Journal of the European Ceramic Society 36 (2016) 4291–4299

Contents lists available at www.sciencedirect.com

Journal of the European Ceramic Society

journal homepage: www.elsevier.com/locate/jeurceramsoc

Spinel saturation of a PbO based slag as a method to mitigate the chemical degradation of magnesia-chromite bricks

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ARTICLE INFO

Article history:
Received 24 February 2016
Received in revised form 6 June 2016
Accepted 19 June 2016
Available online 4 July 2016

Keywords:
Magnesia-chromite
Refractory dissolution
PbO slag
Slag engineering
Chemical wear

ABSTRACT

For nonferrous smelters, the chemical wear of the magnesia-chromite bricks caused by the direct contact with the slag leads to regular replacement of the lining before complete failure. This is a costly and time intensive procedure. Increasing the lining's lifetime, by reducing the chemical wear, would result in a reduction of both the installation cost and the production losses. In this paper, the potential of changing the slag composition to limit the chemical dissolution rate by saturating the slag in spinel components is investigated by isothermal static finger tests. When saturating the slag in spinel by adding Fe_2O_3, a spinel layer forms at the interface between the refractory sample and the liquid slag. As the dissolution of MgO from the refractory in the slag is now controlled by solid state diffusion through the new spinel layer, the chemical wear rate is substantially decreased, thereby increasing the lifetime of the lining.

1. Introduction

Magnesia chromite bricks are commonly used in the lining of smelters in the copper and lead industry [1,2] because of their resistance against the thermal, mechanical and chemical loads inherent to the pyrometallurgical production process. Even despite these favorable properties, the bricks wear over time, eventually requiring a costly and time consuming replacement of the lining. The down time during the replacement of the lining leads to a significant production loss. To increase the profitability of the process, this down time needs to be minimized which, in turn, requires a reduction in the wear rate of the lining.

The wear of linings in pyrometallurgical processes is caused by a combination of thermo-mechanical and chemical degradation [3,4]. The wear mechanisms and rate differs for the bricks, depending if they are in contact with the gas, slag, matte or alloy phase. In the copper and the lead industry the chemical wear caused by the slag is typically the highest [1]. The interaction between the slag and the refractory can be classified in three different types: (1) the dissolution of refractory components into the liquid slag [5], (2) the formation of a solid solution based on components from the slag bath and the phases already present inside the refractory bricks [5–11] and (3) the formation of new solid phases [7,12].

The chemical degradation can be reduced by changing the used brick type [6] but also by modifying the used slag. For the latter several strategies exist. The slag composition can be used to change the properties of the slag and thus indirectly influence the refractory wear. The viscosity of the slag system, for example, is a vital parameter controlling the lifetime of the refractory. Typically lower viscosity systems lead to faster wear rates [5]. The lower viscosity makes it easier for the slag to infiltrate the lining, exposing a larger part of the lining to reaction with the aggressive slag. In the copper industry, for example, the use of calcium ferrite slags allows an easier copper production compared to the classic fayalite slag system but the low viscosity of the slag leads to a significant increase in the wear rate of the lining, limiting the industrial use of this type of slag system. As an alternative, a ferrous calcium silicate slag can be used, which due to its higher viscosity, is less aggressive to the refractory lining [8].

A second method to limit the dissolution of refractory components is to add these components in the slag up to the saturation level of the components [13] or to change the slag composition to limit the solubility of the refractory components in the slag. Yan et al. [14], for example, studied the effect of the pO_2 and Cu_2O concentration on the MgO solubility in a calcium ferrite slag to select conditions that minimize the solubility of MgO and would therefore lead to a longer refractory life.

Besides the solubility of the refractory components into the liquid slag, the kinetics of the dissolution also control the lifetime of the lining. By forming a solid layer between the refractory phases

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http://dx.doi.org/10.1016/j.jeurceramsoc.2016.06.037

and the liquid slag the dissolution rate of the former is lowered, leading to a longer lifetime of the lining. This is called indirect dissolution [5,15]. The continuation of the dissolution process can only take place when the refractory components diffuse through the newly formed solid layer. A process that is significantly slower than the diffusion through the liquid slag, towards the unsaturated bath.

The formation of a new phase depends on the composition of the slag and the composition of the used refractory brick. Not all newly formed phases, however, lead to a protective layer. Previous research [16,17] has shown that the formation of a spinel layer between an MgO refractory brick and a $CaO–Al_2O_3–SiO_2–MgO–FeO$ slag can significantly reduce the dissolution rate of MgO into the bath.

The goal of this work is to determine if the saturation of a $PbO–SiO_2–CaO–ZnO–Al_2O_3$ slag in spinel forming components can be used as a method to slow down the chemical wear at the hot face of a magnesia-chromite brick. Such a slag forms during the 2 stage production of lead from sulfur containing ores. First the ores are oxidized in contact with air to form the slag, which, in a second stage, is reduced to form Pb [18,19]. Because of the industrial importance of this slag system, the $PbO–SiO_2–CaO–ZnO–Al_2O_3–Fe_2O_3$ slag system has been extensively studied to determine the equilibrium phase relations and their composition [18,20–23].

This goal is achieved by comparing the degradation for refractory samples in contact with two different slags: one without the addition of Fe_2O_3 and one with the addition of Fe_2O_3. The latter results in a spinel saturated liquid. In the paper we investigate if this spinel saturation leads to the formation of a protective spinel layer on the entire hot face of the sample and determine what the influence of this spinel layer on the chemical degradation is, by comparing the microstructure and MgO dissolution for both slags. To get the best possible insights into the reaction between the slag and the refractory sample, the interaction is tested on lab scale using synthetic systems allowing optimal control of the conditions during the experiment.

2. Materials and methods

Two different slags are used for the experiments. The selection of the used compositions is made using Fig. 1. It gives the results of thermodynamic calculations, using FactSage 7.0 and its FTOxid database [24,25], by varying the ratio of Fe_2O_3 to ZnO for fixed concentrations of PbO, SiO_2, CaO and Al_2O_3. The first slag composition is selected without the addition of Fe_2O_3 to the system. This composition is completely liquid at the experimental temperature (1300 °C). The second slag is selected to ensure the formation of a solid spinel phase together with the liquid phase. The formation of a spinel phase, with composition AB_2O_4 requires the presence of both divalent and trivalent cations. By varying the ZnO and Fe_2O_3 concentration in the slag, the ratio between divalent and trivalent cations in the slag is changed, resulting in a composition range (seen in Fig. 1) where the liquid becomes (over)saturated in spinel. The experiments are performed in an alumina crucible. The first slag shown in Fig. 1, however, still has a high solubility of Al_2O_3. Al_2O_3 is therefore added to this slag to limit the crucible dissolution and thus the change in liquid composition caused by crucible dissolution during the experiment, while still staying in the fully liquid region. The used slag compositions are given in Table 1.

The experimental setup used during the experiments is schematically shown in Fig. 2. Prior to the experiment the refractory samples are cut in a bar shape (20 × 15 × 100 mm). For both experiments a commercially available fused grain rebonded magnesia-chromite brick is used. Magnesia-chromite bricks are commonly used in both copper and lead smelters [1,2]. A detailed description of the microstructure and the composition of all present phases for the used refractory sample can be found in Scheunis et al. [26]. The synthetic slag is produced by mixing different pure oxide powders in the desired ratio, shown in Table 1. The mixture with a total weight of 1.5 kg is then added in a 1 l alumina crucible and heated in an induction furnace at a rate of 600 °C/h up to 1300 °C. The refractory sample is heated in the same furnace with the alumina crucible but is only submerged when the slag has reached the desired experimental temperature. After 3 h reaction time, the refractory sample is removed from the liquid bath and quenched in water to preserve the microstructure and the composition of the different phases in the best possible way. After the experiment the sample is cut using a diamond saw. The position of the cut is shown in Fig. 2. After polishing the sample, its microstructure is analyzed using a fully quantitative EPMA-WDS (JEOL JXA-8530F) system operated using an acceleration voltage of 15 kV and a probe current of 15 nA. The experimental findings are

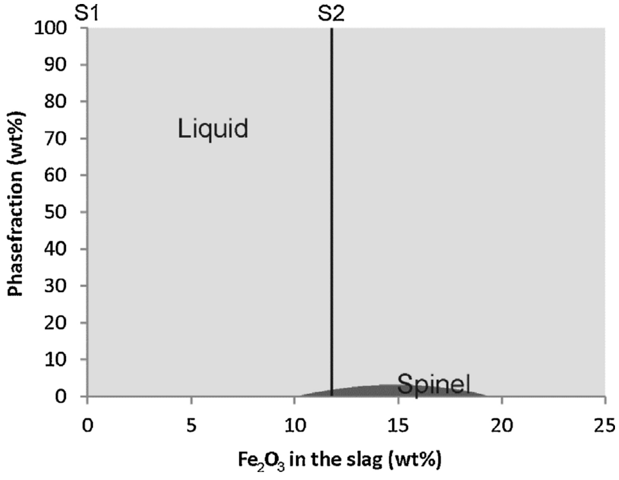

Fig. 1. Equilibrium phase composition at 1300 °C and pO2 = 0.21 atm for a slag with 58.2 wt% PbO, 14.6 SiO_2, 0.9 wt% CaO and 2.9 wt% Al_2O_3. The remaining 23.4 wt% is the combination of Fe_2O_3 and ZnO. The amount of Fe_2O_3 is varied between 0 and 23.4 wt% while ZnO shows the opposite trend (from 23.4 to 0 wt%). S1 and S2 are the 2 slag composition used in the experiments. They are selected to result in only a liquid (S1) and a liquid and spinel phase (S2). The figure is calculated using the FTOxid database from FactSage 7.0 [24,25].

Table 1
Composition of the bulk slag (wt%).

Slag		PbO	SiO_2	CaO	ZnO	Fe_2O_3	Al_2O_3
S1	Wt.%	55.2	13.8	0.9	22.1	–	8.0
	Mole%	29.3	27.2	1.9	32.2	–	9.3
S2	Wt.%	58.2	14.6	0.9	11.7	11.7	2.9
	Mole%	34.1	31.8	2.1	18.8	9.6	3.7

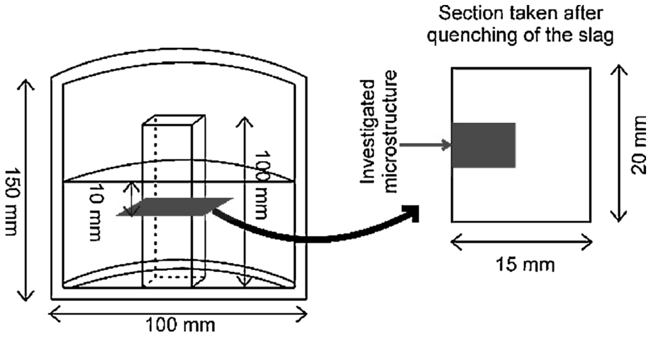

Fig. 2. Schematic representation of the experimental procedure showing the high temperature experimental setup, removal of the sample and the position of the investigated microstructure.