



# Sedimentation of Copper Droplets after their Coagulation and Growth. Laboratory Scale

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Received 03.07.2015; accepted in revised form 17.07.2015

## Abstract

The suspension of copper droplets in the slag is considered. The copper/slug suspension is delivered as the product from the direct-to-blister process which is applied in the KGHM – Polska Miedź (Polish Copper) S.A. factory. The droplets / slag suspension was treated by a special set of reagents (patented by the authors) to improve the coagulation process. On the other hand, the observations are made to estimate if the melting / reduction process in the furnace is sufficiently effective to avoid a remaining of carbon in the copper droplets. The coagulation process was carried out in the crucible (laboratory scale). However, conditions imposed to the coagulation / solidification process in the laboratory scale were to some extent similar to those applied usually in the industry when the suspension is subjected to the analogous treatment in the electric arc-furnace. Some suggestions are formulated how to improve the industrial direct-to-blister process.

**Keywords:** Innovative foundry technologies and materials, Product development, Copper droplets suspension, Droplets coagulation, Droplets solidification.

## 1. Introduction

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, [1]. In fact, 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 sufficiently effective.

The copper droplets evince three typical shapes: a/ star-like droplets are usually formed just at the beginning of coagulation process, b/ irregular spherical droplets form in the middle-time of

the slag decopperisation and c/ regular spherical droplets seem to be the final form of copper suspension.

The mentioned corrections of the droplets shape are accompanied by the increase of copper content and decrease of strange elements in the droplets. Therefore, the copper droplet containing other elements is treated, in the current analysis, as an alloy which modifies its concentration during the coagulation completed by its solidification. When the droplet reaches an optimal / critical diameter then it is settled on the crucible bottom. Settlement occurs because the suspension is incessantly subjected to gravity action. Finally, the solidification process is expected to form a dendritic morphology with some eutectic precipitates in the inter-dendritic regions of the solidified droplet. The adequate theory for solute segregation / redistribution after back-diffusion could be able to estimate amount of eutectic precipitates, [2].

The current analysis is dealing with the suspension treatment by the complex reagent containing phosphate which should improve coagulation. Experiment was made in the laboratory

scale (in crucible) but imposed conditions were similar to those applied in the arc-furnace to imitate fully industrial technology.

## 2. Coagulation and solidification of the copper droplets

The experiments were carried out in the crucible initially heated up to 1300 °C. The slag was put into the crucible and next reagents were introduced into the suspension of copper droplets to accelerate the coagulation. An examination was applied to a given small droplet, coagulation of which did not occur, Fig. 1.

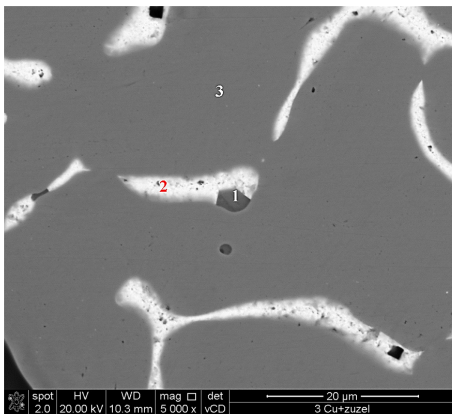


Fig. 1. Morphology of the examined droplet; measurement points evince following elements: 1/ (Cu,Fe)<sub>2</sub>S; 2/ C=34.4, O=16.49, Si=1.22, Pb=23.83, Ca=0.53, Cu=23.54 at.%; 3/ Cu=100 at%

A presence of the (Cu,Fe)<sub>2</sub>S compound proves that the reduction process was not fully carried out in the industrial process. Thus, the (Cu,Fe)<sub>2</sub>S - compound is localized in the precipitate surrounding some grains solidified in a given droplet.

An analysis of the slag located in the neighborhood of the copper droplet was also performed, Fig. 2.

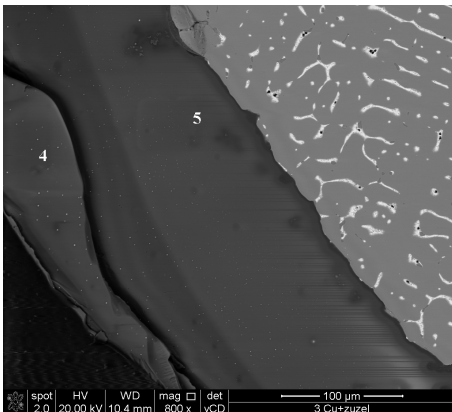


Fig. 2. Morphology of the boundary slag / droplet, points evince: 4/ 5/ C=6.59, O=56.05, Na=3.28, Mg=3.05, Al=4.81, Si=12.74, Pb=0.13, K=1.38, Co=6.19, Fe=4.80, Cu=0,96

The slag morphology evinces also how fine can be copper droplets (visible in the areas 4 and 5), Fig. 2. Further analysis confirm the presence of strange elements in the copper droplet. These elements are situated in the eutectic precipitate, Fig. 3.

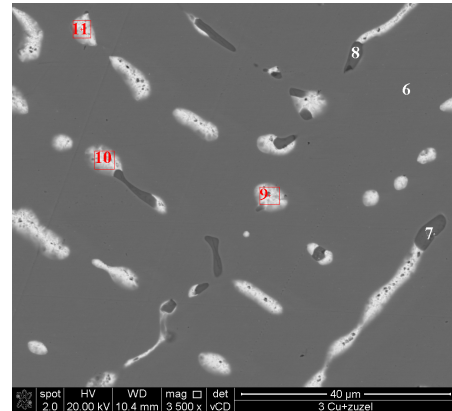


Fig. 3. Dendritic morphology of a copper droplet due to its growth: 6/ Cu=100; 7/ Cu<sub>2</sub>S, 8/ Cu<sub>2</sub>S or in some circumstances: S=28.9, Cu=51.98, Fe=0.82, Zn=18.30; 9/ C=34.92, Cu=34.83, Fe=0.85, Pb=29.52; 10/ C=27.31, Cu=37.3, Pb=35.4; 11/ C=32.15, Cu=38, Pb=29,85; points 7/-11/ are situated in the eutectic precipitate

The copper droplet was solidified to form the equiaxed grains surrounded by the eutectic precipitate as visible in the attached Fig. 1-3. Calculation of the ratio of precipitate to pure copper grains amount is possible while analyzing the droplet as a whole, Fig. 4. It allows to calculate eutectic precipitate fraction and back-diffusion parameter if the adequate phase diagram is known, [2].

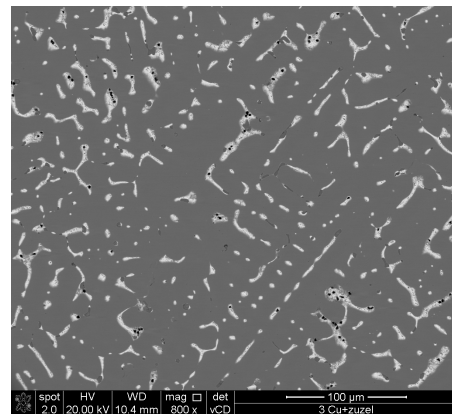


Fig. 4. Morphology of small copper droplet as a whole; precipitate contains a compound which is Cu<sub>2</sub>C<sub>3</sub>O (approximately) and additionally lead which usually is neutral and does not enter into an eutectic compound or eutectic phase; moreover, lead leaves the copper droplet due to further treatment in the electric arc-furnace to form a lead silicate in the surrounding slag; the presence of the Cu<sub>2</sub>C<sub>3</sub>O compound confirms that the Cu<sub>2</sub>S compound was totally reduced by carbon and oxygen in the analyzed area of the droplet

The copper droplets attain a critical diameter due to the influence of the complex reagent and are able to overcome the

buoyancy force to be settled on crucible bottom (laboratory scale). The current experiment confirms this phenomenon and large copper droplets were really found, Fig. 5.

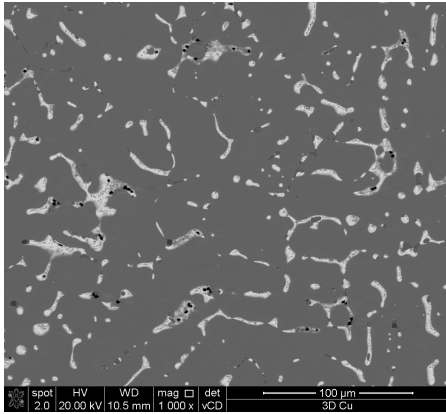


Fig. 5. Morphology of a copper droplet settled on crucible bottom; equiaxed grains of pure copper are surrounded by precipitates

The large copper droplet after sedimentation process, Fig. 5, can be compared with the small copper droplet which is not yet subjected to coagulation with the use of the studied complex reagent, Fig. 4. Moreover, morphology of the large copper droplet, Fig. 5, could be compared with the morphology of the droplet after common coagulation made under industry conditions in the KGHM – Polska Miedź (Polish Copper) S.A., [3], [4], [5].

The current analysis tries to reveal some differences in morphology and solutes concentration between small copper droplet (before coagulation) and large copper droplet subjected to sedimentation on the crucible bottom. Therefore, the solute content measurements and morphologies shown in Fig. 1, Fig. 3 are compared with the similar analysis performed for the large copper droplet, Fig. 6.

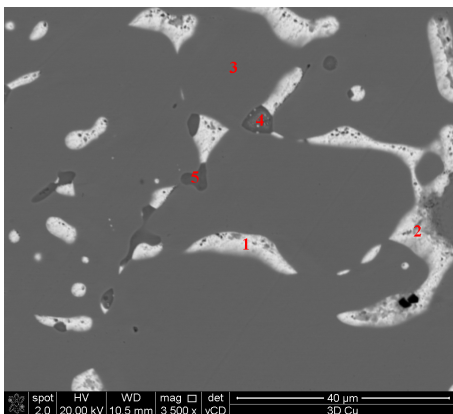


Fig. 6. Morphology of the large copper droplet subjected to the sedimentation on a crucible bottom (laboratory scale experiment)

The pure copper ( $Cu=100$  at.%) is revealed in the 3-area shown in Fig. 6. The precipitate in the 1-area contains  $Cu=37.74$ ,  $C=28.46$ , and  $Pb=33.80$ . The solutes concentration in the 1-area, Fig. 6, is similar to the analogous solutes concentration in the 10-area analyzed in the small copper droplet, Fig. 3. The solutes

concentration in the 2-area is as follows:  $Cu=33.32$ ,  $C=39.72$ , and  $Pb=26.91$ . This analysis corresponds well to the 9,10,11-areas in Fig. 3 and to some extent to the 2-area analysis, Fig. 1. The Cu- $Cu_2S$  eutectic with small addition of zinc is revealed in the 4-area, Fig. 6. The analysis of the 5-area, Fig. 6, confirms the presence of the Cu -  $Cu_2S$  eutectic precipitate, analogously to measurement point, 1, in Fig. 1 and point, 7, in Fig. 3.

The influence of the complex reagent on the decrease of the amount of precipitates can also be envisaged while making the comparison between the middle of the large copper droplet settled on the crucible bottom and the border of this droplet, Fig. 7.

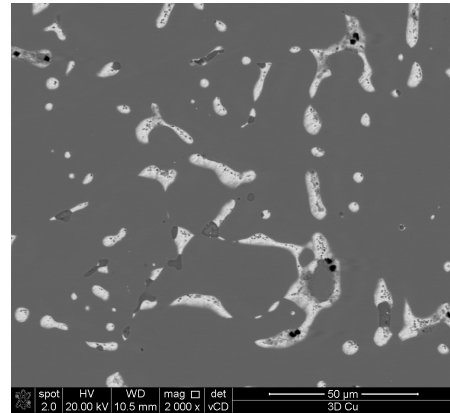


Fig. 7a. Morphology of the middle of the settled droplet

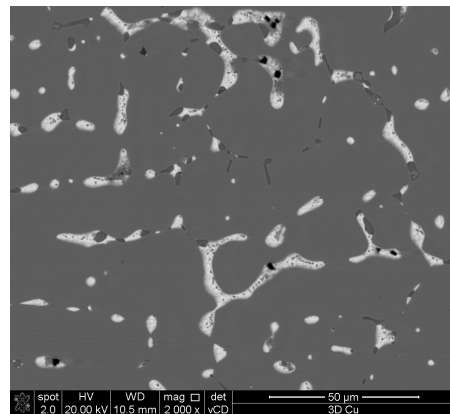


Fig. 7b. Morphology of the border of the settled droplet

It can be concluded that the border-droplet, Fig. 7b, evinces a little less amount of precipitate. It is possible because the droplet border is in the direct contact with the slag and therefore the outside part of the droplet can be partially evacuated of its precipitate. The difference between precipitate fraction in the first morphology, Fig. 7a. and the second, Fig. 7b, is very subtle.

It seems more significant to make the comparison between the precipitate amounts in the small droplet and large droplet settled due to its coagulation and sedimentation on the crucible bottom.

This comparison could be made due to the analysis of the morphology shown in Fig. 4 for the small droplet and that shown in Fig. 5 for the large droplet settled on the crucible bottom. There is no doubt that the coagulation is accompanied by the precipitate removing from the droplet. Thus, the large coagulated

droplet, Fig. 5, possesses less amount of precipitate. It can be concluded that the proper coagulation driven by the complex reagent is possible when the critical / threshold amount of precipitate is reached in each of droplets subjected to coagulation. The critical diminution of the precipitate amount in a droplet is caused by the impact of complex reagent containing phosphate.

The chemical analysis of the slag surrounding a given droplet confirms the presence of following elements: C=32.44, O=28.07, Mg=1.80, Al=2.25, Si=5.00, S=1.10, K=1.63, Ca=1.32, Fe=2.18 and Cu=24.71 at.% in the first area distinguished in the slag.

However, in the second area, the same elements concentration is significantly different: C=4.00, O=27.50, Mg=1.05, Al=1.47, Si=2.64, S=0.00, K=1.23, Ca=0.90, Fe=0.99 and Cu=60.24 at.%.

Some typical areas of the slag morphology are shown in Fig. 8.

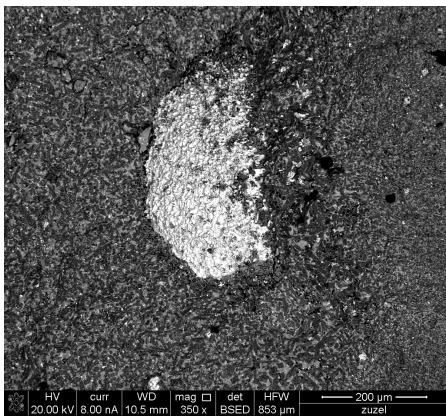


Fig. 8. Typical morphology of the slag; very small copper droplets are dispersed in whole slag volume; droplets before coagulation

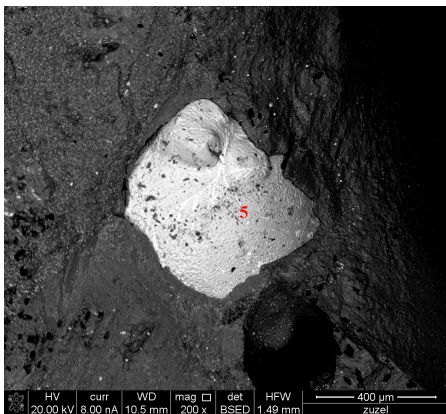


Fig. 9. Large copper droplet just after its sedimentation (area 5); surrounding copper droplets smaller in size are also visible

### 3. Conclusions

- 1) The patented complex reagent is significantly effective in the coagulation if compare the copper droplets morphology before coagulation, Fig. 4, and after coagulation, Fig. 5. The

impact of the reagent leads to decrease of the amount of precipitate up to its threshold / critical amount necessary to initiate coagulation and subsequent sedimentation of the sufficiently large droplet.

- 2) The solutes concentration is practically the same in the small copper droplet as in the large copper droplet.
- 3) Droplets sedimentation after their coagulation up to the critical diameter observed in the laboratory scale (in crucible) should be confirmed in semi industrial and fully industrial conditions.
- 4) The presence of carbon in eutectic precipitate is not desired. The direct-to-blister process is not yet optimized and carbon is not correctly dispersed in furnace shaft as discussed also in [6], [7].
- 5) Lead is typically situated in the precipitate and is rather neutral for the phenomenon of precipitation. Its presence comes from the fact that lead is low melting element.
- 6) At the analyzed stage of sedimentation lead is situated in the precipitate of droplet. Thus, it does not block droplet coagulation. It is well known that lead, which is outside of the droplet, forms the silicate which counteracts coagulation.

### Acknowledgements

The support was provided by the National Center for Research and Development under Grant No. PBS3/244 864/PP/MMB.

### References

- [1] Bydałek, A.W., Bydałek, A., Wołczyński, W., & Biernat, S. (2015). The concept of slag decopperisation in the flash furnace process by use of complex reagents. *Archives of Metallurgy and Materials*. 60(1), 319-322. DOI: 10.1515/amm-2015-0032.
- [2] Wołczyński, W. (2015). Back-diffusion in crystal growth. Eutectics. *Archives of Metallurgy and Materials*. 60(3), (in print).
- [3] Gierek, A., Karwan, T., Rojek, J. & Szymek, J. (2005). Results of test with decopperisation of slag from flash process. *Ores and Non-Ferrous Metals*. 50(12), 669-680.
- [4] Migas, P. (2015). Analysis of the rheological behavior of selected semi-solid slag systems in blast furnace flow conditions. *Archives of Metallurgy and Materials*. 60(1), 85-93. DOI: 10.1515/amm-2015-0014.
- [5] Bydałek, A.W., Biernat, S., Wołczyński, W. & Bydałek, A. (2015). Optimizing of Work Arc Furnace to Decopperisation of Flash Slag. *Archives of Foundry Engineering*. 15(3), 21-24.
- [6] Bydałek, A.W. (2011). Role of carbon in the melting copper processes. *Archives of Foundry Engineering*. 11(SI 3), 37-42.
- [7] Migas, P. & Karbowniczek, M. (2010). Interactions between liquid slag and graphite during the reduction of metallic oxides. *Archives of Metallurgy and Materials*. 55(4), 1147-1157. DOI: 10.2478/v10172-010-0018-0