Freeze-lining formation and microstructure in a direct-to-blister flash smelting slag

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Abstract: Copper smelting in one processing step directly from concentrates to blister copper has been realized on an industrial scale in a few smelters, using concentrates with a high Cu/Fe-ratio. The fluxing of any direct-to-blister slag is demanding task as it must be fluid and maintain suitable properties in the oxidising conditions of copper making, and the reducing conditions of slag cleaning. The smelting slags in the direct-to-blister furnaces contain much more chemically dissolved copper than typical matte making slags.

In this investigation, an industrial direct-to-blister slag was used in a freeze lining growth kinetics study. The freeze lining was formed on a water cooled metal finger at typical smelting temperatures using different dipping times from 5 to 120 min. The growth kinetics of the lining was very fast in the initial stage of the slag contact with the cooled metal surface. The quenched samples showed characteristic solidification zones from the cold end towards the hot side of the freeze lining and the molten slag shown already in other freeze linings and different slag types. The slag chemistry modifies the solidification pattern very much and thus the crystalline phases in the lining included also phases created by the high copper oxide concentration as well as the specific gangue assay of the smelters feed mixture. The thermal stability of the freeze lining in high-in-copper DB slags is discussed as well as the mechanism of delafossite precipitation.

Keywords: Copper, direct-to-blister smelting, slag, microstructure, phase equilibria

1. Introduction

Several authors have investigated freeze lining properties and their formation mechanisms in a number of environments. Most early studies (Thonstad & Rolseth[1], Voller[2] , Solheim & Støen[3]) deal with the Hall-Héroult aluminum smelting cell and its pot lining. Recently, the freeze linings formed in lead and zinc smelting slags have been studied (Verscheure *et al.*[4], Campforts *et al.*[5-10]). Mathematical models have been developed for describing the behaviour of freeze lining in dynamic conditions (Scholey[11], Campbell *et al.*[12], Verscheure *et al.*[13], Zietsman & Pistorius[14], Pan *et al.*[15] and Guevara[16]).

The aim of this study was to investigate the growth kinetics of a silicate slag freeze lining in blister copper smelting conditions where the stability of freeze lining is much more sensitive due to the high copper concentration of the slag than in matte making furnaces. Slag from an industrial direct-to-blister (DB) flash smelting furnace (FSF) was used as the lining forming medium. The water cooled probe technique by Verscheure *et al.*[4] was applied in a rotating crucible, for stabilizing temperature profile of the slag bath.

2. Experimental

A detailed description of the experimental furnace and its instrumentation has been given elsewhere[17], but since the previous research series with copper matte making slags, four PT100 A class temperature sensors were inserted in the water cooled probe close to the slag surface. They are used for measuring heat flux to the cooling water within the slag bath.

Cylindrical crucibles of dense 99.4 % MgO supplied by Ozark Technical Ceramics Inc. 87-100 mm OD and 150 mm H were used. Nitrogen gas with a purity of 99.9 %, containing <20 ppm O_2 and <10 ppm H_2O, was used in all experiments as protective atmosphere for avoiding oxidation of the slag during experiments. The flow rate of nitrogen to the furnace varied in the experiments from 3 to 6 L/min (STP).

Water flow into the probe was adjusted by controlling water pressure in the probe with manual valves. The 700 mm long probe used in experiments was ϕ_o=14 mm and the inner tube for water feed to the tip was ϕ_o=8 mm. The probe and the inner sheath were made of AISI 316L stainless steel and the walls were 1 mm thick. Schematic construction of the probe is shown in Fig. 1. The probe was insulated with Kaowool fiber rope, starting 100 mm upwards from the tip of the cold finger.

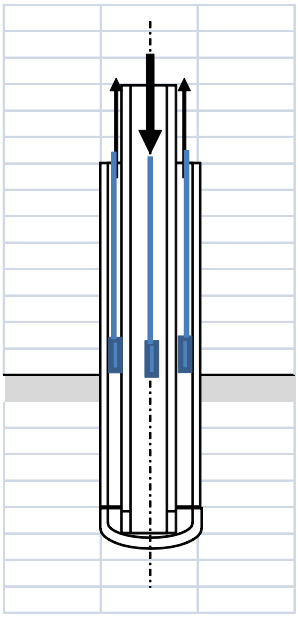

Figure 1. A schematic construction of the cooled probe with the four PT100 temperature sensors (blue) in the water channels for heat flux measurements.

The solidified freeze linings were broken for preparation of samples from the top and bottom parts. The specimens were examined with a LEO 1450 scanning electron microscope (SEM) with a tungsten cathode, in backscattered electron mode using 15 kV acceleration voltage. The microstructures and compositions of the phases were determined using an INCA X-Max EDS-analyser from polished sections, prepared using standard wet methods. SPI Supplies Inc. (PA) mineral standards were used for the elements analysed by EDS. Chemical analyses of the slag were made by ICP and Satmagan was used for their magnetite content. Selected slags were investigated by X-ray diffractometry (XRD) for their phase assembly.

The experiments were carried out at 1350 °C furnace temperature and the immersion time of the cold finger varied from 5 to 120 min. Before immersion, the crucible with molten slag was allowed to stabilise for 30 min at 1350 °C. The crucible was rotating (10 rpm) during the heating up period and experiments, in order to smoothen the temperature profile. The heating up rate was 250 °C/h. The flow rate of cooling water to the cold finger 2-3 L/min and its accurate rate was measured before each test with a known volume and timer. After each test, the freeze lining sample was immediately quenched in water. The final cooling was done in air, in order to remove water and humidity from the sample porosity and its surfaces. The crucible with the rest slag was cooled down in flowing nitrogen with the furnace.

3. Results

The average main component analyses of the slag before and after the test are collected in Table I. The calculated concentrations of ferric and ferrous oxide have also been included in table I, based on the analysed total iron and magnetite concentrations and assuming that half of dissolved copper is bound with ferric oxide not seen in the magnetite analysis, and 2% of copper is present as dispersion. The effect of delafossite to the magnetite analysis was not taken into account.

Table I. The DB slag chemistries prior to and post freeze lining tests; averages of the quenched dip rod samples.

		ICP	ICP	ICP	ICP	ICP	ICP	S/C analyser	Satmagan	
		Cu	Fe(tot)	Al_2O_3	CaO	K_2O	MgO	S(tot)	Fe_3O_4	SiO_2
		%	%	%	%	%	%	%	%	%
Start sample - average, dip rod		19.1	27.8	4.8	3.8	2.6	2.0	0.0	32.7	25.4
End sample - average, dip rod		19.0	26.9	4.8	3.8	2.5	2.0	0.0	29.1	25.7
									%FeO	$\%Fe_2O_3$
									5.86	33.23

The dimensions of the freeze lining obtained were measured with slide gauge. Due to the uneven surface structure the dimensions were determined from several points representing various cross sections. The relative measuring error, however, is large as the thermocouple sheaths inserted in the slag caused clear non-symmetry to the slag mixing and the freeze lining layer growth.

The thickness of the freeze lining grown on the water cooled metal surface at 1350 °C slag temperature as a function of time is shown in Fig. 2. The steady-state thickness of the lining is only 18 - 20 mm in this geometry and with an OD 14 mm cooled probe, when overheating of the DB slag is 100 - 120 °C.

As shown in Fig. 2, the growth rate achieves steady state with zero growth rate during the first 30-40 minutes of the probe-slag contact. The lining does not grow in thickness when overheating of the slag and cooling power of the probe are kept constant. The selected dense MgO as crucible material was found to be very compatible with the high-copper DB slag which initially did have some dissolved magnesia in the assay.

The microstructures of the freeze linings formed on the cooled probe were examined with SEM and the micrographs were collected to panoramas from the cold face towards hot face. An example is shown in Figure 3 and it reveals the development of the freeze lining microstructure as a function of the distance from the cooled metal surface. The chemical compositions of the formed crystalline phases were also analysed using EDS techniques, as a function of the lining thickness from the cooled probe surface.

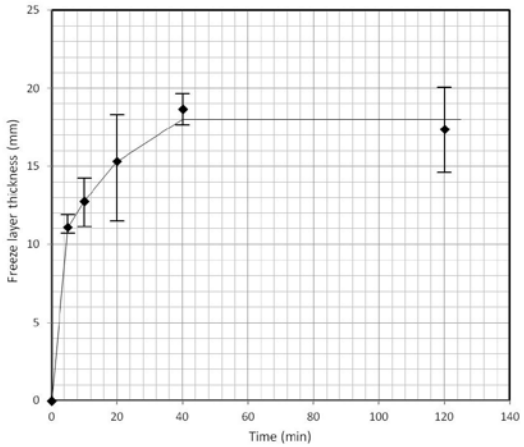

Figure 2. Growth rate of the freeze lining thickness in the direct-to-blister flash smelting slag at 1350 °C on an OD 14 mm water-cooled stainless steel probe.

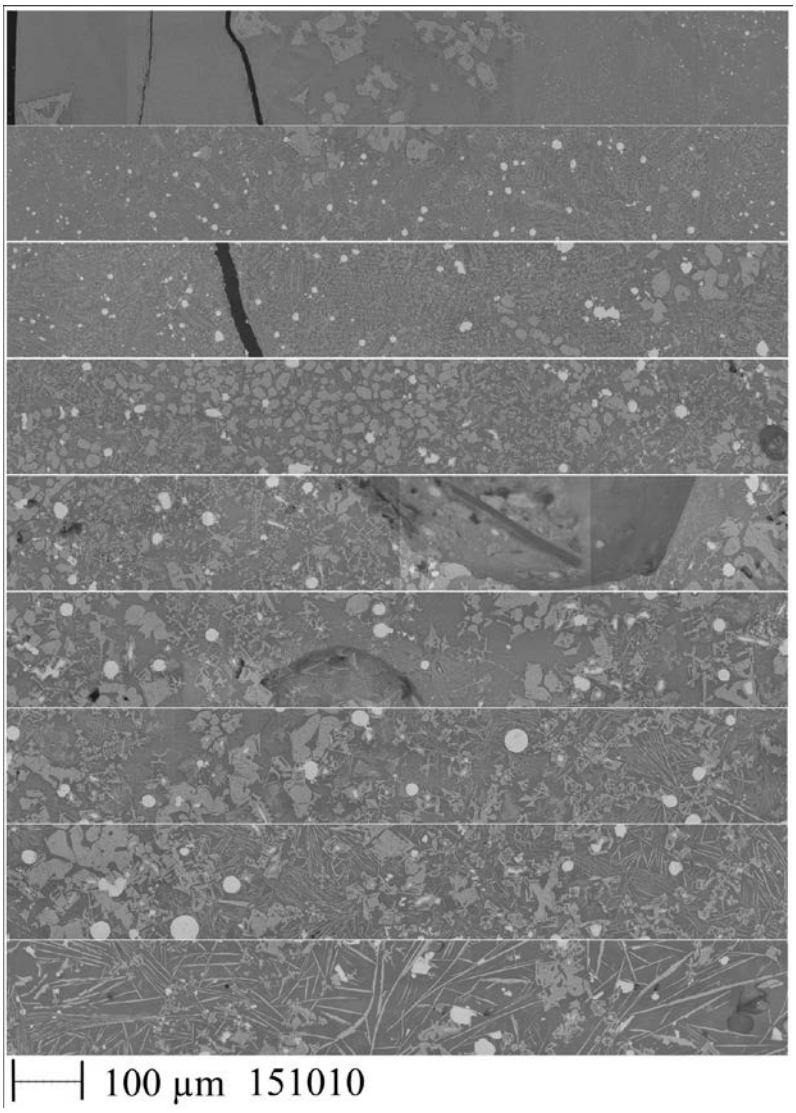

Figure 3. Panorama SEM micrograph of the cooler half of a freeze lining formed during 40 min contact time; the cold face is in the upper left corner of the slice and each horizontal strip is 1 mm long.

X-ray diffraction data of the slowly cooled end slag show in all cases magnetite and delafossite ($CuFeO_2$). In several end slags, those were the only crystalline phases detected by XRD.

Figure 3 shows a selected panorama over the well developed freeze lining micro structure formed on the cold finger over a relative long contact time of 40 min, covering about half of the whole lining thickness formed in the experiment. The mineralogical structure of the freeze lining is very different when compared with the matte smelting slag freeze linings studied earlier[17], due to two reasons: firstly, the conditions in direct-to-blister furnace, where metallic, sulphur-lean blister copper is stable, and secondly, the chemistry of feed mixture gangue of the smelter. It differs from most copper concentrates, in particular as to its concentrations of alumina as well as magnesia. The fluxing practices at the smelter also include lime additions[18]. The slag also has a relatively high K_2O concentration.

Microstructures of the essentially amorphous or glassy inner layers at a distance of 0.1 - 0.3 mm and 1 mm from the cooled metal surface is shown in Fig. 4 and 5, respectively. The immersion time of this freeze lining was 10 minutes. The micro structure at the cold face is formed of very fine crystalline or amorphous glass phases where a few relatively large magnetite (spinel) crystals are embedded.

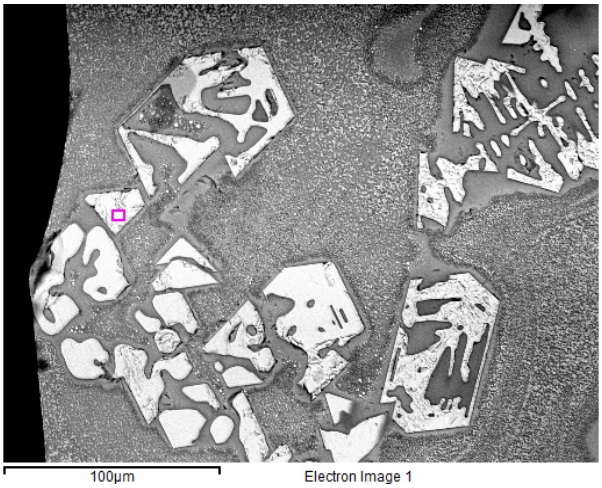

Figure 4. DB-slag microstructure next to the cooled surface: spinel crystals in ’amorphous’ or ’micro crystalline’ matrix; 10 min contact time at 1350 °C slag temperature; notice the diffusion zone around the spinel phase.

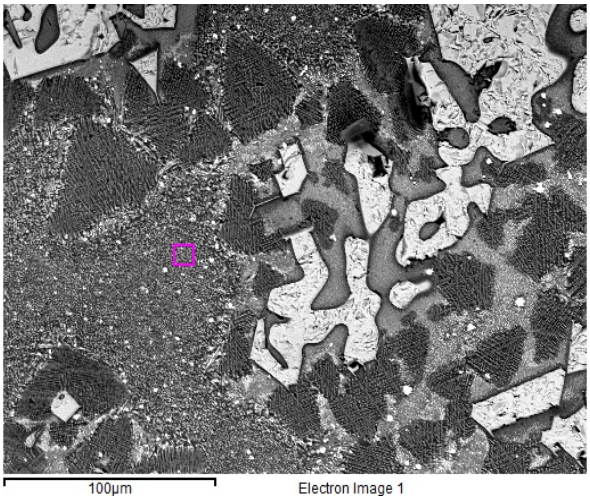

Figure 5. DB-slag microstructure on the outer rim of the amorphous zone: 10 min contact time at 1350 °C (distance about 1 mm from the cold metal surface).

The chemistry of precipitated magnetite (spinel) differs significantly from that in the traditional matte smelting freeze linings[17]: it contains a high (>5 %) concentration of copper, dissolved as oxide, Fig. 6, and occasionally cobalt which is typical minority component of the concentrates used at the smelter. It is oxidised from the metal phase in the blister making conditions. The formed spinel also contains 2-3 % alumina and magnesia throughout the freeze lining layer, Fig. 6, as well as 1-2 % cobalt and traces of titania and silica.

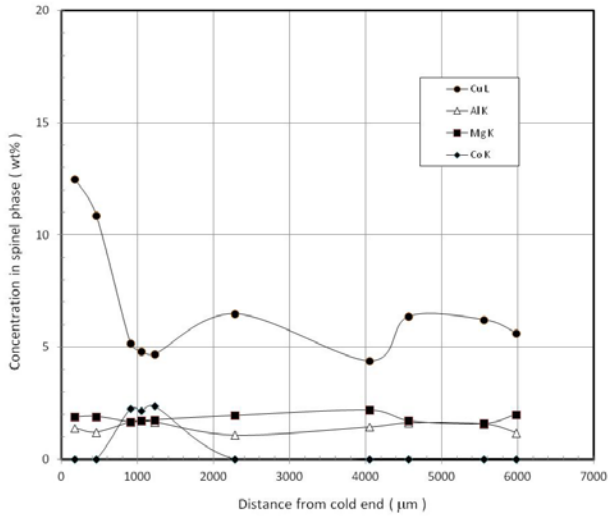

Figure 6. The development of the spinel assay as a function of distance from the cold surface (5 minute contact time with the molten slag).

The thickness of the glassy zone against the cooled metal surface is much wider than in the matte making slags studied earlier[17] and it extends to about 1 – 1.5 mm from the cold face. At about 1 mm from the cold surface outwards, the glassy matrix starts to crystallise and spinel phase is coarsened, Fig. 5. Its crystals are relatively small and thus they do not allow any accurate EDS analysis, but it gives an average assay with elements from the surrounding glassy matrix.

At a distance of 2-3 mm from the cold surface, the freeze lining grain structure turns again into fine and it contains solidified iron-bearing blister copper, see Fig. 7, but only few coarse magnetite (spinel) cystals. The analysed iron concentration of blister copper is up to 4-5 %. The spinel dendrites are densely distributed and very fine (<10 µm).

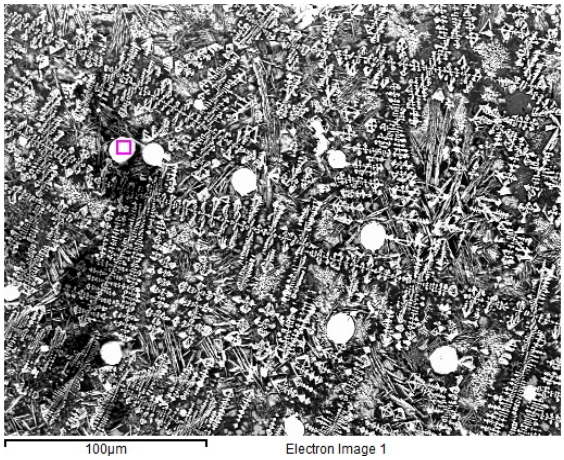

Figure 7. Microstructure of the freeze lining at a distance of 2-3 mm from the cold face; 10 minute contact time with the direct-to-blister flash smelting slag: spinel crystallites with a few blister copper droplets (white) embedded in glassy matrix.

At a distance of 4-6 mm from the cold face the solidified freeze lining contains increasing fractions of a new phase delafossite, which has morphology of needles or plates and it forms bundles in the glassy intergranular matrix, as shown in Fig. 8 (10 minutes contact time). A detailed EDS analysis was carried out at a large magnification and the composition of delafossite as obtained in two different experimental runs was found to be 32.3 ±1.9 % Fe and 45.4 ±1.9 % Cu. It also contained about 1 % Ti, Si and Al as well as less than 0.5% Mg, K and Ca. The phase is slightly copper-rich with regard to stoichiometric delafossite which has 41.97 % copper.

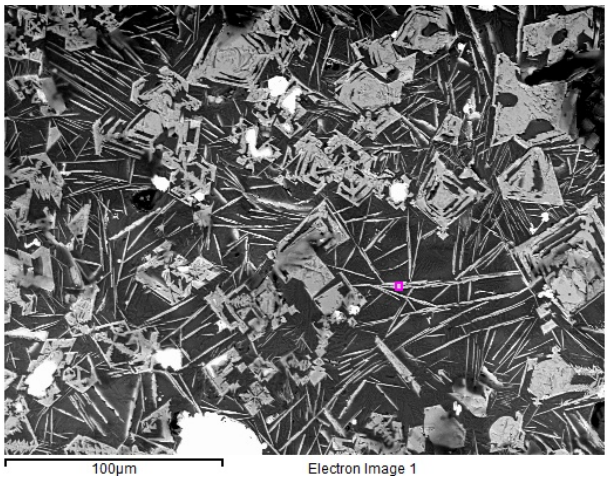

Figure 8. Needle-like delafossite crystals in the freeze lining together with spinel dendrites and copper droplets (10 minutes contact time).

The amorphous layer next to the cold face contains a high fraction of copper(oxide) and it is higher (>20 %) than the average slag concentration. The freeze lining assay towards the cold face has also a high silica concentration, of the order 30-35 % SiO_2, and it rises even more at a distance of 1-2 mm from the cold face towards the hot face, reaching concentrations of >45 % SiO_2.

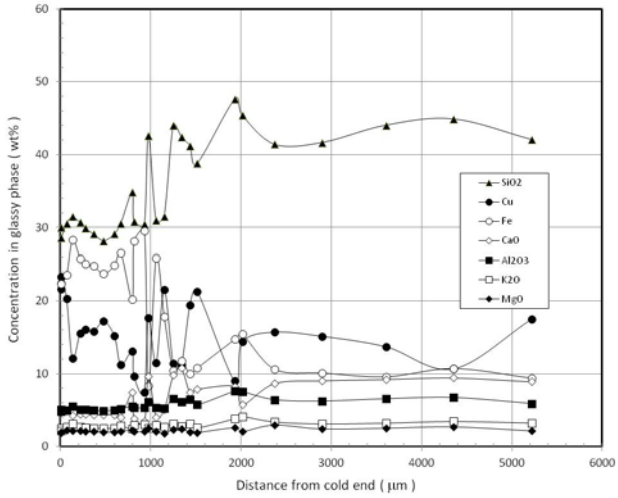

Figure 9. Development of the assay of the glassy phase in a test with 5 min duration; the 1 - 1.5 mm thick, fully glassy zone can be distinguished also here, in particular from its silica concentration.

Figure 9 shows the assay of the glassy matrix in a test run with duration of 10 minutes, as a function of distance (µm) from the cold face. The scatter from one point to another is relatively large, but in spite of that the lines have been

drawn from point to point. In addition to the elements plotted in Fig. 9, the glassy phase contains small concentrations of titanium (0.2 %) and in particular close to the hot face also sodium (0.2-0.3 %) as trace elements.

4. Discussion and conclusions

The growth kinetics of freeze lining in DB slags is rapid, and a steady state thickness is reached within 30-40 min of the slag-cooled metal surface contact.

Silica concentration of the DB freeze lining is slightly larger (25-30 % SiO_2) in the amorphous inner zone towards the cooled metal surface than in the average slag analysis, and it rises even further in the layers closer to the hot face. Silica concentrations in excess of 40 % were analysed in the DB slag freeze linings. The strong scattering of copper and iron concentrations over the fully glassy zone and the locally variable concentrations are due to precipitation of spinel (magnetite) or its absence in the vicinity of the analysis point. Copper of the lining drops at a distance of 1.5 - 2 mm below concentrations less than 10 % (Cu), which in turn is less than the average concentration of the DB slag. In the fast solidified zone it is close to the average slag concentration.

The refractory components of the glassy matrix (MgO ja Al_2O_3) in the freeze lining are evenly distributed and no trends can be detected throughout the layer. The lime concentration in the hot face, on the other hand, is much higher than the average assay of the slag (≈4 %). The analysed potassia concentration is also essentially constant over whole thickness of the freeze lining and the level of K_2O is relatively high in this slag.

The copper precipitates in the freeze lining contain about 4 % iron. They are slightly more iron-rich than the peritectic point of the liquid alloy of the copper-iron binary system[19], but close to its solid solubility (4.2 % Fe).

The formation and precipitation of delafossite from the slag requires a high oxygen partial pressure or high copper (oxide) concentration in the slag, and it is characteristic to DB slags. It does not have solubility with spinel (or 'magnetite', Fe_3O_4), but precipitates as an own substance from the slag. Thus it at low temperatures contains a fraction of the slags ferric oxide and as a non-magnetic phase it is not detected in the Satmagan magnetite analysis.

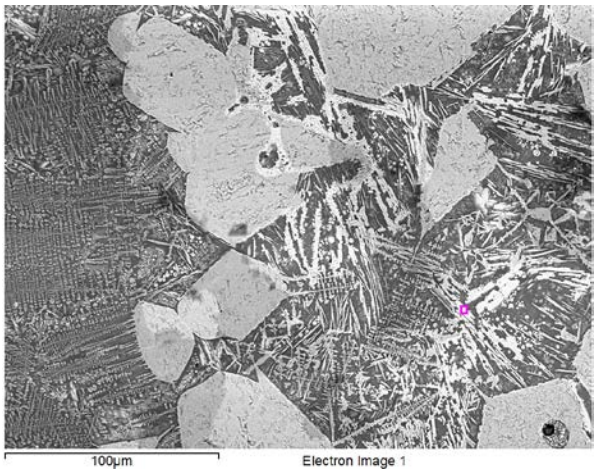

Figure 10. Delafossite needles (white phase, $CuFeO_2$) in the glassy matrix and surface layers on large spinel crystals (grey).

Delafossite is precipitated as thin needles and their bundles and it covers primary magnetite crystals, as shown clearly in Fig. 10. Due to its morphology, the accurate determination of its composition in thin needles and on spinel grains is very demanding by EDS techniques. Therefore, no accurate composition was determined from the precipitated delafossite, which in the ternary copper-iron-oxygen system is essentially stoichiometric $Cu_2O{\cdot}Fe_2O_3$. EDS-analyses show small concentrations of silica, alumina, potassia, titania and magnesia in delafossite, but they may be only echoes from the phases behind the delafossite grains.

Delafossite grows on spinel grains as well as homogeneously nucleated crystals of its own. This is due to the incongruent equilibrium of delafossite with the molten slag phase[20]. This reaction can be written as

$$Fe_3O_4(s) + 1½\ (Cu_2O) + ¼O_2(g) = 3CuFeO_2(s). \quad (1)$$

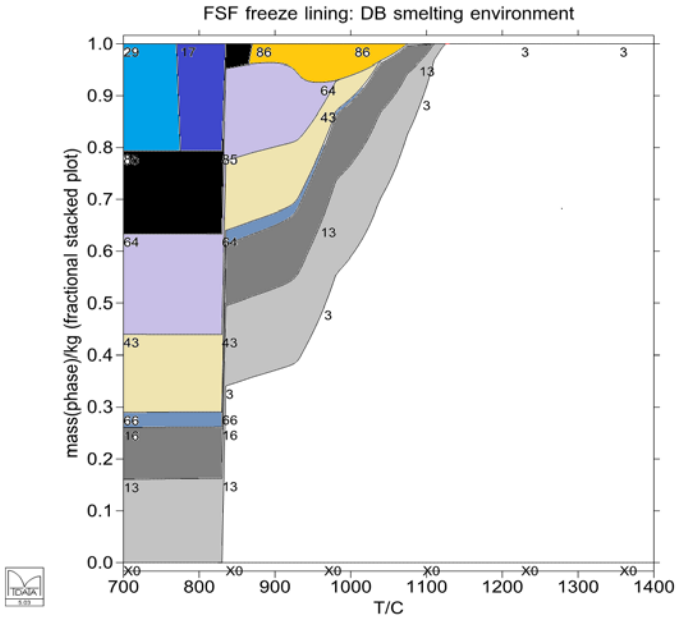

Figure 11. Equilibrium solidification plot of the stable phases in outer (hot face) layer of the freeze lining formed in the DB slag studied in this work; calculated using MTDATA and Mtox 7.0 database; the phase labels refer to: #3-liquid oxide, #13-clinopyroxene, #17-feldspar, #29-microcline, #43-wollastonite, #64-delafossite, #66-solid copper, #85, 86-silica.

Thus it is not generated directly from the molten slag phase, in a similar way as magnetite precipitates. Delafossite has typically needle-like structure[21] when it precipitates homogeneously in the glassy slag matrix or nucleates on spinel crystals below about 1170-1100 °C, depending on the prevailing oxygen partial pressure[22].

The refractoriness of the formed freeze lining was evaluated by equilibrium simulations using the Mtox database and MTDATA software[23]. The lining assay was taken as an average of the EDS analyses of the last solidifying fraction of the lining, the glassy, intergranular matrix. The results of the equilibrium analysis is shown in Fig. 11 which indicates that the final solidification of the freeze lining matrix takes place at about 850 °C. The solidification and thus the softening temperature of DB freeze lining is 200-300 °C lower than that of the freeze lining formed in copper matte

making furnaces[17]. It is thus not surprising that the stability of freeze lining in DB furnaces is poor and very sensitive to any temperature variation in the smelting vessel.

Acknowledgements

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