

# CRYSTALLISATION BEHAVIOUR OF LIQUID CaO-SiO<sub>2</sub>-FeO-MnO SLAGS IN MOIST GAS ATMOSPHERES

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## Introduction

Steelmaking slags, the main by-product from steelmaking process, contain significant thermal energy (~1600°C) and considerable amount of target metals in oxide forms (e.g. ~30% FeO). No process known so far has been commercialised to recover either the huge thermal energy or the valuable metal oxides contained in the waste slags. As previously reported<sup>1</sup>, we are aiming to develop a novel process to recover energy (in the form of H<sub>2</sub> gas) and materials (in the form of magnetite Fe<sub>3</sub>O<sub>4</sub>) from steelmaking slags through integrating the heat recovery process by Bhattacharjee *et al.*<sup>2</sup> with the materials recovery process by Semykina *et al.*<sup>3</sup>. The process is dependent on the structure and properties of the slag, of which the crystallisation tendency is key. This is because surface phases affect the slag's reactivity with the gas and it enables selective formation of solid phases containing transition metals. The present work investigated the crystallisation behaviour of synthetic molten CaO-SiO<sub>2</sub>-FeO -MnO slags after reacting with moisture.

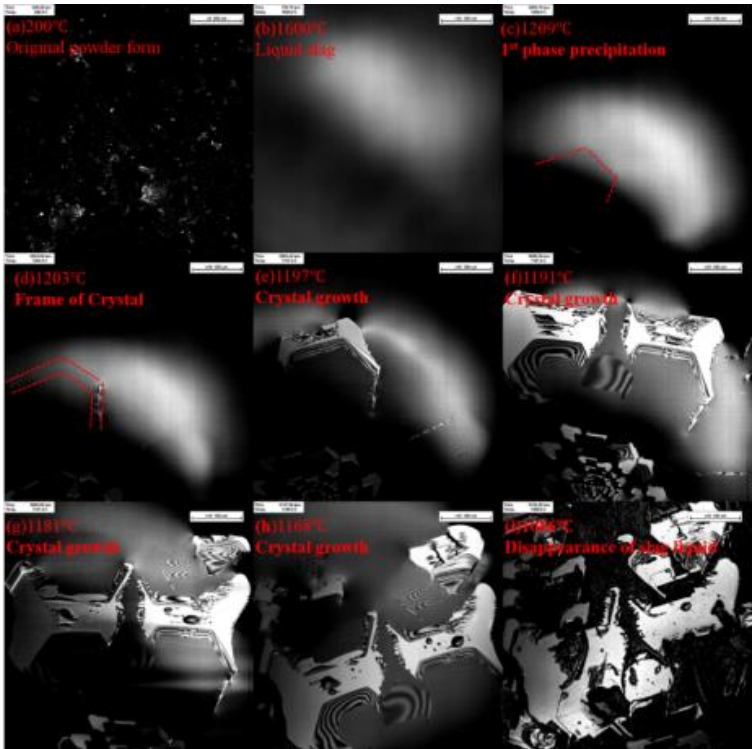
## Experimental

The crystallisation behaviour of the CaO-SiO<sub>2</sub>-27.78%FeO-5.56%MnO (wt%) slags with different basicities (CaO/SiO<sub>2</sub>) of 1.0, 1.25 and 1.5 was in situ observed under the confocal laser scanning microscope (CLSM) and recorded at various temperatures in Ar atmosphere after reacting with moisture. The pre-melted slag in a Pt crucible was heated to and kept at 1600°C under Ar gas for 5 minutes. Then the Ar gas was switched to H<sub>2</sub>O-Ar gas to react with molten slag for 10 minutes at 1600°C. After the reaction, the H<sub>2</sub>O-Ar gas was switched to Ar gas and the slag was quenched by two different cooling processes, namely continuous cooling and isothermal cooling. In the continuous cooling experiment, a fixed cooling rate was applied to the molten slag sample from 1600°C to the end of the slag solidification to plot the CCT diagrams. As for the isothermal cooling, the molten slag sample was quenched at a cooling rate of 50°C/s to a pre-set temperature and was held for 5-30 minutes to construct the TTT diagrams. The microstructure and mineral composition of the quenched slags were

analysed by SEM-EDS and XRD respectively. The slag preparation and experimental procedure are detailed elsewhere<sup>1</sup>.

### Crystallisation of reacted slags under continuous cooling

Figure 1 shows the crystallisation behaviour of the reacted slag with basicity of 1.0 observed by CLSM at the cooling rate of 10°C/min. Figure 1a and 1b show its morphology at room temperature and at 1600°C under Ar atmosphere respectively. The nucleus of the primary crystal phase was observed to form at 1209°C (Figure 1c), and the frame of crystal formed at 1203°C (Figure 1d). With decreasing the temperature from 1197°C to 1168°C, the volume of the crystal nucleus increased gradually (Figure 1(e-h)). The liquid slag finally appeared to have fully crystallised at 1086°C (Figure 1i).

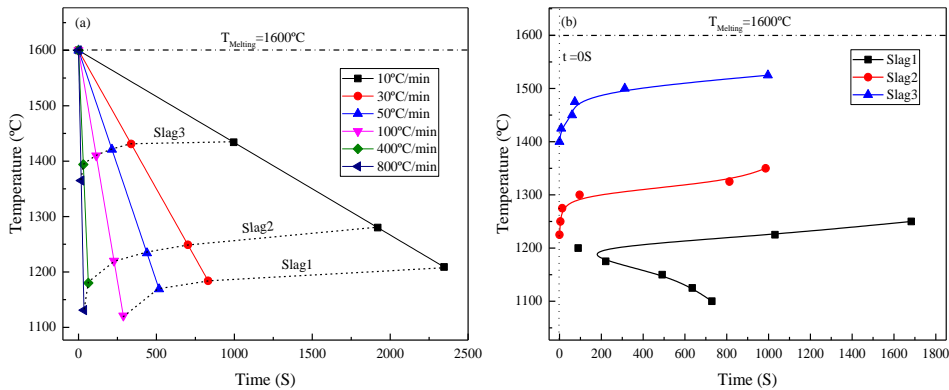


**Figure 1:** Crystallisation of the slag (basicity=1.0) in continuous cooling (10°C/min)

CCT diagrams of the reacted slags with different basicities were determined at different cooling rates. Figure 2a is as an example the results for the slag with basicity of 1.00. In general, the crystallisation temperatures of precipitated phases decreased with increasing the cooling rate from 10°C/min to 100°C/min, which is to be expected. Increasing cooling rates resulted in larger increase in slag viscosity as temperature was lowered before crystallisation commenced enabling a higher degree of undercooling (a lower crystallisation temperature). Melts with higher basicities have a higher tendency for crystallisation. This agrees with the fact that a great number of breakage of Si-O bonds and re-ordering of silicate structure, resulting in a lower viscosity ( $\eta$ ), occurs with the increase of basicity.

# Crystallisation of reacted slags under isothermal cooling

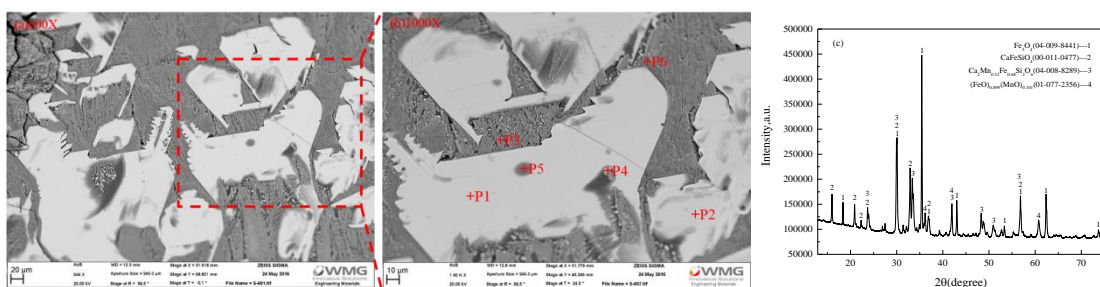
Onsets of slag crystallisation under isothermal cooling conditions were observed under CLSM and recorded to construct the TTT diagrams for the reacted slags with different basicities. The reacted slag with basicity of 1.00 (Figure 2b) showed a typical ‘C’-shaped TTT curve, with its apparent nose located at 1200°C and 89 seconds. A half-‘C’-shaped TTT curves presented in the slag basicity of 1.25 and 1.50, and the nose temperature and critical time for nucleation increased with the slag basicity increasing from 1.25 to 1.50. As shown in Figure 2b, with increasing slag basicity, not only did the TTT curves of glassy to crystalline transformation shift to the left, but also the TTT diagrams shifted to higher temperatures, indicating higher tendency for crystallisation. With increasing slag basicity, the crystallisation temperature increases while the incubation time decreases. The critical cooling rate, *i.e.* the minimum cooling rate that results in a completely glassy slag (*i.e.* no crystalline content) can be obtained from Figure 2b.



**Figure 2:** (a) CCT diagram of reacted slag with basicity =1.00, and (b) TTT diagram

## Phase characterisation

Figure 3a and 3b show the SEM photographs of reacted slag with the basicity of 1.00 at the continuous cooling rate of 10°C/min with different magnification factors. It should be pointed out that Figure 3a is the corresponding image of Figure 1i observed by CLSM. In order to determine the elementary distribution in different phases, EDS spot analysis indicated that the white phase was close to  $\text{Fe}_3\text{O}_{3.8}$ , while the grey dendritic crystal and slag matrix were approaching  $\text{CaMn}_{1.14}\text{Fe}_{1.70}\text{Si}_{1.89}\text{O}_{6.25}$  and  $\text{CaSiFe}_{0.62}\text{O}_{3.67}$  respectively. As shown in Figure 3c, the main phases in the reacted slag were detected to be spinel (magnetite  $\text{Fe}_3\text{O}_4$ ),  $\text{CaMn}_{0.32}\text{Fe}_{0.68}\text{Si}_2\text{O}_6$  and  $\text{CaFeSiO}_4$  with a small amount of  $(\text{FeO})_{0.899}(\text{MnO})_{0.101}$ , which is in agreement with the SEM-EDS analysis. By combining the crystallisation behaviour observed by CLSM, the microstructure analysed by SEM-EDS and the phases presented in the slag characterised by XRD, for the reacted slag with basicity of 1.00, the primary phase formed at (1209°C) in Figure 1c can be considered as  $\text{Fe}_3\text{O}_4$ . Similarly, the primary phases formed in the reacted slags with basicity of 1.25 and 1.50 can be considered as  $\text{Fe}_3\text{O}_4$  and  $\text{Ca}_2\text{SiO}_4$  respectively but were not reproduced here for the brevity of the paper.



**Figure 3:** Morphologies and minerals of the reacted slag with basicity of 1.0 at continuous cooling rate of 10°C/min (a) SEM image with magnification factor of 600X (b) SEM image with magnification factor of 1000X, and (c) XRD patterns

## Conclusions

1. For the slags (reacted with moisture) under continuous cooling conditions, CCT curves indicated that the crystallisation temperatures increased with decreasing the cooling rate from 100°C/min to 10°C/min.
2. For the slags (reacted with moisture) under isothermal cooling conditions, TTT curves indicated the nose temperature and critical time for nucleation located at 1200°C and 89 seconds when the slag basicity is 1.00, while those increased with the slag basicity increasing from 1.25 to 1.50.
3. The findings of this study provide different solutions for the slags with different basicities to control crystallisation behaviour for the recovery of targeted metals.

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