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THE DECOPPERIZATION AND COAGULATION BY USE THE CARBON-N-Ox METHOD

This paper discusses the impact of complex chemical reagents during the process of decopperisation of slag. The beneficial effect of carbide response factors with the participation of nitrogen was indicated as well as the role of stimulators surfactants. Based on the results of the research the basic structure of the slag during decopperisation was systematized. The effects of coagulation of droplets of copper in the slag were shown in this paper.

Keywords: crystals morphology, calcium compounds, copper slag, salts

1. Introduction

The article presents an outline of the new technology of pyrometallurgical processing of slag in the direct-to-blister process. A new way of implementing the technology of recovery of copper from the flash furnace slag by means of different charges has been proposed. An extraction process carried out in the industrial furnace leads to the formation of the copper droplets suspension in the liquid slag. Next, the formed suspension is delivered into the electric arc-furnace where the final coagulation of the copper droplets suspend in the liquid slag occurs. The copper droplets coagulation is completed by their growth / solidification usually accompanied by segregation of some elements which are present inside these droplets. The presented concept intensifies the reactions, using the Carbon-N-Ox method of copper compounds to forms of metallic phases in the slag [1]. The processes of coagulation are accelerated and the crystallization processes of metallic phases are under control. The formation of the chilled grains zone is the result of unconstrained rapid solidification and was not the subject of simulation [2].

The discussed concept takes into consideration the impact of the carbon reagents, and this constitutes the next aspect of its originality. Most of the methods of pyrometallurgical recovery of copper from by-product slag, including those applied in copper smelter in Głogow (Poland), uses coal in the form of coke or coal briquettes. It is used in conjunction with the fluxes that correct physico-chemical properties of the processed slag. However, in the light of the experience of the authors and other scientists, as well as theoretical analysis, which form of carbon reagent appears to be very inefficient. Reacting only with the agents of the melting atmosphere, solid carbonaceous/carbon does not dissolve itself, and, therefore, it does not react so effectives in the slag. That is why some different reagents, such as the carbides – nitrogen carbides ones, have been introduced. As several studies on the conditions of liquid/molten cooper and its alloys have shown, carbon ions $\{C^{2+}\}$ and $\{C^{4+}\}$ are the decisive components of the reactions that take place in slag (Fig. 1).

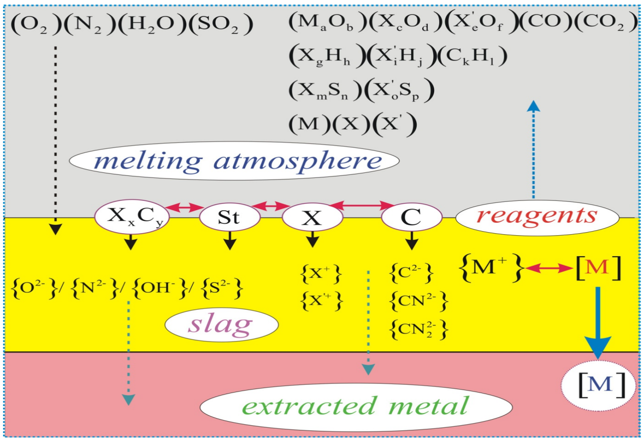

Fig. 1. A proposed scheme [2] of refining-extracted Carbon-N-Ox process of a slag with a carbide-cyjanamide slag solution where: ( ) – gas, M – extracted metal, X – reagent, St – reaction stimulator, { } – ions in the slag

The method of tracing changes of the physical properties of processing and post-process slag [3-5], and the program for mathematical modeling of the phenomenon of crystallization of metallic phases in the slag, together with the simultaneous application of complex, carbide reagents, allows to reach the content of 0.3% copper in slag.

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2. Analysis of issues

The complexity of the interactions of nitrogen in the slag were indicated by D.J. Min and R.J Fruehan's results [6] who observed the decrease of solubility of nitrogen in the crucible with the increase of CaO in it. From the results published in another paper [7] one might think about decreasing the nitrogen solubility in the slag with an increase in the SiO_2 content and decreasing f CaO. Reports from the Authors work [8] seems to be very interesting point of view – that in the presence of carbon or metals carbides, nitrogen combines in the slag systems CaO-Al_2O_3-SiO_2 with carbon in the form cyanamides. The authors of these works assumed that nitrogen substrates occurs mainly in two forms: nitride and cyanide with the formation of $\{N^{-3}\}$ and $\{CN^{-1}\}$. In studying matrix systems CaO-Al_2O_3-SiO_2 assigned were to process of chemical bonding of nitrogen in slag the following reactions:

$$3\langle C\rangle + 3\,[O^{2-}] + (N_2) - 2e \rightarrow 2\{N^{2-}\} + 3(CO) \qquad (1)$$

$$5\langle C\rangle + 3\,[O^{2-}] + 2\,(N_2) - 2e \rightarrow 2\{CN_2^{\,2-}\} + 3(CO) \qquad (2)$$

$$5\langle C\rangle + 3\,[O^{2-}] + 2(N_2) - 4e \rightarrow 2\{CN_2^{\,1-}\} + 3(CO) \qquad (3)$$

Based on data from the literature and own research [8] the following schema of mechanism of the impact of nitrogen with the participation of carbon in the slag oxide was developed:

$$(N_2) \rightarrow 2\{N\}\text{absorbed} \qquad (4)$$

$$\langle C\rangle + [O^{2-}] - 2e \rightarrow (CO) \qquad (5)$$

$$2\langle C\rangle + 4\{N\}_{\text{adsorbed}} + 2e \rightarrow 2\{CN_2^{\,2-}\} \qquad (6)$$

Slightly different position was taken by S. Kurita [9], which is also stated in the slag occurrence of such compounds as Si_3N_4, AlN, $Ca(CN)_2$ and $CaCN_2$. Author [9] accepted the hypothesis that chemisorbtion of nitrogen, after the adsorption at the interface according to formula 4, proceeds at the carbon content according to two variants:

– formation of nitrides

$$2\{N\}_{\text{ads.}} + 3\langle C\rangle + 3\,[O^{2-}] \rightarrow 2\{N^{3-}\} + 3\,(CO) \qquad (7)$$

or in writing ion: $2\{N\}\ \text{absorbed} + 6e \rightarrow 2\{N^{3-}\}$

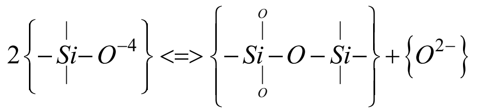
– formation of cyanamides,

$$2\{N\}_{\text{ads.}} + 2\langle C\rangle + [O^{2-}] \rightarrow \{CN_2^{\,2-}\} + (CO) \qquad (8)$$

or in writing ion:
$2\{N\}_{\text{ads.}} + \langle C\rangle + 2e \rightarrow \{CN_2^{\,2-}\}$, which was also established in the previously cited work [2].

Validation of these mechanisms can be found in A. Yazawa research [10], according to which the dissolution of nitrogen is described by reactions 7 and 8 wherein the content of such phase $\{CN_2^{\,2-}\}$ the author described as extremely low, not more than 0.001 wt%. R. Barryman [11] for indirect downstream nitriding Author recognized carbide. The Authors [12, 13] also pointed to the increase in the intensity of nitriding in the system CaO-CaF_2. At the same time in other studies a marked catalytic effect of halogen compounds of calcium on the process of nitriding carbide was indicated. Placing the unstable compounds such as CaF_2 and $CaCl_2$ significantly lowered the initiation temperature reaction of nitrogen fixation by carbide to approx. 950 K, while the product was easier to dissociate at higher temperatures. Analysis of compounds used as flux for carbide, taking into account the atmosphere melting containing approx. 78% nitrogen, the question has hypothesized that the nitriding carbide can also take place in other conditions, and even more in pyrometalurgical processes of refining copper and its alloys involving this reagent and carbon. On the basis of analytically documented work it can be assumed that the most important step in the mechanism of adsorption of nitrogen in the ionic form N^{-3} and $CN_2^{\,-2}$. Researches of R. Inoue and H. and other [7] demonstrated the possibility of strong interaction of nitrogen in systems: CaO-SiO_2, CaO-MgO-SiO_2, BaO-MgO-SiO_2, CaO -SiO_2-Al_2O_3. From the analysis presented in this work it can be concluded that it is possible to replace oxygen in slag with nitrogen, an exchange thorough the surfaces of Nitrogen-Slag interface. This means that for the higher nitrogen content in the atmosphere the content of oxygen in the slag should undergo decrease.

A. Bydałek [1], analyzing the formulas of 1-8 came to similar conclusions. They found in fact that a decisive influence on the rate of chemisorptions of nitrogen is determined by the electron supply quantity and type of oxygen ions. This issue is directly related to the problem of the coordination of ions Si^{+4}, $Ca^{+\,2}$, $Al^{+\,3}$ Na^{+}, K^{+} and O^{-2} in the systems concerned. It has been demonstrated that in breaking bridges, particularly by joining calcium, sodium or potassium ions to the negatively charged oxygen atoms at the corners of SiO_4 tetrahedral, it was followed by rapid depolymerisation of the structure. The effect of increasing the basics oxide content should finish, when the ratio of corresponding orthosilicates is reached according to the following scheme [14]:



$$2\left\{-\overset{|}{\underset{|}{Si}}-O^{-4}\right\} <=> \left\{-\overset{\overset{O}{|}}{\underset{\underset{O}{|}}{Si}}-O-\overset{|}{\underset{|}{Si}}-\right\} + \left\{O^{2-}\right\} \qquad (9)$$

The basic weakness of the promoted concept, which was shown among others by Y. Iguchi and Y.I. Ueda [15] and Migas and Korolczuk [16], provided the fact that the reaction described above (9) was dependent not only on changes of slag composition appearing during refining but also on the temperature. We found that the cross-linking Si^{+4} is associated with the absorption of oxygen ions. Therefore it inhibits the adsorption of nitrogen due to the absence of electron carriers. The introduction of calcium ions, the breaking chains silicate releases oxygen ions, thereby intensifying the adsorption process. In the processes of decopperisation of slag is slurry process, which is a fundamental process in Poland in the production of copper from the ore, the electric furnace is charge predominantly with limestone (calcium carbonate), sodium carbonate and carbon.

Taking to account the analysis, in the presence of calcium ions, nitrogen should dissolve better, and in the presence of carbon ions it should form cyanamides compounds. This thesis became the basis for the formulation of a concept of research – technology called Carbon-N-Ox [17]. Additionally, based on its own experience, we found that the ions $\{CN_2^{2-}\}$ is not only promote to oxide reduction, but also to the interfacial tension change and decrease the melting temperature. Therefore, in regard to the conditions of de-coppering of slag, following mechanism of the changes taking place in the furnace at a temperature of approx. 1200-1300°C was proposed with application of the Carbon-N-Ox method:

A – reduction of copper oxides with the participation of carbon-nitrogen compounds (according to the equations 1-8),
B – the formation of metallic copper droplets,
C – droplets coagulation,
D – deposition of copper drops on the bottom of the furnace.

Contrary to the expectations, the most difficult to optimize are the stages C and D, because of the “closing-trapping” droplets of copper by slag structure, mainly the so-called ferrites which are compounds of iron-silicon-oxygen. They are structurally equivalent to orthosilicates widely described in the literature [11-15], and therefore, by analogy, it was decided to propose a scheme of interactions in a suspension slag – reagents of Carbon-N-Ox system (Fig. 2):

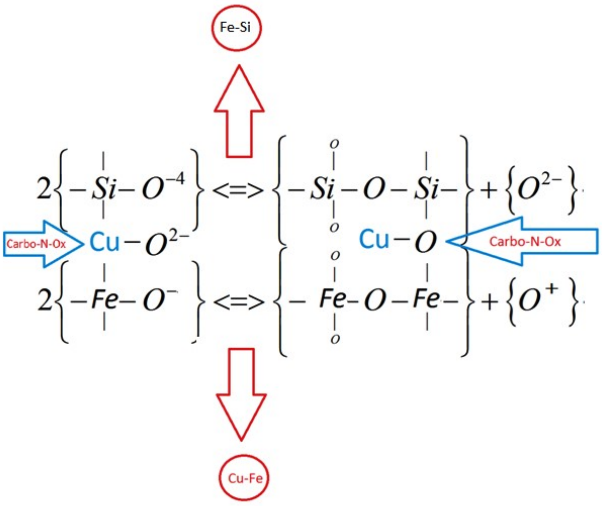


Fig. 2. Scheme of interactions in a suspension slag – reagents of Carbon-N-Ox system

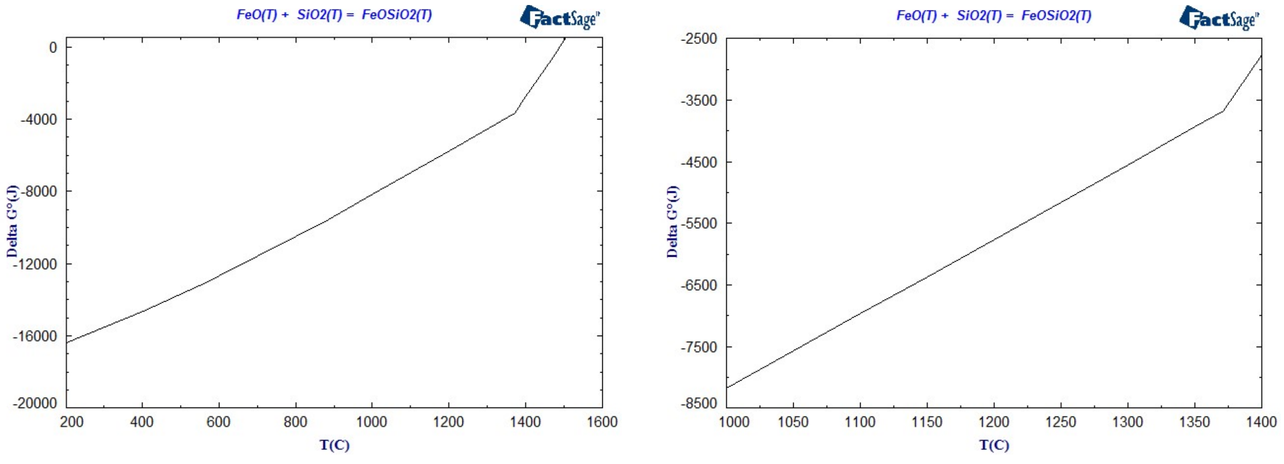
3. Analysis of thermodynamically aspects of selected compounds

Thermodynamic analysis of the possibilities of reaction and formation of selected compounds in the assumed conditions systems were performed. Thermodynamic database FactSage with Reaction module was used. Calculations are based on minimizing Gibbs energy and thermo-chemical functions. The calculations can be continued until chemical equilibrium is reached with selected reagents or chemicals spices. Likewise up to identify the inversion temperature for a given system of substrates, also for different selected units (K, C, bar, atm., J, etc) of physical and chemical variables: T, p, H, S, G. Calculations can be performed for increase temperature of systems as well as opposite for single and multi-component mixtures. The following selected cases were analyzed.

3.a. Reactions of ferric silicates

The changes of the thermodynamic potential (enthalpy of reactions) of iron silicate formation reaction (reaction occurred) have been presented on the (Fig. 3a,b).

With increase of temperature, the changes in potential increases towards more positive values that it’s possible to observe in the (Fig. 3a,b). Conversely, the rate of change of DG changes at 1370°C, the relationship becomes more “steep”, the stability of iron silicate is decreases above this temperature.



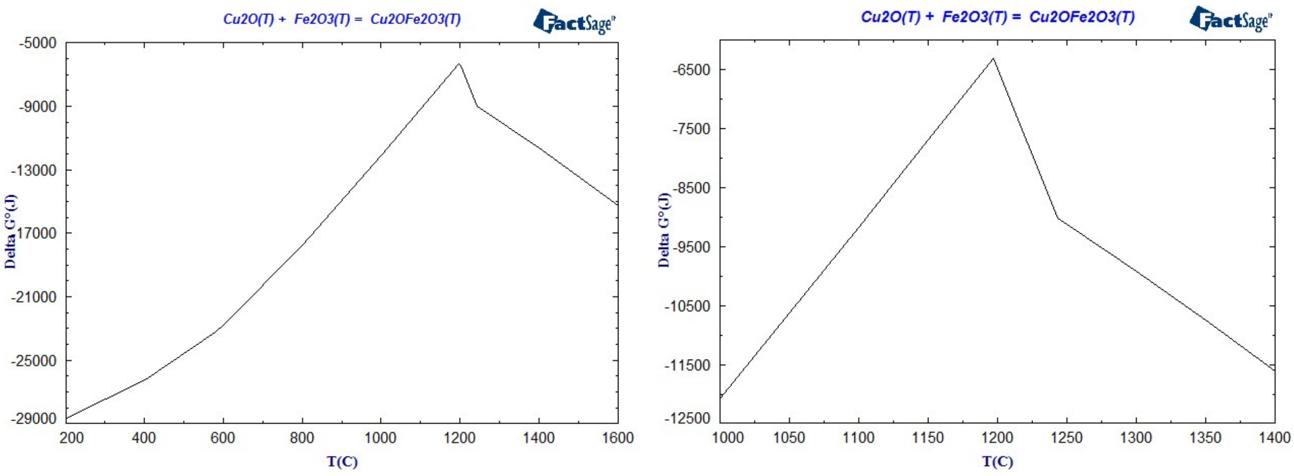
a) b)

Fig. 3. The changes of the thermodynamic potential (enthalpy of reactions) of iron silicate formation reaction

3.b. Reactions of copper ferrites

In (Fig. 4a,b) enthalpy of copper ferrites reactions formation were presented. Compounds change their stability under given conditions in the temperature range 1000-1200°C and above that temperature also.

In the range of temperatures 1000-1200°C, the copper ferrites stability decreases obtained a maximum up to 1200°C, but once it is exceeded, the value of changes in the thermodynamic potential gradually increases. Therefore compounds seems to become more stable with temperature rise.



a) b)

Fig. 4. The changes of the thermodynamic potential (enthalpy of reactions) of copper ferrites formation reaction

3.c. Findings of structure

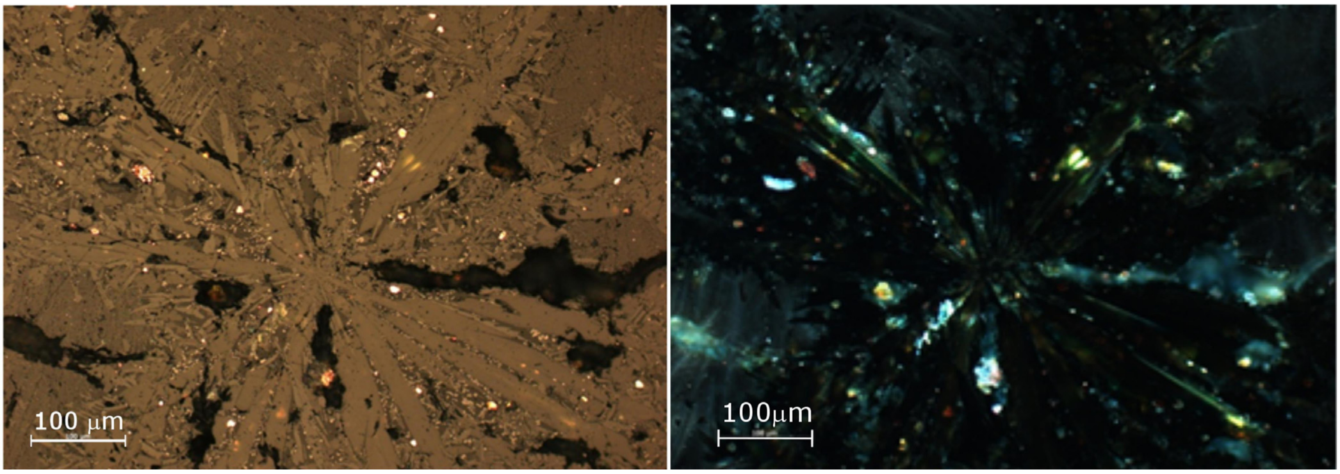
Slag and metals are subject to a crystallization process. Assuming that the liquid slag consists of short-alignment structures (SRO) in analogy to the solid phase, the sample for structural analysis was collected from the electric furnace and subjected to rapid cooling – so-called frizzing. This procedure allowed to obtain a structure similar to that which occurs temporarily in a liquid state. The samples were cooled in liquid nitrogen. In the course of structural analysis there were differentiated the suspension solidified slag and slag occurring during de-coppering in an electric furnace, the following structures:

Zone I – "octopus" structure – (Fig. 5a,b),

Zone II – equiaxed structure – (Fig. 6a,b),

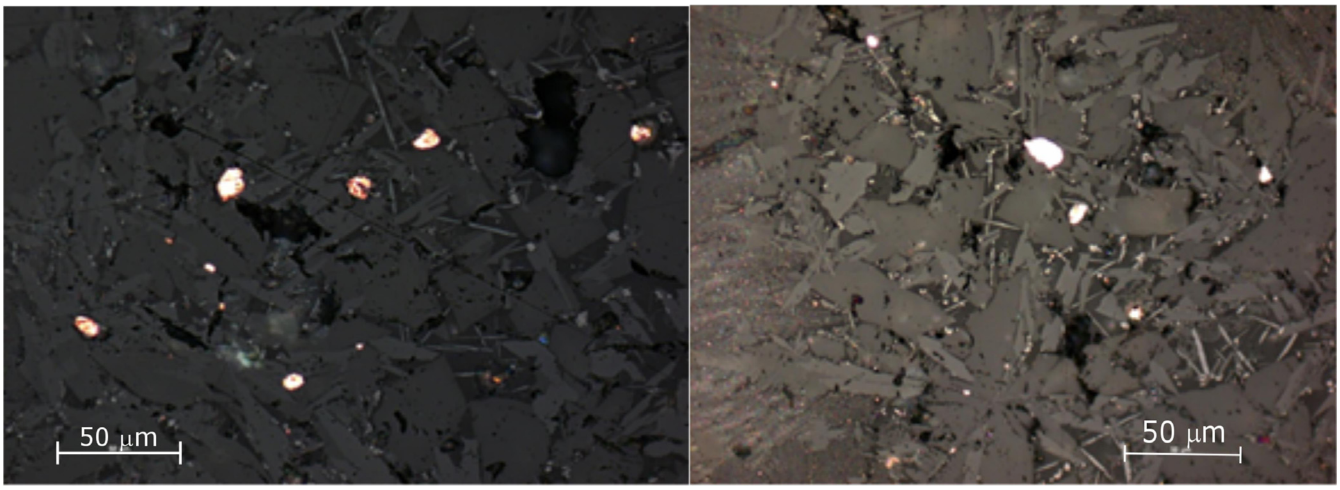
Zone III – column structure – (Fig. 7a,b).

A characteristic feature of the structures was the occurrence, as in the case of metals, the respective structures in the preferred areas of solidifying slag. In places with a large temperature gradient there were the column structure observed, in places with little gradient – equiaxed and "octopus" structures. Samples for structural studies were collected for the areas immediately close to the electrode (there appeared even, high (approx. 1350°C) temperature, and areas remote from the electrodes (there was a large temperature gradient of 250°C). The exact distinction of zones I and II was difficult, and often a mixed structure was obtained (Fig. 3b).



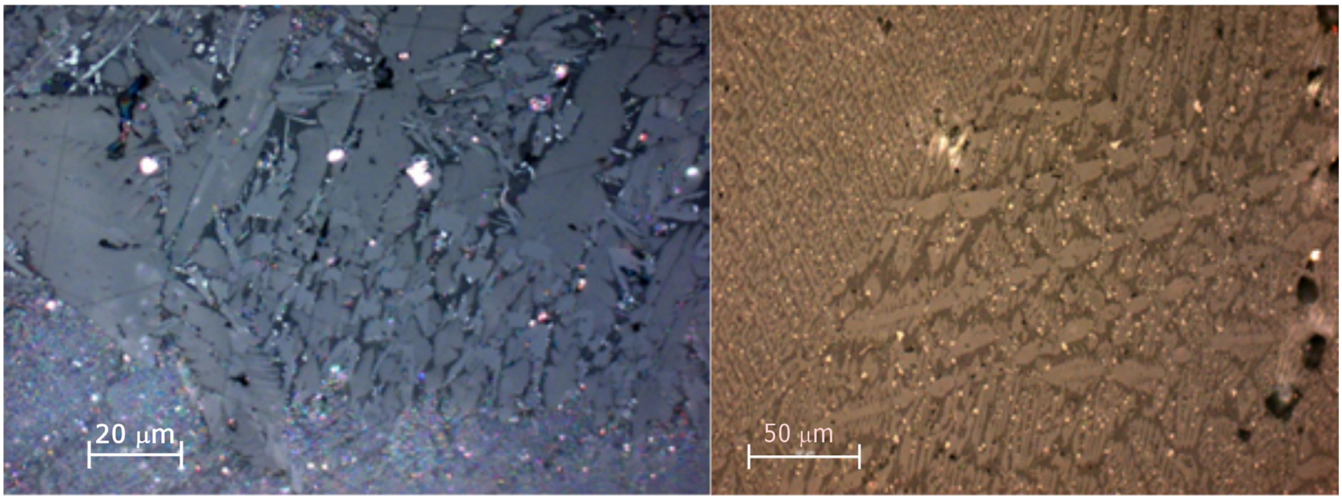
a) b)

Fig. 5. Zone I – "octopus" structure: a) – plain optical image, 400×, b) image in polarized light, 400×



a) b)

Fig. 6. Zone II: a) equiaxed structure – 800×, b) the composite structure from the zones I and II, 1000×



a) b)

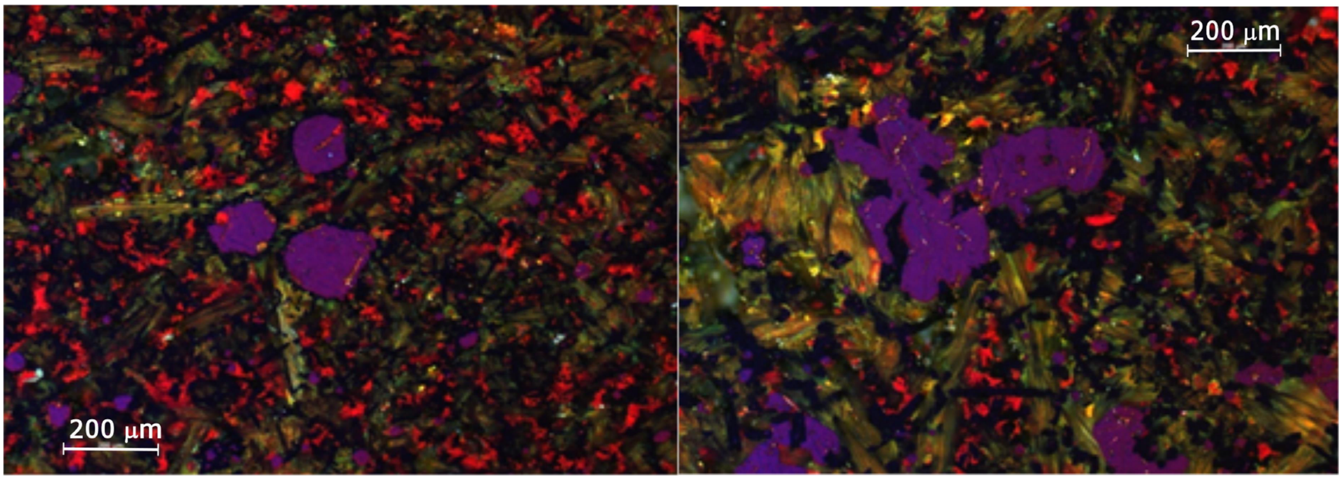
Fig. 7. Zone III with distinction: a) zone of large columnar crystals with visible at the bottom zone of fine crystalline, 1250×, b) fine crystalline structure, 1000×

Analysis of different crystal forms present in the slag during the de-coppering shows the dependence of the dimension of droplets of metallic copper separating in slag. The problem of slag decoppering consists of the elimination of the drops of the metal small precipitates with a size smaller than 5 μm, and such are present in the structure I and structure III. Only in equiaxed structure (marked II) in the final stages of de-coppering droplets not smaller than 10 μm can be observed. Therefore, Carbon-N-Ox technology was found to impact the surface parameters, including the interfacial surface tension, for the formation of structures similar to those of equiaxed slag. This issue is directly related to the above-described problem of the coordination of ions SiO^{4-}, Ca^{+2}, Na^{+}, K^{+} and O^{-2} in the slag. Based on own research [2] phosphorous ions were selected for this system as well. Finally, set of the reactants affecting the structure of slags consist of calcium, ferrum and aluminum carbides, in coordination with the stimulators in the form of phosphorus and calcium. The role of the carbide reactants is the reduction of copper oxides (Fig. 8a), whereas the role of the surface impacts stimulator were both the impact on the matrix of slags, and on the coagulation of droplets of metallic copper (Fig. 8b).

The results indicated that in the case of "octopus" structure (zone I) combining even large particles of copper (about 100 μm) proceeded very slowly. Fig. 5 and 8a shows the skeleton of dendritic structure, the shape of "octopus", with a visible nucleus in the middle – exactly the way to connect copper particles. Fig. 8b,f shows the effect of combining indicates a lack of dendritic structure, which makes it impossible to connect.

4. Summary and conclusions

The article shows the necessity of taking into account the procedures of slag de-coppering both impacts – reducing capacity and surfactant. We discussed basic types of crystalline structures formed during slags re-melting. Structures which positively



a) b)

Fig. 8. a) photo polarized light indicating the copper oxides (red areas) 400× b) coagulation area of copper precipitates in the slag, 400×

influence the coagulation, and which obstruct the process were distinguished here. Shown was the mechanism of metallic copper particles coagulation in the slag. Decrease amount of copper in the post-process slags was obtained from 0.6% to 0.3% as results of all combined actions. If would be taking account one batch charged to electric furnace/refining process in 500 Mg slag – at theoretical simulations shows additions amount of copper was 1,5 Mg per one melt.

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