PHASE CHEMISTRY STUDY OF THE INTERACTIONS BETWEEN SLAG AND REFRACTORY IN COPPERMAKING PROCESSES

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Abstract

The molten oxides (slag), matte and metal charges during smelting, converting and refining stages of the pyrometallurgical coppermaking processes are contained in refractory-lined vessels. The refractory materials are selected so as to provide resistance to corrosion by molten phases and thermal insulation to minimize heat losses while maintaining the charge in a molten state. However, high process temperature, highly agitated and chemically aggressive melts in furnaces can result in rapid degradation of the refractory and premature shutdown of the reactor for relining; imposing additional costs on processes in the form of planned and unplanned maintenance.

The focus of the present study is on detailed characterization of the phase chemistry and slag interactions with refractories. The rate of reactions between refractories and liquids depends on the phase equilibria. Post-mortem analysis of the spent brick from Isa smelter was followed by isothermal finger laboratory test under controlled conditions. Electron probe X-ray microanalysis (EPMA) is used to measure the compositions of the phases across the samples. This information is linked to the phase equilibria. Thermodynamic modelling is carried out by FactSage to assist in interpretation of the results.

Phase analysis of used refractory and laboratory tests for Isa smelter indicate formation of a protective spinel layer on the hot face slowing refractory dissolution.

Introduction

Most pyrometallurgical coppermaking processes involve smelting and converting stages. Isa and flash smelters are primarily used for the smelting stage, forming two different liquid phases i.e. copper matte and slag. The ISASMELT reactor is primarily used for lead and copper-containing materials [1]. The furnace consists of a top submerged lance (TSL), and a refractory-lined vessels in the shape of a vertical cylinder. Refractory materials are selected so as to provide (1) high resistance to abrasion effects due to the strong bath convection, corrosion and chemical attacks by the low viscosity slag phase and (2) thermal insulation to minimize heat losses to the surroundings. However, high process temperature and highly agitated bath in both ISA and Pierce-Smith furnaces may give rise to rapid degradation of the refractory and premature shutdown of the reactor for relining; imposing additional costs on processes in the form of planned and unplanned maintenance [2].

The rate of refractory degradation is a function of several variables such as liquid bath temperature, chemical composition on of the liquid bath, liquid properties (density, viscosity, and diffusivity) and degree of bath agitation. The infiltration of the liquid slag/matte phases into the brick occurs through the in-the matrix-brick pores acting as channels speed up the chemical degradation of the brick [3, 4]. Therefore, firstly minimization of porosity in the prefabricated brick is of significance to decrease infiltration depth of low viscosity liquid into refractory. Secondly, formation of a protective solid phase layer on the interface between refractory and molten slag may slow down the process of slag infiltration into the brick [5-7]. In the current study, the effects of slag chemistry on the formation of the protective layer has been investigated through carrying out the post-mortem analysis of the used brick, measurements of as received well-quenched slag samples and isothermal laboratory finger tests samples.

Methodology of analysis and experiment

Isa smelter fresh brick and the spent one from in-contact-with-slag area were sectioned, mounted in epoxy resin, and polished for metallographic examination and microanalysis. Electron probe X-ray micro analysis (EPMA) was used to characterize microstructures and to measure the phase chemistry. An electron-probe X-ray microanalyzer, Superprobe JEOL (a trademark of Japan Electron Optics Ltd., Tokyo) 8200L EPMA equipped with five wavelength dispersive X-ray detectors was used to determine the phase compositions.

Isothermal laboratory experiment was performed using static finger test (see Figure 1). 2 kg of as-received industrial slag from Isa smelter was placed in MgO crucible using an electric furnace until a temperature of 1170 ˚C was reached. The preheated refractory finger was partially immersed into the liquid slag bath for 6 hours. After designated time the sample was pulled out of the bath and quenched in water. The sections were prepared similar to spent brick and then analyzed.
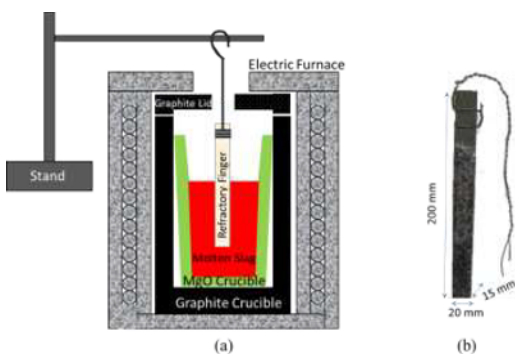

Figure 1. Apparatus of the Iso-thermal refractory test for Isa smelter and PS convertor brick at 1170 ˚C and immersion time: 6h, (b) refractory finger after the test

Result

<u>Characterization of fresh Isa smelter smelting brick</u>

The microstructure of a direct-bonded magnesia-chromite bricks (see Figure 2) is made up of large fused grains (periclase plus secondary chromite, 2-4mm), primary chromite (0.5-2mm), secondary chromite, monticellite, and pores. The bulk and the compositions of the phases are shown in Table 1. The periclase phase is highly rich in MgO ($\approx$ 97 wt pct) and has relatively low iron content (2 wt pct).Compared to the primary chromite [(Fe, Mg, Ca)O.(Cr, Fe, Al, As)$_2$O$_3$] the secondary chromite phase has higher FeO and lower Cr$_2$O$_3$. Primary and secondary chromite phases also have different morphologies. The latter is observed either on the edge of the periclase sub-grains or inside the periclase sub-grains. The source of silica and lime in the starting materials leads to formation of forsterite and monticellite phases during the brick production process. Monticellite phase (CaMgSiO$_4$, belongs to the olivine crystal group) has a plate-shaped morphology formed around the primary chromite phase.
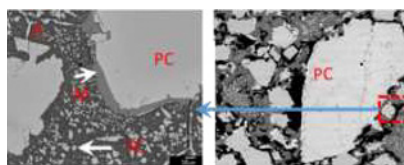

Figure 2: Back-scatter microstructures of (a) Isa smelter fresh brick (direct bond) from smelting area. Fused periclase (P), primary chromite (PC), secondary chromite (SC), monticellite (M).

Table 1: Chemical composition of phases in Isa smelter fresh brick using EPMA.

wt pct	Cu$_2$O	**FeO	S	SiO$_2$	CaO	Al$_2$O$_3$	MgO	Cr$_2$O$_3$	As$_2$O$_3$
*Bulk composition	0.0	12.8	0.0	0.9	0.8	8.1	50.9	26.4	0.0
Periclase	0.0	2.0	0.0	0.0	0.0	0.1	96.8	0.0	0.9
Primary Chromite	0.0	9.7	0.0	0.0	0.1	11.8	18.9	59.4	0.1
Secondary Chromite	0.1	28.1	0.0	0.1	0.2	10.0	20.6	40.5	0.2
Monticellite	0.0	0.9	0.0	38.5	34.5	0.2	25.5	0.4	0.2

* Bulk composition is taken from the refractory supplier datasheet.
** Iron was calculated as FeO

<u>Used ISA Slag Brick</u>

The back-scattered image (see Figure 3) illustrates the formation of several microstructural types starting from hot face; the reaction zone, infiltration zone and unaffected zone. The reaction zone delineates the boundary between the brick and the liquid slag phase. This layer is approximately

1mm thick starting from the hot face towards the slag/brick interface. The main phases formed in the slag/refractory reaction zone are the spinel phase, entrapped liquid and metallic copper. In addition, entrapped primary chromite from the brick (0.6 mm away from the hot face) is observed in this section.

The infiltration zone consists of original brick phases, infiltrated slag and newly formed solid phases. The infiltration depth seems to be relatively shallow (3 mm). The liquid slag infiltrated into the brick through the pores and cracks and the new phases such as spinel, and forsterite formed within the zone. Newly formed forsterite is a solid solution phase [2(Fe, Mg)O.SiO$_2$] crystallized due to the chemical reaction between the slag phase (Iron oxide and silica) and MgO from the periclase matrix. The microstructure of the brick in the unaffected zone is very similar to the fresh brick; no liquid slag or newly formed phases were observed on this zone.
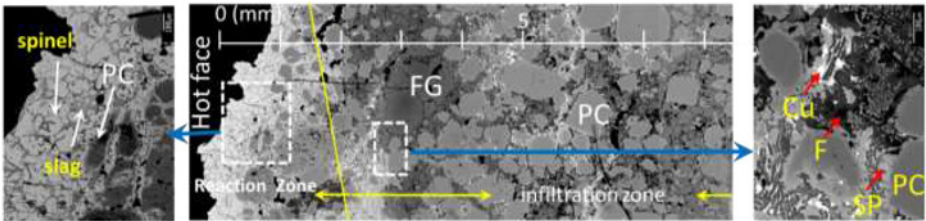

Figure 3. Back-scatter microstructures of Isa smelter-used brick taken from slag/matte area. Fused grain (FG), primary chromite (PC), spinel (Sp), and forsterite (F).

Isothermal laboratory experiment brick

Similar to the Isa spent brick microstructure, protective layer of spinel in the reaction zone, infiltration zone (newly formed forsterite and spinel) and unreacted (or unaffected) zone were observed (see Figure 4).
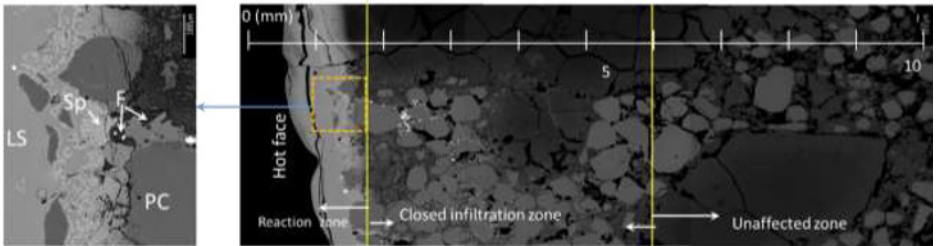

Figure 4: Back-scatter microstructure of (a) laboratory experiments with Isa slag and brick at 1170 ˚C, and 6h immersion. Primary chromite (PC), forsterite (F), liquid slag (LS), fused grain (FG), and spinel (Sp)

Discussions

In spent brick and also laboratory test brick, the spinel phase was formed on the slag/refractory interface as a result of the interaction between refractory components (primary chromite and periclase) and slag phase. The spinel phase seems to separate molten slag from refractory phases

slowing down further reaction (degradation) between brick and aggressive slag. Formation of forsterite in the infiltrated area seems to block open liquid channels, thus decreasing the dissolution rates and the infiltration rates of the slag phase into the brick.

Figure 5 shows the Fe/SiO_2 as a function of MgO in well-quenched bulk slag phases from the Isa smelter, the bulk samples from before and after the laboratory experiment, as well as thermodynamic model prediction with FactSage [8] for the given conditions. Fe/SiO_2 in bulk slag samples indicates that the slag phase is located on the spinel side as a primary phase crystals with MgO concentration between 1 to 1.5 wt pct in the bulk liquid slag. This is consistent with the formation of spinel in the reactive layer of Isa spent brick (see Figure 3).

For laboratory tests, the slag composition moved to the olivine and spinel sides since the bulk liquid phase was saturated with MgO (2.7 wt pct) due to carrying out the isothermal experiment in the MgO crucible. This is also consistent with the microstructural observations (see Figure 4).

The results from post-mortem analysis and the laboratory test indicate the significant effect of slag chemistry on refractory degradation. To increase the service life of the reactor it seems that fluxing recipe should be set in a way to encourage formation of spinel on the hot face of the refractory. This may slow down the dissolution of the refractory into the aggressive slag.
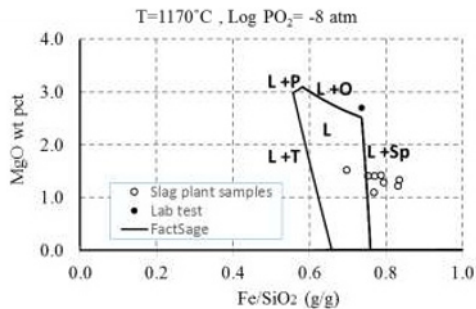

Figure 5: Fe/SiO_2 as a function of MgO in bulk slag phases of laboratory experiment, plant samples and thermodynamics calculation by FactSage [8]. Liquid (L), spinel (Sp), olivine (O), pyroxene (P) and tridymite (T).

Summary

Post-mortem analysis of the spent brick, isothermal laboratory tests along with analysis of the well-quenched slag samples from smelter were undertaken to characterize the effects of slag composition and process temperature on slag-refractory interactions. The results were related to the slag-refractory phase chemistry.

Phase analysis of used refractory and refractory after laboratory test indicated that spinel, and forsterite phases are formed due to the interaction between slag and refractory material. These solid phases block the pores in refractory leading to slowing down the refractory dissolution. This is indirect dissolution process; desired type of the refractory/slag interactions. It seems that service life of the reactor may be longer if the slag composition is moved into the primary phase field that can be formed from the refractory and slag material into spinel, or olivine phase fields.

References

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