-ray analyses data it was defined that the main phases formed on slag cooling are iron silicates, pyroxene and magnetite. Copper and zinc solubility in the main phases is not higher then 0.8% and 4.9%, respectively. Sulphide phases are represented by bulk matte inclusions and minor sulphides, which are formed out as a result of slag cooling. Minor sulphides have similar composition as sphalerite and christophite. Sulphide zinc-containing phases might be segregated by flotation methods.

Acknowledgement

The work was support by the Russian Foundation for Basic Research (grant No 11-08-12062).

References

[1] A. V. Vanyukov, V. Ya. Zaitsev. Theory of Metallurgical Processes, Metallurgiya, Moscow, 1993, in Russian.

[2] A. V. Vanyukov, V. Ya. Zaitsev. Slags and Mattes of Nonferrous Metallurgy, Metallurgiya, Moscow, 1969, in Russian.

[3] A.V. Vanyukov, V.P. Bystrov, A.D. Vaskevich. Smelting in the liquid bath, Metallurgiya, Moscow, 1988, in Russian.

[4] E.N. Selivanov, R.I. Gulyaeva, D.I. Zelytin, V.V. Belyaev, N.I. Selmenskich. Effect of speed of cooling on structure of slag from of copper-zinc concentrates in Vanukov furnace. *Tsvetnye Metally*, 2009 (12), p27-31, in Russian.

[5] B.K. Mohapatra, B.D. Nayak, G.V. Rao. Microstructure of and metal distribution in Indian copper converter slags – study by scanning-electron microscopy. *Mineral Processing and Extractive Metallurgy*, 1994, 103, pC217-C220.

[6] J. Elliott. Phase relationships in the pyrometallurgy of copper. *Metallurgical Transactions*, 1976, 7B, p17-33.

[7] E.N. Selivanov, R.I. Gulyaeva, D.A. Toloknov Magnetite precipitation during copper - zinc concentrates autogenous smelting in Vanyukov's furnace. *Tsvetnaya Metallurgia*, 2010 (7), p3-9, in Russian.
[8] U.B. Schmonin. Pyrometallurgical slag depletion of non-ferrous metals, Metallurgiya, Moscow, 1981, in Russian.
[9] A.M. Khalemskiy, A.V. Tarasov, A.N. Kazantsev, V.D. Kinev. Copper-zinc sulphide material smelting in Vanyukov's furnace. Ekaterinburg: Kedr, 1993, in Russian.
[10] R.W. Ruddle. The Physical Chemistry of Copper Smelting, Institution of mining and metallurgy, London. 1953.
[11] R. Rüffler, J. Dávalos. Phase Analytical Studies of Inductrial Copper Smelting slags: Part I: Silicate slags, *Hyperfine Interac*. 1998, 111, p299–307.
[12] P. Spira, N.J. Themelis. The Solubility of Copper in Slags. *Journal of Metals*, 1969, 29 (4), p35-42.
[13] A.I. Okunev, M.D. Galimov. Oxidation of iron and sulfur oxide-sulfide system, Nauka, Moscow, 1983, in Russian.
[14] A. Yazawa. Thermodynamic considerations of copper smelting, *Canadian Metallurgical Quarterly*, 1974, 13 (3), p443-455.
[15] A. Roine, P. Lamderg, J. Mansikka-aho. Outokumpu HSC Chemistry for Windows, Outotec Research OY, Pori, 2007. www.outotec.com.
[16] E.N. Selivanov, V.V. Belyaev, N.I. Selmenskikh, A.A. Pankratov. Forms of Metals in the Slag of Combined Melting–Converting of Copper Concentrates. *Rasplavy*, 2004 (1), p33–41, in Russian.