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DYNAMIC MODE OF COPPER RECOVERY FROM THE POST-PROCESSING SLAGS

The post-processing slags containing about 0.8 wt.% of copper were subjected to the treatment of a complex reagent. The chemical composition of the complex reagent has been elaborated and patented in frame of the Grant No. PBS3/A5/45/2015. The slags had an industrial origin and were delivered by the Smelter and Refinery Plant, Głogów, as a product of the direct-to-blister technology performed in the flash furnace assisted by the arc furnace. An agglomeration of copper droplets suspended in the liquid slag, their coagulation, and deposition on the bottom of furnace were observed after the treatment this post-processing slag by the mentioned reagent. The treatment of the post-processing slags by the complex reagent was performed in the arc furnace equipped with some additional electrodes situated at the furnace bottom (additional, in comparison with the arc furnace usually applied in the Smelter and Refinery Plant, Głogów). The behaviour of the copper droplets in the liquid slag within the competition between buoyancy force and gravity was studied from the viewpoint of the required deposition of coagulated copper droplets. The applied complex reagent improves sufficiently the surface free energy of the copper droplets. In the result, the mechanical equilibrium between coagulated copper droplets and surrounding liquid slag is properly modified. Eventually, sufficiently large copper droplets are subjected to a settlement on the furnace bottom according to the requirements. The agglomeration and coagulation of the copper droplets were significantly improved by an optimized tilting of the upper electrodes and even by their rotation. Moreover, the settlement was substantially facilitated and improved by the employment of both upper and lower system of electrodes with the simultaneous substitution of the variable current by the direct current.

Keywords: post-processing slags, complex reagent, copper recovery, arc furnace, rotating tilted electrode

1. Introduction

The analysis connected with the efficiency of the stimulators and reagents onto the agglomeration, coagulation and sedimentation of the copper droplets in the liquid post-processing slags is continued in frame of the Grant No. PBS3/A5/45/2015. The slags used in the experiment were delivered by the Smelter and Refinery Plant, Głogów after the so-called direct-to-blister process assisted by the slag treatment in the arc furnace. The direct-to-blister technology is an extraction process and delivers the primary suspension of the copper droplets in the liquid slag. The following agglomeration, coagulation and sedimentation of the copper droplets are significantly influenced by the extraction technology [1,2].

The mentioned industrial process of decopperisation is able to diminish the copper content in the slags from about 12 wt.% (obtained due to the direct-to-blister process) to 0.8 wt.% obtained in the arc furnace (the Smelter and Refinery Plant, Głogów).

An additional problem which accompanies the decopperisation is the removing of lead and iron from the copper droplets [3]. Moreover, carbon is also frequently present in the copper droplets [4], especially, when reduction of oxides is not sufficiently effective in the direct-to-blister process [5,7,10]. The interfacial phenomena have also significant influence on the copper recovery from the slags [6,8,9].

It should be emphasized that the copper droplets geometry is strictly connected with the copper concentration. Therefore, an evolution of droplet shape is expected during droplets coagulation, Fig. 1. An observation of the changing in copper droplets geometry facilitates the estimation of the copper droplets self-cleaning. The recorded copper droplet shapes are: rod-like, star-like, irregular spherical, regular spherical one.

The evolution of the mentioned geometry from the rod-like to the spherical regular one can be improved by imposing some dynamic conditions upon the process of the copper recovery from the post-processing slags. So, the geometry of copper droplets is a good factor which determines their approximate purity, Fig. 1, Fig. 2.

The dominant large copper droplet is just in the course of coagulation through swallowing the rod-like droplets. This main droplet tries to diminish its surface free energy (surface tension).

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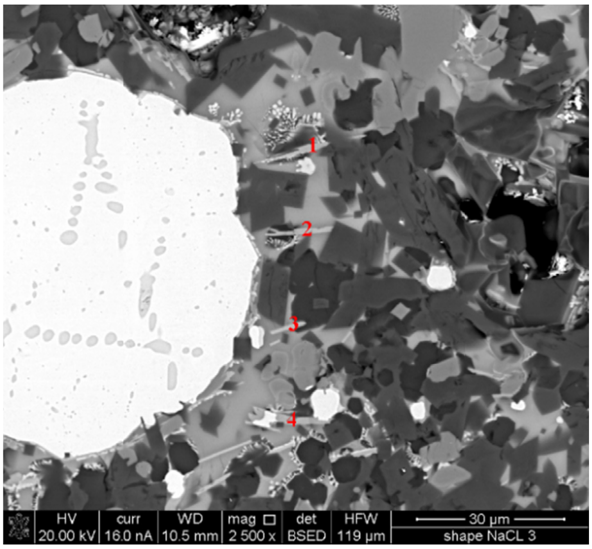

Fig. 1. Copper droplets shape; (1,2,3,4 – rods) – containing below 15 wt.% Cu tend towards the spherical irregular dominant droplet

The star-like copper droplets contain usually about 25 wt.% Cu. When the droplet evinces irregular spherical geometry, Fig. 1, then it may contain almost 50 wt.% Cu.

Fully spherical shape of the droplet is connected with the highest purity. This purity may be equal to about 70 wt.% Cu or more, Fig. 2.

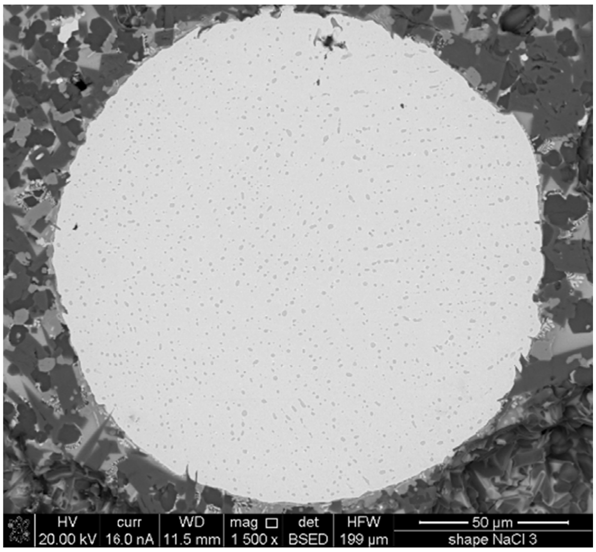

Fig. 2. Fully spherical coagulated droplet containing about 85 wt.% Cu with some agglomerations of the $Cu\text{-}Cu_2O$ – rod-like eutectic

The current experiment with the imposed dynamic conditions tries to explain not only the evolution of the copper droplets shape but also the phenomenon of the droplets self-cleaning as well. First of all, however, the experiment tries to explain how to improve the sedimentation of copper droplets. It is expected that the post-processing slags may diminish the copper content from about 0.8 wt.% Cu to 0.2 wt.% Cu and even to 0.1 wt.% Cu. For that reason, an innovative design of the arc furnace is proposed in the current experiment.

2. Phenomenon of the droplet self-cleaning

The copper droplets suspended in the liquid slag tend to diminish their surface tension. Thus, the smaller droplets are swallowed by the bigger dominant copper droplets, Fig. 1, Fig. 3.

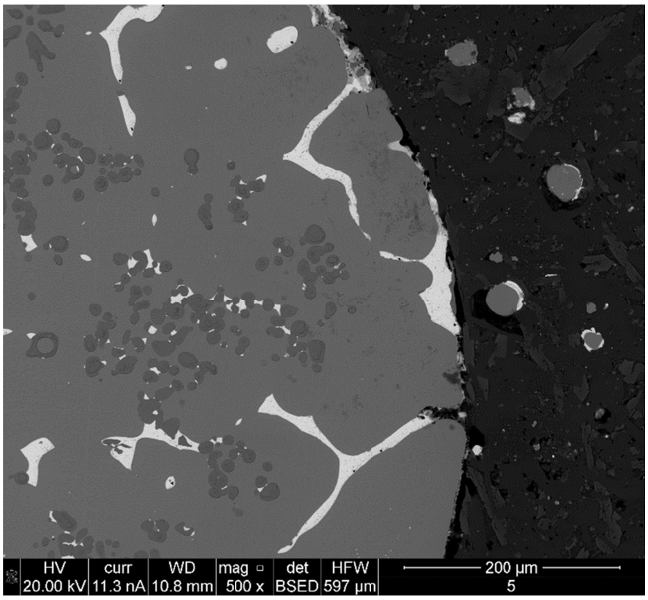

Fig. 3. Small copper droplets tending to be swallowed by the dominant droplet in order to diminish its surface tension

The diminishing of the surface tension is easier when the droplet contains low melting phases: $Cu\text{-}Cu_2O$ – eutectic and lead, Fig. 4.

All the areas of lead try to be localized at the copper droplets periphery according to the phenomenon of self-cleaning, Fig. 5.

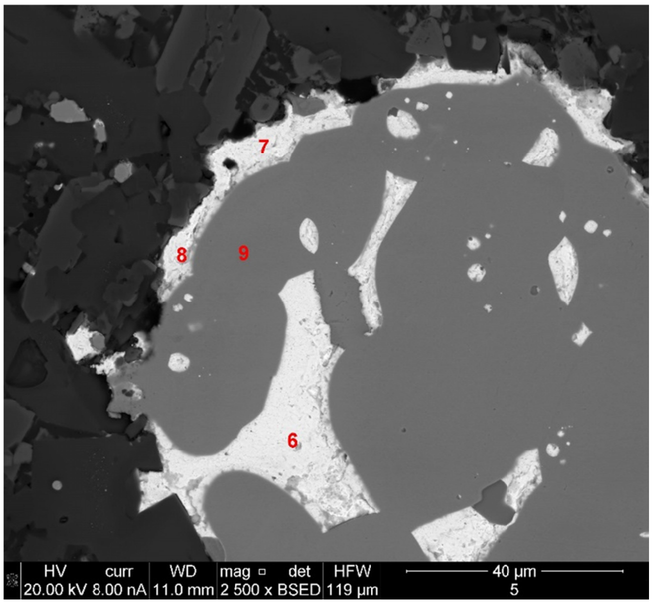

Fig. 4. Copper droplets in the course of the self-cleaning with the simultaneous tendency to attend a fully regular spherical shape due to the presence of $Cu\text{-}Cu_2O$ eutectic and lead; (6, 7, 8 – areas contain $Cu\text{-}Cu_2O$, and additionally Ca, Fe, Si, Al inside lead), (9 – area contains pure copper)

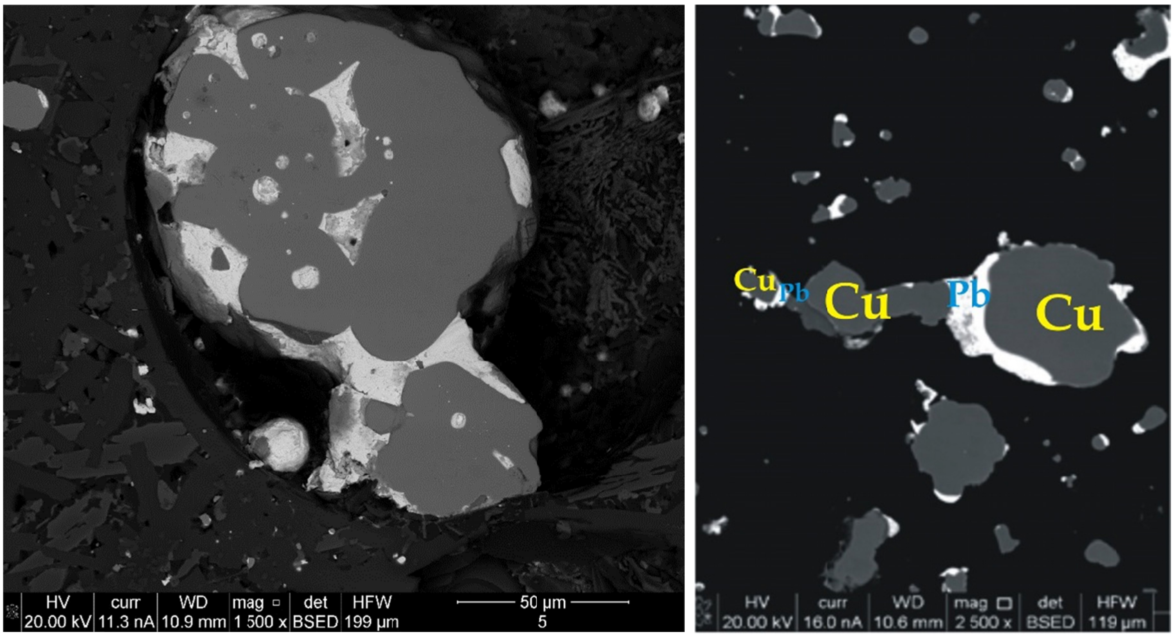

Fig. 5. Lead areas mainly situated at the copper droplet periphery

Unfortunately, sometimes, lead located at the bigger droplet periphery stops the way to incorporation a smaller droplet (it leads to creation as if a joint Cu-Pb-Cu), Fig. 5.

It is evident that the copper droplet rotation makes the self-cleaning easier, Fig. 6.

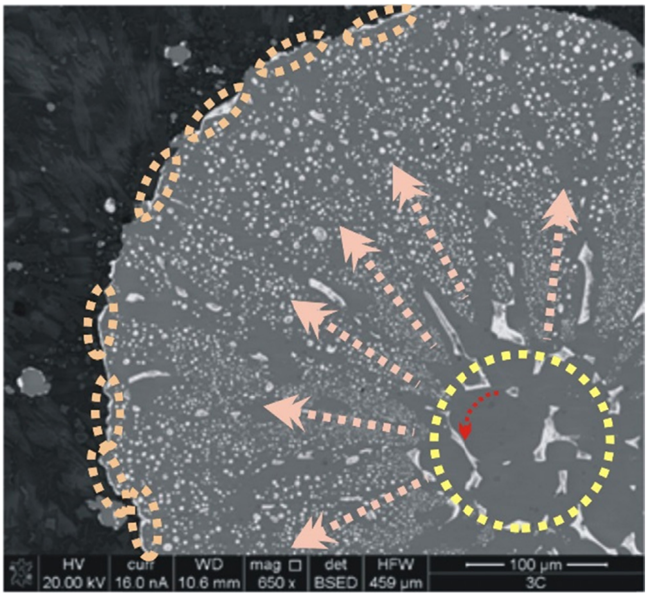

Fig. 6. Rotating copper droplet and resulting centrifugal force (arrows)

The centrifugal force promotes the localization of lead at the periphery of droplet, Fig. 6. The activity of the centrifugal force is accompanied by the activity of the chemical stimulators and reagents. It is well visible that the core of the droplet is cleaned and contains pure copper, only. An example of the almost completely cleaned droplets suspended in the liquid slag is shown in Fig. 7.

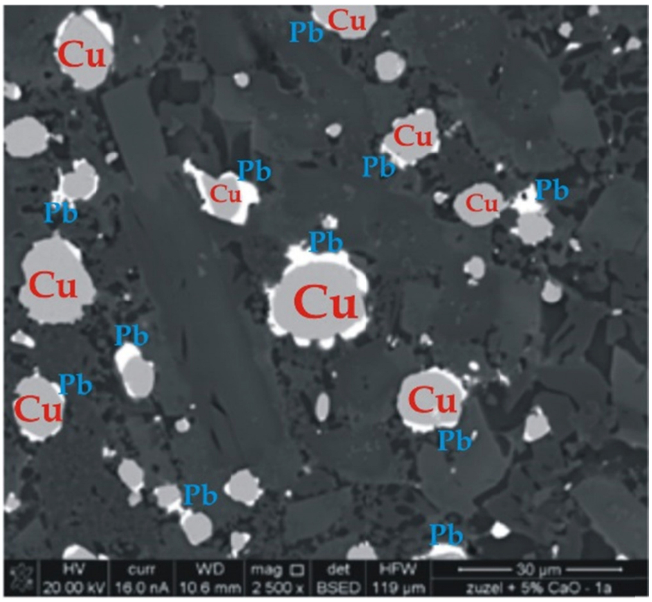

Fig. 7. Copper droplets with some areas of lead situated exclusively at the droplets periphery

Sometimes, when the copper droplet contains large amount of iron then self-cleaning leads to the formation of the Cu(Fe) envelope, Fig. 8. In this case, the envelope makes a barrier for further coagulation. Eventually, buoyancy force pushes the droplet onto the liquid slag surface, and droplet sedimentation is not possible, Fig. 8.

In some situations, the copper droplets may be attached to the Fe- or Al – spinel (from the slag) [12]. It complicates the phenomenon of self-cleaning.

When the rotation is significantly strong the lead envelope tries to fall off the droplet and to tear away, Fig. 9.

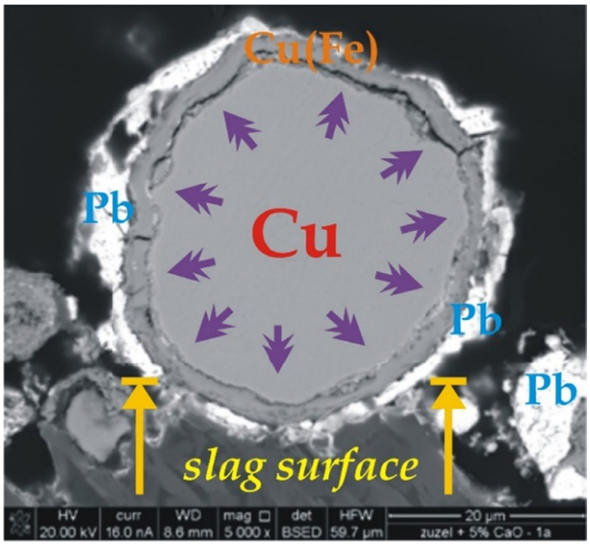

Fig. 8. Fully cleaned droplet surrounded by the double envelope: Cu(Fe) + Pb due to the activity of the centrifugal force (arrows) and with the pure copper in its core

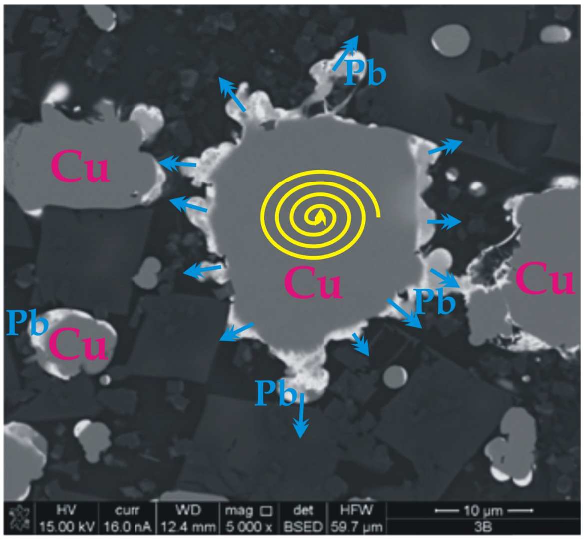

Fig. 9. Lead envelope in the course of detaching the copper droplet

The detached areas of lead may be effectively surrounded by carbon if present in the liquid slag, Fig. 10.

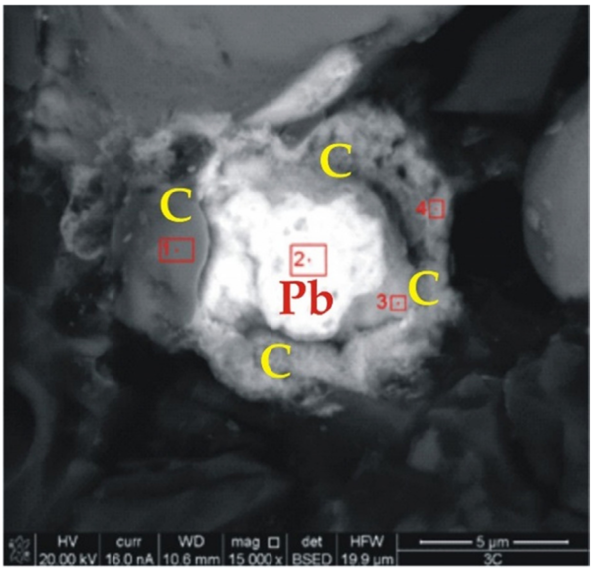

Fig. 10. Phenomenon of an isolation of the lead – particle by carbon

All mentioned phenomena are usually preceded by the agglomeration of copper droplets suspended in the liquid slag, Fig. 11.

The more intensive is rotation of the copper droplets the more significant is the centrifugal force and tendency to detach lead from the droplet core as well as periphery. Therefore, the rotation of the copper droplets was significantly accelerated in the current experiment by creating some dynamic conditions of the copper droplets agglomeration, coagulation and final sedimentation.

Additionally, the efficiency of the complex reagent ingredients (recently patented [13]) was also studied since the chemical usually used in the industrial conditions seems to promote an agglomeration and coagulation of droplets, mainly [11].

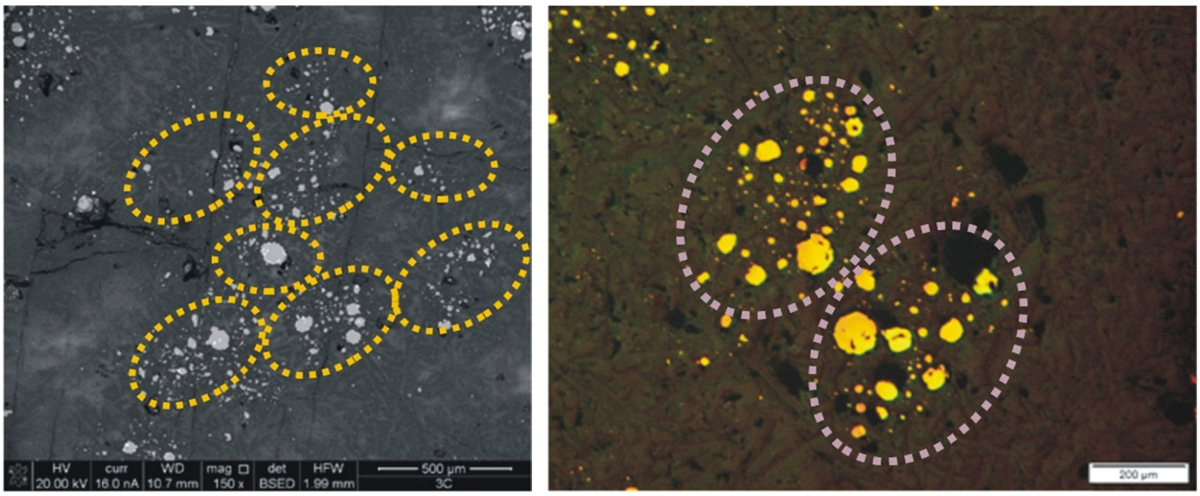

Fig. 11. Agglomeration of copper droplets in the liquid slag promoted by the activity of the complex reagent (chemical stimulators + chemical reagents)

3. Recovery of copper droplets in dynamic conditions

The dynamic conditions of copper droplets agglomeration, coagulation and sedimentation were ensured by the system of tilted electrodes (upper system of electrodes) in the arc furnace designed in BOLMET S.A. Company, Wiechlice, Fig. 12. Generally, the technology was divided into two steps. In the first step, the upper electrodes system (tilted and rotating electrodes) was employed to assist in the process of copper droplets agglomeration and coagulation. The tilting of electrodes had been subjected to an optimization. It is shown schematically in Fig. 12, where smaller particles denote the agglomeration, bigger particles denote the coagulation and an initial amount of deposited copper is situated at the furnace bottom. The variable current was delivered to the upper electrodes system, only. So, the agglomeration and coagulation occur mainly during this first period of time.

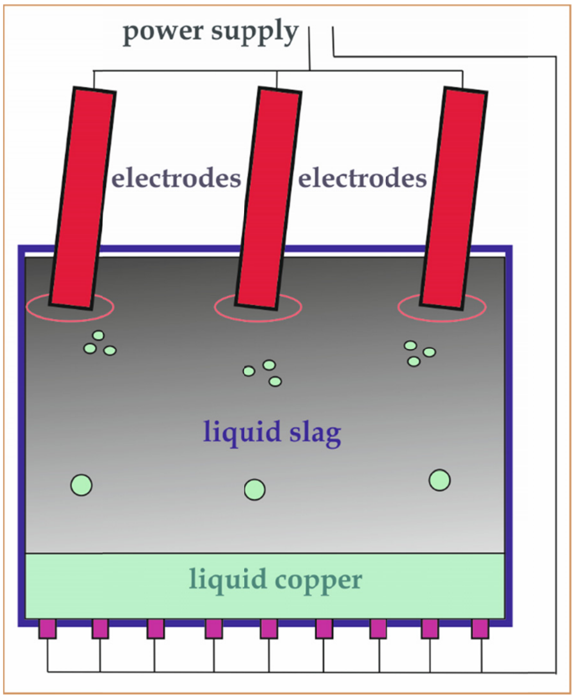

Fig. 12. System of the tilted and rotating upper electrodes in the arc furnace applied to the first step of the experiment

In the second step, when the intensive deposition of the coagulated droplets was expected, then the variable current was replaced by the direct current. The direct current supplied both upper and lower electrodes systems, Fig. 13.

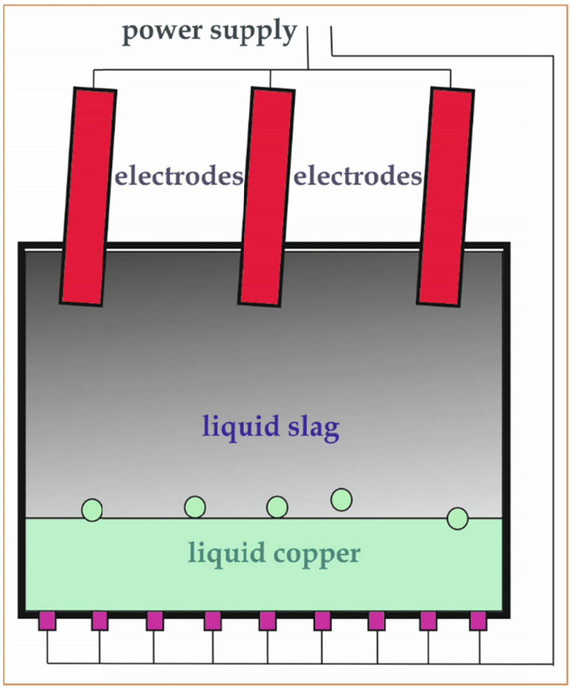

Fig. 13. Intensive sedimentation of the coagulated copper droplets assisted by the direct current field during the second step of the experiment

The current experiment was performed in the dynamic condition at 1320°C. First, the suspension of the copper droplets in the liquid slag was melted and subsequently treated by the industrial chemicals like: fine coal, CaO from the $CaCO_3$ decomposition, and Na_2CO_3. Subsequently, some components / ingredients of the patented complex reagent were applied, respectively.

The treatment of the liquid slag by the industrial chemicals is not so efficient. The cooled slag (after chemical treatment) still contained many copper droplets gathered in some agglomerations, (about 0.7 wt.%), Fig. 14. Coagulation of droplets is also visible.

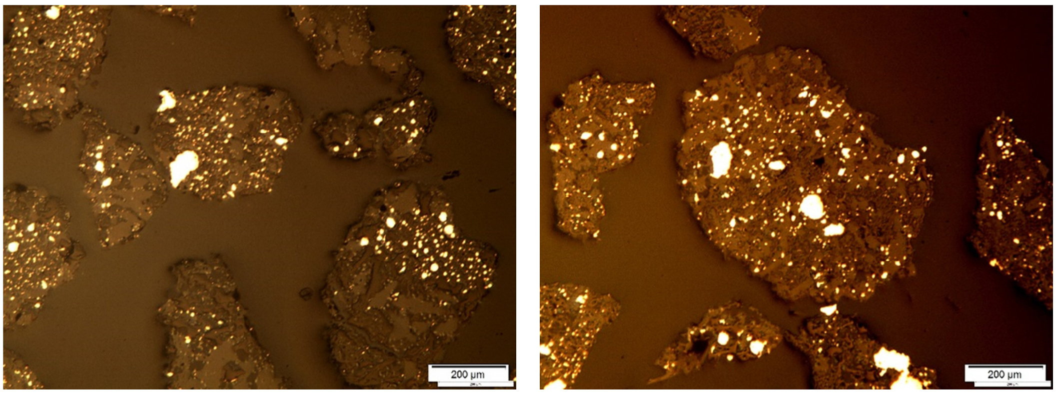

Fig. 14. Cooled slag with some distinguished areas containing agglomerations of copper droplets

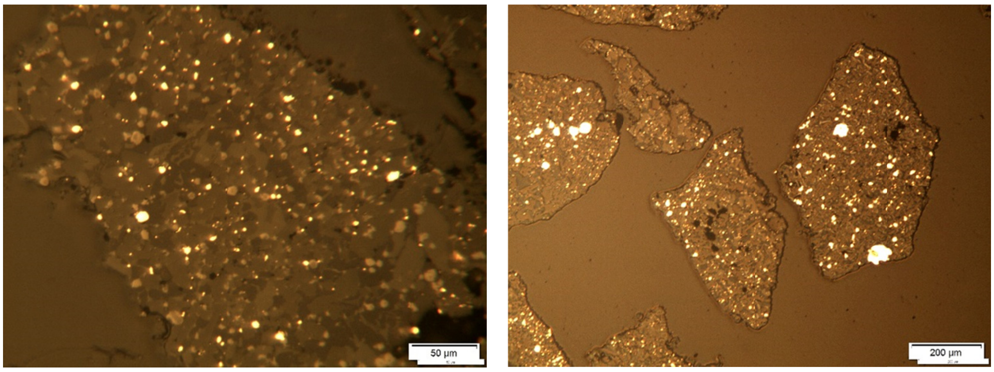

Fig. 15a. Distinguished areas of the cooled slag containing agglomerations of copper droplets after $CaCO_3$, and Na_2CO_3 (5% of each) – chemicals treatment (for 10 minutes)

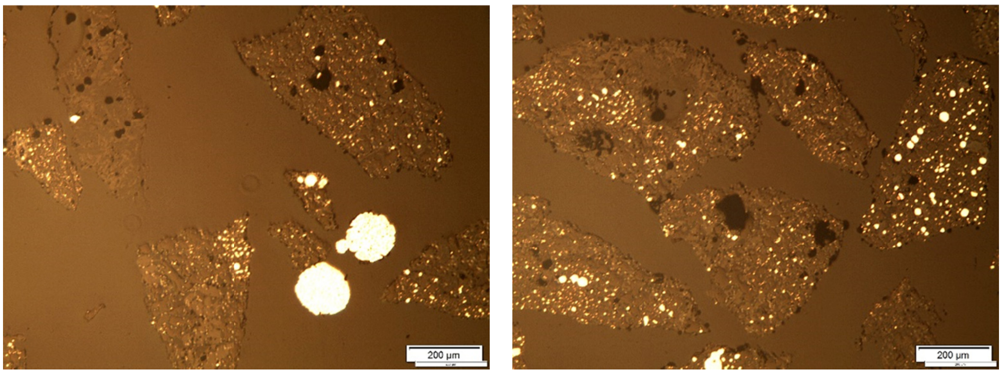

Fig. 15b. Distinguished areas of the cooled slag containing agglomerations of copper droplets after $CaCO_3$, CaC_2, and Na_2CO_3 (5% of each) – chemicals treatment (for 10 minutes)

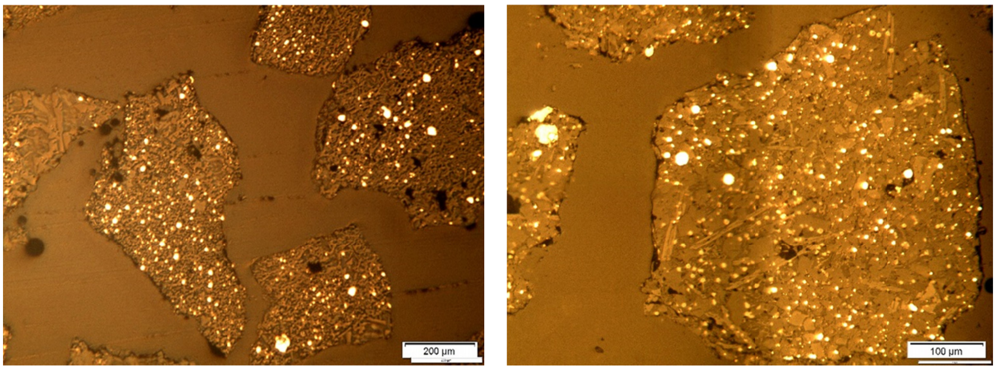

Fig. 15c. Distinguished areas of the cooled slag containing agglomerations of copper droplets after $CaCO_3$, and Na_2CO_3 (5% of each), NaCl (2%) – chemicals treatment (for 10 minutes)

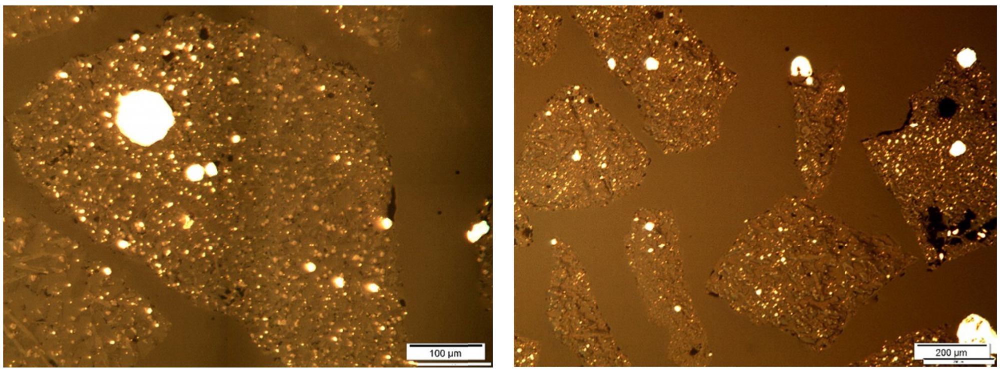

Fig. 15d. Distinguished areas of the cooled slag containing agglomerations of copper droplets after $CaCO_3$, CaC_2, and Na_2CO_3 (5% of each), NaCl (2%) – chemicals treatment (for 10 minutes)

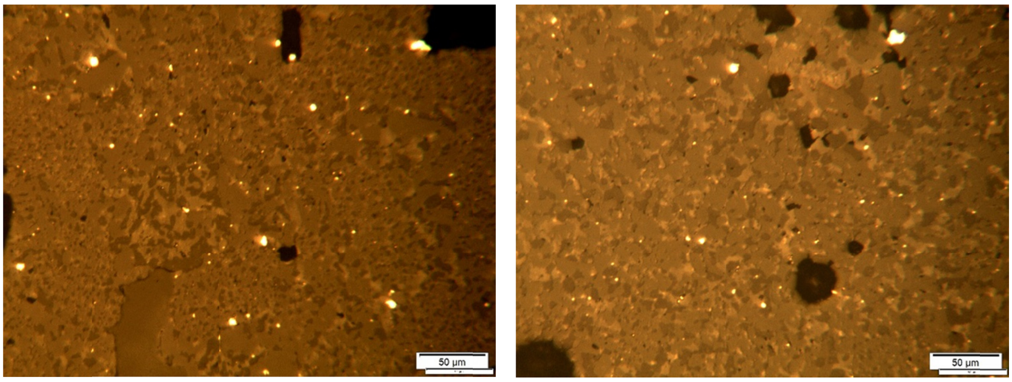

Fig. 15e. Distinguished areas of the cooled slag containing agglomerations of copper droplets after $CaCO_3$, K_3PO_4, and Na_2CO_3 (5% of each), NaCl (2%) – chemicals treatment (for 10 minutes)

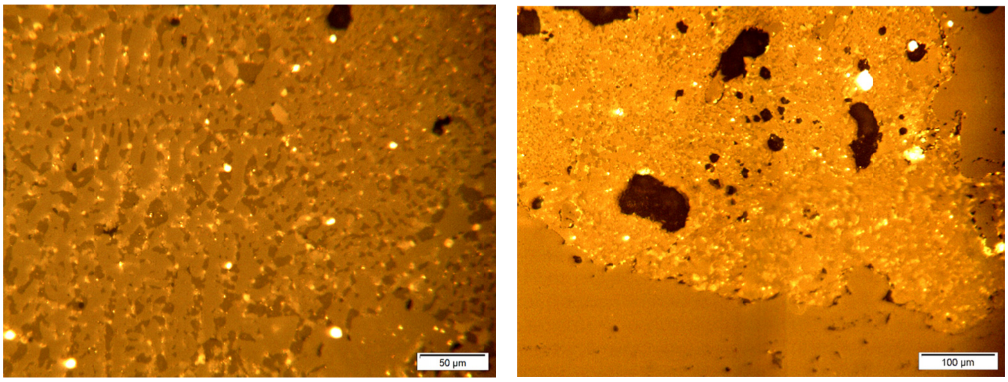

Fig. 15f. Distinguished areas of the cooled slag containing agglomerations of copper droplets after $CaCO_3$, K_3PO_4, and Na_2CO_3 (5% of each), NaCl (2%) – chemicals treatment (for 10 minutes)

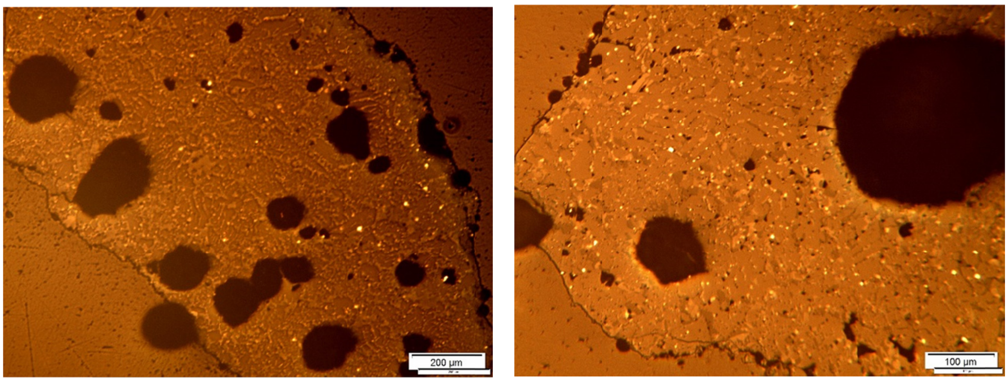

Fig. 15g. Distinguished areas of the cooled slag containing copper droplets without the chemicals treatment but maintained at the elevated temperature for 20 minutes

Next, the studied suspension of the copper droplets in the liquid slag was subjected to activity of the complex reagent (chemical) containing the following stimulators and reagents: NaCl, $CaCO_3$, K_3PO_4, CaC_2, Na_2CO_3, $CaCN_2$, and Mn_3C. The efficiency of the copper recovery is more visible than in the case of the industrial chemical treatment, Fig. 15a, Fig 15b, Fig. 15c, Fig 15d, Fig. 15e, and Fig. 15f. The post-processing slag subjected to the thermal treatment only (without use of the complex reagent ingredients) is shown in Fig. 15g to compare it visually with the slag for which all the ingredients of the complex reagent were applied, Fig. 15h.

4. Concluding remarks

The complex reagent is satisfactorily effective in the recovery of copper from the post-processing slags. The reagent is able to diminish the copper content from about 0.8-0.9 wt.% even up to 0.10-0.15 wt.%, Fig. 15h. This result suggests the possibility of an improvement of the current technology of copper recovery applied in the Smelter and Refinery Plant, Głogów, and reproduced in the current experiment (performed in the BOLMET Company), Fig. 14.

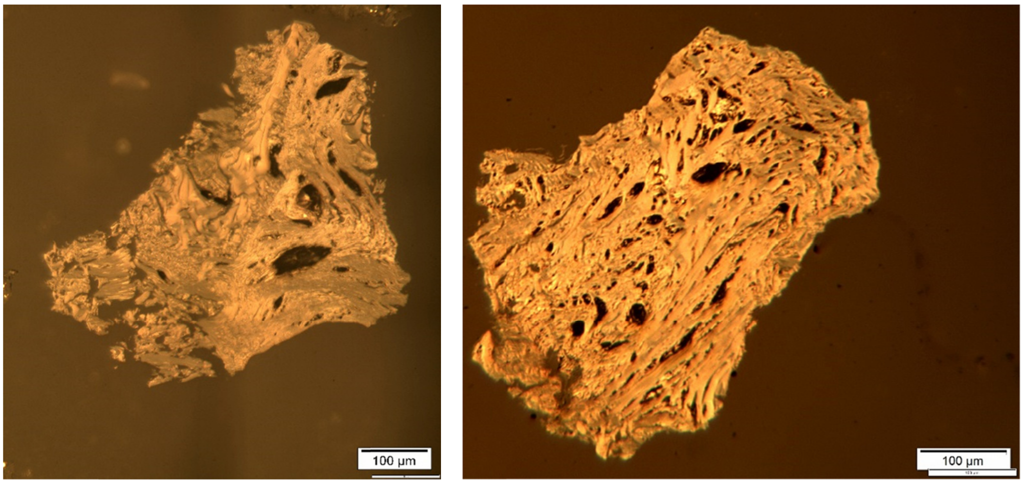

Fig. 15h. Distinguished areas of the cooled slag with the remaining copper droplets (about 0.15 wt.%) after the complex reagent (equipped with the all ingredients) treatment (for 20 minutes)

The proposed two steps mode of the copper droplets suspension maintenance, Fig. 12, Fig. 13, not only, significantly improves the self-cleaning of the copper droplets but has a positive influence on the agglomeration, and coagulation of copper droplets as well. Sufficiently rapidly coagulating droplets (due to their intensive rotation during the first step of technology) are able to overcome the buoyancy force and not to be pushed towards the liquid slag surface. Contrary, these large droplets are easily subjected to gravity and tend to be deposited onto the furnace bottom. Moreover, the second step of the current technology succours efficiently the mentioned deposition / sedimentation due to the direct current field imposed on the system.

Although, the intensive rotation of copper droplets resulting from the imposed variable current field (first step of the technology) improves the self-cleaning of the copper droplets, the deposited liquid copper still contains iron and lead. These last mentioned elements are to be remove from the copper bath by another technology.

A contribution of the stimulators and reagents in the patented complex reagent / chemical can be controlled by the computer assisted program. This computer program is predicted to analyze a given composition of the liquid slag and eventually may suggest how to modify / adjust the contribution of the complex reagent ingredients to ensure the efficient recovery of copper from this slag.

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