

EFFECT OF Al_2O_3 ADDITION ON THE CRYSTALLISATION OF A HIGH BASICITY BOF SLAG: PERSPECTIVE OF GLASS FORMING ABILITY FOR SLAG VALORISATION

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Introduction

BOF slag is the main by-product from primary steelmaking. Approximately 21 million tonne steel slag is produced annually in the EUROSLAG Association members, and BOF slag accounts for almost half of the volume¹. Disposal of the slags is a financial burden for the industry, and leaking of heavy metals (such as Cr and V) from the slag is a potential threat to human health. Alternatively, valorisation of BOF slag, benefiting both the steel industry and the environment, is a promising development direction.

The cementitious nature of silicates in the BOF slag suggests that it is possible to be used in cement application. In the solidified slag, the glassy compound has improved hydration potential compared with the crystalline compounds². Subsequently, the glassy slag can be applied in manufacturing blended cement, creating higher added value³. However, the strong crystallisation ability of the high basicity BOF slag leaves the glassy formation of the slag a challenge. Even under rapid cooling condition (water quenching), the major phase is dicalcium silicate (C_2S) and the glass phase is hardly formed⁴.

In this work, the effect of Al_2O_3 addition on the crystallisation of a high basicity BOF slag was studied in-situ using a Confocal Scanning Laser Microscopy (CSLM) and the Time Temperature Transformation (TTT) curves were constructed. The CSLM has been successfully applied in the study of TTT curves of slags. In addition, the liquidus temperature of the slags was determined. The viscosity of each slag at the nose temperature was estimated by using FactSage. The critical cooling rate, as an indicator of the glass forming ability, was also determined. The result implies that Al_2O_3 addition improves the glass forming ability appreciably.

Materials and Experimental procedure

The composition of the starting slag is given in Table 1. The slag composition represents a typical industrial BOF slag, which was sampled at the slag yard. The slags were then milled to a particle size less than 200 μm . The content of Fe^{2+} and Fe^{3+} were measured using chemical titration by potassium dichromate. 5, 10, and 15 wt% Al_2O_3

(Sasol, Germany, 25 μm) was mixed with the industrial slag to investigate the influence of Al_2O_3 on the crystallisation of BOF slag. The slags were labelled as 5A, 10A and 15A, respectively.

Table 1: Chemical composition of the master slag, wt%

CaO	FeO	Fe ₂ O ₃	SiO ₂	MnO	MgO	Al ₂ O ₃	P ₂ O ₅	TiO ₂	V ₂ O ₅
42-55	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. Measured by the X-ray Fluorescence spectroscopy (Panalytical PW2400).

The slag was charged into a high purity magnesia crucible (32 mm ID, 70 mm H) and melted in a vertical tube furnace (100-250/18, HTRV, GERO, Germany) under purified Ar with the flow rate of 0.4 L/min. After melting at 1600°C for 1 hour, the slag was then quenched into water. Then the crystallisation behaviour of the slag was investigated in-situ using the CSLM (1LM21-SVF17SP, Lasertec, Japan) equipment. Technical description and temperature calibration of the CSLM has been reported in our previous work⁵. In this study, a tiny piece (approximately 50 mg) of the quenched slag was loaded in a 10×10 mm Pt foil. Each slag was pre-melted at 1600°C in ambient air atmosphere. To estimate the liquidus temperature, the slag was heated up to 1300°C with a heating rate of 200°C/min, then slowly heated up to 1600°C with a heating rate of 5°C/min. To investigate the TTT diagrams, the slag was melted in air at the temperature 50°C above its liquidus for 2 min, followed by decreasing the temperature rapidly to the desired temperature and held at that temperature until the first crystallisation was observed, as indicated in Figure 1 a. The onset of the crystallisation was defined as the moment when the first crystal was visualised.

The mineralogical and microstructural analysis was done by the EPMA (JXA-8530F, JEOL Ltd, Japan). FactSage 7.0 was used to calculate the thermodynamic equilibrium and the slag viscosity at the nose temperature by using FactPs and FToxid database.

Results and Discussions

Schematic diagram of the temperature history and TTT curves of the original and Al_2O_3 modified slag are shown in Figure 1a and 1b, respectively. The crystallisation temperature of the slags was remarkably decreased by adding Al_2O_3 . Within 20 min, the highest temperature to visualise the crystallisation of the original slag is 1510°C, while it decreases to 1270°C for the sample 15A. The nose temperature (T_n , at which the incubation time is shortest) and liquidus temperature (T_l) also decreased with Al_2O_3 addition. The influences of Al_2O_3 addition on T_n and T_l are shown in Table 2.

The typical observations of the iso-thermal crystallisation in the CSLM were given in Figure 2, where the iso-thermal temperature of 1270°C for sample 15A was taken as an example. The crystal precipitated from the melt has a faceted morphology. Previous

research confirmed that with increasing undercooling, morphology of the precipitated crystal from CaO–Al₂O₃–SiO₂ melts changes from faceted to dendritic shape⁵.

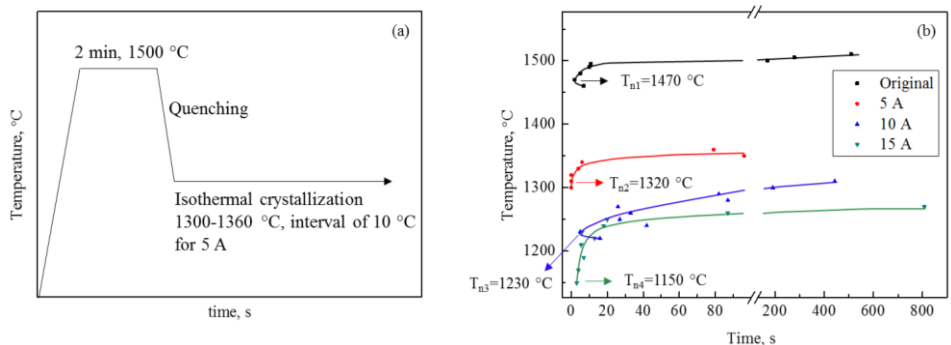


Figure 1: (a) Schematic diagram of the temperature profile for constructing TTT curve (sample 5A as an example); (b) TTT diagram of the original and modified BOF slags. T_{n1} , T_{n2} , T_{n3} , and T_{n4} are the nose temperature of original, 5, 10, and 15 wt% Al₂O₃ modified slags. The line is drawn as a guide for the eye

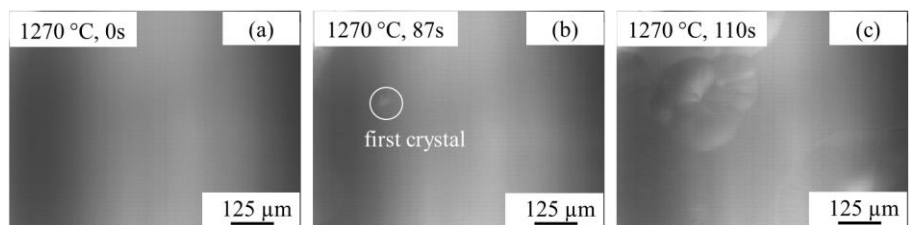


Figure 2: Observation of the crystallisation at 1270 °C of 15A. (a) the moment when the sample is rapidly cooled to a temperature of 1270 °C; (b) the onset of crystallisation; (c) 110 s after the rapid cooling

Critical cooling rate (R_c) is a key parameter to examine the glass forming ability. When the cooling rate is larger than R_c , no crystal forms during the cooling process. Therefore, R_c is of fundamental importance to describe the glassy formation ability. Equation (1) has been established to calculate R_c ⁶.

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

where $A = 40,000 \text{ J} \cdot \text{m}^{-3} \cdot \text{K}^{-1}$, T_l the liquidus temperature of the slag (°C), η the viscosity at the nose temperature (Pa·s), B a kinetic barrier to form the critical nucleus, and ΔS_m is the melting entropy of the oxide ($\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$). B can be estimated by relating to the entropy of fusion via $B \approx 12.6 \times (\Delta S_m / R)^7$. T_l and T_n are the measured data, η_n , B and ΔS_m are the calculated values by FactSage. The values for each parameter and the calculated results are shown in Table 2.

R_c is decreased rapidly with increasing Al₂O₃ additions. The magnitude of R_c decreases from $45077^\circ\text{C} \cdot \text{s}^{-1}$ for the original slag to $1188^\circ\text{C} \cdot \text{s}^{-1}$ for the 15 Al₂O₃ modified slags. Additionally, since the Fe²⁺ is oxidised to Fe³⁺ and forms C₂AF in air, R_c decreases (glass forming ability increases) and cementitious behaviour of slag can be enhanced³.

Table 2: Parameters used to calculate the critical cooling rate to produce glassy slag

	T_l , °C	T_n , °C	η_n , Pa·s	B	ΔS_m , J·K ⁻¹ ·mol ⁻¹	R_c , °C·s ⁻¹
Original	1556	1470	0.033	66.7	54.0	45077
5A	1406	1320	0.126	56.5	50.1	25020
10A	1318	1230	0.379	51.8	49.6	7224
15A	1300	1150	1.391	50.6	51.2	1188

According to the Equation (1), a better glass forming ability can be enhanced in the condition with a lower liquidus temperature (T_l), a higher viscosity of the melt at the nose temperature of the TTT curve (η_n), a higher kinetic barrier of the critical nucleus formation (B) and a lower melting entropy (ΔS_m). As seen in Table 2 and Figure 1b, with increasing Al₂O₃, η_n increases but T_l and B decrease. Meanwhile, the melting entropy of slag (ΔS_m) firstly decreases and then increases slightly. In this study, the combined effect of Al₂O₃ is favour for forming the glass phase in the slag. This can be understood through Equation (1), where R_c is proportional to the square of the T_l and reversely proportional to η_n . Therefore, the decrease of T_l and increase of η_n induced by Al₂O₃ addition improves the glass forming ability.

Conclusions

The influence of Al₂O₃ addition on the crystallisation of a high basicity BOF slag was studied in-situ. The glass formation ability is found to be enhanced by Al₂O₃. This is because of the decrease of liquidus temperature and the increase of viscosity at nose temperature in the TTT curves. The improved glass forming ability suggests a potential application of BOF slag for high-quality blended cement production.

References

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