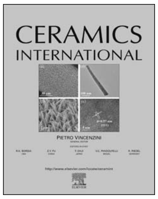
Ceramics International (xxxx) xxxx–xxxx

Contents lists available at ScienceDirect

Ceramics International

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



Slag corrosion of alumina-magnesia-carbon refractory bricks: Experimental data and thermodynamic simulation

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ARTICLE INFO

Keywords:
Alumina-magnesia-carbon refractories
Slag corrosion
Crucible test
Thermodynamic simulation

ABSTRACT

Alumina-magnesia-carbon (AMC) bricks are used in steelmaking ladles, where they are part of the bottom and sidewalls working linings. These refractories can be corroded by liquid slag, especially during tapping and casting. In order to contribute with information regarding the reaction mechanisms and the formed phases when they are in contact with a molten slag, the slag corrosion at high temperatures of three AMC refractories is analyzed in this paper. A crucible test was performed at 1600 °C using an industrial basic slag, and the results were compared with those obtained in testing at 1450 °C. In addition, thermodynamic simulations of the slag-refractory contact were performed using FactSage software and a model which considers the global chemical composition of each refractory. Differences in the materials wear associated with differences in composition were predicted by the simulation. Other determining factors, such as microstructure and texture of the evaluated AMC refractories, were also discussed.

1. Introduction

Alumina-magnesia-carbon (Al_2O_3-MgO-C, AMC) refractory bricks are used in the metal line and the bottom of the working linings of steelmaking ladles [1–5]. Their application in the slag line is limited due their susceptibility to basic melt attack at high temperature [2]. However, depending on the logistics of the steelshop, AMC refractories can be corroded by liquid slag, especially during tapping and casting. Although some works have been reported on the corrosion of AMC refractories [6–9], information regarding the reaction mechanisms and the characterization of the formed phases in the refractories' microstructure at high temperatures is still rather limited.

The thermodynamic simulation of refractory corrosion by melts using commercial software packages (such as Thermocalc or Factsage) is a very powerful tool that can be used to explain and predict the mineralogical composition of the refractory-slag system and even corrosion wear [10,11]. There are several models available for slag corrosion simulation, which have been mainly applied to the study of castables, with each one trying to reproduce the practical conditions better each time [10–13]. For example, Luz et al. [10] introduced the saturation of slag by the refractory components and its chemical composition change after the reaction with the refractory in the simulation model. Once the thermodynamic model has proved to be adequate for describing a refractory-slag system, it can be used to predict the final equilibrium state for different experimental conditions (changes in temperature, slag or refractory compositions, for instance), thus reducing the number of expensive and time-consuming experimental tests. Of course, the model cannot consider all the factors involved in the corrosion process, especially those related to kinetic aspects. Nevertheless, the corrosion mechanism and main determining factors regarding corrosion behavior may be also inferred from thermodynamic simulation data [10,11].

This work deals the evaluation of the corrosion of three AMC refractories in contact with an industrial typical slag at 1600 °C, in air. The results are compared with experimental data obtained at 1450 °C which were previously reported and discussed [9]. In addition, the thermodynamic simulation of the refractory-slag system at both temperatures, 1450 and 1600 °C, is performed using a model which considers the overall chemical composition of the refractory and the liquid slag composition changes due to the interaction with the refractory. In order to point out the advantages of the thermodynamic analyses, and use it to explain corrosion behavior, the results of experimental corrosion crucible tests are also compared to the calculated ones.

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http://dx.doi.org/10.1016/j.ceramint.2016.12.114
Received 9 August 2016; Received in revised form 22 December 2016; Accepted 22 December 2016

Please cite this article as: Muñoz, V., Ceramics International (2016), http://dx.doi.org/10.1016/j.ceramint.2016.12.114

Table 1
Composition and texture data of AMC refractories.

		AMC1	**AMC2**	**AMC3**
Main phases (wt %)	Corundum (Al_2O_3)	82.7 ± 0.3	57.6 ± 0.3	70.5 ± 0.3
	Periclase (MgO)	5.40 ± 0.02	27.0 ± 0.1	6.8 ± 0.1
Secondary phases (wt%)	Mullite ($3Al_2O_3.2SiO_2$)	–	–	8.6 ± 0.3
	Graphite (C)	1.7 ± 0.1	3.5 ± 0.1	3.0 ± 0.1
	Resin (C, O, H)	5.4 ± 0.1	5.6 ± 0.1	5.0 ± 0.1
	Aluminium (Al)	1.39 ± 0.02	1.37 ± 0.02	1.60 ± 0.02
Impurities (wt%)	Fe_2O_3, SiO_2, CaO, TiO_2[a]	3.4 ± 0.3	4.9 ± 0.3	4.5 ± 0.3
Apparent porosity (%)		6.7 ± 0.1	7.8 ± 0.5	4.0 ± 0.1
Permeability (m^3/Nw/s)[b]		0.013	0.015	0.008
Minimum pore diameter (μm)		0.060	0.055	0.003

[a] Impurities expressed as oxides with contents > 0.1 wt%; others impurities are: K_2O, P_2O_5, Cr_2O_3, MnO, ZrO_2, SrO, ZnO.

[b] For ΔP of 3 MPa; ΔP is the pressure drop when the gas used in the measurement (N_2) passes through the sample.

2. Experimental procedures

2.1. Materials

Three alumina-magnesia-carbon (Al_2O_3-MgO-C, AMC) commercial refractory bricks manufactured by the same supplier and labeled as AMC1, AMC2 and AMC3 were analyzed. The bricks have different MgO content and different raw materials as sources of alumina.

Bearing in mind the aim of this work, these materials were characterized using a vast group of analysis techniques: X-ray fluorescence (XRF), plasma emission spectroscopy (ICP-OES), gravimetry, X-ray diffraction (XRD), differential thermal and thermogravimetric analyses (DTA/TGA), reflection optical microscopy and scanning electron microscopy coupled with X-ray dispersive energy (SEM/EDS), measurements of density and porosity, Hg-intrusion porosimetry, dilatometric analysis and permanent linear change (PLC). The refractory characterization results have been previously reported [14], and the main data are summarized in Table 1.

From these analyses, it was determined that every refractory contains brown fused alumina (Ea) plus tabular alumina (Ta). AMC1 has a higher proportion of the last type of aggregate with respect to Ea aggregates, and with respect to Ta aggregates present in the other two materials as well. Furthermore, it was confirmed that only AMC3 possesses bauxite (with a mullite content estimated around 8–9 wt%), and that aluminium is used as an antioxidant in the three materials in similar proportions. The higher amount of sintered magnesia in AMC2 is distributed in the medium-fine fraction whereas this component is present only as fine particles in the matrix of AMC1 and AMC3.

Graphite, whose particles have a similar aspect ratio in the three materials, is present at a higher content in AMC2, but its flakes are the smallest. The amount of graphite in AMC3 is somewhat lower and its particles are the purest. Furthermore, the bricks contain a similar amount of resins as organic binders, although it was not possible to determine what kind of phenolic resin they are (novolaka or resol).

Regarding the texture, AMC2 has a larger amount of open pores, although they are similar in size to those of AMC1. Conversely to what could be expected considering the presence of bauxite as source of alumina in AMC3, which has rather higher porosity (10–15%) than the other two sources of alumina (tabular and fused aluminas, with porosities < 3%), this is the brick with the lowest values of open porosity, permeability and pore size. This fact was attributed to a better granulometric fractions packing which would lead to lower levels and sizes of inter-particle pores.

The tortuosity parameter (determined by the Hg-intrusion porosimetry) was ~ 2 for each AMC refractory.

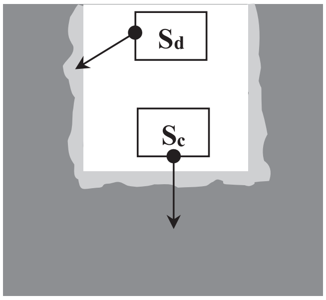

Fig. 1. Cross section of the corroded crucible.

2.2. Slag corrosion test

The corrosion behavior of AMC refractory bricks in contact with a typical ladle slag was studied at 1600 °C in air, employing the static crucible test. Crucibles of 6×6×5 cm^3 with a hole 3.6–3.7 cm in diameter and 2.3–2.5 cm in height, into which the slag in powder was placed, were used for the corrosion tests. These crucibles were thermally treated in an electric chamber furnace (SiC heating elements; Carbolite HTF 1700) at 1600 °C for 2 h. After the thermal treatment, the crucibles were cut transversally and then packed in epoxy resin in vacuum. The cross surfaces were ground with SiC papers up to 4000 grit of abrasive grade and polished with diamond paste up to 3 μm, using kerosene as a lubricant.

Corrosion was measured by the worn cross-area of the crucible (in percentage), which is a consequence of the irreversible loss of the refractory particles attacked by the slag. Photos were taken of the cross sections and the images were analyzed using Image Pro Plus 6.0 software. The new inner surface of the crucible was delimited on the cross section image and used to calculate the worn area S_d as a percentage of the original cross-area of the crucible, S_c (Fig. 1).

The slag used in the corrosion tests was that left in the ladle after the end of the continuous casting. It was characterized by several experimental techniques (XRF, XRD, DTA-TGA and critical temperature determination), and the results have been previously reported [9]. From the chemical composition (Table 2), the basicity index IB_2 (CaO/SiO_2 ratio) was calculated giving a value of 10.8, which indicates its basic character. The softening temperature of the slag was 1366 ± 5 °C, and its viscosity (η) at 1600 °C was estimated at 0.152 Pa s using the Urbain model [15], which has been extensively used to achieve a very good approximation of this property for steelmaking slags.

2.3. Thermodynamic simulation

The calculations performed in this work were based on the minimization of the free energy of the system in order to find out the chemical composition of the solid, liquid and gaseous phases, as well as their proportions at the thermodynamic equilibrium. Simulations have been carried out using FactSage (version 6.4), a fully integrated database and software developed between Thermfact/CRCT (Montreal) and GTT-Technologies (Aachen). The equilibrium phases, as well as the lowest temperature of liquid formation of the slag (equivalent to its melting point), were predicted using the Equilib module.

An iterative procedure which considers the liquid composition changes due to the brick corrosion [10] was used in the thermodynamic calculations. Firstly, 100 g of each AMC brick and 100 g of a slag composition (taking only those components ≥0.50 wt%) were considered in the first reaction stage. All calculations were performed for a constant temperature of 1450 or 1600 °C and a pressure of 1 atm. After the first reaction step, the resulting liquid (considered as the modified slag) was again put in contact with the same amount (100 g) of the original brick composition used before, and a further thermodynamic calculation step (CS) was carried out. This procedure was constantly