Sulphide Capacity and Mineralogy of BaO and B₂O₃ Modified CaO–Al₂O₃ Top Slag

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BaO and B₂O₃ were used to improve the metallurgical properties and valorisation potential of CaO–Al₂O₃ based top slag. The sulphide capacity of BaO–B₂O₃ modified CaO–Al₂O₃ based top slag was measured and compared with calculated values using the FactSage software. The effect of slag basicity ($\text{CaO} + \text{MgO}/(\text{Al}_2\text{O}_3 + \text{B}_2\text{O}_3) = 0.6\text{--}1.4$) and BaO content on sulphide capacity was discussed. The mineralogy of the slag after experiments was observed. The crystallisation path of the slag during cooling was predicted based on a Scheil-Gulliver model. Consequently, the effect of the slag basicity and B₂O₃ on slag mineralogy and glass formation ability was discussed. It is found that the sulphide capacity is mainly influenced by slag basicity. BaO addition improves the slag sulphide capacity only for slag with low basicity (< 1.2). B₂O₃ addition enlarges the liquid region at 1600°C but decreases the slag sulphide capacity. High basicity and B₂O₃ addition benefit the glass formation and would improve the slag valorisation potential in applications where the glass content is important.

KEY WORDS: sulphide capacity; mineralogy; slag valorisation; BaO–B₂O₃ addition.

1. Introduction

Top slag used in a ladle refining process improves the steel cleanliness by (i) preventing metal reoxidation through impeding air infiltration; and (ii) absorbing impurities like sulphur/phosphorus and non-metallic inclusions. In general, slags with a low melting temperature, low viscosity, low oxidation potential and high sulphide capacity are preferable.^{1–3)} The low melting temperature and low viscosity ensure the fluidity during the metallurgical processing; the high sulphide capacity and low oxidation potential benefit the thermodynamics of sulphur impurity removal. CaF₂ (less than 10 wt%) modified CaO–SiO₂ (CSF) based slag fulfils these requirements and therefore exhibits excellent metallurgical properties. This CSF slag, however, is so basic that $\beta\text{-C}_2\text{S}$ is formed during the post-metallurgical cooling process. The $\beta\text{-C}_2\text{S}$ transforms upon cooling into $\gamma\text{-C}_2\text{S}$ and this transformation is accompanied with a considerable volume increase, leading to material disintegration.⁴⁾ Thus, the valorisation of this slag as aggregate becomes a challenge. In addition, the use of CaF₂ may increase environment risks. To solve the slag valorisation and environmental issues, an option is to develop a fluorine free and non-disintegrating slag while at the same time not jeopardizing the metallurgical quality (e.g. desulphurisation) of the steel production.

CaO–Al₂O₃ (CA) based top slag has been considered as a potential substitute due to its good refining properties.⁵⁾ In the first phase of our studies,^{6–8)} the desulphurisation of

stainless steel (45–150 ppm sulphur) by using the current CSF slag and an optimised CA based synthetic slag (with 50% CaO, 40.4% Al₂O₃, 4.3% SiO₂, 2.1% Fe₂O₃, 1.7% TiO₂ and 0.6% MgO) has been performed to prove the concept of substitution. Although a relatively low sulphide capacity was obtained for the CA slag due to its low basicity (the RO/M₂O₃ ratio is used to represent the slag basicity hereinafter, $R = \text{Ca} + \text{Mg}$, $M = \text{Al} + \text{B}$), an equivalent desulphurisation efficiency and an improved steel cleanliness were obtained with this optimised CA slag. The optimised CA slag remains on the lime saturated liquidus and therefore provides a constant desulphurisation capacity, while the sulphide capacity of CSF slag decreases as the reaction proceeds. The kinetics condition for desulphurisation is also improved using CA slag due to its fast fluxing. This CA slag however was found to easily crystallize during cooling (even using water quenching), which limits its further valorisation. It has been reported that amorphous slags have excellent valorisation potential due to their low solubility of heavy metals and good hydrating properties.^{9–11)} Therefore, this CA based slag has to be further modified to improve (i) its valorisation potential by enhancing the glass formation ability and (ii) its metallurgical performance by increasing the sulphide capacity.

B₂O₃ is an effective flux agent to improve the slag fluidity and glass formation ability.^{12–15)} Wang *et al.* compared the effect of CaF₂ and B₂O₃ on viscosity and melting temperature of CA based slags ($\text{C/A} = 1.1\text{--}4.0$).¹²⁾ By substituting the CaF₂ with B₂O₃, they found that (1) the melting temperature of the slag decreased remarkably; (2) the temperature range for low viscosity was expanded and the stability of

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slag viscosity varying with temperature was improved; and (3) slag could be controlled in a higher basicity range while still maintaining a good fluidity. Sung *et al.* found that the number of Si–O and Al–O broken bonds increased in Al₂O₃–SiO₂ melts with B₂O₃ addition, which decreases the crystallization temperature and benefits the glass formation.¹³⁾ On the other hand, Arturo reported the effect of CaF₂ and B₂O₃ on sulphide capacity.¹⁴⁾ They pointed out that the addition of B₂O₃ decreases the free O²⁻ in the melt and the substitution of CaF₂ with B₂O₃ lowered sulphide capacity of CaO–SiO₂ based slags. Thus, B₂O₃ can be used to improve the slag valorisation potential but jeopardizes the metallurgical quality (*e.g.* desulphurisation) of the steel production. The latter might be solved by BaO addition. Gao *et al.* measured the effect of BaO on sulphide capacity and concluded that BaO had strong affinity for sulphur and could release a large amount of free O²⁻. Its addition consequently increases the sulphide capacity.¹⁵⁾ However for the combined use of BaO and B₂O₃, *i.e.* BaO–B₂O₃ modified CaO–Al₂O₃ slag, knowledge on the sulphide capacity and the glass formation is still limited.

In the present work, the sulphide capacity of the BaO–B₂O₃ modified CA based top slag was measured through gas-slag-metal interactions and calculated with the aid of FactSage software. The slag mineralogy and microstructure after the experiments were evaluated. The effect of BaO, B₂O₃ and slag basicity on sulphide capacity and slag mineralogy was discussed based on thermodynamic considerations. This work is expected to improve the slag valorisation and metallurgical properties of top slag used in ladle refining.

2. Experimental

2.1. Materials Preparation

A few grades of synthetic slag were prepared. Analytical reagent grade CaCO₃ was first calcined at 1000°C for 10 hours to obtain high purity CaO. The obtained CaO powder was then mixed with Al₂O₃, MgO, B₂O₃ and BaO oxides in ethanol for 24 hours in a multi-direction tubular mixer, using ZrO₂ milling balls. The suspension was then dried in a rotary evaporator, thereafter the mixed powder (50 g) was

pre-melted at 1600°C for 1 h in a platinum crucible in air in a bottom loading furnace (AGNI-ELT 160-02, spring type). The pre-melted slag was then further size reduced to below 40 µm by a centrifugal grinding mill. Detailed chemical composition of the slag is listed in **Table 1**. The slags were varied with basicity, BaO and B₂O₃ contents to investigate their effects on sulphide capacity and slag mineralogy.

2.2. Sulphide Capacity Measurement

The sulphide capacity (*C_S*), *i.e.* the sulphur absorption ability of metallurgical slag, is described by Fincham and Richardson as follows:¹⁶⁾

$$C_s = \exp\left(-\frac{\Delta G_2^\circ}{RT}\right) \cdot \left(\frac{a_{(O^{2-})}}{f_{(S^{2-})}}\right) \dots\dots\dots (1)$$

where $a_{(O^{2-})}$ is the activity of oxide ions in the slag; $f_{(S^{2-})}$ the activity coefficient of sulphide ions in the slag; R the gas constant, 8.314 J/(mol·K); T the temperature in K; ΔG_2° the Gibbs energy of the gas-slag reaction (2),^{16,17)} J/mol. Combining the definition of sulphide capacity and the reaction (2), the sulphide capacity can be expressed as Eq. (3):

$$\frac{1}{2}S_2(g) + (O^{2-}) = (S^{2-}) + \frac{1}{2}O_2(g) \quad \Delta G_2^\circ = 118\,535 - 58.8T \dots\dots\dots (2)$$

$$C_s = (\%S) \sqrt{\frac{P_{O_2}}{P_{S_2}}} \dots\dots\dots (3)$$

where (%S) is the weight percentage of sulphur content in the slag; P_{O_2} and P_{S_2} respectively the partial pressure of O₂ and of S₂ gas in the system, Pa. Therefore, the sulphide capacity can be measured with Eq. (3) through the desulphurisation equilibrium of gas-slag interaction. On the other hand, the gas-metal (usually Cu) equilibrium with respect to desulphurisation can be expressed as reaction (4):¹⁸⁾

$$\frac{1}{2}S_2(g) = [S]_{Cu} \quad \log K_4 = \frac{5\,430}{T} - 0.815 \dots\dots\dots (4)$$

combining Eqs. (3) and (4), the sulphide capacity can be also expressed in the form of Eq. (5):

Table 1. The pre-melted slag composition used in the experiment.

Slag No.	Slag composition (wt%)						RO/M ₂ O ₃ = (CaO + MgO)/(Al ₂ O ₃ + B ₂ O ₃)
	CaO	Al ₂ O ₃	BaO	MgO	B ₂ O ₃	Others	
1	31.0	51.6	4.8	7.6	5.0	0	0.68
2	36.7	45.9	4.8	7.6	5.0	0	0.87
3	41.3	41.3	4.8	7.6	5.0	0	1.06
4	45.0	37.6	4.8	7.6	5.0	0	1.23
5	48.2	34.4	4.8	7.6	5.0	0	1.42
6*	50.0	40.4	0	0.6	0	9	1.09
7	47.2	39.3	1.0	7.6	5.0	0	1.24
8	50.4	36.0	1.0	7.6	5.0	0	1.41
9	49.3	35.2	2.9	7.6	5.0	0	1.42

* measured with XRF, others = 4.3% SiO₂ + 2.1% Fe₂O₃ + 1.7% TiO₂ + 0.9% impurity, and basicity = (CaO + MgO)/(Al₂O₃ + SiO₂ + TiO₂)

Fig. 1. The schematic diagram of the experimental set-up.

$$C_S = \frac{(\%S)}{[\%S]_{Cu}} (P_{O_2})^{\frac{1}{2}} K_4 \quad \dots\dots\dots (5)$$

where $[\%S]_{Cu}$ is the weight percentage of sulphur content in the copper phase. Thus, the sulphide capacity can also be obtained by Eq. (5) based on the measured sulphur distribution ratio and oxygen partial pressure, *i.e.* by means of gas-slag-metal equilibrium.

In the present study, the sulphide capacity was measured based on gas-slag-metal equilibrium (Eq. (5)). The gas-slag-metal equilibrium experiment was performed with a high temperature vertical tube furnace (Fig. 1, Gero HTRV 100-250/18, with MoSi₂ heating elements). 15 g of copper (containing 0.15 wt% S in the form of FeS) covered with 3 g of the pre-melted synthetic slag was melted in a molybdenum crucible (the ID is 30 mm, OD 35 mm and the height 50 mm) at 1 600°C under a flowing CO–CO₂–Ar gas mixtures. The volume ratio of CO and CO₂ was set to 30 to control the partial pressure of oxygen. The equilibrium oxygen partial pressure at 1 600°C was 1.91×10^{-10} Pa. According to results obtained in the preliminary experiment (Fig. 2), the sulphur distribution between slag and metal (L_S , open triangle) remained more or less constant beyond 6 hours of interaction. It should be mentioned that more sulphur (around 0.8 wt%) is added in the metal phase in the preliminary tests. The equilibration time was therefore set to be 6 hours for the gas-slag-metal interaction with respect to desulphurisation. After the equilibration, the crucible was lifted to the cold part of the furnace for cooling. The furnace chamber was rinsed with Ar to remove the remaining CO, the crucible was then taken out of the furnace chamber and sprayed with flushing argon gas.

2.3. Sample Analysis and Characterisation

The equilibrated copper and slag samples were collected after the experiments. The obtained slag sample was divided

Fig. 2. The evolution of sulphur in metal and slag and sulphur distribution ratio ($T.S_{slag}/T.S_{Cu}$) as a function of equilibration time.

into two parts. The first part was used for slag mineralogy and microstructure characterisation by X-ray diffraction (XRD, Siemens D500 SC40 equipped with a Cu tube) and electron probe microanalysis (EPMA, JEOL JXA-8530F). The second part of slag sample was crushed and milled to a size below 40 μ m, then measured with a LECO combustion analyser (CS-230) for the total sulphur content (T.S). At least two samples were measured for each test. The average value was then used for the T.S if the relative error between these two measurements is less than 10%, otherwise more samples were measured. The total sulphur content of the copper phase was measured similarly.

3. Results and Discussion

3.1. Sulphide Capacity and Its Significant Factors

3.1.1. The Calculated and Measured Sulphide Capacity of the BaO and B₂O₃ Modified CaO–Al₂O₃ Top Slag

The sulphide capacity can be calculated with the aid of FactSage software by using a gas-slag equilibrium method. During the calculation, the thermodynamic equilibrium between the slag and a gas mixture (O₂–S₂) at a specific temperature (1 600°C) was calculated using the equilibrium module. The partial pressure of the O₂ and S₂ were fixed at 10^{-10} and 10^{-6} respectively. The FactSage 6.3 version and the database of FactPS and FToxid were used during the calculation. On substitution of the equilibrated partial pressure of O₂ (g) and S₂ (g), as well as the equilibrated sulphur content in the slag phase into Eq. (3), the sulphide capacity can be calculated (denoted as ‘calculated value’). Figure 3 shows the calculated iso-log C_S diagram for CaO–Al₂O₃–MgO–5 wt% B₂O₃ slag system at 1 600°C. The influence of BaO on the liquidus temperature, as well as on the sulphide capacity is not considered during the calculation due to a lack of relevant thermodynamic data, *i.e.* the composition of other components was kept constant and the amount of BaO was set to zero during the FactSage calculation.

It can be seen from Fig. 3 that the liquidus area at 1 600°C (marked with a dotted line) is enlarged by B₂O₃ addition. This is believed to be the result of the interaction between B₂O₃ and MgO/CaO. The formation of low melting temperature eutectic compounds, *e.g.* CaO·B₂O₃ ($T_m = 1\,100^\circ\text{C}$)

and $\text{MgO} \cdot \text{B}_2\text{O}_3$ ($T_m = 988^\circ\text{C}$) lowers the liquidus of the slag.^{12,19)} On the other hand, since B_2O_3 has a relatively low melting point (around 450°C), its addition can promote slag melting in steelmaking practice. Secondly, the sulphide capacity increases with increasing CaO content. The basic component CaO provides free oxygen ions (O^{2-}) for the desulphurisation reaction (Eq. (6)), and therefore raises the slag sulphide capacity. The iso-log C_s curves shown in Fig. 3 are approximately parallel to the lime saturated portion of the liquidus and the C_s value increases as the slag composition approaches the lime saturated liquidus. From a thermodynamic viewpoint, the lime saturated slag therefore can be recommended to maximize the desulphurisation.

On the other hand, the sulphur content of slag and metal after the gas-slag-metal equilibration experiment was measured with LECO and has been listed in **Table 2**, in which T.S represents the total sulphur content; and L_s the measured sulphur distribution ratio between slag and metal phase. It

should be noted that a small amount of Cu droplets was entrapped in the slag phase. These Cu droplets, however, have limited influence on the measured T.S in slag phase (< 10 ppm assuming Cu contains 3 000 ppm sulphur, Table 2) and on the measured sulphide capacity due to their small amount, *i.e.* less than 0.2 vol.% based on image analysis. Based on these experimental data, the sulphide capacity can be obtained through Eq. (5), and is denoted as ‘measured value’. The calculated and measured sulphide capacity values are given in Table 2 as well. The comparison of the calculated and measured sulphide capacity is shown in **Fig. 4**. It can be seen that the data points slightly diverge from the one by one relation (the dash line). This is probably due to the BaO addition, which has a complex influence on sulphide capacity. This complex effect however cannot be taken into account during the calculation of FactSage (version 6.3) due to the lack of thermodynamic data. The influence of additives on sulphide capacity is discussed in detail in the following section. The disagreement between the calculated and measured C_s for slag 6 without BaO is probably due to the inaccuracy of its composition (Table 1), *i.e.* around 1% impurity and 2.3% Fe_2O_3 . The divergence would be around 1.1% assuming the impurity and Fe_2O_3 to be SiO_2 and FeO respectively during the calculation.

Fig. 3. The calculated iso-log C_s of $\text{CaO-Al}_2\text{O}_3\text{-MgO-5\% B}_2\text{O}_3$ slag (wt%) with FactSage at 1600°C , the solid circles represent the experimental slag compositions.

Fig. 4. Comparison of measured and calculated sulphide capacity at 1600°C .

Table 2. The sulphur content after gas-metal-slag equilibrium, the measured and calculated sulphide capacity (C_s).

Slag No.	T ($^\circ\text{C}$)	T.S (ppm)		L_s	log C_s		Divergence (Meas. – Calc.)/Meas.
		Slag	Metal		Measured	Calculated	
1	1 600	620	3 050	0.203	–3.47	–3.54	–2.1%
2		1 150	2 800	0.411	–3.16	–3.20	–1.3%
3		2 250	2 650	0.849	–2.85	–2.88	–1.2%
4		3 950	2 200	1.795	–2.52	–2.62	–4.1%
5		5 300	1 900	2.789	–2.33	–2.31	0.7%
6		2 680	2 080	0.889	–2.67	–2.55	4.6%
7		3 150	2 250	1.400	–2.63	–2.62	0.6%
8		5 150	1 800	2.861	–2.32	–2.26	2.4%
9		5 050	1 950	2.590	–2.36	–2.32	1.8%

3.1.2. Influence of Basicity, B_2O_3 and BaO on Sulphide Capacity

Figure 5 gives the influence of the B_2O_3 addition on the calculated sulphide capacity. Two approaches are used during the calculation: A1 and A2 where CaO:Al₂O₃:MgO ratio (A1) and RO/M₂O₃ ratio (A2) are kept constant respectively. In both cases, the B_2O_3 addition decreases the sulphide capacity, indicating that (1) B_2O_3 is an acid oxide^{20,21)} and decreases the sulphide capacity (2) B_2O_3 is more acid than Al₂O₃,²²⁾ and therefore the substitution of Al₂O₃ with B_2O_3 (*i.e.* keeping RO/M₂O₃ ratio constant) still decreases the sulphide capacity. Although Fig. 3 shows that the B_2O_3 addition enlarges the liquid region of CaO–Al₂O₃–MgO slag system at 1 600°C, the calculated highest log C_s without any CaO precipitation is around –2.0 at 1 600°C in CaO–Al₂O₃–MgO slag system, while it decreases to around –2.1 for CaO–Al₂O₃–MgO–5 wt% B_2O_3 slags. Therefore, the B_2O_3 addition decreases the sulphide capacity of the CA based slags.

The measured sulphide capacity as a function of RO/M₂O₃ and (RO + BaO)/M₂O₃ ratios are illustrated respectively in the upper and lower diagrams of **Fig. 6**. The logarithm of the sulphide capacity shows a linear relationship

with both the RO/M₂O₃ and (RO + BaO)/M₂O₃ ratios, indicating that the sulphide capacity of a slag system strongly depends on the slag basicity. The basicity represents the level of free O^{2–} ions in liquid slag, and high basicity means high content of free O^{2–} for desulphurisation reaction (Eq. (6)). As basic oxides, CaO and MgO release free O^{2–} in molten slag, while B_2O_3 is an acid oxide and absorbs free O^{2–}.^{20,21)} Al₂O₃ is an amphoteric oxide and its behaviour depends on the basicity of the slag. In case of RO/M₂O₃ > 1, Al₂O₃ would behave as an acid oxide and absorb free O^{2–} to form AlO₄^{5–} tetrahedral units. Al₂O₃ would also behave as a basic oxide and release free O^{2–} in case of RO/M₂O₃ < 1.²²⁾ The linear relation between the log C_s and (RO + BaO)/M₂O₃ in the lower part of Fig. 6 suggests that BaO acts as a basic component in the present slag systems. Thermodynamically, BaO releases free oxygen ions at high temperature and has a strong affinity for sulphide ions, and therefore enhances the desulphurisation ability of slag.²³⁾ **Figure 7** shows the influence of BaO content on slag sulphide capacity. Through the comparison of the calculated and measured sulphide capacity, it can be seen that BaO addition has limited effect on the sulphide capacity of slag with a high basicity (the solid dot with RO/M₂O₃ = 1.4), while it increases the sulphide capacity of the slag with a low basicity (the solid square symbol with RO/M₂O₃ = 1.2). Moreover, the sulphide capacity is increased with increasing BaO content for low basicity slag. This is probably related with the thermodynamic nature of the desulphurisation product (*i.e.* BaS) in the case of BaO addition. The BaS is not stable and tends to decompose after its formation, especially in slag with a high CaO content.¹⁵⁾ Therefore, the addition of BaO is more effective on increasing sulphide capacity for the slags with low basicity. In addition, BaO could increase the polymerization of aluminosilicate anions, increasing the slag viscosity,²⁰⁾ which affects the desulphurisation kinetics. Sukenaga *et al.*²⁰⁾ found that the addition of BaO in CaO–Al₂O₃–SiO₂ slag increases aluminosilicate anions (Q²(1Al)) and consequently increases slag viscosity. Taking into account the limited effect of BaO on the increase of sulphide capacity at high basicity and its negative effect on the desulphurisation kinetics, it can be concluded that it is not very helpful to use

Fig. 5. Influence of the B_2O_3 addition on the calculated sulphide capacity at 1 600°C, A1 and A2 represent CaO:Al₂O₃:MgO ratio and RO/M₂O₃ ratio kept constant during calculation.

Fig. 6. Relation between sulphide capacity and RO/M₂O₃ ratio, where R = Ca + Mg, M = Al + B.

Fig. 7. Effect of BaO addition on slag sulphide capacity.

BaO. Nevertheless, BaO may be used for low basicity ($RO/M_2O_3 < 1.2$) slags to increase their sulphide capacity.

3.2. Slag Mineralogy

3.2.1. Effect of Basicity on Slag Mineralogy

Figure 8 shows the microstructure of slags for different basicity. $MgAl_2O_4$ spinel phase is distributed in $CaAl_2O_4$ (CA) matrix in low basicity slag ($RO/M_2O_3 = 0.68$, Fig. 8(a)); $Ca_3Al_4MgO_{10}$ (C_3A_2M) is crystallized in glassy matrix in the slag with moderate basicity ($RO/M_2O_3 = 1.06$, Fig. 8(b)); and limited amount of periclase phase (unassimilated

MgO) is formed in glassy matrix with high basicity ($RO/M_2O_3 = 1.42$, Fig. 8(c)).

The XRD patterns of the slags with different basicity are shown in **Fig. 9**. It can be seen that diffraction peaks of the crystal phases have gradually disappeared, which implies that the amount of crystalline phase decreases and the slag is transformed into an amorphous glassy phase by increasing basicity from $RO/M_2O_3 = 0.6$ to 1.0 – 1.4 . In general, glass transformation is governed by the nucleation and crystal growth that takes place during cooling of the melt.^{24,25} The glass phase can be regarded as the supercooled liquid with relatively higher viscosity, and an interrupted phase transformation would benefit its formation. The phase transformation during the cooling is directly linked to slag composition, which determines the transition temperature, *e.g.* liquidus, solidus and glass transition temperatures. **Figure 10** shows the calculated phase transition temperatures of the present slags. The solidus temperature (solid dot in Fig. 10) decreases with increasing slag basicity, while the liquidus temperature (solid squares) first decreases and subsequently increases. The increase of liquidus temperature is due to the formation of the periclase phase, which is less than 4 wt%.

Fig. 8. The microstructure of the slag at different basicity: a) S1 ($RO/M_2O_3 = 0.68$), b) S3 ($RO/M_2O_3 = 1.06$) and c) S9 ($RO/M_2O_3 = 1.42$).

Fig. 9. XRD patterns of the slags with different RO/M_2O_3 ratio, 1: $MgAl_2O_4$; 2: $CaAl_2O_4$; 3: $Ca_3B_2O_6$; 4: MgO ; 5: $Ca_3MgAl_4O_{10}$.

Fig. 10. The transition temperature as a function of RO/M_2O_3 ratio.

Fig. 11. The crystallization path of the slag predicted with Scheil-Gulliver model: a) lower basicity (S1 with $RO/M_2O_3 = 0.68$) and b) higher basicity (S9 with $RO/M_2O_3 = 1.42$).

By taking account of the low solidus temperature and limited periclase phase (open square in Fig. 10, *i.e.* low liquidus temperature), it is reasonable to conclude that the glassy phase is more easily formed in the slag with high basicity.

In order to better understand the mineralogy and micro-structure of the slag, thermodynamic consideration on the slag solidification and phase transformation was made with the aid of FactSage. The solidification of liquid slag was calculated with a Scheil-Gulliver model, in which solid state transformations are not considered; the database of FactPS and FToxid were used during the calculation. The evolution of phases as a function of temperature with the highest (S9, $RO/M_2O_3 = 1.4$) and the lowest basicity (S1, $RO/M_2O_3 = 0.6$) is shown in Fig. 11. It can be seen that the slag basicity has a significant influence on the slag solidification, and consequently on the solidified mineralogy. In all the studied slags, MgO containing phases are initially precipitated, *i.e.* as spinel ($MgAl_2O_4$) in the acidic ($RO/M_2O_3 < 1$, Fig. 11(a)) slag and as periclase (MgO) in the basic ($RO/M_2O_3 > 1$, Fig. 11(b)) slag, respectively. Since the MgO content is at a similar level in all the slags, the Al_2O_3 content becomes the key factor to determine the mineralogy of the precipitation. A relatively low Al_2O_3 activity is obtained in high basicity slag ($RO/M_2O_3 > 1$), and therefore MgO precipitates in the form of periclase during the cooling, whereas at low slag basicity

Fig. 12. XRD patterns of the slags with additives, 1: $Ca_5Al_6O_{14}$; 2: $Ca_3Al_2O_6$; 3: MgO ; 4: $CaAl_2O_4$; 5: $Ca_3MgAl_4O_{10}$.

($RO/M_2O_3 < 1$), there is sufficient Al_2O_3 to react with MgO to form spinel. With further solidification, the CA ($CaO \cdot Al_2O_3$) phase is precipitated in acidic slag, while C_3A_2M , C_3A and CA phases are formed in basic slag. At the end of solidification, the C_3B ($3CaO \cdot B_2O_3$) phase is formed in both cases while a small amount of C_3A_2M is also precipitated in acidic slag. Considering the fast cooling, the solid phase transformation might be interrupted and high temperature phases are retained. Therefore, the CA, spinel phases and C_3B would be dominant in acidic slag, which qualitatively agrees with the XRD measurement (see Fig. 9). For basic slag, although the C_3A phase is not experimentally identified, other phases qualitatively agree with the calculation. Comparing Figs. 11(a) and 11(b), it can be seen that the solidus temperature with higher basicity slag is much lower than that with lower basicity one, suggesting an improvement of glassy formation ability by increasing the slag basicity.

3.2.2. Influence of Additives on the Slag Mineralogy

In the present work, a small amount of additives, *e.g.* BaO and B_2O_3 was introduced in the slag to modify the thermodynamic and kinetic properties of the slag with the aim to improve the desulphurisation and slag valorisation potential. Figure 12 shows the XRD pattern for the equilibrated slag with different amount of additives. As shown in the lower part of Fig. 12, no significant influence of BaO content on the slag mineralogy was found (all slags in lower part of Fig. 12 contain 5 wt% B_2O_3 addition). On the other hand, the addition of B_2O_3 significantly influences the slag mineralogy (upper part of Fig. 12). It depresses the formation of crystalline phase and induces the formation of amorphous glassy phase. This is due to the fact that B_2O_3 lowers down the slag melting temperature and induces the glass formation,^{12,24,25} and consequently improves the valorisation potential in application where glass content is important.

4. Conclusions

The sulphur capacity of BaO– B_2O_3 modified CaO– Al_2O_3 based top slag was measured and calculated with aid of the FactSage software. The influence of slag basicity and additives on the sulphide capacity was discussed based on ther-

mododynamic considerations. The mineralogy of the slag after equilibration was evaluated, and the effects of slag basicity, BaO and B₂O₃ additions on the mineralogy were discussed. The main results can be summarized as follows:

(1) The sulphide capacity is mainly influenced by slag basicity. The addition of BaO has a complex effect on sulphide capacity, it increases the sulphide capacity of the slag at low basicity, *i.e.* R/M = 1.2 while it has limited effect for slag with high basicity, *i.e.* R/M = 1.4. The addition of B₂O₃ decreases the sulphide capacity of the CA slags.

(2) The slag mineralogy was considerably influenced by the slag basicity. The periclase and MgAl₂O₃ spinel are formed in slags with higher and lower basicity, respectively. High basicity induces the formation of the glassy phase. The obtained mineralogy qualitatively agrees with the prediction using a Scheil-Gulliver model.

(3) A small amount of B₂O₃ addition could significantly depress the crystallization during the cooling and therefore improves the valorisation potential. BaO has limited effect on slag mineralogy.

REFERENCES

- 1) T. Miki, J. Björklund, M. Andersson and P. Jönsson: Proc. 3rd Int. Conf. Process Development Iron Steelmaking, Vol. 2, MEFOS, Lulea, (2008), 581.
- 2) J. Lehmann and M. Nadif: *Rev. Miner. Geochem.*, **73** (2011), 493.
- 3) B. Yoon, K. Heo, J. Kim and H. Sohn: *Ironmaking Steelmaking*, **29** (2002), 215.
- 4) D. Durinck, F. Engström, S. Arnout, J. Heulens, P. T. Jones, B. Björkman, B. Blanpain and P. Wollants: *Resour. Conserv. Recy.*, **52** (2008), 1121.
- 5) M. Hino and S. Ban-Ya: Ultra High Purity Base Metal, The Japan Institute of Metals, Sendai, (1995).
- 6) P. Yan, M. Guo, X. Guo, S. Huang, J. V. Dyck and B. Blanpain: *ISIJ Int.*, **53** (2013), 459.
- 7) P. Yan, S. Huang, L. Pandelaers, J. V. Dyck, M. Guo and B. Blanpain: *Metall. Mater. Trans. B*, **44** (2013), 1105.
- 8) P. Yan, S. Huang, J. V. Dyck, M. Guo and B. Blanpain: *ISIJ Int.*, **54** (2014), 72.
- 9) M. Tossavainen, F. Engstrom, Q. Yand, N. Menad, M. L. Larsson and B. Bjorkman: *Waste Manage.*, **27** (2007), 1335.
- 10) J. N. Murphy, T. R. Meadowcroft and P. V. Barr: *Can. Metall. Q.*, **36** (1997), 315.
- 11) C. Shi: *J. Mater. Civil. Eng.*, **16** (2004), 230.
- 12) H. Wang, T. Zhang, H. Zhu, G. Li, Y. Yan and J. Wang: *ISIJ Int.*, **51** (2011), 702.
- 13) Y. Sung: *J. Mater. Sci.*, **37** (2002), 699.
- 14) A. Bronson and G. R. Pierre: *Metall. Trans. B*, **10** (1979), 375.
- 15) Y. Gao, Q. Liu and L. Bian: *Metall. Mater. Trans. B*, **43** (2012), 229.
- 16) C. J. B. Fincham and F. D. Richardson: *Proc. R. Soc. London, Math. Phys. Sci.*, **223** (1954), 40.
- 17) M. Nzotta, D. Sichen and S. Seetharaman: *Metall. Mater. Trans. B*, **30** (1999), 909.
- 18) M. Ohta and K. Morita: *ISIJ Int.*, **39** (1999), 1231.
- 19) A. S. Sunkar and K. Morita: *ISIJ Int.*, **49** (2009), 1649.
- 20) S. Sukenaga, N. Saito, K. Kawakami and K. Nakashima: *ISIJ Int.*, **46** (2006), 352.
- 21) D. D. Ebbing and M. S. Wrighton: General Chemistry, Houghton Mifflin Press, Boston, (1996).
- 22) L. Teixeira, Y. Tokuda, T. Yoko and K. Morita: *ISIJ Int.*, **49** (2009), 77.
- 23) S. Oguchi and D. G. C. Robertson: *Ironmaking Steelmaking*, **11** (1984), 262.
- 24) S. Lee, K. Shim and K. Auh: *J. Mater. Sci.*, **37** (2002), 2011.
- 25) L. D. Pye, H. J. Stevens and W. C. Lacourse: Introduction to Glass Science, The Vitreous State Plenum Press, New York, (1972).