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Understanding the bottom buildup in an electric copper smelting furnace by thermodynamic calculations

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ABSTRACT
Thermodynamic calculations were used to investigate the liquidus temperature of the slag and the possible influence on the buildup formation in an electric copper smelting furnace. The impact of parameters such as Fe/SiO_2 ratio, partial pressure of oxygen and the content of the oxides ZnO, Al_2O_3 and Cr_2O_3 in the slag were investigated with respect to the liquidus temperature of the slag. Results show that the chromium content in the slag has the greatest impact on the liquidus temperature and on the formation of solid particles. The characterisation of the buildup done earlier showed that spinel phases were among the dominating phases. This is supported by the thermodynamic calculations in the present paper, where the chromite solid solution was found to be the primary precipitation phase.

RÉSUMÉ
On a utilisé des calculs thermodynamiques pour étudier la température de liquidus du laitier et l'influence possible sur la formation de l'accumulation dans un four électrique de fusion de cuivre. On a examiné l'impact de paramètres tels que le rapport Fe/SiO_2, la pression partielle d'oxygène et la teneur en oxydes ZnO, Al_2O_3 et Cr_2O_3 dans le laitier en fonction de la température de liquidus du laitier. Les résultats montrent que la teneur en chrome du laitier a le plus grand impact sur la température du liquidus et sur la formation de particules solides. La caractérisation de l'accumulation, effectuée plus tôt, a montré que les phases spinelles se trouvaient parmi les phases dominantes. Ceci est soutenu par les calculs thermodynamiques dans cet article, où l'on a trouvé que la solution solide de chromite était la phase de précipitation primaire.

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Copper smelting; FactSage; buildup; thermodynamic calculation; spinel; pyrometallurgy; electric furnace

1. Introduction

The Rönnskär smelter is located in the north part of Sweden. The plant processes both primary and secondary raw materials to produce copper, zinc clinker, lead and precious metals. The smelting of copper-rich feed material is carried out in either an Outokumpu flash furnace or a fluidised bed roaster followed by an electric smelting furnace. The produced matte is transferred to Peirce-Smith converters, with the resulting blister copper refined in an anode furnace before anode casting and subsequent electrorefining to high-purity cathode copper [1].

The two basic and widely applied smelting processes for copper concentrates today are flash smelting and bath smelting [2,3]. During the 1970s, bath smelting of copper concentrates using electric furnaces was common. Most are now closed due to the prohibitively high cost of electricity. However, the electric smelting furnace at the Rönnskär plant is still in operation and, since the furnace utilises an external heat source, oxidic and metallic materials can also be smelted.

A known challenge with operating electric smelting furnaces is the formation of buildup at the bottom, which, amongst other factors, prevents normal flow within the furnace and makes tapping more difficult. Therefore, Boliden Rönnskär and Luleå University of Technology started a joint project to characterise the buildup in the furnace with the aim of understanding more about the formation and how to control the buildup. The work started during 2013, when Boliden rebuilt their electric smelting furnace. The results from the characterisation are presented in a separate paper [4].

The characterisation showed that the buildup mainly consisted of spinel solid solutions with varying chemical composition together with solidified slag, matte and metallic phases. The last three phases were believed to have solidified during contact with the already existing buildup or refractory material. The major crystalline phases in the buildup were different spinel solid solutions, where chromite and magnetite dominated.

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Zonation between Cr-rich and Fe-rich areas within the same grain could be observed. The same tendencies could also be seen for aluminium and zinc. Table 1 summarises the key findings from the characterisation study.

The formation and precipitation of solid spinel, such as chromite or magnetite, from the liquid slag can contribute to the buildup [5]. Therefore, it is of interest to know how the slag system within the present electric smelting furnace is influenced by variation of the main element seen in the spinel solid solutions. Thermodynamic calculations using the software FactSage™ 6.4 [6,7] were therefore used to evaluate the influence Cr_2O_3, Al_2O_3 and ZnO have on the buildup formation.

The phase diagram for the FeO-Fe_2O_3-SiO_2 system is the basis for practical evaluation of copper smelting systems. Most slags also contain a few per cent of lime, magnesia and/or alumina together with other minor elements that are oxidised to the slag phase, such as Pb, Zn and Ni [3]. Although phase diagrams are a useful guide for prediction of the behaviour of slags, they are not always applicable to complex systems for industrial purposes, where the weight ratio of Fe/SiO_2, presence of minor elements and oxygen partial pressure play important roles in the stability region of the liquid phase. However, a great deal of work has been undertaken to increase the theoretical knowledge of more complex systems. Jak and co-workers have done extensive studies on determination of liquidus temperature and phase equilibria in systems relevant to base–metal extraction slags [8-15]. Zhao *et al.* [14,15] have studied the influence of alumina on the phase equilibria in fayalite slag containing high levels of zinc in equilibrium with metallic iron. They found that the presence of alumina resulted in the formation of a spinel phase, which was not the case without alumina addition. The formed spinel was a solid solution between the end members hercynite ($FeAl_2O_4$) and franklenite ($ZnFe_2O_4$). The liquidus temperature in the spinel primary phase field increased with increasing Al_2O_3 and ZnO concentration. However, the CaO content in their system was higher compared to the slag studied in the current paper. Zhao *et al.* [16] have also studied the influence of Al_2O_3 on the Al_2O_3-FeO-CaO-SiO_2 system in equilibrium with metallic iron. They found that the fayalite primary phase field expanded towards lower iron oxide concentration and also that the liquidus temperature decreased with an increasing Al_2O_3 content up to 6 wt-%. Henao *et al.* [10] investigated the liquidus temperatures and phase equilibria of copper smelting slags in the FeO_x-SiO_2-CaO-MgO-Al_2O_3 system at pO_2 10^{-8} atm. They found that the spinel liquidus temperature increased with an increasing content of MgO or CaO. The formed spinel was a solid solution between the end members Magnetite (Fe_3O_4), Hercynite ($FeAl_2O_4$) and Magnesioferrite ($MgFe_2O_4$). Chen *et al.* [17] studied the effect of Al_2O_3 and Cr_2O_3 on the liquidus temperature in the system MgO-FeO-SiO_2 with focus on the cristobalite and tridymite primary phase field in equilibrium with metallic iron. They found that an increased Cr_2O_3 content lowered the liquidus temperature in the primary phase field. However, the MgO content in their system was much higher compared to the slag studied in the present paper. Ilyushechkin *et al.* [18] studied the influence of Al_2O_3, CaO and Cr_2O_3 on the Fe-Mg-Si-O slags relevant for the platinum industry and found, for instance, that chromia increased the liquidus temperature by about 60 K in an oxygen-reduced atmosphere (CO_2:H_2 ratio = 132:1). The gas mixture corresponds to a calculated pO_2 between $8*10^{-7}$ and $3*10^{-4}$ at the temperatures used in the study.

The influence of minor oxides on slag liquidus temperature in processes has been studied with the aid of thermodynamic calculations. Cardona *et al.* [19] used thermodynamic modelling to understand the behaviour of minor oxides at the Paipote smelter. At the smelter, an electric furnace is operated as a slag cleaning furnace. Kongoli and Yazawa [20] have also used thermodynamic calculations to investigate the liquidus temperature of slags at intermediate oxygen partial pressure (pO_2 10^{-8}–10^{-6}) relevant for copper extraction. Their calculations showed that an increased content of Al_2O_3, CaO or MgO increases the liquidus temperature.

In the studies reported in the above-mentioned papers dealing with liquidus temperature either synthetic slag compositions are used or minor elements, such as Cr, are not included, which is of interest for the present work. It is known that chromium is a strong nucleation agent and will probably therefore influence the liquidus

Table 1. Characterisation summary of buildup.

Phase	Chemical nature	Morphology and association
Chromite (ss)	Cr-spinel with Fe, Zn, Al, Mg	Single crystals or agglomerates. Zonation between Cr-rich and Al-rich areas as well as Zn-rich.
Magnetite (ss)	Fe-spinel with Cr, Zn, Al	Single crystals or agglomerates.
Olivine (ss)	Fayalite with Zn, Ca, Cr, Mn, Mg	Solidified slag
Copper (ss)	Alloy with high Cu content	Droplets or matrix-type formation
Pyroxene (ss)	Pyroxene with Al, Ca, Mg, Zn	Inclusions between spinel phases and fayalite
Matte	Copper sulphide with Fe, Zn	Zonation between Cu-rich and Zn-rich sulphide
Speiss	Cu-rich with As, Sb, Sn, Ni	Droplets or thin strings

temperature to a large extent. Karamanov *et al.* [21] showed that chromia has a strong nucleation effect for spinels in high-iron-content glasses. Zhang *et al.* [22] investigated the precipitation and growth of spinel crystals in vanadium slag and found that $FeCr_2O_4$ crystals precipitated before crystals of FeV_2O_4 and Fe_2TiO_4. Among the members of the spinel group there is a wide range of solid solubility. For instance, there is a complete range of solubility between magnetite, zinc ferrite and between $ZnAl_2O_4$ and $ZnFe_2O_4$ [8,23]. In the current work the result from the characterisation[4] of the buildup in an electric smelting furnace, together with thermodynamic calculations, is applied to aid understanding of the formation mechanism.

2. Methodology

Thermodynamic calculations were used to understand the influence of Cr_2O_3, Al_2O_3 and ZnO on the buildup in the electric smelting furnace. The liquidus temperature of the slag and the primary precipitation phase as a function of Fe/SiO2 ratio were found by varying one parameter at a time. In the calculations, minor elements such as Sb, As and Bi, as well as S, were neglected. Cr is included, since it is expected to be of importance for the precipitation phase [21,22].

The thermodynamic calculations were performed using the software FactSage™ 6.4 and its databases FToxid and FactPS [6,7]. In order to establish the liquidus temperature all possible stoichiometric solid phases (152 in total) from FToxid and FactPS were used together with the liquid solution slag (FToxid-SLAGA) and the condensed solid solutions spinel (FToxid-SPINA), olivine (FToxid-OlivA), pyroxenes (FToxid-cPyrA, FToxid-oPyr, FToxidpPyrA) and monoxide (FT-Oxid-MeO_A) from FToxid. The solution phases were selected based on the findings in the previous characterisation. The gas phase was suppressed, except for O_2(g), which was used to set the partial pressure of oxygen.

Table 2 shows the average slag composition for the electric smelting furnace that was used for the parameter study. The composition is an average for the year 2012 and was chosen because 2012 was the last whole year with full operation before the rebuilding of the furnace in 2013. The entrained matte and dissolved copper were omitted in the calculation. The original analysis was normalised to 100%. The parameter of interest was then changed and the analysis was again normalised to 100% keeping the changed value fixed. The Fe/SiO_2 ratio was changed with the new total weight of Fe and SiO_2 being kept constant. When varying the content of Cr_2O_3, Al_2O_3 and ZnO, other components have been changed in such a way as to keep the proportions of all other components constant. The partial pressure of oxygen in the calculations was set to 10^{-9}, based on the result from the previous study [4], except when $p(O_2)$ was used as a variable.

All data were provided by Boliden Rönnskär and come from the normal production sampling.

The mineralogy of the samples was studied on polished samples using a Zeiss Gemini Merlin scanning electron microscope (SEM). Semi-quantitative and qualitative analyses were carried out using an energy dispersive spectrometer (EDS). The acceleration voltage was set to 20 keV and the emission current was 1.0 nA.

3. Results

At the Rönnskär smelter the electric furnace is operated with a weight ratio of Fe/SiO_2 in the slag of around 1. The monthly average for the year 2012 varied between 0.91 and 1.08 with the average of 0.99. The slag tapping temperature varied between 1229°C and 1367°C with an average of 1288°C. To investigate the influence of the changed parameters, the average slag compositions for 2012 were used, see Table 2.

The influence of the oxygen partial pressure has on the liquidus temperature can be seen in Figure 1. The liquidus temperature rises with an increasing partial pressure of oxygen. The primary precipitation phases are tridymite and spinel, depending on the Fe/SiO_2 ratio.

The chromium content in the slag has a large impact on the liquidus temperature. As can be seen in Figure 2, the temperature increases more than 20°C for an increase in Cr_2O_3 by 0.1 wt-% at the Fe/SiO_2 ratio relevant to the process. The primary precipitation phases are tridymite and spinel. For comparison, the calculated liquidus temperatures for the base case can be found in Figure 2.

The composition of the precipitated spinel phase one degree below the calculated precipitation temperature

Table 2. Average slag composition for the year 2012. Entrained matte and dissolved copper and sulphur have been omitted. Assay in wt-%.

	Al_2O_3	CaO	Cr_2O_3	Fetot	MgO	NiO	PbO	SiO_2	ZnO	Sum	Fe/SiO_2
Original	3.7	2.4	0.3	28.7	0.9	0.1	1.3	29.8	11.9	79.1	0.962
Normalised / base case	4.7	3.0	0.3	36.3	1.1	0.1	1.7	37.7	15.1	100.0	0.962

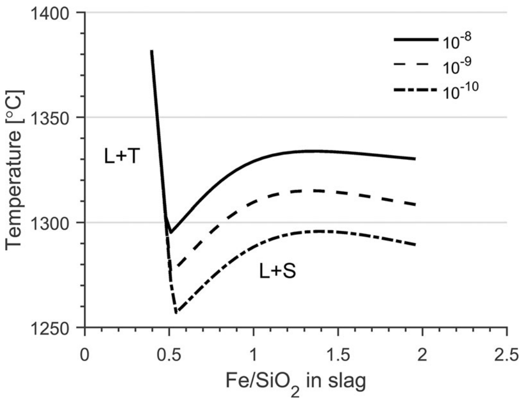

Figure 1. Calculated slag liquidus with varying Fe/SiO$_2$ weight ratio and pO$_2$. L (Liquid), T (Tridymite), S (Spinel).

seen in Figure 2 is presented in Figure 3. For a slag with Cr_2O_3 content higher than 0.1 wt-% (see Figure 3 b, c and d) chromium is a major component in the spinel phase at a Fe/SiO2 ratio of around 1. It can also be seen that as the Fe/SiO$_2$ ratio increases, the Fe and Al content within the spinel phase increases.

The effect of changed alumina and zinc oxide content can be seen in Figures 4 and 5, respectively. The influence on the liquidus temperature is not as large as with changed chromium content. The main precipitation phase is tridymite and spinel, depending on the Fe/SiO$_2$ ratio. For comparison, the calculated liquidus temperatures for the base case are also presented.

EDS point analysis data of different spinel grains detected during the previous characterisation [4] are presented in Table 3. The result is given as at-% and recalculated as element by stoichiometry with oxygen as base and valances given as in Table 3. The calculation is done with the INCA software from Oxford Instruments. Measurements below 0.5 at-% have been excluded due to instrument limitations. Most of the points correspond by chemistry to the spinel phase chromite with substitution of zinc and aluminium.

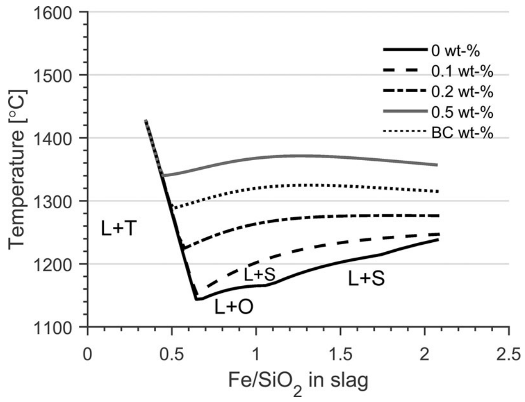

Figure 2. Calculated slag liquidus with varying Fe/SiO$_2$ weight ratio and Cr_2O_3. Base case corresponds to approximately 0.3 wt-% Cr_2O_3. L (Liquid), T (Tridymite), S (Spinel), O (Olivine).

4. Discussion

The results from the thermodynamic calculations showed that the primary precipitation phase formed at a Fe/SiO$_2$ ratio higher than about 0.5 for all changed parameters is a spinel phase. The exception is a chromia-free slag, see Figure 2, where olivine is the primary precipitation phase at Fe/SiO$_2$ ratio between 0.6 and 1.1. That the spinel phase is involved and also contribute to the buildup is evident both from the previous characterisation [4] and the calculations in the present paper. Comparing Figures 1, 2, 4 and 5 it can be seen that chromia has the largest influence on the liquidus temperature at the Fe/SiO2 ratio relevant for the process with a rise in liquidus temperature of about 20 degrees with an increased chromia concentration of 0.1 wt-%.

The characterisation of the buildup showed, as mentioned earlier, that large parts were spinel phases. EDS point analysis data of different spinel grains found during the characterisation are presented in Table 3. The composition in the different points indicates that the majority of spinel grains could be said to belong to the end member chromite by chemistry with substitution of Zn and Al. This corresponds well to the result from the calculation, see Figure 3. Already at low concentration of chromia (0.1 wt-% according to calculation) in the current system, chromite spinel is formed and can contribute to buildup. Based on this it can be concluded that the buildup is primarily formed by settling of precipitates from the bulk slag and not by deposition due to cooler furnace walls. However, it should be remembered that the calculations done in the present paper is restricted to changes in the liquid slag only. In the real process the slag can interact with both matte and metal which is the case for the data presented in Table 3. The changes seen in the calculations can therefore be both larger and smaller.

Chromia is a strong nucleation agent, which has been demonstrated by Karamanov *et al.* [21] for high iron content glasses. It is also known that chromia is a source for hearth buildup in, for instance, the smelting of PGM concentrates, where Cr_2O_3 content can reach up to a few per cent [5,24]. In the previous characterisation, the majority of the spinel crystals found were chromium-rich and had a varying composition.

A varying chrome content in the feed could therefore lead to formation of spinel at different temperatures and, therefore, also with varying composition. This would explain the varying composition seen between different spinel grains in the characterisation. Similar findings

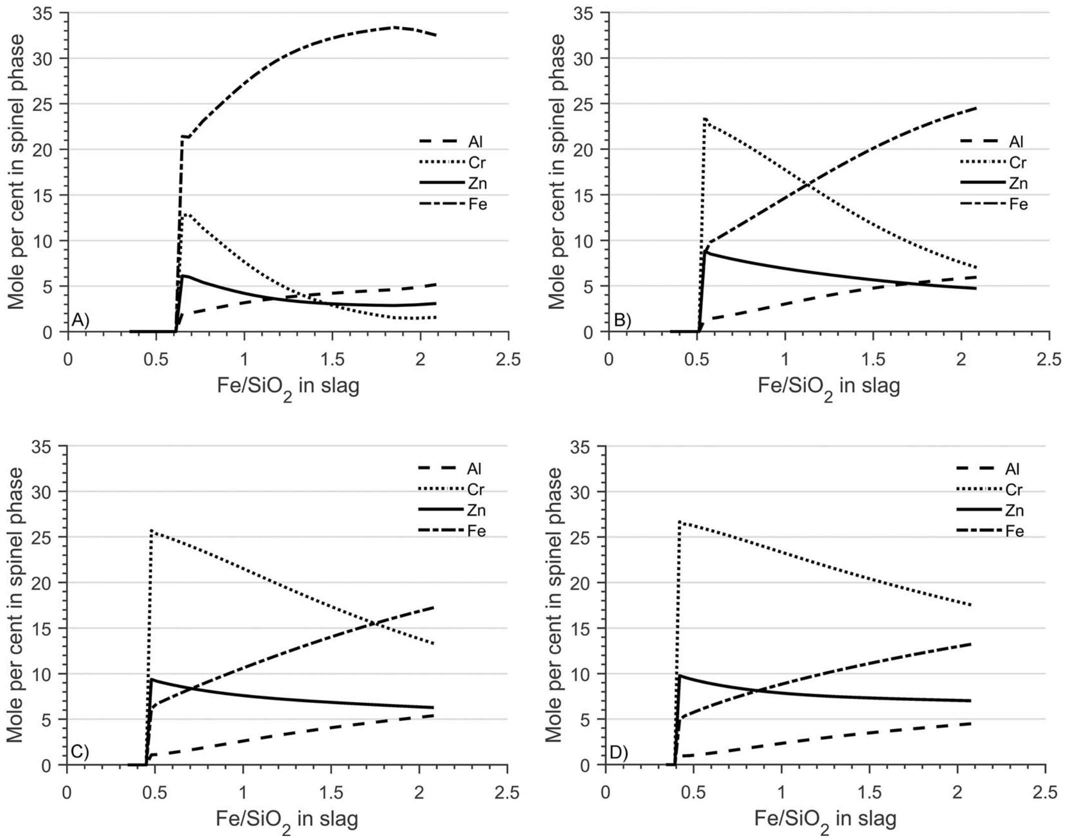

Figure 3. Composition of the first precipitated spinel phase from a slag with varying Fe/SiO_2 weight ratio. A) 0.1 wt-% Cr_2O_3 B) 0.2 wt-% Cr_2O_3 C) Base case (approximately 0.3 wt-% Cr_2O_3) D) 0.5 wt-% Cr_2O_3. The temperature is one degree below the precipitation temperature in Figure 2.

are reported by Nell [5] for smelting PGM concentrate in an electric smelting furnace. During equilibrium experiments, it has been verified that the bulk composition and temperature have an effect on the chromium content in the formed spinel phase [18].

Zhao *et al.* [16] studied the influence of alumina on synthetic fayalite slag and found that additions of up to 6 wt-% lowered the liquidus temperature. Similar results were found in studies with industrial fayalite slag samples by Mostaghel *et al.* [25]. However, at additions above 10 wt-%, the liquidus temperature increased. The explanation was that the system changed the primary crystallization phase field from fayalite to hercynite, which has a higher liquidus temperature compared to

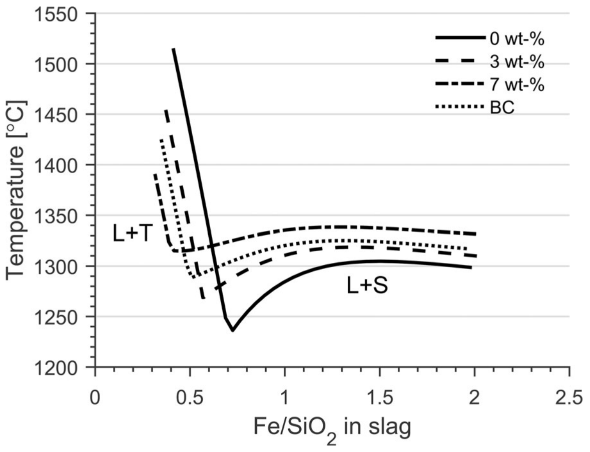

Figure 4. Calculated slag liquidus with varying Fe/SiO_2 weight ratio and Al_2O_3. Base case corresponds to approximately 5 wt-% Al_2O_3. L (Liquid), T (Tridymite), S (Spinel).

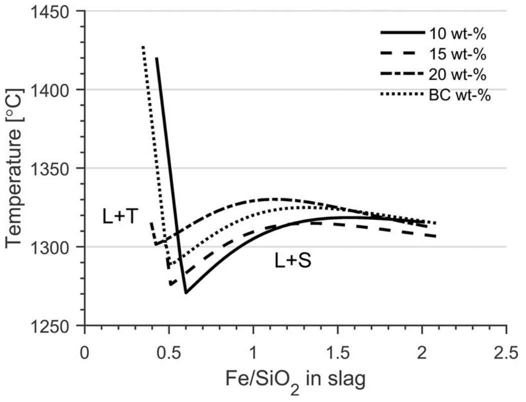

Figure 5. Calculated slag liquidus with varying Fe/SiO_2 weight ratio and ZnO. Base case corresponds to approximately 15 wt-% ZnO. L (Liquid), T (Tridymite), S (Spinel).

Table 3. EDS point analysis data of different spinel grains. The result is given as at-% and recalculated as element by stoichiometry with oxygen as base and valances as given.

Sample	Al^{3+}	Cr^{3+}	Fe^{2+}	Mg^{2+}	O^{2-}	Zn^{2+}	SUM
A	8.2	16.5	11.8	0.9	56.2	6.5	100.0
B	7.3	17.8	11.2	0.7	56.3	6.7	100.0
C	9.2	15.3	11.7	1.0	56.1	6.7	100.0
D	8.7	14.6	13.4	1.0	55.8	6.4	100.0
E	7.2	18.2	10.7	0.9	56.3	6.7	100.0
F	7.7	16.1	13.0	1.0	55.9	6.4	100.0
G	6.2	19.3	10.5	0.8	56.4	6.8	100.0
H	21.9	2.3	10.3		56.1	9.4	100.0
I	4.3	10.6	25.2		53.7	6.3	100.0
J	4.9	18.2	13.9	0.5	55.8	6.7	100.0
K	1.6	23.1	11.8		56.2	7.3	100.0
L	1.5	23.2	12.3		56.2	6.9	100.0
M	4.0	22.4	9.4	0.7	56.6	6.8	100.0
N	4.0	22.2	9.9	0.7	56.6	6.6	100.0
O	3.0	15.6	18.8		54.7	8.0	100.0
P	5.2	21.2	9.0	0.9	56.6	7.1	100.0
Q		25.7	10.1		56.4	7.8	100.0
R	7.2	18.6	9.9	1.2	56.4	6.7	100.0
S	12.8	12.9	10.0	1.1	56.4	6.8	100.0
T	12.7	12.9	10.2	1.0	56.4	6.9	100.0
U	6.2	19.2	11.2	0.9	56.4	6.1	100.0
V	0.9	2.8	42.5		50.9	2.8	100.0
X	1.0	4.7	39.7		51.4	3.2	100.0
Y		2.5	45.0		50.6	1.9	100.0
Z	0.9	25.4	9.6	0.5	56.6	7.0	100.0
Min	0.9	2.3	9.0	0.5	50.6	1.9	
Max	21.9	25.7	45.0	1.2	56.6	9.4	

fayalite. The simulated influence on the liquidus temperature in this study differs from the above. The reason for the difference is inclusion of chromium and, as can be seen in Figure 2, even a low amount of chromium increases the liquidus temperature substantially.

The characterisation of the buildup in an electric copper smelting furnace was described earlier [4]. The characterisation showed that the buildup mainly consisted of spinel solid solutions, solidified fayalite slag, matte and metal phases. The major crystalline phase found was spinel phase. The spinel grains had no homogenous chemical composition; instead, the composition varied both between different grains and also within the grains. The main elements that varied were Fe, Cr, Al and Zn. With the thermodynamic calculations done in the present paper, the objective was to improve knowledge and understanding as to why the buildup is formed and, subsequently, also how to control the buildup. It should be mentioned that the calculations in the present paper are limited to the composition of the slag phase. In the real process, the slag is in contact with, for instance, matte and concentrate. A change in the slag composition will influence the matte composition and vice versa and this was not taken into consideration in the present calculations.

5. Conclusions

Based on the present study, the chrome content is the most important factor that influences the formation of the buildup, since it has a significant effect on the liquidus temperature and by controlling the chrome intake it would therefore be possible to control the formation of the buildup. The thermodynamic calculations done in the present paper support the characterisation performed in an earlier paper.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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