Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 42 (2016) 743–751

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Comparison of the chemical corrosion resistance of magnesia-based refractories by stainless steelmaking slags under vacuum conditions

Liugang Chen*, Annelies Malfliet, Peter Tom Jones, Bart Blanpain, Muxing Guo

Department of Materials Engineering, KU Leuven, Kasteelpark Arenberg 44, BE-3001 Leuven, Belgium

Received 1 July 2015; accepted 31 August 2015
Available online 6 September 2015

Abstract

This study evaluates commercially available magnesia–chromite, magnesia–carbon and magnesia–doloma bricks for their use in a Vacuum Oxygen Decarburisation ladle. The corrosion behaviour of these bricks by stainless steelmaking slags is, therefore, investigated through crucible tests in a vacuum induction furnace at elevated temperatures (1650 and 1750 °C) and low oxygen partial pressures (5.3 and 3.0×10^{-11} atm). The results reveal that magnesia–carbon bricks are severely corroded due to the high dissolution of MgO, while magnesia–chromite and magnesia–doloma refractories exhibit an excellent corrosion resistance. The MgO enrichment in the slag is believed to be the reason of the low wear rate of the MgO–doloma refractories. Rebonded and direct-bonded MgO–chromite refractories show similar corrosion resistance against the slags because of the 'secondary chromite inactivation'. Decreasing the slag basicity enhances the dissolution of MgO into the slag, thereby increasing the corrosion of the magnesia-based refractories.

Keywords: B. Electron microscopy; C. Corrosion; D. MgO; E. Refractories; Stainless steelmaking slag

1. Introduction

The 'slagline' is the most critical wear zone in Vacuum Oxygen Decarburisation (VOD) ladles which are used in the secondary refining process of stainless steel. In the selection of a refractory brick for this zone the demanding VOD process conditions should be considered. These include high temperatures (≥1650 °C), low pressures (1–200 mbar), turbulent motion of the bath and aggressive fluid slags. Until recently, fired magnesia–chromite (MgO–chromite) bricks are the most extensively used material in the VOD slaglines, showing an excellent slag resistance and thermal stability. However, the high cost of MgO–chromite bricks and the potential formation of Cr^{6+} during use and/or cooling are providing an impetus for replacement of MgO–chromite by chromite-free bricks [1–3]. In response to this incentive, Parada and co-workers [2,3] studied the performance of different types of fired magnesia–doloma (MgO–doloma) and magnesia–carbon (MgO–C) bricks in the linings of a VOD ladle where they were in contact with $CaO–MgO–SiO_2–Al_2O_3–CrO_x$ stainless steelmaking slags. Post-mortem characterisation of industrially worn specimens has shown that fired MgO–doloma bricks may be used in the slagline of the VOD ladles, while MgO–C bricks perform poorly in the slagline. Although these studies have generated crucial insights in refractory wear under industrial conditions, a drawback of this research procedure is that it is practically difficult to find out the influence of temperature or slag composition, e.g. basicity (CaO/SiO_2 ratio) or Al_2O_3 content on the refractory degradation. In addition, the reason why MgO–doloma refractories exhibit an excellent chemical corrosion resistance against the stainless steelmaking slags is not clear from these studies.

Laboratory rotating refractory finger tests have been proven to be very useful to investigate the fundamental degradation mechanisms of specific refractory materials for distinct metallurgical purposes [4–7]. Following this line of thought, Guo et al. [4,5] have performed rotating finger tests in a vacuum induction furnace to simulate the industrial vacuum refining conditions. This allowed studying the corrosion behaviour of

---

*Corresponding author. Tel.: +32 16 377706; fax: +32 16 321991.
E-mail address: liugang.chen@mtm.kuleuven.be (L. Chen).

http://dx.doi.org/10.1016/j.ceramint.2015.08.175
0272-8842/

high quality rebonded MgO–chromite and pitch bonded MgO–C bricks in contact with Al_2O_3-rich (15–20 wt%) stainless steelmaking slags. The influence of temperature and corrosion time on the refractory wear was successfully investigated. Nonetheless, it is very difficult with rotating finger tests to exactly control the experimental conditions, e.g. Al_2O_3 contents, for the sake of comparing different refractory materials. Besides, the prospects of MgO–doloma refractories as an alternative for MgO–chromite bricks for the VOD slagline were not investigated in these studies.

In the present study a different experimental approach is considered to investigate the degradation behaviour of several commercially available magnesia-based refractory bricks under exactly the same conditions. As such, a crucible set-up in a vacuum induction furnace with all brick types (MgO–chromite, MgO–C and MgO–doloma) in one assembly was prepared. The objective of this study is three-fold. Firstly, the corrosion behaviour of the different MgO-based refractories can be compared under the same experimental conditions. The combination of the chemical corrosion resistance of the bricks from this study and from previously performed industrial *post-mortem* studies [2,3,8] provides the basis to select the refractory, which would perform best in industrial operation. Secondly, the degradation mechanisms of MgO–doloma refractories can be investigated. Thirdly, the influence of the Al_2O_3 content and the basicity (CaO/SiO_2 ratio) of the $CaO–MgO–SiO_2–Al_2O_3–CrO_x$ slags on the corrosion behaviour can be studied for all bricks in the same experimental run.

2. Experimental

2.1. Materials preparation

Refractory bricks, metallurgical slags and stainless steel charge (AISI 304) were supplied by a stainless steel company. In order to investigate the effect of slag composition on the refractory corrosion, three different metallurgical slags were used. Their compositions are listed in Table 1. The basicity (C/S: CaO/SiO_2 ratio) and Al_2O_3 content of the slags are the main variables. The three slags V1, V2 and V3 have a basicity of 1.25, 1 and 0.75, respectively. The Al_2O_3 content is 3.7 wt% in V1, and 10.0 wt% in V2 and V3.

The refractory segments for the crucible tests were cut from seven different types of commercially available MgO–chromite (MK), MgO–C (MC) and MgO–doloma (MD) refractory bricks (Table 2). The parameters of the refractory segments are shown in Fig. 1. Each crucible assembly is constructed with eight refractory segments (Fig. 1). The details for the crucible construction are shown in Table 3. More specifically, the MgO–chromite bricks (MK1, MK2) and MgO–C bricks (MC1, MC2) were investigated in the three tests, the MgO–doloma bricks (MD1, MD2, MD3) were only examined in the test V3 (Table 3).

Table 1
Chemical composition of the (as-delivered) stainless steel slags initially charged in the experiments, as determined by ICP-AES analysis (in wt%).

Exp. no.	MgO	Al_2O_3	SiO_2	CaO	Cr_2O_3	MnO	Total Fe	Basicity (C/S)
V1	14.7	3.7	32.1	39.8	2.6	1.3	1.6	1.25
V2	11.3	10.0	37.1	37.0	1.7	0.4	0.1	1.00
V3	9.4	10.0	37.0	27.7	2.8	1.7	1.9	0.75

2.2. Experimental set-up and procedure

Crucible tests were carried out in a vacuum induction furnace (Balzers, type VSG 30, 60 kW power supply, 4 kHz frequency). A schematic drawing of the experimental set-up is shown in Fig. 2. The experimental conditions are listed in Table 3. Each test was carried out in a crucible assembly constructed with eight refractory samples as shown in Fig. 1. Before each test, the crucible containing a charge of graphite was preheated at 1200 °C for 24 h in an argon atmosphere to remove the volatile species from the MgO–C bricks. 14 kg of stainless steel and 2.5 kg of VOD-reduction slag was held in the preheated crucible and then heated to the desired temperature. The target temperature for the test was controlled by the power input, according to a previously experimentally determined power–temperature curve [9]. The temperature of the melt was measured by a dip thermocouple (type B: Pt 30% Rh/Pt 6% Rh) every 30 minutes. A gas mixture of CO and CO_2 was blown into the furnace at a flowrate of 40 L/min CO and 1 L/min CO_2, controlled by mass-flow metres, to simulate the atmosphere in the VOD process. The oxygen partial pressure was thus set to be approximately 10^{-11} atm (5.3 and 3.0×10^{-11} atm, Table 3). Three tests were carried out with different temperatures (V1 and V2: 1650 °C, and V3: 1750 °C) and exposure times (60 and 90 min), as shown in Table 3.

2.3. Sample analysis techniques

After the tests, the refractory samples were taken from the worn crucible and visually examined. Specimens were cut perpendicularly to the refractory/slag interface from the slag zone, embedded in a low-viscosity resin (Epofix) by vacuum impregnation, ground with silicon carbide grinding paper and polished with diamond paste. The polished refractory specimens were carbon coated, and characterised with high resolution scanning electron microscopy (SEM, Philips XL-30 FEG), equipped with an energy dispersive spectroscopy (EDS, EDAX) system with an ultra-thin window. Initial slags and final slags after the tests were analysed with inductively coupled plasma atomic emission spectroscopy (ICP-AES).

3. Results and discussion

3.1. Macroscopical observations of the refractory degradation

The strongest refractory wear is observed at the slag–metal interface. This is due to the combined effects of the strong agitation caused by the induction currents and the Marangoni convection generated by the interfacial tension gradient [4,10]. The wear depth (ΔL) at the slag–metal interface was