Effect of Al_2O_3 addition on mineralogical modification and crystallization kinetics of a high basicity BOF steel slag

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Abstract

Basic oxygen furnace (BOF) steel slag is a main by-product produced during the converter steelmaking process. The volume instability and fast crystallization property of the BOF slag limit its added-value application. The present study investigates the effect of Al_2O_3 addition on the microstructure modification and crystallization kinetics of a high basicity BOF steel slag. Continuous cooling transformation (CCT) and time-temperature-transformation (TTT) curves have been constructed using a confocal scanning laser microscopy (CSLM) to determine the relation between cooling rate and behavior of the crystallization process. The critical cooling rate to vitrify the slags was experimentally obtained. The crystallization sequence has been clarified by integrating the *in-situ* and post-mortem observations with thermodynamic calculation. This article provides a fundamental understanding on the effect of Al_2O_3 on mineralogical and morphological modification, aiming to improve the hydration potential of the high basicity BOF steel slag.

Key words: recycling; BOF steel slag; Al_2O_3 addition; crystallization kinetics;

1. Introduction

Over the past decade, the world crude steel production increases from 1.25 billion tonnes (year of 2006) to 1.62 billion tonnes (year of 2015) [1]. Concurrently, the steel slag, as a main by-product during the steelmaking process, has a huge output. The EUROSLAG (European Slag Association) members produces around 20 million tonnes steel slag annually, among which approximately 10 million tonnes is BOF slag [2]. Storage of such tremendous amount of slag is a big issue for both the company and the environment. Therefore it is of great importance to recycle the steel slag and explore possibility of its added value applications.

By hot stage engineering, the BOF steel slag has been successfully reused in different applications, such as aggregates for road construction pavement [3,4], cement for building purpose [5–7], fertilizer for agricultural application [8]. The high strength and mechanical resistance of the slag due to its high contents of silicate enables its applications in civil engineering. Also, the phosphorus in the slag is favorable to nourish plant and improve soil quality. The volume disintegration of the high basicity (mass ratio of CaO/SiO_2) BOF steel slag, however, raises challenges in its reutilization as added-value constructional materials. Up to 10 pct expansion is induced due to the hydration and carbonation of free lime and magnesia [9], resulting in the “dusting” of the slag. According to the previous work, 4 wt pct free lime was suggested as the tolerance to avoid the general expansion [10]. Several different methods have been carried out with the goal to chemically stabilize the free lime. Accelerated carbonation treatment of slag has been demonstrated as an efficient way to eliminate the free lime by reacting with CO_2 [11–13]. Basicity modifier such as SiO_2 was examined as an effective agent by transforming the free lime and diacalcium silicate to merwinite and akermanite [14,15]. Recently, the present authors reported a novel lime stabilization method by cooling the slag in air, where wustite in the slag is oxidized

to hematite and then stabilizes the free lime by forming calcium aluminoferrite [16]. On the other hand, another issue that limits the added-value application of the BOF slag is its fast crystallization property due to the high mass ratio of CaO/SiO_2 in the slag [17]. Although the crystalline compounds with less hydraulic potential can be used as an aggregate for concrete [14], by forming more amorphous phase that has improved hydration potential, the slag can be applied in manufacturing inorganic polymer [18], which may add the slag application value. Therefore, the latter is more favorable. Rapid cooling is the most common method to vitrify the slag, enhancing the cementitious property [19–21]. To manipulate cooling condition for maximizing amorphous phase of the solidified slag, many efforts have been attempted to construct CCT and TTT diagrams of the slags by using CLSM [22–25], single hot thermocouple technique (SHTT) [26,27] and double hot thermocouple technique (DHTT) techniques [28,29]. These CCT and TTT curves provide fundamental understandings of the crystallization kinetics of the slag during cooling. Jung *et al.* have studied the crystallization behavior of electric arc furnace (EAF) slags with various basicity (ranged from 0.7 to 1.1), and found that higher basicity slags have a delayed crystallization due to the enhanced polymerization of slag structure [30]. Jiang *et al.* investigated the effect of $\text{CaO}/\text{Al}_2\text{O}_3$ mass ratio (ranged from 0.8 to 1.2) on the crystallization behavior of a $\text{CaO}-\text{Al}_2\text{O}_3$ based slag system, where Al_2O_3 has been reported to facilitate the crystallization and increase the crystallization temperature [31]. The rapid crystallization property of BOF slag challenges the laboratory study technique on its crystallization kinetics. Therefore, research work is limited on the crystallization behavior of a high basicity BOF slag system. This, however, is imperative for exploring the added-value application of the BOF slag.

In summary of the previous studies, it can be concluded that (1) high basicity induces volume instability and fast crystallization of the BOF slag, which is limited its added-value application as constructional materials; (2) rapid cooling is a promising method to vitrify the BOF slag that helps to improve hydration potential; (3) Al_2O_3 has been reported to facilitate the crystallization and increase the crystallization temperature for lower basicity slags, but its effect on the crystallization kinetics of a high basicity BOF slag is unclear.

This paper has attempted to investigate the role of Al_2O_3 in the mineralogical modification and crystallization kinetics of the high basicity BOF slag. A typical BOF master slags mixed with different amount of Al_2O_3 have been melted and equilibrated at elevated temperatures, followed by water quenching. The mineralogical and morphological modification by the Al_2O_3 addition has been revealed. *In situ* observation of the crystallization process of both the original and Al_2O_3 modified slags was performed by a confocal scanning laser microscopy combined with infrared image heating (CSLM-IIH) to construct the CCT diagram of the slags. The microstructure of the solidified slags at a certain cooling rate was analyzed by a field-emission electron probe micro analysis (FE-EPMA). By integrating the *in situ* observation and post-mortem analysis of the furnace and CLSM experimental samples with thermodynamic calculation using FactSage, the mineralogical evolution of the slags under distinct test condition has been identified. With the aim to improve the potential of the hydration of a high basicity BOF steel slag, the present study provides an in-depth knowledge about the effect of Al_2O_3 on mineralogical and morphological modification of the BOF slag. The result suggests that by steering Al_2O_3 addition and cooling rate, the BOF steel slag can be recycled towards added-value application.

2. Experimental methods and thermodynamic calculations

Materials preparation

A typical BOF steel slag was used as the starting material. The slag was sampled at different positions from a slag yard of a steel plant. Then the bulk slag was milled to below 200 μm and mixed thoroughly.

Table 1 gives the chemical composition range of the master slag, which was determined by the X-ray Fluorescence spectroscopy (Panalytical PW2400). Concentration of Fe^{2+} and Fe^{3+} in the slag were measured using chemical titration by potassium dichromate. 10.2 wt pct Fe^{2+} and 10.4 wt pct Fe^{3+} were respectively determined for the master slag.

Table 1. Chemical composition of the master slag (wt pct)

CaO	*Fe	Fe^{2+}	Fe^{3+}	SiO_2	MnO	MgO	Al_2O_3	P_2O_5	TiO_2	V_2O_5
42-55	14-25	7-18	5-11	12-18	0-8	0-5	0-3	0-2	0-1	0-0.5

*Fe is the total iron in the oxides.

5, 10 and 15 wt pct Al_2O_3 (Sasol, Germany, 25 μm) were respectively mixed with the master slag in ethanol. The mixtures were then mixed in a multidirectional mixer (Turbula type) for 24 h, followed by drying in a rotating evaporator at 338 K (65 °C) and further dried in a muffle furnace at 353 K (80 °C) for 24 h.

Furnace experiments

To study the effect of Al_2O_3 addition on the mineralogy of BOF slag under a rapid cooling condition, 30 g slag was loaded in a high purity magnesia crucible (32 mm ID, 70 mm H), which was suspended by Mo hooks in a vertical tube furnace (100-250/18, HTRV, GERO, Germany) under an Ar flow rate of 0.4 L/min. The Ar was pre-purified by passing through a Mg furnace at 773 K (500 °C). The slag was melted and held at 1873 K (1600 °C) for 1 h to homogenize the composition, followed by water quenching.

In-Situ CLSM observation

To investigate the crystallization kinetics, *in situ* observation of the BOF slag crystallization was performed to construct the CCT and TTT diagrams. Technical description and temperature calibration of CSLM has been reported in our previous work [22,32]. The schematic representation of the sample holder used in the present study is given in Figure 1. A 10×10 mm Pt foil was used as the holder and the center of the foil was mechanically curved, allowing to hold a small piece (~0.1 g) of slag. The slag was pre-melted at 1873 K (1600 °C) for 5 min to homogenize the chemical composition, release the gas and determine the melting temperature of the slag for the afterward observation. The slag was then re-melted again at the temperature 50-100 K higher than the pre-determined melting temperature. Figure 2 (a) and (b) present a schematic temperature profile used in the construction of the CCT and TTT diagrams, respectively. To determine the CCT diagram, the molten slag was cooled at various cooling rate, *i.e.* from 30 K/min to 1600 K/min. Program cooling rate and the corresponding actual cooling rate are given in Table 2. The actual cooling rate is used in this work. To investigate temperature and time dependences of the crystallization under isothermal condition, the molten slag was cooled rapidly to the temperature of interest and held at that temperature to observe the isothermal crystallization. During the entire process, the sample was continuously monitored and images were captured at a frequency of 30 frames/minute. The on-set temperature of the phase transition (liquid-solid) is defined as the temperature at which the crystal was firstly observed. The ending point of the phase transition is considered to be at the temperature at which the crystals stop growing.

Figure 1. Schematic representation of the slag specimen holder used in CSLM.

Table 2. Cooling rates of the CSLM.

Program cooling rate, K/s	Actual cooling rate, K/s
0.5	0.49
1.0	0.98
2.0	2.0
3.3	3.3
5.0	4.4
10.0	8.6
20.0	19.4
26.7	21.0

Figure 2. Temperature profile to construct (a) CCT and (b) TTT curves in CSLM.

Sample analysis and characterization

The mineralogical composition of the quenched slags was identified by X-ray Diffraction (XRD, D2 Phaser, Bruker, Germany), with 2θ in the range of $5-70^\circ$ using Cu $K\alpha$ radiation at 30 kV and 10 mA. The step size was set at 0.02° within 0.6 second. Approximate 10 wt pct ZnO powder (purity 99.9 pct, Sigma-Aldrich BVBA, Belgium) was wet-mixed with the samples as a reference to identify the amount of amorphous. Rietveld refinement was applied to achieve the quantitative analysis of the XRD pattern. Mahieux *et al* have evaluated the chemical composition of a BOF slag by QXRD and XRF analysis, and justified the accuracy of the Rietveld refinement [33]. Microstructural analysis of the slags was done by the EPMA (JXA-8530F, JEOL Ltd, Japan). The accelerating voltage was 15 kV and beam current was 15 nA.

Thermodynamic calculation

FactSage 7.0 was used to calculate the thermodynamic equilibrium by selecting databases of FactPs and FToxid. The commercial FactSage software has been successfully used in thermodynamically

modelling slag system in recent years [34,35]. “Equilibrium” and “Scheil-Gulliver” solidification modules coupled with FactSage modelling were adopted to investigate the slag crystallization behavior. The “Equilibrium” module assumes mass diffusion is infinitely fast, so that the global system is at thermodynamic equilibrium. The “Scheil-Gulliver” module, on the other hand, assumes that infinite diffusion takes place in liquid slag, but there is no diffusion in the solids. Therefore in “Scheil-Gulliver” module, thermodynamic equilibrium is achieved within the liquid slag, but not in the global system [36].

3. Results and discussion

3.1 Effect of Al_2O_3 addition on mineralogy of the quenched BOF slag

Figure 3 shows the XRD spectra of the original and Al_2O_3 modified slags after water quenching at 1873 K (1600 °C). The theoretical interplanar distances corresponding to the strongest diffraction level of lime is $d_l = 2.4059 \text{ \AA}$ (h, k, l = 2, 0, 0), and the corresponding 2 theta position is at 37.34° using Cu $K\alpha$ radiation. For the present slags, the 2 theta positions of free lime shifted to diffraction angles of 37.51° (see dashed line) due to the incorporation of FeO, MnO and MgO in the lime phase. This was in agreement with the previous studies [37–39]. Free lime was detected in the original slag, but it was completely eliminated in the modified slags. The other phases in the slags are similar, including brownmillerite (formula $\text{Ca}_2(\text{Al}_x\text{Fe}_{1-x})_2\text{O}_5$, in short C_2AF , x is in range of 0-0.7) [40], belite (formula Ca_2SiO_4 , in short C_2S), monoxide (FeO and/or MgO-based solid solution, in short RO) and zincite (ZnO). ZnO was intendedly added into the slag as a standard oxides for mineral/phase quantification. Figure 4 shows the quantified contents of minerals in the original and Al_2O_3 modified slags. With increasing Al_2O_3 additions, C_2AF and C_2S decrease markedly, and RO remains at an approximately constant level (around 15 wt pct). The amorphous phase, however, increases from 2.7 wt pct for the sample with 0 wt pct Al_2O_3 addition to 38.0 wt pct for that with 15 wt pct Al_2O_3 addition.

Figure 3. XRD spectra of the original BOF slag and Al_2O_3 modified BOF slags as quenched at 1600 °C. 5 A, 10 A and 15 A represent 5, 10 and 15 wt pct Al_2O_3 modified slags.

Figure 4. Comparison of the major phases of the original BOF slag and modified slags, as quantified by Rietveld refinement of XRD spectra. 5 A, 10 A and 15 A represent 5, 10 and 15 wt pct Al₂O₃ modified BOF slags. C₂AF, C₂S and RO represent calcium aluminoferrite, belite, and monoxide, respectively.

The elimination of free lime by adding Al₂O₃ is attributed to the reaction as shown in reaction (1)

where x is in the range of 0-0.7 [40]. From the stoichiometric consideration, to stabilize 5.6 wt pct free lime, the maximum consumption of Al₂O₃ should be 3.57 wt pct. Therefore, 5 wt pct Al₂O₃ addition is enough to stabilize all the free lime, which has been confirmed in the present study (see Figure 3 and Figure 4).

Figure 5 shows the liquidus surface of the Al₂O₃-CaO-FeO_x ternary system in air. The composition of C₂AF minerals generated from the original and the Al₂O₃ modified BOF slags are indicated by the green dots. As shown by the arrows, the C₂AF composition moves towards lower-liquidus area with increasing Al₂O₃ addition, implying that the liquid fraction in the slag at elevated temperature is increased with quantity of the Al₂O₃ addition. The mass ratio of A/F in the C₂AF phase (Figure 6) with various Al₂O₃ addition was determined by WDS analysis. It is clear that the ratio increases significantly with increasing Al₂O₃ addition. That the decreased liquidus temperature of C₂AF with higher mass ratio of Al₂O₃/Fe₂O₃ (A/F) is in an agreement with the finding of the experimental study by Fukuda *et al* [41]. Figure 6 also shows the thermodynamically calculated melting temperature of the slags as a function of Al₂O₃ addition amount. By increasing the Al₂O₃ addition, melting temperature of the slags decreases from 1766 K (1493 °C) of the original slag to 1522 K (1249 °C) of the 15 wt pct Al₂O₃ modified slag. The decrease of melting temperature is considered to be an important reason for the increase of the amorphous phase in the quenched slag, as observed in our experimental study (Figure 4). On the other hand, it has been reported that with the increased A/F ratio in C₂AF, the hydration reaction rate of C₂AF increases [42]. Therefore, the hydration reaction can be manipulated by controlling the A/F ratio through Al₂O₃ addition, tailoring the slag product property for its high added value application.

Figure 5. Liquidus surface in the Al_2O_3 - CaO - FeO_x system in air. Adapted from ref [43]. The green arrows indicate the evolution of C_2AF with different A/F ratios caused by Al_2O_3 modification. A: Al_2O_3 ; C: CaO ; F: Fe_2O_3 .

Figure 6. Change of A/F in the C_2AF phase and melting temperature of the slags with different Al_2O_3 additions.

3.2 Construction of CCT and TTT diagrams of the Al_2O_3 modified BOF slag in air

Crystallization behavior of the original and the Al_2O_3 modified BOF slags under continuous cooling and isothermal conditions in air atmosphere has been *in situ* observed using the CSLM-IIH. Figure 7. Illustration of crystallization of the 15 wt pct Al_2O_3 modified BOF slag with a continuous cooling rate of 2 K/s in CSLM test. 15 wt pct Al_2O_3 modified BOF slag is taken as an example to illustrate the crystallization process. The slag was cooled from 1723 K (1450 °C) with a continuous cooling rate of 2 K/s. Figure 7 (a) shows the slag before cooling, where the slag is fully liquid. As temperature decreases, a solid crystal appeared at 1477 K (1204 °C), which is defined as the onset crystallization temperature under such a cooling rate. The precipitated crystal then started growing, forming a larger crystal with an equiaxial shape. According to thermodynamic calculation (FactSage) and post-mortem analysis of the quenched

slag sample, the firstly predicated crystal was identified as the C_2S , which grows with crystallization time (Figure 7 (c)). As shown in Figure 7 (d), with further cooling, the second C_2S crystal with a similar morphology appeared in the observation view and was connected to the firstly precipitated C_2S crystal. At the temperature of 1442 K, the crystals with a different morphology precipitated from the melt, as seen in Figure 7 (e). FactSage calculation and post-mortem analysis of the sample after test confirm that these crystals are melilite (C_2FAS). No significant change was observed after temperature below 1402 K (1129 °C).

Figure 7. Illustration of crystallization of the 15 wt pct Al_2O_3 modified BOF slag with a continuous cooling rate of 2 K/s in CSLM test.

Using the images captured from the CLSM crystallization experiments, the CCT diagrams of the different slags (*i.e.* onset crystallization temperature as a function of time under continuous cooling conditions) are constructed and given in Figure 8 (a). 5 A, 10 A, and 15 A refer to the 5, 10, and 15 wt pct Al_2O_3 modified slags, respectively. In the CCT diagram, the solid symbols and corresponding open symbols respectively represent the onset and ending temperature of crystallization under a certain cooling rate. The narrow temperature range between the onset and ending temperatures for each slag implies rapid crystallization of the slags.. The fast crystallization characteristic of BOF slag is not significantly changed by adding Al_2O_3 . For a given slag, increasing cooling rate results in a decrease of the onset crystallization temperature as indicated by the solid lines in Figure 8 (a). The theoretical crystallization temperatures of slags with different Al_2O_3 addition were calculated by FactSage 7.0 using the database of FactPs and FToxid, and the results are given by the horizontal dashed lines in Figure 8 (a). The melting temperature of the original and the Al_2O_3 modified slags are, respectively 1800 K (1527 °C, T_1 , original slag), 1723 K (1450 °C, T_2 , 5 A), 1673 K (1400 °C, T_3 , 10 A), 1638 K (1365 °C, T_4 , 15 A). Based on these calculated melting temperature data, the undercooling (**temperature difference between the melting point and actual solidification temperature**) of each slag at various cooling rates can be estimated as shown in Figure 8 (b). The undercooling is increased with increasing cooling rate and Al_2O_3 addition. For the original slags, by increasing cooling rate from 29.4 K/min to 1260 K/min, the undercooling increased from 80 K to 247 K. While for the 15 wt pct Al_2O_3 modified slag, the undercooling increased from 128 K to 277 K by increasing the cooling rate from 29.4 K/min to 1260 K/min. According to the classical nucleation theory, the undercooling implies the resistance of a liquid for solid precipitate nucleation, which is much larger than the resistance of crystal growth [44]. The steady frequency of nucleus formation, I , can be expressed by equation (1)

$$I = \frac{k}{\eta} \exp[-b\alpha^3\beta T_l^3/T\Delta T^2] \quad (1)$$

where k is a constant [44]; b is a nucleus shape factor; T , T_l , and ΔT are, respectively the temperature at a given moment, the liquidus temperature, and the undercooling (K). α and β are dimensionless parameters defined as $\alpha = \frac{(NV^2)^{1/3}\sigma}{\Delta H_m}$, $\beta = \frac{\Delta H_m}{RT_m}$, where N is Avogadro's number, V is the nucleus' volume (m^3), σ is the interfacial energy between crystal and liquid (N/m), ΔH_m is the melting enthalpy at the liquidus temperature (J/mol), R is the gas constant (8.314 J/mol·K). It has been reported that Al_2O_3 can increase the viscosity of the BOF slag at high temperature, where the slag is mostly liquid [45,46]. According to Equation (1), the steady frequency of nucleus is reversely proportional to the viscosity, so that the nucleation frequency may be decreased by the viscosity increase caused by Al_2O_3 addition. In this way, for a given cooling rate the undercooling of the slag is increased with Al_2O_3 addition.

Figure 8. (a) CCT diagram of the original and the modified BOF slags. The solid and open symbols represent the starting and ending crystallization temperatures, respectively. T_1 , T_2 , T_3 and T_4 indicate the calculated liquidus temperature of original, 5 wt pct, 10 wt pct, and 15 wt pct Al_2O_3 modified BOF slags. The line is drawn as a guide for reading. (b) Undercooling of the original and modified BOF slags under various cooling rates. 5 A, 10 A, and 15 A indicate the 5 wt pct, 10 wt pct, and 15 wt pct Al_2O_3 modified BOF slags, respectively.

Figure 9. TTT diagram of the original and the modified BOF slags. 5 A, 10 A, and 15 A indicate the 5 wt pct, 10 wt pct, and 15 wt pct Al_2O_3 modified BOF slags, respectively. T_{n1} , T_{n2} , T_{n3} , and T_{n4} are the nose temperature of original, 5 wt pct, 10 wt pct, and 15 wt pct Al_2O_3 modified BOF slags. The line is drawn as a guide for reading.

The TTT diagram with respect to the crystallization behaviour of the present slags under isothermal condition is presented in Figure 9. It is clear that the onset crystallization temperature of the slags was remarkably decreased by adding Al_2O_3 . The highest temperature to visualize the crystallization of the original slag is 1783 K (1510 °C), while it became 1543 K (1270 °C) for the slag with 15 Al_2O_3 addition. For a given slag, the incubation time of the crystallization decreases significantly with the isothermal temperature. The kinetics of isothermal crystallization is well described by the Johnson-Mehl-Avrami (JMA) model under the assumption that during crystallization, there is only one dominant crystalline phase [47]. This assumption suits crystallization of the presently investigated slag, where the C_2S is the dominant crystalline phase. According to the JMA model,

$$\ln\left(\ln\frac{1}{1-\varphi}\right) = n \ln \lambda + n \ln(t - \tau) \quad (2)$$

where φ is the crystallized fraction, t the isothermal crystallization time, τ the incubation time, λ the crystallization rate constant related with the crystal nucleation and growth, n the Avrami parameter. The crystal fraction obtained from CSLM tests are defined as $\varphi = A_c/A_t$, where A_c is the area of crystals and A_t is the total area. A_c and A_t are measured with the aid of image analysis software. n is used to describe the nucleation and growth mechanism, as shown in Table 3. To simplify the calculation, n is assumed not to change with the isothermal crystallization time. By plotting $\ln\left(\ln\frac{1}{1-\varphi}\right)$ against $\ln(t - \tau)$, n and λ can be determined as the slope and interception of the regression function, respectively. The plots of $\ln\left(\ln\frac{1}{1-\varphi}\right)$ vs $\ln(t - \tau)$ are shown in Figure 10. Accordingly, by using Figure 10, the values of Avrami parameter and crystallization rate constant are obtained as listed in Table 4. Since the value of Avrami parameter ranges mostly from approximately 1.00 to 2.00, we may concluded that under the present experimental condition it is a bulk nucleation and the growth is controlled by diffusion [47,48]. $n = 3.08$, however, was obtained at isothermal temperature 1513 K in the 15 wt pct Al_2O_3 modified BOF slag, implying that the crystal growth may change from 2-dimension to 3-dimension. In addition, the crystallization rate constant is decreased considerably as temperature increases (see Table 3 and Figure 11). This is probably due to the decreasing in the crystallization driving force with decreasing in the undercooling of the slag solidification.

Table 3. Values of Avrami parameter for different nucleation and growth mechanism

	Crystallization mechanism	
	Diffusion controlled	Interface reaction controlled
Bulk crystallization with an increasing number of nuclei (constant nucleation rate)		
3d growth	2.5	4
2d growth	2	3
1d growth	1.5	2
Bulk crystallization with a constant number of nuclei (instantaneous nucleation)		
3d growth	1.5	3
2d growth	1	2
1d growth	0.5	1
Surface nucleation	0.5	1

Figure 10. Plots of JMA model for isothermal crystallization at various temperatures. (a) Original BOF slag; (b) 5 wt pce Al_2O_3 modified BOF slag; (c) 10 wt pce Al_2O_3 modified BOF slag; (d) 15 wt pce Al_2O_3 modified BOF slag. The least-square method was used to fit the dataset.

Table 4. The crystallization rate constant n and the Avrami parameter λ for the isothermal crystallization of the original and modified BOF slags.

Sample	Temperature, K	n	λ
Original	1753	1.43	0.104
	1763	0.89	0.039
	1773	1.36	0.056
	1783	1.26	0.005
5A	1603	2.25	0.063
	1613	2.15	0.021
	1623	1.58	0.024
	1633	1.00	0.001
10A	1543	1.72	0.037
	1553	1.97	0.041
	1563	1.41	0.012
	1573	1.99	0.007
15A	1513	3.08	0.054
	1523	1.74	0.034
	1533	1.96	0.028
	1543	1.11	0.005

Figure 11. Change of crystallization rate constant with temperature for the original and modified slag. The least-square method was used to fit the dataset.

According to the measured TTT diagram, the nose temperature (indicated as T_n , at which the incubation time is shortest) was also decreased substantially with Al_2O_3 addition, *i.e.* from 1740 K (1467 °C) of the original slag to 1423 K (1150 °C) of the slag 15 A (the nose temperature decreased by 317 K). The nose temperature can be used to estimate the critical cooling rate (R_c), which is a key parameter to examine the glass forming ability of the slag. Theoretically, when the cooling rate is larger than R_c , no crystal can form during the cooling process [44]. R_c is, therefore, of fundamental importance to describe the glassy formation ability. Based on the theory of crystallization kinetics, Uhlmann and Onorato developed a model to estimate the critical cooling rate (R_c) for glass formation [30]:

$$R_c = \frac{AT_l^2}{\eta_n} \exp(-0.212B) \left[1 - \exp\left(\frac{-0.3\Delta S_m}{R}\right) \right]^{3/4} \quad (3)$$

where $A = 40,000 \text{ J}\cdot\text{m}^{-3}\cdot\text{K}^{-1}$, T_l is the liquidus temperature of the slag (K), η the viscosity at the nose temperature (Pa·s), R the universal gas constant ($8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$). B a parameter to measure a kinetic barrier of forming the critical nucleus [50], and ΔS_m the melting entropy of the precipitated oxide ($\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$). B can be estimated by the entropy of fusion via $B \approx 12.6 \times (\Delta S_m/R)$ [51]. After plugging the values of the relevant parameters into Equation (3), it can be simplified as

$$R_c = \frac{AT_l^2}{\eta_n} 0.975\Delta S_m [1 - 0.965\Delta S_m]^{3/4} \quad (4)$$

where T_l and T_n can be determined by the CSLM tests, η_n , and ΔS_m can be calculated by FactSage. The obtained values of these parameters (*i.e.* T_l , T_n , η_n , and ΔS_m) in Equation (4) are shown in Table 5. By using the data in Table 3, the critical cooling rate as a function of Al_2O_3 addition amount is calculated as shown in Figure 12. Apparently, R_c decreases dramatically with adding Al_2O_3 into the slag, *i.e.* from 45077 K/s of the original BOF slag to 1188 K/s of the slag 15 A. A smaller R_c with a lower Al_2O_3 slag implies that the Al_2O_3 modified BOF slag is easier to be vitrified.

Table 5. Parameters used to calculate the critical cooling rate to produce amorphous slag.

	T_l , °C	T_n , °C	η_n , Pa·s	ΔS_m , $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
Original	1556	1470	0.033	54.0
5A	1406	1320	0.126	50.1

10A	1318	1230	0.379	49.6
15A	1300	1150	1.391	51.2

Figure 12. Change in the critical cooling rate of forming fully amorphous slag in air with different Al₂O₃ additions.

According to Equation (4), the critical cooling rate R_c (better glass forming ability) is proportional to the liquidus temperature (T_l) squared and melting entropy (ΔS_m), and reversely proportional to the viscosity of the slag at the nose temperature (η_n). As shown in Figure 13 (a), both the liquidus and nose temperature of the slag was decreased by adding Al₂O₃, whereas the slag viscosity η_n increases remarkably (see Figure 13 (b)). On the other hand, the melting entropy of slag (ΔS_m) firstly decreases and then increases slightly (Figure 13 (b)). According to the results in Figure 13, the combined effect of Al₂O₃ (*i.e.* increases viscosity and decreases melting temperature) is favorable to form the glass phase in the slag. Since the changing in ΔS_m with Al₂O₃ is negligible in the present work (see Figure 13 (b)) it can be concluded that the decrease in T_l and increase in η_n with Al₂O₃ addition are the origins of the increase in the glass forming ability of the slag.

Figure 13. Change of key parameters, which are applied for the calculation on the critical cooling rate of the original and the Al₂O₃ modified BOF slags, as a function of Al₂O₃ addition amount. (a) liquidus and nose temperature; (b) viscosity and change of entropy.

3.3 Crystallization sequence during continuous cooling of the slag

To have a fundamental understanding of the effects of Al_2O_3 addition on the crystallization kinetics, the crystallization sequence during continuous slag cooling was further investigated. The *in situ* observation of the mineral evolution during the solidification process with a cooling rate of 0.98 K/s is shown in Figure 14. To identify the mineral, WDS analysis was performed and the microstructure of the slags after solidification is also demonstrated in the figure.

Figure 14 (a-1) and (a-2) respectively exhibit the morphologies of the firstly and secondly precipitated crystals (CLSM images) during the solidification of the original BOF slag. They were identified as C_2S and C_2AF , as shown in Figure 14 (a-3). Under the cooling rate of 0.98K/s, the crystallization temperatures of C_2S and C_2AF are measured to be 1715 K (1442 °C) and 1561 K (1288 °C) respectively. As shown in Figure 14 (a-1), during the crystallization process, C_2S has an equiaxed morphology and grows rapidly, forming a matrix phase of the solidified slag. C_2AF is more bright compared to the surrounding matrix. As presented in Figure 14 (b) and (c), the crystallization sequence of the 5 and 10 wt pct Al_2O_3 modified BOF slag is similar to that of the original slag, *i.e.* C_2S firstly precipitates followed by C_2AF . But the precipitation temperature of both C_2S and C_2AF was gradually decreased by Al_2O_3 addition. In the original BOF slag, the onset crystallization temperature of C_2S was measured to be 1715 K (1462 °C), but it drops to 1532 K (1259 °C) with 10 wt pct Al_2O_3 addition. Similarly as for C_2S crystallization, onset crystallization temperature of C_2AF drops from 1561 K of the original slag to 1335 K (1062 °C) of the 10 wt pct Al_2O_3 modified slag. It should be noted that a grey phase was also identified as melilite in the 10 wt pct Al_2O_3 modified slag after the CSLM test. Due to the small amount of melilite, it was not observed in the CSLM test but it was identified in the post-mortem analysis (see Figure 14 (c-3)). Most of these melilite was analyzed to be solid solutions of a series of calcium silicates, including akermanite (formula $\text{Ca}_2(\text{MgSi}_2\text{O}_7)$), gehlenite (formula $\text{Ca}_2(\text{Al}_2\text{SiO}_7)$, in short C_2AS), and ferri-gehlenite (formula $\text{Ca}_2\text{FeAlSiO}_7$, in short C_2FAS) [52,53]. WDS analysis of the slag samples confirms that the melilite in the present study is C_2FAS . Figure 14 (d-1 to 3) shows the crystallization sequence of the 15 wt pct Al_2O_3 modified BOF slag at the cooling rate of 0.98 K/s in air. The faceted C_2S crystals precipitates at 1503 K (1230 °C), followed by melilite precipitating from 1449 K (1176 °C). In the CSLM, melilite is darker than C_2S . Compared with other slags, the onset crystallization temperature of C_2S is further decreased with adding 15 wt pct Al_2O_3 , but its morphology has changed from the equiaxed to faceted shape. Also, the secondly precipitated crystal is melilite rather than C_2AF . Based on the present observation, it is clear that adding Al_2O_3 into the slag decreases the crystallization temperature of C_2S , changes the crystal morphology and alters crystallization sequence of the different solid crystals during the slag solidification.

Figure 14. Crystallization sequence of the (a) original BOF slag, (b) 5 A, (c) 10 A and (d) 15 A slags during continuous cooling condition (0.98 K/s) in air, as observed in the CSLM and EPMA. C: CaO; S: SiO₂; F: Fe₂O₃; A: Al₂O₃.

Thermodynamic calculation on the slag solidification process was performed by using FactSage software. The “Equilibrium” solidification model was used for the solidification from 1973 K (1700 °C) to 773 K (500 °C), while the “Scheil-Gulliver” model was applied for the solidification from 1973 K (1700 °C) till the temperature at which the liquid slag disappears. Figure 15 presents comparison of the crystallization sequence and slag mineralogy of the original, 5, 10 and 15 wt pct Al₂O₃ modified BOF slags as experimentally determined and calculated by “Scheil-Gulliver” and “Equilibrium” models. The image analysis software was used to obtain the mineralogical fraction of the experimental slag samples. According to the calculation, C₂S is the firstly precipitated crystal in all the cases, regardless of Al₂O₃ addition quantity. The secondly precipitated crystal, however, differs in different models. In the “Scheil-Gulliver” modelling, the secondly precipitated crystal is, respectively MgO (for the original BOF slag), C₂AF (for the 5 and 10 wt pct Al₂O₃ modified BOF slags) and C₂FAS (for the 15 wt pct Al₂O₃ modified BOF slags). This simulated crystallization sequence is in a reasonable agreement with the experimental results (see Figure 14). In the “Equilibrium” modelling, however, the secondly precipitated crystal is

merwinite (formula $\text{Ca}_3\text{Mg}(\text{SiO}_4)_2$, in short C_3MS_2) for the original, 5 and 10 wt pct Al_2O_3 modified BOF slags, which is not the case with our experimental observation. With respect to the mineralogical fraction, C_2S and C_2AF are the main minerals in the experimental results. As shown in Figure 15, C_2S and C_2AF are the main minerals in “Scheil-Gulliver” model, but C_2S becomes a minor mineral in the “Equilibrium” model, where the main minerals are C_2AF , C_3MS_2 and C_2FAS . Therefore, it can be concluded that “Scheil-Gulliver” model has more correctly predicted the slag solidification behavior than the “Equilibrium” model for the present experimental conditions. The reason is probably because of that “Scheil-Gulliver” model assumes infinite diffusion takes place in the liquid slag, but no diffusion in the solids. In the “Equilibrium” model, however, it assumes thermodynamic equilibrium can be achieved in the global system [36]. Under the continuous cooling condition, solid phase can hardly participate in the reactions occurring in the remained liquid, so that the assumption of “Scheil-Gulliver” model is closer to the reality of the BOF slag solidification under the present experimental condition.

Figure 15. Comparison of crystallization sequence and slag mineralogy for original and modified slags as experimentally determined and simulated by the equilibrium model and the Scheil-Gulliver model. Ex: experimental results; SG: Scheil-Gulliver model; Eq: Equilibrium model. C: CaO; S: SiO₂; F: Fe₂O₃; A: Al₂O₃; M: MgO.

Conclusions

The influence of Al_2O_3 additions on the mineralogy and crystallization kinetics of the BOF slag has been systematically studied through quenching experiments and the *in situ* CSLM observation of the slag solidification. The mineral changes with Al_2O_3 additions were revealed. The CCT and TTT diagrams have been constructed to understand the crystallization behavior (e. g. identify the primary crystal phase of the slag at different compositions and cooling rates) of the original and modified BOF slags using the CSLM. Effect of the cooling rate on the undercooling of slag solidification was discussed. The isothermal crystallization kinetics was studied, and the critical cooling rate to vitrify the BOF slag was determined based on the measured TTT diagrams. Also, the crystallization sequence during continuous cooling process has been discussed through CSLM observation combined with the slag solidification modelling. The main conclusions are summarized as follows.

(1) 5 percent Al_2O_3 addition can effectively remove free lime from the high basicity BOF slag, and increases the liquid fraction of the slag. With further Al_2O_3 additions, the amorphous phase increases while the C_2S and C_2AF decrease in the solidified slag. The reason is that the melting point of the slag

is decreased with increasing Al_2O_3 additions. The hydration property of the quenched slag can be manipulated by controlling of the A/F ratio through Al_2O_3 addition.

(2) Under the current continuous cooling condition, the original and modified BOF slags crystallize rapidly. Increasing cooling rate and Al_2O_3 addition amount can appreciably increase the undercooling of the slag during solidification. The slag crystallization kinetics follows well with the JMA model. The crystallization of the original and modified BOF slags is deduced to be a bulk nucleation and the crystal growth is controlled by diffusion. The crystallization rate constant is significantly decreased as temperature increases. The glass formation ability of the slag is found to be enhanced by adding Al_2O_3 . This is attributed to that Al_2O_3 causes decreasing in liquidus temperature and increasing in viscosity of the slag at nose temperature. The increasing in glass forming ability of the slag with Al_2O_3 addition suggests a potential application of BOF slag for high-quality blended cement production.

(3) To have a fundamental understanding of the effects of Al_2O_3 addition on the crystallization kinetics, the crystallization sequence during continuous slag cooling was further investigated. C_2S crystal firstly precipitated from the slag in the continuous cooling condition with a cooling rate of 0.98 K/s, regardless of Al_2O_3 addition. Yet the secondly precipitated phase can be C_2AF or C_2FAS , which is dependent on the slag composition. “Scheil-Gulliver” modelling predicts a better result than that of “Equilibrium” modelling results in the continuous cooling condition.

Acknowledgments

The authors gratefully acknowledge the support from the Agency for Innovation by Science and Technology of Belgium (IWT grant NO. 140514). Chunwei Liu would like to acknowledge the support of the China Scholarship Council (CSC, No.201306080002).

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