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MICROSTRUCTURE CHARACTERISATION OF FREEZE LININGS FORMED IN A COPPER SLAG CLEANING SLAG

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Abstract

The initial growth rate of freeze linings on water-cooled elements submerged in molten iron silicate slag is fast. The freeze lining microstructure forming on water cooled steel surface in a high-silica, slag cleaning furnace slag of a direct-to-blister copper smelter is mostly glassy or amorphous. It contains 5-30 µm magnetite crystals, very small and larger copper droplets as well as small magnetite and silicate nuclei embedded in the glassy silica-rich matrix. Chemically the formed freeze linings are more silica-rich than the slag from which they were generated. Magnetite (spinel) is the primary phase of the solidifying SCF slag but it does not form a continuous network through the freeze lining. Its strength is given by the intergranular silica-rich phase which initially is glassy or microcrystalline. Due to only partial slag reduction in the SCF process, large magnetite crystals are present in the freeze lining and seem to interact physically with copper droplets.

Key words: copper smelting, slag, cooling element, freeze lining

1. Introduction

In the direct-to-blister (DB) Flash Smelting processes the concentrate is oxidised in one step into metallic, low-sulphur blister copper in a Flash Smelting Furnace (FSF), without separate converting step for treating sulphidic matte into crude metal [1,2]. It is feasible option for a limited number of copper concentrates with a high Cu/Fe ratio [3]. By combining the smelting and converting operations, the operating and capital costs of smelting are reduced while simultaneously improving the energy efficiency. In the DB Flash Smelting processes the FSF slags contain a lot of chemically dissolved copper, and their total copper content may be 15 - 25 wt-% depending on the utilized slag-chemistry and the actual oxygen potential or the sulphur end-point [4]. Therefore, the slag from the DB primary smelting furnace is usually cleaned in an electrical slag-cleaning furnace (SCF) in one or two stages [1] where copper concentration is decreased to less than 1 % (Cu).

In all intensive copper smelting and slag cleaning furnaces water-cooled copper elements are used in various locations to stabilise refractory wear and extend campaign life. The microstructures of freeze linings formed in various smelting slags have been studied experimentally by a few authors. Campforts *et al.* [5-7] have carried out detailed studies in lead smelting slags in oxidising and reducing conditions. Pistorius *et al.* [8, 9] have evaluated the maintenance and properties of freeze linings in ilmenite smelting. In copper and nickel smelting slags the freeze lining formation and their properties are less frequently studied. Guevara and Irons [10] as well as Pan *et al.* [11] modelled freeze layer formation in six-in-line electric furnaces in the calcine and sulphide smelting environments, respectively. Their performance has been evaluated in some cases [7, 12] but only limited experimental data are available on the microstructures formed in iron silicate slags typical to copper smelting in matte and direct-to-blister conditions, as well as in slag cleaning furnaces [13, 14]. It is generally assumed that microstructure of the freeze lining depends on its growth rate and thus on the heat flow rate [12].

In this paper, the details of microstructures and growth rates of the freeze-linings on a water cooled metal surface in an industrial SCF slag will be reported. The heat conductivity measurements have been published already earlier elsewhere [15].

2. Experimental

The experiments were carried out in a 25 kVA vertical tube furnace delivered by Entech (Ängelholm, Sweden) and heated with $MoSi_2$ heating elements. The furnace temperature was controlled by a Eurotherm 2408 PID unit and the maximum

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temperature of the furnace is 1700°C. The studied slags were melted under flowing dry nitrogen in cylindrical 99.4 % MgO crucibles, supplied by Ozark Technical Ceramics Inc., MO (USA), with outer diameters from 80 to 100 mm. The mixing of slag was maintained during submersion by fixing the crucible to the rotating pedestal which also acted as a bottom of the furnace working tube. The rotation rate used was 10 rpm. The experimental setup is illustrated in Figure 1. More detailed information on the experimental setup can be found elsewhere [3, 14].

The freeze-lining sample was solidified on the surface of a water-cooled probe built from two concentric AISI 316L tubes with the outer diameters of 8 and 14 mm, and wall thickness of 1 mm. The temperature of the water-flow inside the probe was monitored with six A Class PT100 temperature sensors (platinum resistance thermometer, PRT) manufactured by SKS Automation Oy (Finland). The temperature of the freeze-lining was monitored with two calibrated S-type thermocouples (Johnson-Matthey, UK) at fixed distances, on one side of the probe. The assembly of the thermal sensors is shown in Figure 2.

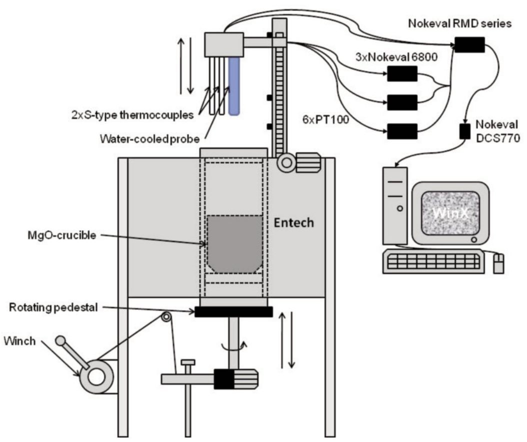

Figure 1. *The experimental furnace with the water-cooled probe and data-logging circuits for temperature measurements.*

The freeze lining growth runs were carried out with 1.6 - 2.4 kg slag weighted in the crucible, see Table 1. The furnace was heated up with a rate of 3 - 4 °C/min in nitrogen atmosphere. After reaching the experimental temperature the furnace was allowed to stabilise for 30 minutes so that the temperature inside the furnace and the slag had enough time to get uniform and constant. The cooling water flow rate was kept constant, on the average at 2.0 L/min, from one experiment to another, and measured accurately prior to each experiment. Growth rate of the freeze-lining was obtained by varying the submerging time of the probe. For more detailed information, see Table 1.

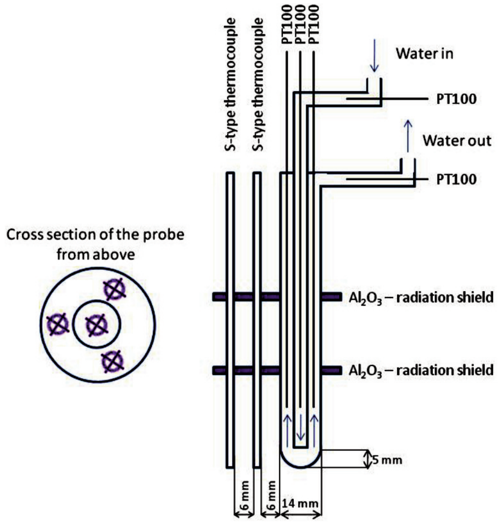

Figure 2. *A schematic design of the water-cooled probe: its water temperatures were measured with six A class PRTs and temperatures in freeze-lining with two S-type thermocouples.*

Before and after submerging the probe, a dip rod sample was taken. Those samples were used for monitoring the slag composition before and after submerging. The freeze-lining sample solidified on the probe surface was quenched in water after a desired time of immersion, dried, broken and prepared with standard wet methods for microstructure analyses. More detailed information on the experimental procedures, sample preparation and analytical methods used can be found in reference [3].

The start and end samples were sent for ICP, Satmagan, SiO_2 and chemical analysis. The freeze-lining samples were examined with a LEO 1450 scanning electron microscope (SEM) with tungsten cathode (Zeiss, Germany) using polished sections. For imaging, the backscattered electron (BSE) mode and 15 kV acceleration voltage at 15 mm working distance were used. The chemical compositions of phases were studied with an INCA X-Max EDS-analyser (Oxford Instruments, UK), using mineral standards manufactured by SPI Supplies Inc. (West Chester, PA). INCA Energy uses the XPP matrix correction scheme developed by Pouchou and Pichoir [16] and supplied by Oxford Instruments.

The experimental studies consisted of two different lots of slag from KCM smelter in Zambia. In the first shipment studied, the magnetite content of the slag was found to be too high compared to the reported copper level of the slag [2] and the slag was oxidized after sampling from the SCF launder. Therefore, another lot of the slag was acquired for the second series of experiments. In the second batch, the magnetite content was comparable to the analysed copper level of the slag, see Table 1.

Table 1. *Experimental details of the SCF slag freeze lining growth tests.*

Date	Slag lot #	Subm. time /min	Slag temp. /°C	Crucible OD /mm	Depth of probe in slag /mm	Weight of slag /g	FL sample weight /g	Water flow/ L/min	N_2 flow/ L/min
9.5.2011	1	5	1375	80	23.7	1308.7	134	2.02	3
11.5.2011	1	10	1390	80	33.85	1400.7	260.9	2.04	3
16.5.2011	1	20	1390	100	18.97	1636.1	155.2	2.09	3
18.5.2011	1	40	1390	100	22.54	1766	170.8	2.01	3
25.5.2011	1	120	1390	100	25.2	1620.1	304.3	2.08	3
5.8.2011	1	5	1390	80	32.78	1473.2	218.3	2.04	4
10.8.2011	1	10	1390	80	36.79	1544	336.3	2.07	4
12.8.2011	1	20	1390	100	35.39	1994	314.2	2.12	4
17.8.2011	1	40	1390	100	30.1	1886.5	255.8	2.09	4
19.8.2011	1	120	1390	100	35.17	1997.4	624.7	2.09	4
5.7.2012	2	40	1375	100	43.99	1792.6	585.3	2	5
10.7.2012	2	40	1390	100	39.61	2365.5	580.6	2.02	5
12.7.2012	2	20	1390	100	40.32	2309.1	442.4	2	5
26.7.2012	2	20	1390	100	36.59	2404.2	382.1	2.03	4

The stability of obtained freeze linings in prolonged annealing was tested by a 16 hour heat treatment at 918 ±5 °C in flowing, dry 99.999 % argon. The microstructures were examined as described above.

3. Results

Features of the freeze lining growth kinetics test program carried out in this work with the DB smelter slag cleaning furnace slag, using the two lots of the industrial SCF slag received, were compiled in Table 1. The compositions of the SCF slags studied were collected in Table 2. They are averages of the analysed chemical compositions of the start and end dip rod samples, taken in each experiment prior to submerging the probe in the slag and post lifting it from the crucible.

From Table 1 it can be concluded that the MgO crucible was chemically compatible with the slag and did not dissolve into it too much, i.e. the MgO concentration is only 0.5 percentage units higher in the end samples compared to the start samples. It is also interesting to notice that Fe_3O_4 contents of the slag baths were lower in the end of the experiment. The total iron content of the slag bath was constant during the test. This suggests that dissolved magnetite or ferric oxide tends to precipitate from the bath and solidify in the forming freeze-lining layer. No other trends and signs of selective solidification can be seen in the obtained slag compositions.

3.1 Freeze lining growth kinetics

The freeze-lining thickness studied in the two SCF slag systems behaves as expected, based on our previous experience on the DB slag freeze linings growth [14]. The solid slag layer grows very quickly and the freeze-lining is approximately 15 mm thick already just after 5 minutes of the probe-slag contact. Based on the results with freeze-lining thicknesses only, it is impossible to estimate exactly whether the

Table 2. *Compositions of the SCF slag studied based on average start and end sample analyses (wt-%).*

Sample type	Cu	Fe_{tot}	Al_2O_3	CaO	K_2O	MgO	Fe_3O_4	SiO_2
	(ICP)	(ICP)	(ICP)	(ICP)	(ICP)	(ICP)	(Satmagan)	
Start, 1st lot	5.4	28.9	6.3	5.1	2.8	2.5	25.9	34.2
End, 1st lot	5.4	29	6.3	5.1	2.8	3	21	34.7
Start, 2nd lot	5.6	23.4	6.2	5	2.9	3.9	15.8	38.9
End, 2nd lot	5.5	23.6	6.3	4.9	3	4.4	12.1	40.3

steady-state conditions in the freeze lining were reached or not. The evolution of the freeze-lining thickness with the studied SCF slags is represented in Figure 3 as a function of submersion time.

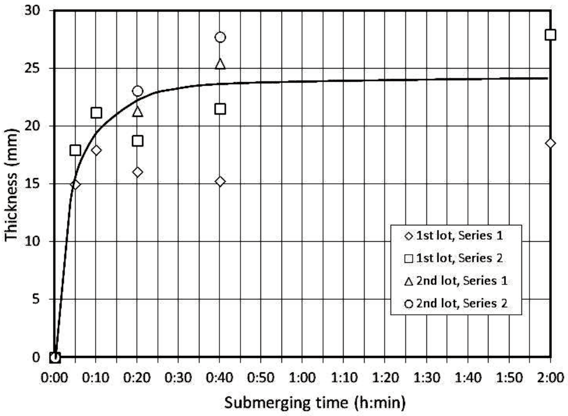

Figure 3. *The freeze-lining thickness in the studied SCF slags; the 5 and 10 min submersion tests were done in crucibles with a smaller OD and therefore the growth was quicker than in longer experiments.*

Figure 3 indicates that within the first 30-40 minutes the freeze lining thickness has reached a value of 23 ±5 mm and its growth has essentially ceased.

3.2 Freeze lining microstructure

Typical microstructures obtained in the SCF slag freeze linings are represented as panoramas throughout the entire lining layer in Figures 4-5. Figure 4 shows a well-developed freeze lining after submerging time in the molten slag of 40 minutes. Figure 5 displays the freeze lining in its developing stage, after 20 minutes of submersion.

The solidified and quenched freeze-linings formed in the molten industrial SCF-slag system studied in this work consisted of magnetite (Fe_3O_4) crystals (an end member of the spinel solid solution series), metallic copper and an amorphous (microcrystalline) or glassy silicate matrix throughout the layer. In a similar way as in matte smelting conditions [12] the freeze layer formed in the iron silicate slag in SCF could be divided into three zones: The first 1-2 mm from the water cooled probe is mostly glassy, containing only random magnetite crystals and in some linings random clusters of metallic copper precipitates against the water cooled probe surface; the hot face has a 2-4 mm thick layer of the bulk slag layer attached on the actual freeze lining; its boundary against the freeze lining is indicated by absence of the microcrystalline precipitates in the glassy matrix. The actual body of the freeze lining in steady-state conditions is therefore only 15-20 mm thick and its chemical composition is essentially constant over the whole thickness, except the glassy layer against the probe.

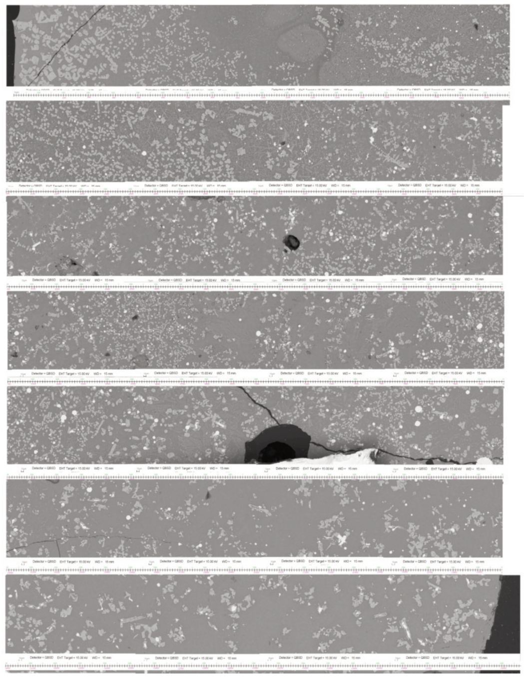

Figure 4. *Micrograph of freeze-lining sample from an experiment with 1st SCF slag batch (40 minutes); upper-left corner of the panorama was in direct contact with the probe surface and its hot face is in the lower right; each horizontal strip shows a length of 2 mm in the actual freeze-lining sample*

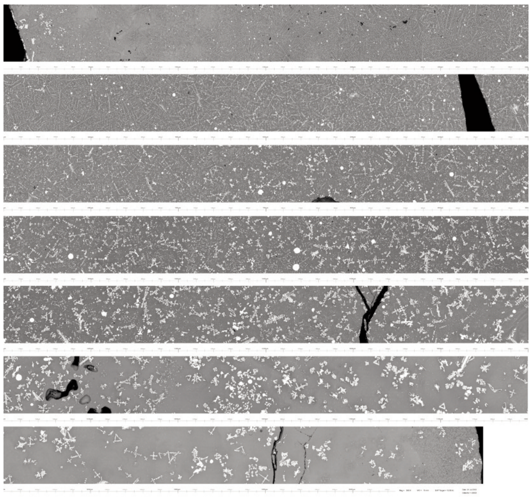

Figure 5. *A cross section of the freeze-lining from an experiment with 2nd SCF slag lot (20 minutes); upper-left corner of the panorama was in direct contact with the probe surface and its hot face is in the lower right; each horizontal strip of the panorama represents a length of 2 mm in the actual freeze-lining sample.*

For this reason, the obtained freeze linings were divided for EDS analyses and determination of the phase compositions into cold-end and hot-end sections as well as the middle section, denoting the actual well-developed freeze layer. In order to show the compositional variations in the well-developed zone, the EDS analyses were collected from its center-line (‘middle’) as well as from a radius of 75% from the cold face.

The freeze linings formed from the SCF slag batches studied were similar as to their microstructures. The only noticeable difference between the slag lots was that the fraction of magnetite observed in the lining was less in the second lot. The finding is in line with the chemical analyses and thus the oxidation degrees of the two slags received from the DB smelter, see Table 2.

The fraction of glassy phase in the freeze lining within the first 1-2 mm distance from the cold end is >90 %. In that fast solidified zone; no large metallic copper droplets can be seen, but small (<1-2 μm) copper globules are present. Their distribution is also essentially random. The volume fraction of metallic copper is low, much less than 5 %, as shown in Figure 6.

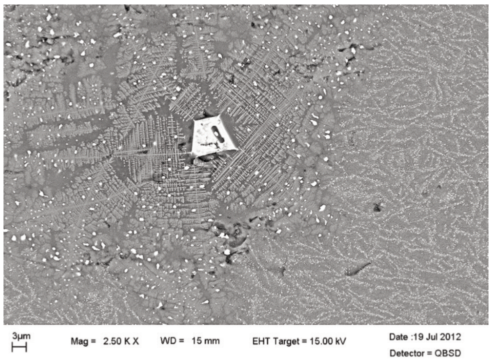

Figure 6. *A detail of microstructure of the predominantly microcrystalline slag close to the water cooled probe in a 40 min freeze lining run with the 2nd slag batch, showing a small spinel crystal (white) and its dendrite arms extending to the slag matrix, and chains of sub-microcrystalline silicates (×2500).*

The freeze lining formed from an industrial slag cleaning furnace slag of a DB smelter contains also large spinel (magnetite) crystals with diameters up to 20-40 μm, see Figure 7. They entrap metallic copper droplets precipitated from the slag in the SCF treatment, due to suitable copper-magnetite wetting properties. The spinel crystals prevent the metallic copper from coalescing and thus settling by gravity [17]. The secondary spinel arms formed during freeze lining solidification and crystallization of the intergranular slag are much smaller, less than 1 μm in diameter, as can be seen in Figure 6.

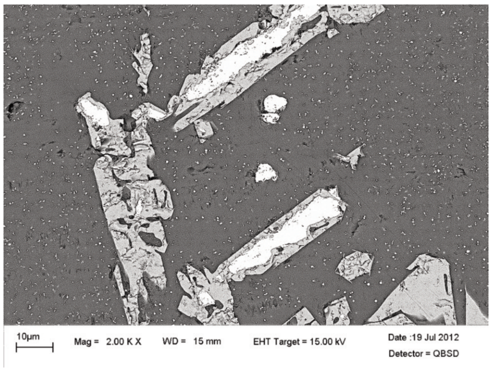

Figure 7. *Microstructure of a glassy hot-face slag in the freeze lining: very small copper droplets embedded in the slag matrix and large spinel crystals (light grey) entrapping metallic copper (white) within their dendrite arms (×2000).*

The glassy inter-granular phase in the freeze lining is enriched by silica. Its silica concentration is 50 wt-% SiO_2 or above throughout the lining thickness. The concentration analysed is much higher if compared with the average chemistry of the studied 2nd lot SCF slag of about 40 % SiO_2. The EDS analyses from the glassy phase, recalculated to oxides in cases the element is present with one oxidation degree only, were collected in Table 3. It also shows that the zone next to the water cooled probe is enriched with magnesia, lime and alumina, but its potassia concentration is clearly less than that of the bulk slag. This indicates high mobility of potassia in the slag.

Table 3. *Analysed composition of the intergranular phase in the SCF freeze lining by EDS (wt-%).*

	Cold end	Middle	End-to-middle	Hot end
MgO	5.97	1.17	1.52	4.87
Al_2O_3	8.6	11.86	11.19	8.44
SiO_2	50.18	62.05	57.58	49.73
K_2O	1.93	5.21	4.87	3.34
CaO	7.98	5.02	5.32	6.23
Fe	17.65	9.12	12.67	17.4
Cu	1.38	1.53	0.79	2.56

Due to the relatively high concentrations of alumina, lime and magnesia in the slag as compared with ordinary iron silicate slags in the copper smelting, the spinel precipitates dissolve also significant fractions of them, see Table 4. The concentrations of non-iron oxides in the large spinel crystals are essentially constant, from the cold face to the hot end. The spinel precipitates are mostly typical euhedral in shape, exhibiting as long dendrites in the polished sections.

Table 4. *Dissolution of other oxides in magnetite (spinel) crystals by EDS (wt-%).*

	Cold end	Middle	End-to-middle	Hot end
MgO	2.62	2.28	2.19	2.21
Al_2O_3	3.5	3.64	3.5	3.63
SiO_2	0.53	0.39	0.23	0.47
Fe	66.74	67.84	68.51	67.93
Cu	0.85	0	0	0.08

Metallic copper droplets and small precipitates contain a lot iron dissolved in the alloy. Table 5 shows the analysed iron and oxygen concentrations in large copper droplets obtained in the experimental runs. It is not clear whether the large metal droplets, see Figure 7, originate from the cooling process of the slag when the freeze lining is formed, or were they present already in the initial slag obtained from the smelter. This is a consequence of copper saturation of the SCF slag and the fact that smelting slags always contain some mechanically entrapped metal [17]. This may be possible because all droplets found in the freeze lining were less than 100 μm in diameter and the particles of that size will not settle in molten iron silicate slags [18].

Table 5. *EDS analyses of the metallic copper droplets in the SCF slag freeze lining (wt-%).*

	Cold end	Middle	End-to-middle	Hot end
O	0.82	0.48	0.53	0.5
Fe	3.34	2.42	3.19	2.78
Cu	95.84	97.11	96.28	96.71

3.3 Thermal stability of the freeze lining

The maximum duration of the freeze lining growth tests was two hours. In order to get an idea of the lining microstructure after a longer annealing, a sample from 1st lot slag freeze lining grown in contact with molten slag for 120 minutes was heat treated for 16 hours in an inert atmosphere of flowing dry argon at 918 °C. The glassy intergranular matrix reveals clear signs of crystallization after this treatment, as shown in Figure 8.

New spinel (light grey) has stacked on the primary spinel crystals (darker grey), and a lot of chains of nuclei are visible in the glassy continuous phase around the dendrites. The grain sizes of the new phases in the matrix are <5 μm and thus their assays are impossible to measure by SEM-EDS techniques accurately. EDS point analyses suggest that their compositions are close to olivine and pyroxene type silicates with stoichiometries $(Me)_2SiO_4$ and $(Me)SiO_3$, respectively, where Me is Al, Ca, Fe and Mg.

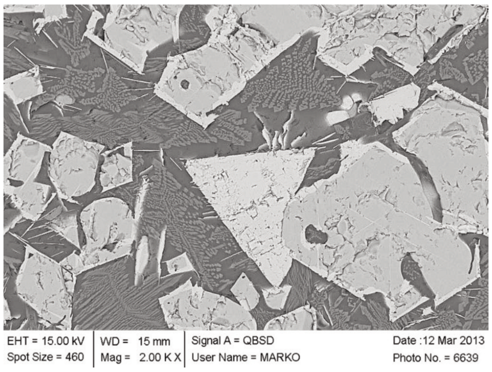

Figure 8. *Large spinel dendrites in partially glassy intergranular matrix of a freeze lining annealed at 918 °C, formed initially within 120 minutes on water cooled probe at 1390 °C slag temperature (×2000).*

4. Discussion

The slag cleaning furnace slag solidifies to the freeze lining largely as a glassy or amorphous intergranular phase from where only spinel (magnetite) crystals have been able to precipitate in large quantities. The other features of the freeze layer do not resemble those of the equilibrium solidification of the bulk slag. In order to generate a firm equilibrium background to the freeze lining formation processes, the thermodynamic solidification pattern was generated to the slag using the analysed average starting composition of the 2nd SCF slag lot, as shown in Table 2. The calculations were carried out with MTDATA software [19] (vers. 5.10) using Gibbs energy minimization techniques. The thermodynamic property data were extracted from the extensive slag database Mtox (vers 7.1) by NPL [20]. The computational system used was composed of 38 non-ideal solid or molten solution phases and seven pure (solid) substances.

The obtained equilibrium solidification path of the studied SCF slag is shown in Figure 9, displaying masses of the stable phases as a function of temperature. The calculations indicate that the melting range of the SCF slag is large, extending from the liquidus temperature of 1190 °C to the solidus temperature, at about 840 °C. The low melting point in comparison with pure iron silicate slags is due to its high potassium oxide and lime concentrations which extend the solidification clearly to temperatures below 1100 °C. Due to the high silica content and high viscosity, a significant superheat had to be used in the experiments.

As Figure 9 proves, the primary phase of the SCF slag solidification is spinel. Metallic copper is stabilised in the slag essentially at the same temperatures as magnetite, indicating that the slag precipitates out elemental copper during the equilibrium solidification due to ferrous-ferric oxide equilibria [21] and their redox reactions. The next solids coming out from the molten phase in the equilibrium solidification are various pyroxene-type silicates [22]. It is obvious based on the solidification equilibria of the SCF slag that the hot face of the freeze lining is below the liquidus temperature of the bulk slag.

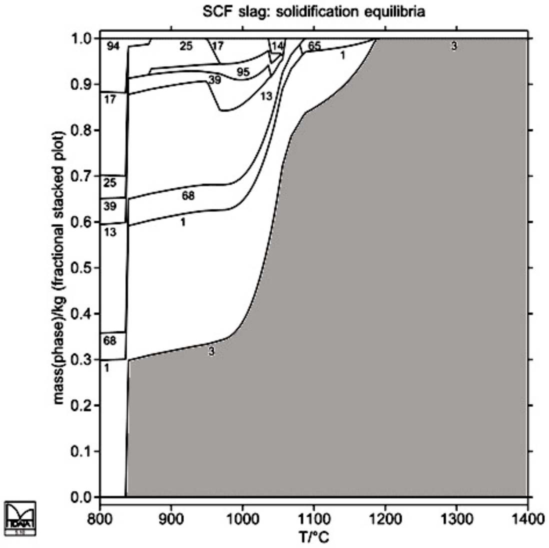

Figure 9. Equilibrium solidification path and stable phases of the studied SCF slag at 800 to 1400 °C; the phase labels refer to: 1-spinel, 3-liquid slag, 13 & 14-clinopyroxene, 17-feldspar, 25-cordierite, 39-orthopyroxene, 66-liquid metal, 68-Cu(s) and 94 & 95-SiO_2.

5. Conclusions

All industrial high-intensity electric furnaces are equipped with cooling elements and therefore the properties and management of the freeze linings is essential. The freeze lining growth rate in the SCF slag on a water-cooled metal surface is high which enables healing of a damaged electric furnace lining rapidly, within 10-30 minutes of the molten slag to cooling element contact. As the first step of freeze lining formation, an amorphous or glassy layer with a thickness of about 2 mm is formed. The solidification rate is slowed down after the initial contact of the slag with the stainless steel probe, and the freeze layer thickness is stabilized to a steady-state value within 30-40 minutes.

The solidification pattern of an industrial, high-silica SCF slag in the rapid growth of the freeze lining layer on a metallic cooling element is not a thermodynamic equilibrium process. Only primary spinel (magnetite) crystals are precipitating fast enough and able to form euhedral dendrites with diameters of about 5-30 μm. Majority of the freeze lining is formed by an amorphous or glassy phase which has clearly higher silica concentration than the average slag assay. It forms the rigid continuous freeze lining layer on the cooling element. This indicates that fast material transport processes occur in the solidifying slag. Spinel crystals do not generate a continuous network through the freeze lining and thus the glassy, continuous silica-rich intergranular phase gives strength to the freeze lining. Its precipitation from the bulk slag must thus dominate the growth rate, together with the heat flux through the lining [15].

It is evident, based on the equilibrium assemblages of the matrix, that in long-term exposure to smelting conditions parts of the glassy matrix will precipitate crystalline phases. Some initial signs of various pyroxene and olivine-type phases could be seen in current laboratory tests, with the maximum duration of 120 minutes at the molten slag contact, as well as in subsequent annealing for 16 hours in an inert gas atmosphere at 918 °C.

Acknowledgements

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