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Gravity/buoyancy competition within coagulation of copper droplets in slag

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ABSTRACT

Purpose: A suspension of copper droplets in the slag coming from the direct-to-blister process was subjected to the treatment analogous to that usually applied to the electric arc-furnace process. In particular, recently patented by authors, complex reagent was applied and verified.

Design/methodology/approach: The suspension was subjected to coagulation and solidification. Both processes were studied, independently. The suspension of droplets was treated not only by the recently patented complex reagent but by the CaO – industrial compound (in the amount of 5 %wt.) as well, to make comparison between both substances effectiveness.

Findings: The observation was focused on the behavior of droplets to conclude whether the droplets are settled on the crucible bottom due to the effect of gravity or pushed to the liquid slag's surface due to buoyancy force influence. In the case of the patented reagent application, the coagulation mainly was completed by the droplets' settlement on the crucible bottom. The treatment performed with the use of the CaO – compound promoted the influence of buoyancy force. The coagulated copper droplets were pushed to the liquid slag's surface.

Research limitations/implications: Rest reagents known in the industry practice will be subjected to the analogous analysis in order to make further comparison with the effect of the patented chemical.

Practical implications: Conclusion from the performed experiment made in the crucible (laboratory scale) allow to suggest how to improve not only the semi- or fully industrial direct-to-blister technology but the treatment of the slag in the electric arc-furnace as well.

Keywords: Thermo-chemical treatment; Copper droplets coagulation; Solidification

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MATERIALS MANUFACTURING AND PROCESSING

1. Introduction

An extraction technology, named as the direct-to-blister process, carried out in the flash furnace leads to the formation of the primary suspension of the copper droplets in the liquid slag (Fig. 1). The extraction technology is of fundamental significance for the subsequent coagulation process carried out during the second step of the slag treatment performed with the use of a complex reagent [1,2]. The copper droplets' coagulation is completed by their growth/solidification accompanied by segregation of some elements which are present inside theme. Especially, some eutectic precipitates are expected inside the solidified droplets. Usually, a part of the appeared eutectic is the so-called equilibrium precipitate and the second is non-equilibrium precipitate [3].

The droplets are not consisted of pure copper but contain lead and iron [4]. In the industrial practice, iron and lead cannot be easily removed from the copper droplets. Sometimes, carbon is also present in the droplets when the direct-to-blister process and accompanying reduction of oxides is not effective [5,6].

An evolution of the copper concentration in the suspend droplets (Fig. 1), can be subjected, first, to general valuation by the observation of the droplets' shape [1]. For example, the star-like shape of the copper droplets is typical for the droplets which contain at least 20% wt. Cu. The spherical droplets, irregular in their shape, contain about 50%wt. Cu. Fully regular droplets evince up to 70% wt. Cu [1].

The mentioned evolution of both droplets' shape and copper content is accompanying the synchronous droplets' coagulation [7]. Coagulation is the fundamental phenomenon which leads to the sedimentation of droplets on the crucible or electric arc-furnace bottom, however, under condition that droplets reach/cross over the critical diameter/weight. The obtaining of the critical weight is a necessary condition to overcome the buoyancy force and make the desired droplets' sedimentation possible. The intensity of mentioned phenomena depend strongly on the slag viscosity [8]. Therefore, the applied complex reagent should promote not only the coagulation itself but some changes of the slag properties as well. Moreover, some metallic additions contained in a slag have a positive effect on reduction of copper oxides [4].

Carbon which is added to combustion reactor in the flash furnace should be dispersed uniformly in the furnace shaft and completely consumed in the process under investigation. When this condition is not satisfied then some excess particles of carbon can be present/visible in the slag coming from the direct-to-blister process and even inside the copper droplets [9-13].

In the current analysis an effect of two compounds/ reagents on the copper droplets coagulation and finally on the competition between gravity and buoyancy force is studied. The first compound is the complex reagent recently patented by the authors and second the CaO-compound in the amount of 5% wt., both added to the suspension of small copper droplets in the slag coming from the flash furnace (from KGHM - Polska Miedź, S.A., Lubin) (Fig. 1). The experiment was performed in the crucible, so, in the laboratory scale. The laboratory condition imitated conditions usually applied to the industrial electric arc-furnace or to semi-industrial process.

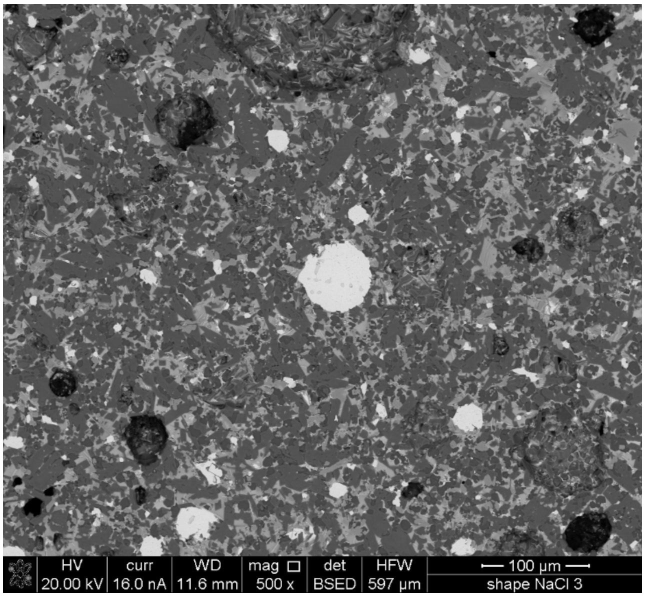

Fig. 1. Copper droplets suspend in the liquid slag coming from the direct-to-blister process usually performed in the flash furnace

2. Coagulation/solidification of droplets

The experiments dealing with the copper droplets coagulation were performed in the laboratory scale with the use of a proper crucible initially heated up to 1300°C. The slag was put into the crucible and next the complex reagent or the CaO-compound was introduced into the suspension of copper droplets, respectively. An examination was applied to both slags treated by mentioned reagents to state whether the settlement of the coagulated droplets is sufficiently effective.

The results of solidification were also subjected to examination in order to confirm the presence of some precipitates and to analyze their morphology. Formation of the equiaxed, dendritic structure was expected in the coagulated droplets. Each of grains formed in the solidified droplet was predicted to be surrounded by eutectic precipitates containing low-melting phases typical for a given suspension (droplets in the slag) coming from an industrial process.

2.1. Coagulation assisted by a complex reagent

The complex reagent has been patented by the authors after many initial tests. It is expected that this chemical should be very effective in experiment of: coagulation, refining of copper droplets and finally in sedimentation of the coagulated and refined droplets.

The fragmental morphology of the examined suspension is shown in Figure 1. A general view of the sample as a whole is also presented (Fig. 2).

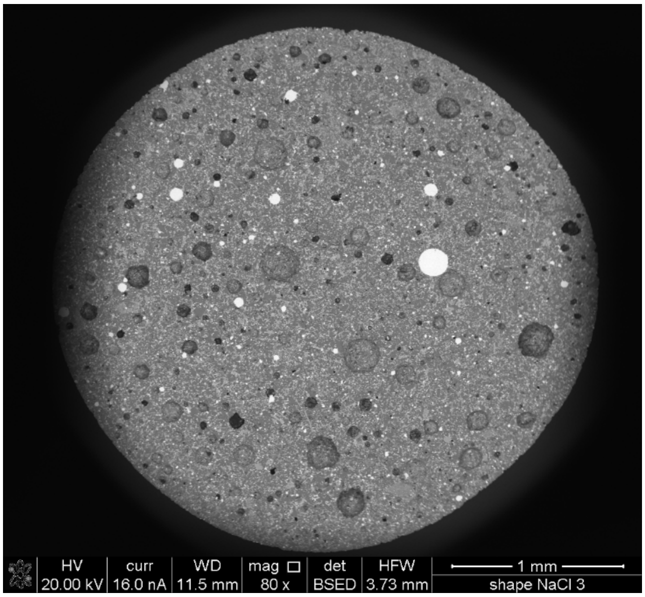

Fig. 2. Total view of the sample containing the copper droplets (not settled on the crucible bottom) suspend in the slag subjected to the treatment by the considered complex reagent; droplets seem to be dispersed uniformly in the droplet's volume

Generally, there were not star-like in shape droplets (Fig. 2). It seems that almost all the droplets evince a regular spherical shape. Some of them have been subjected to the detailed morphological analysis. A representative example of regular droplets is shown in Figure 3. This almost ideally regular, spherical in shape droplet (in macro-scale) is slightly deformed at its periphery (in micro-scale).

The mentioned deformation at the droplet's periphery is the result of the interaction of droplet itself with different slag's particles. These slag's particles are shown in a grey-scale which depends on the differentiated solutes concentration in them.

All the particles interact with the droplet to settle a mechanical equilibrium between both interacting bodies that is, between a given slag's particle and a droplet. This mechanical equilibrium results from the local interplay between surface tension of the slag's particle and surface tension of a given copper droplets. The darker particle the more intensive penetration of this particle into the copper droplet (Fig. 3). Moreover, the more regular in shape droplet the higher content of copper in the droplet, as mentioned. Thus, it is obvious that the refinement of the droplet depends on the mechanical equilibrium at its periphery. Therefore, it seems also important to form an envelope in the slag surrounding a droplet.

This envelope should be able to modify the mechanical equilibrium in such a way that this newly formed equilibrium would better promote droplet's coagulation and refining.

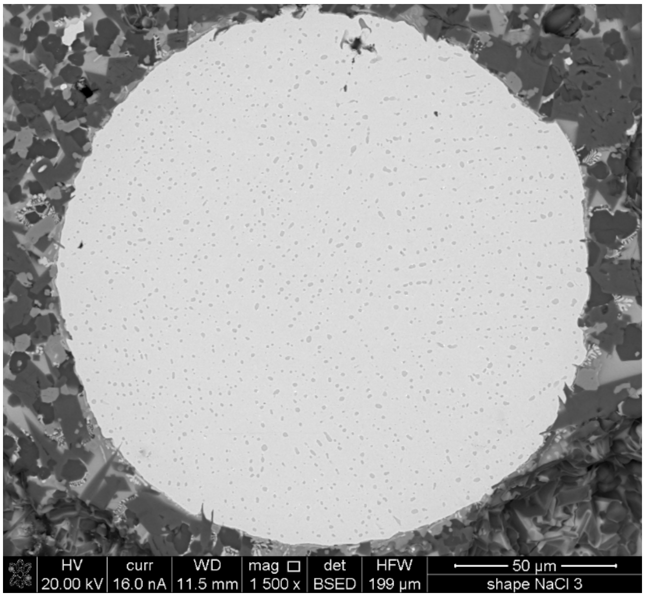

Fig. 3. A distinguished copper droplet regular in its spherical shape; some precipitates are steadily dispersed in its volume

The droplet shown in Figure 3 seems to be ready to be settled on the crucible bottom. However, this phenomenon was arrested because the gravity action was interrupted by the sample freezing.

The discussed interaction between a copper droplet and the slag's particles in frame of the mechanical equilibrium creation is very well-marked (visible) in Figure 4.

The regular droplet's formation was arrested in the course of a critical weight/diameter attainment. Thereby, the mechanical equilibrium is in evolution to its final state which corresponds with the critical droplet's weight. Thus, at this stage of droplet's shape evolution, some slag's particles penetrate into the copper droplet significantly (Fig. 4). It should be emphasized that darker particles of the slag penetrate more intensively into the copper droplet, as expected. At the same time a copper droplet refinement occurs simultaneously with the droplet's drift to shape regularity. It confirms that a given droplet contains some strange elements like: lead, iron and others.

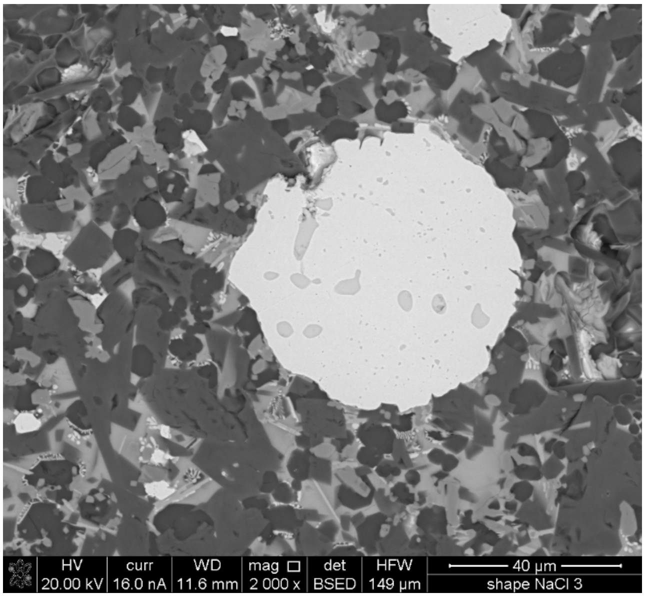

Fig. 4. Copper droplet in course to a critical weight attainment; local mechanical equilibria are created at the boundary between a given slag's particle and neighbouring part of the copper droplet and visible as the concave-or convex interface; some eutectic (low melting phases) precipitates are also visible in the droplet

The discussed both concentration-and shape evolution are not identical/similar in each of the droplets suspend in the liquid slag. Some of droplets-manifest violent change whereas other evince slow development of their size (Fig. 5). However, it seems obvious that better formed droplets of regular spherical shape are larger than irregular droplets which are smaller and differ significantly in the copper concentration from that which are regular.

The tested complex reagent seems to be very effective in the process of coagulation of small copper droplets which initially are irregular in their spherical shape (Fig. 6). Moreover, these small irregular droplets contain about 50% wt. Cu, only, as mentioned. However, the small in size particles tend towards a dominant large, distinguished particle which is the best not only in its regularity of shape but in its content of copper (up to 70% wt.) as well (Fig. 6).

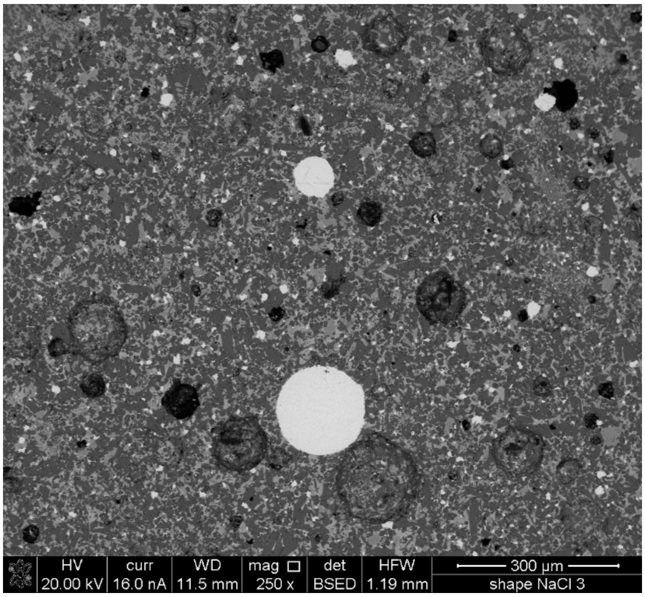

Fig. 5. Two copper droplets in course of their betterment in shape, size, copper content, mechanical equilibrium, and consumption of small droplets; these dominant two droplets were previously surrounded by the small (consumed) droplets close to them; the bigger droplet the better its spherical shape regularity

Also the betterment of the mechanical equilibrium is far-gone for these large copper droplets in comparison with the mechanical equilibrium established at the droplet/slag's particles interface for the small particles. Additionally, some numerous rod-like droplets also appear in the neighbourhood of the distinguished large particle and tend to be swallowed by this dominant droplet (Fig. 6).

It is supposed that rod-like shape of droplets results from their very low copper content and movement towards dominant droplet.

The planetary arrangement of small copper droplets as well as rod-like small droplets (Fig. 7), were subjected to the detailed analysis of their composition. The small irregular droplets contain at least 20% wt. Cu as expected.

The chemical composition of the small rod-like droplets is approximately as follows: C = 4.68, O = 40.86, Al = 5.17, Si = 9.51, Ca = 2.75, Fe = 14.10, Cu = 18.17, Mg = 1.50, K = 1.65, Ti = 0.98, and Pb = 0.62% at.

When these rod-like droplets become swallowed by the large droplet then the contained additional elements form the low melting eutectic phases which are well visible inside this dominant droplet (Fig. 4, Fig. 6 and Fig. 7).

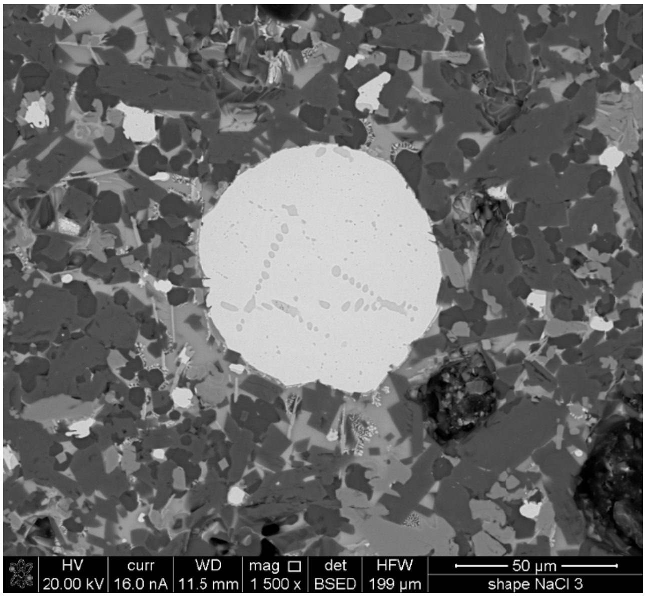

Fig. 6. Planetary arrangement of small copper droplets irregular in their shape and rod-like copper droplets; all mentioned droplets are situated close to a large distinguished droplet, dominant, and almost regular in its spherical shape

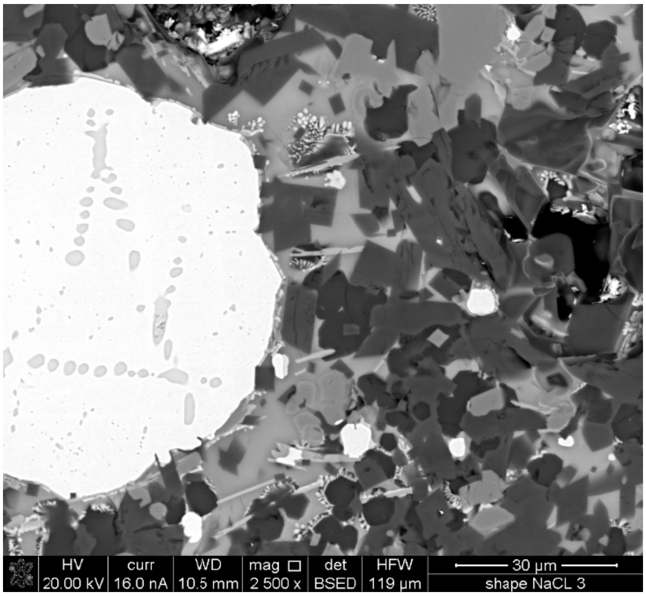

Fig. 7. Large dominant copper droplet and localization of the surrounding rod-like small droplets which tend to be swallowed

2.2. Coagulation of the copper droplets assisted by the CaO-compound/reagent

An application/use of the CaO-compound, well known in the industrial practice, has also been subjected to the examination analogous to that performed for the complex reagent.

Surprisingly, the CaO-compound/reagent promotes formation of droplets' agglomerations (Fig. 8).

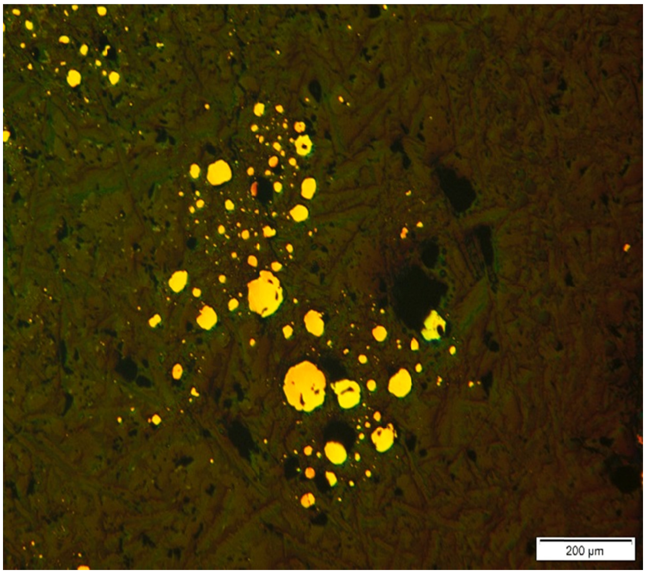

Fig. 8. Agglomerations of the copper droplets as a positive result of the CaO-compound/reagent interaction with the suspension

Initial interaction of the CaO-compound with the suspension of droplets in the liquid slag is positive. Almost all the droplets form some agglomerations.

This phenomenon seems to be an arrangement of droplets preceding their subsequent coagulation. However, an undesirable phenomenon appears at the same time (Fig. 9). The droplets become continuously wrapped round in a new phase.

The detailed analysis of this envelope confirms the presence of following elements C = 26.1, O = 32.1, Al = 3.43, Pb = 29.14, Ca = 1.65, Fe = 2.89, and Cu = 4.69. So, lead is the dominant element in the formed envelope.

It is obvious that appearance of the envelope counteracts not only to formation of the local mechanical equilibrium between slag particles and a given copper droplet (as it has taken place in the case of application of the studied complex reagent (Fig. 4, Fig. 6, and Fig. 7) but opposites against the coagulation of droplets in a given agglomeration as well.

Moreover, a mid-envelope forms between the main envelope and droplet (Fig. 10). This complex system attracts/absorbs some black particles, mainly, from the neighbouring slag (Fig. 10).

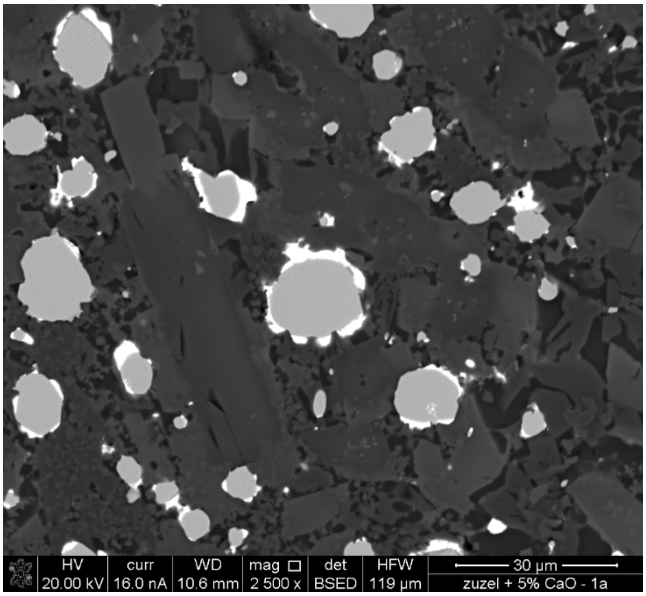

Fig. 9. Envelopes of the copper droplets in a given agglomeration

Mid-envelope seems to be a kind of an interconnection, [14-20], which could be a product of a diffusional reaction between copper, and some elements from the main envelope.

The copper droplet, shown in Figure 10, contains the following elements: C = 5.91, O = 4.41, Mg = 2.65, Al = 1.80, Si = 3.45, Ca = 0.98, Fe = 1.58, and Cu = 79.22%at. So, the copper droplet is not yet sufficiently refined. The refinement of the droplet seems to be difficult or even impossible since the exchange of some elements between droplet and slag is blocked by the envelopes' system.

Size of one distinguished droplet has been measured (Fig. 11), to prove that the envelopes' system is the barrier that prevents the droplet against possible coagulation/sedimentation.

The diameter of the distinguished droplet (Fig. 11), points that this droplet can have some troubles to be settled on the crucible/furnace bottom because is still too small.

On the other hand, the buoyancy force has a chance to win gravity and push this droplet up to the slag's surface (Fig. 12). However, the largest droplet is situated centrally at the lowest part of the locally depressed slag's surface. Small droplets are located a little higher than this dominant copper droplet.

Two droplet's types can be differentiated among all droplets located at the slag's surface due to buoyancy force activity (Fig. 12).

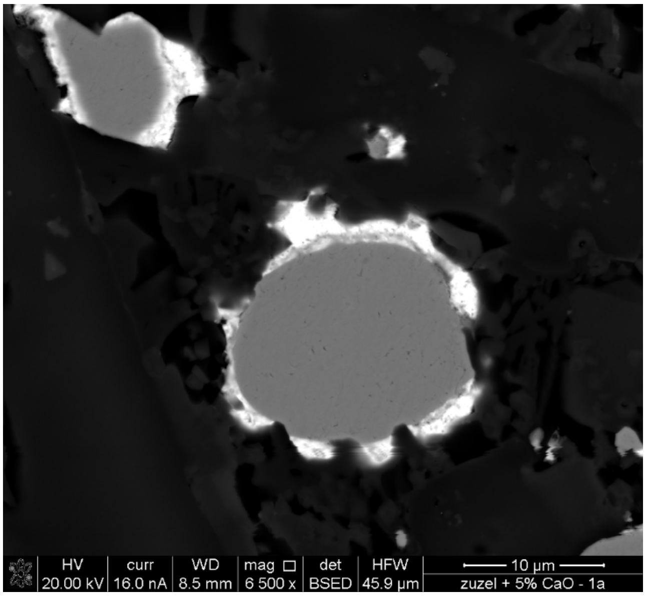

Fig. 10. Complex system of the envelopes: black slag's particles envelope, white main envelope, grey mid-envelope, surrounding a given copper droplet distinguished in the agglomeration

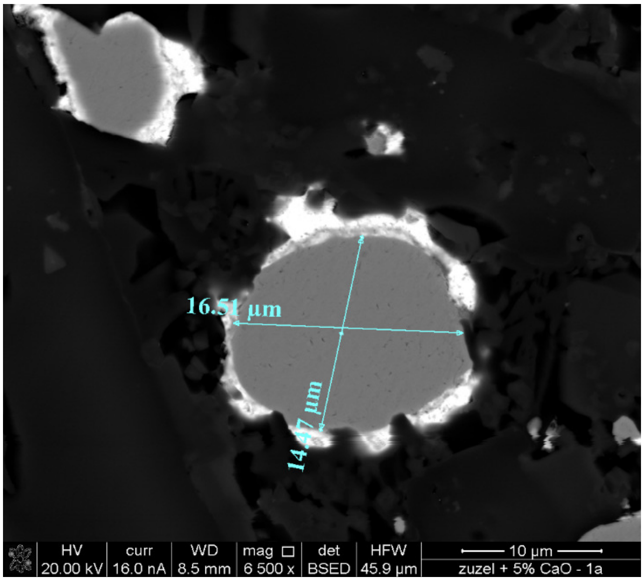

Fig. 11. Size of a distinguished/studied copper droplet

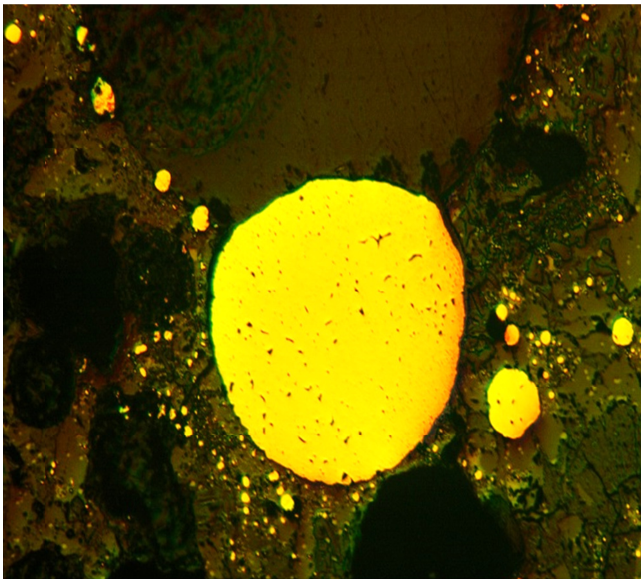

Fig. 12. Copper droplets located at the liquid slag's surface due to buoyancy force activity

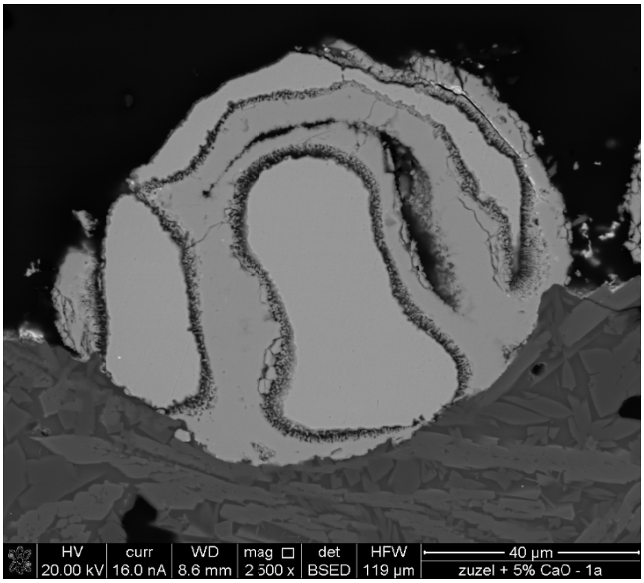

Fig. 13. Droplet situated on the slag's surface due to buoyancy force activity; small droplets are joint to form this larger droplet

First of all, there are some droplets already described in details and shown in Figure 10. Yet, completely different type of droplets is also visible at the slag surface (Fig. 13).

Surprisingly, the mechanism of the formation of this complex, enough large droplet (consisted of a few small droplets) leads to loss of all envelops. This is a very advantageous phenomenon. Sometimes, morphology of this complex, enough large droplet is more complicated (Fig. 14). It occurs when the partial droplets are much more equipped with additions, especially with carbon.

Unfortunately, these complex droplets (Fig. 13, Fig. 14) are still too small to be settled on the crucible bottom due to desired gravity force victory over buoyancy force activity.

Solidification of this complex droplet is completed by the precipitation of some eutectic law melting phases (Fig. 13, Fig. 14).

The precipitates surround each of the fragmentary droplets. Detailed analysis of precipitates confirms the presence of the following elements: Mg = 1.97, Pb = 0.23, Si = 2.46, Fe = 0.87, Ca = 0.96, C = 41.18, Cu = 34.44, O = 16.81, and Al = 1.09. Thus, the Cu_2O/Cu - eutectic is expected there.

On the other hand, the small fragmentary droplets evince some differences in copper content. The copper concentration oscillates between 25% at., and 50% at., in these integrant droplets (Fig. 13). It is sometimes possible to reveal joint/coagulated, small copper droplets which were not able to loss the envelopes (Fig. 15).

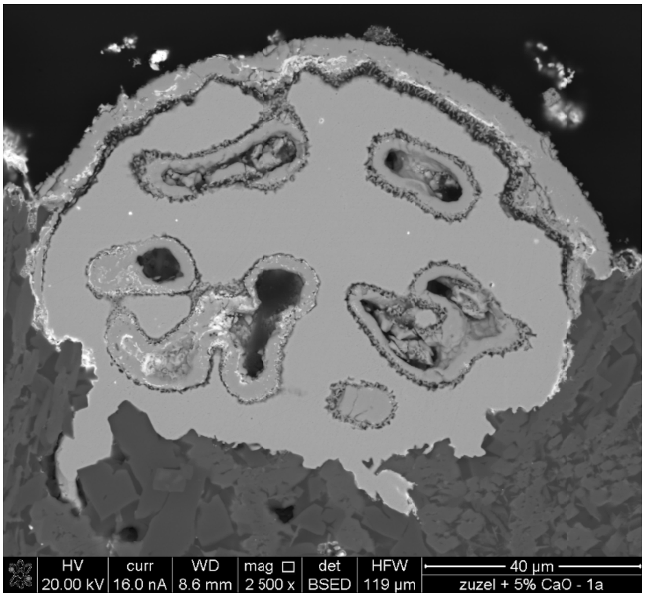

Fig. 14. Complex copper droplet consisted of a few small copper droplets containing elevated amount of additions

The copper droplet, shown in Figure 15, seems to be enough large. Therefore, the size of this droplet has been examined (Fig. 16).

A diameter of this droplet is almost twenty times greater that the diameter of an individual, small droplet also measured, and shown in Figure 11. The elevated size of the examined copper droplet is not enough big to be subjected to gravity force activity.

This droplet is not settled on the crucible bottom. It tends towards the slag's surface as shown in Figure 17. It becomes obvious that the CaO-compound interacts not effectively with the copper droplets suspension in the liquid slag. Majority of the droplets are situated at the slag's surface (Fig. 17).

The revealed droplets' agglomerations (Fig. 8) do not tend to a fusion of small droplets and their final coagulation. Therefore, the exclusive application of the CaO-compound/reagent is not reasonable. However, it could be used together with other reagents.

Its positive interaction has been already mentioned. It was revealed that its activity leads to the formation of the droplets' agglomerations. Further activity should be intercepted by another reagent which is able to counteract the formation of envelopes.

The detailed analysis of the suspension morphology (Fig. 17) confirms, once again, that the droplets in agglomerations remain as small as they were at the moment of envelope formation round their periphery.

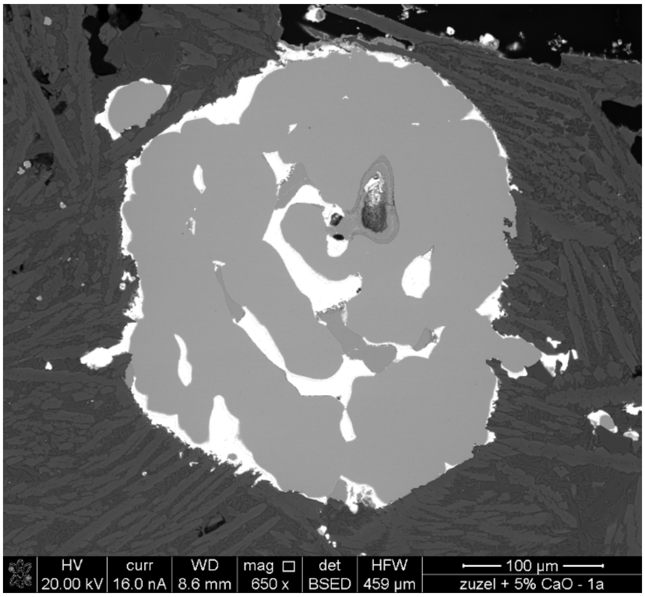

Fig. 15. Enough large copper droplet as a result of the fusion of a few small droplets, each surrounded by envelope; droplet arrested just at the liquid slag's surface

The coagulated complex droplets are situated at the slag's surface being too small in size to be settled on the bottom.

Even enough large droplets, after the fusion, tend towards the slag's surface. They are not able to develop their size/weight and to cross a critical weight enabling them desired sedimentation.

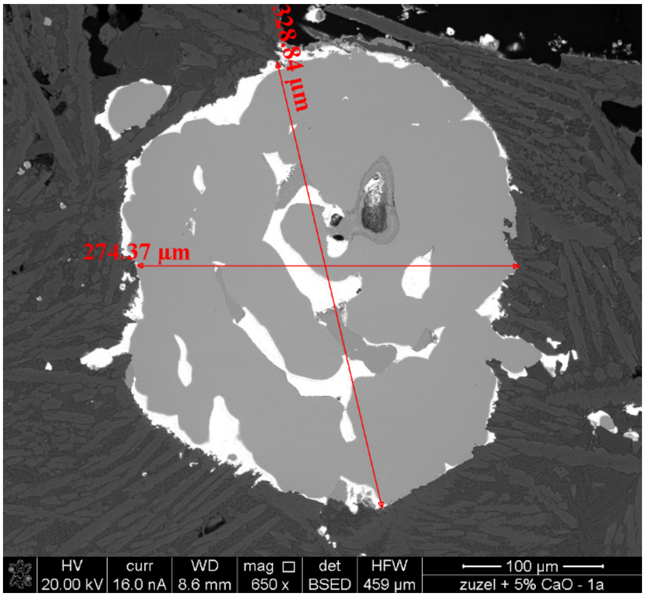

Fig. 16. Copper droplet as a result of fusion of a few small droplets each surrounded by an envelope; diameter measurement

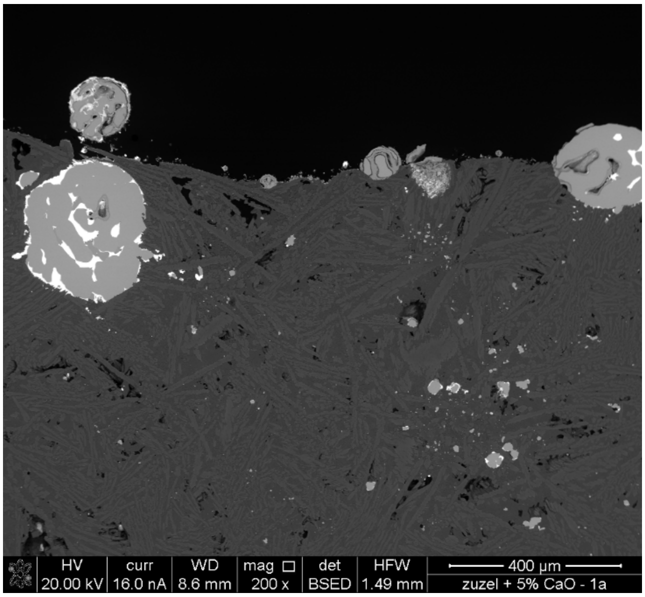

Fig. 17. Copper droplets situation on/at the liquid slag's surface; even a distinguished large enough droplet tends towards the liquid slag's surface (not to the crucible bottom)

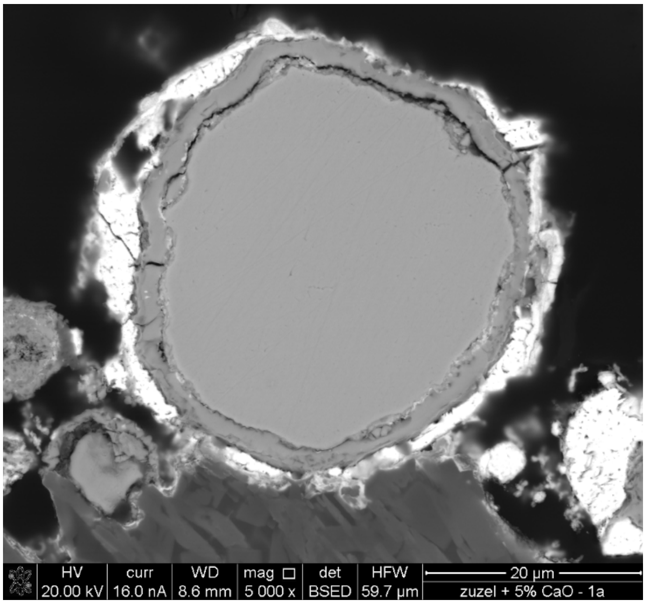

Fig. 18. Formation of the interlayer between the total, converging envelope and droplet; the droplet situated on the slag's surface

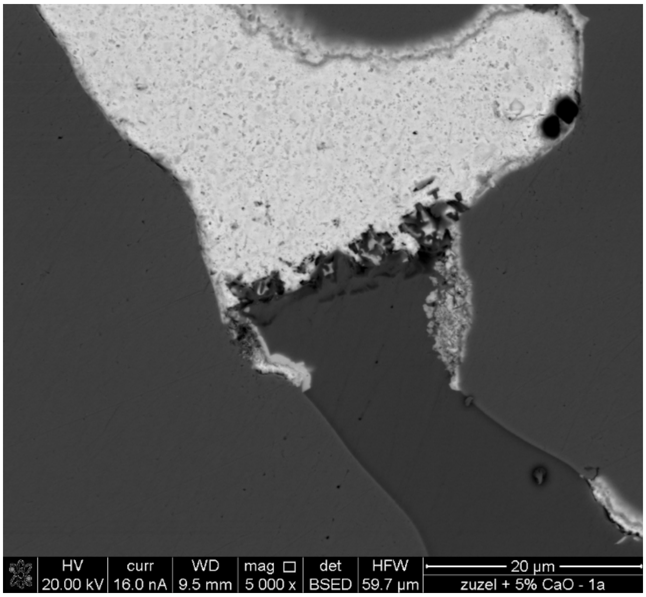

Fig. 19. Precipitates inside the enough large droplets being the result of some small droplets fusion (as that shown in Fig. 15)

The small droplets which are completely surrounded by their envelopes are blocked against coagulation and easily/rapidly located at/on the slag's surface (Fig. 18). Time and temperature promote the formation of the intermediate layer located between envelope and droplet itself. In this unusual situation, a kind of interconnection is formed [14-20].

Formation of other interconnections has also been revealed. A kind of diffusion joint can be found in the precipitates which are the result of copper droplet solidification (Fig. 19).

Diffusion of some elements from envelope into the intermediate layer and diffusion of some elements from the droplet took place during formation of the revealed layer [16] (Fig. 18). The analogous phenomenon took also place within precipitates shown in Figure 19. Some elements diffused from white phase as well as from grey phase to form a new intermediate, black phase (Fig. 19).

3. Concluding remarks

The comparison of the interaction of both complex reagent and the CaO-compound with the studied suspension proves that the complex reagent is satisfactorily effective in the process of coagulation and further sedimentation of the copper droplets suspend in the liquid slag.

Alas, in the case of the CaO-compound formation of some agglomerations of droplets is possible, mainly. Next, the droplets go to the liquid slag's surface from these agglomeration due to the victory of the buoyancy force over gravity force activity as both forces are in the continuous competition with each other.

In fact, the performed experiments demonstrate that in the case of the application of the complex reagent almost all the droplets subjected to the competition between buoyancy - and gravity force were settled on the crucible bottom as expected.

In the case of the application of the CaO-compound as a reagent majority of the coagulated droplets were found at the slag's surface.

Therefore, the patented, complex reagent is recommended for the industrial practice. The reagent is effective not only in coagulation but in the desired sedimentation of droplets as well. It is obvious that this reagent interacts with the victory of the gravity over buoyancy force which are in continuous competition in the described technology.

Unfortunately, the CaO-compound's application as a reagent leads to formation of some envelopes containing lead. The envelopes effectively block the coagulation of copper droplets. The droplets are not able to overcome the critical weight required by the sedimentation.

Solidification of copper droplets leads to formation of equiaxed grains surrounded by precipitates containing low-melting phases. In the case of the application of the complex reagent the so-called mechanical equilibrium promotes/controls the tendency of the formation of spherical droplets' shape. It is advantageous phenomenon. The more spherical shape of droplet the higher content of copper.

Kinetics of the coagulation is well illustrated by the planetary configuration of the small droplets and rod-like droplets which tend to join (to be swallowed) the dominant droplet (Fig. 6, Fig. 7).

Unfortunately, the rod-like droplets evince a high content of additions. Finally, additions form low-melting phases in precipitates.

Acknowledgements

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Additional information

Selected issues related to this paper are planned to be presented at the 22nd Winter International Scientific Conference on Achievements in Mechanical and Materials Engineering Winter-AMME'2015 in the framework of the Bidisciplinary Occasional Scientific Session BOSS'2015 celebrating the 10th anniversary of the foundation of the Association of Computational Materials Science and Surface Engineering and the World Academy of Materials and Manufacturing Engineering and of the foundation of the Worldwide Journal of Achievements in Materials and Manufacturing Engineering.

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