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Thermodynamic simulation models for predicting Al_2O_3–MgO castable chemical corrosion

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Abstract

The chemical corrosion of two Al_2O_3–MgO castables (containing distinct binder sources: hydratable alumina or calcium aluminate cement) were evaluated in this work via thermodynamic calculations. Two simulation models were proposed according to the following procedures: (1) firstly the matrix and later the aggregates of the castables were placed, separately, in contact with an industrial basic slag, and (2) the overall chemical composition of the design castables was directly reacted with the molten slag. The theoretical results were further compared with experimental data collected after corrosion cup tests. Although the thermodynamic evaluation of the overall castable compositions was able to identify the phase transformations correctly, a two-step analysis of the matrix components and aggregates particles seems to be the best alternative to evaluate the binder source effect on the corrosion performance of the two Al_2O_3–MgO refractory materials.

Keywords: C. Corrosion; Spinel containing castables; Thermodynamic simulation; Spinel

1. Introduction

Corrosion of refractory castables is a complex phenomenon which has been extensively studied [1–6]. Depending on the system, refractory wear may comprise chemical (corrosion) and physical or mechanical (erosion) processes. Chemical corrosion takes place as the evaluated system attempts to attain the equilibrium when the molten liquid is not saturated with a refractory component. Therefore, the thermodynamic equilibrium will only be achieved by the dissolution of that refractory component up to the liquid saturation [5].

Although the bulk slag has an important influence on the corrosion process, the composition of the local molten slag penetrating the refractory is also critical. The local liquid may present some changes due to the dissolution of the binder and grains or the incorporation of species as for the spinel (which can accommodate Al_2O_3, FeO or MnO in its structure) [1]. Moreover, iron and manganese ions, which diffuse faster than others, may penetrate farther into the refractory. Therefore, the corrosion rate is a function of many variables including temperature, refractory/liquid/interface composition, and liquid density, viscosity, diffusivity and stirring rate [5–8].

Spinel containing castables are heterogeneous materials comprised by coarse alumina aggregates and a finer, more porous intergranular matrix. The higher porosity and fine texture of the matrix make it more reactive than the aggregates. Consequently, castable wear also depends on the microstructure of the refractory and its physicochemical properties, including type of bond and grain size distribution [2,4,9].

The reaction between refractory and molten slags should be described taking into account both the thermodynamic (equilibrium conditions) and the kinetic aspects (reaction rates). Thermodynamic calculations are particularly suitable to understand the corrosion phenomena. By analyzing the reactions at equilibrium, better knowledge of the corrosion mechanisms can be attained by improving industrial performance and reducing the need of experimental tests [4].

Recently, some work has focused on developing simulation models to evaluate refractory corrosion behavior [2,3,9]. Although the proposed procedures provide very useful information, they do not take into account the slag saturation and the changes of its chemical composition during the reaction

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with the refractory. Thus, in a previous study a new modeling approach was suggested by the present authors [10], when successive calculations, simulating the liquid penetration and its compositional changes, were carried out. According to that article, the predictions attained by the thermodynamic calculations for the spinel containing castable corrosion behavior were in agreement with the experimental tests, but it was also highlighted that some improvements (such as previous evaluation of the molten slag interaction with the matrix compounds and later with the aggregates of the castables) could still be implemented.

Considering these aspects, this work addresses the investigation of a novel thermodynamic simulation procedure, where firstly the matrix and later the aggregates are taken into account during contact between an industrial steel ladle basic slag with two different Al_2O_3–MgO castable compositions. Additionally, the collected results attained by this procedure were compared with the data of simulations involving the interaction between the liquid slag and the overall chemical compositions of the refractories and also with experimental tests (corrosion cup-tests) in order to evaluate the advantages and drawbacks of each calculation procedure.

2. Experimental and thermodynamic calculations

For the two designed vibratable castables (Alfred particle packing model, $q = 0.26$ [11]) coarse tabular alumina was added as aggregates ($d \leq 6$ mm, Almatis, USA) and dead-burnt magnesia ($d < 45$ μm, 95 wt% of MgO, $CaO/SiO_2 = 0.37$, Magnesita Refratários S.A., Brazil), silica fume (971U, Elkem, Norway), reactive alumina (CL370, Almatis, USA) and fine tabular alumina ($d < 200$ μm, Almatis, USA) comprised the matrix of these compositions. Moreover, calcium aluminate cement – *CAC* – (Secar 71, Kerneos, France) or hydratable alumina – *HA* – (AlphaBond 300, Almatis, USA) were selected as binders and their influence on the corrosion behavior were investigated. Table 1 shows their overall compositions.

During the processing step, 0.2 wt% of a polycarboxylate-based dispersant was added to the castable suspensions (Bayer, Germany) in order to ensure suitable dispersion of the fine particles. Additionally, 3.9 and 5.3 wt% of distilled water was required for the IS-6C1S and IS-6H1S mixing, respectively. The prismatic samples used in the corrosion tests (150 mm × 25 mm × 25 mm) were molded, cured at 50 °C for 24 h, dried at 110 °C for 24 h and pre-fired for 5 h at 600 °C. In order to ensure the formation of in situ spinel and calcium hexaluminate (CA_6) in the castable microstructure [12,13], the prepared samples were also thermally treated at 1500 °C for 5 h.

Table 1
General information of the castables compositions.

	Designed compositions	IS-6C1S	IS-6H1S
Raw materials	Tabular ($d < 3$ mm) and reactive alumina ($d_{50} = 4$ μm)	87	87
	Dead-burnt magnesia ($d < 45$ μm)	6	6
	Calcium aluminate cement	6	–
	Hydratable alumina	–	6
	Silica fume	1	1

Before the corrosion tests, small cups were drilled into the fired samples (central inner diameter of 10 mm and 10 mm deep), which were filled with a mixture of 90 wt% of the slag (Table 2) and 10 wt% of iron oxide. The corrosion cup tests were conducted in a vertical tube furnace in a controlled oxidizing atmosphere (oxygen partial pressure = 0.21 atm) (HTRV 100-250/18 GERO) at 1550 °C for 2 h. The corroded samples were also cut and their cross sections were polished for scanning electron microscopy evaluation (JEOL JSM – 5900 LV, The Netherlands).

Thermodynamic simulations were carried out using FactSage [version 6.2, Thermfact/CRCT (Montreal) and GTT-Technologies (Aachen)], which comprises a series of modules that access and cross link thermodynamic databases and allow various calculations. For this study, the databases used were Fact53, SGTE and FToxid, and the Equilib and Viscosity modules were selected for the chosen simulations.

Two calculation procedures were developed by the present authors and compared considering the liquid composition changes during the contact between the refractory–slag at high temperatures. According to a first proposed model [10], 100 g of each designed castable (in this case, only the overall compositions was evaluated – Table 1) and 100 g of a slag composition (comprised of a mixture of 90 wt% of an industrial secondary metallurgy slag – Table 2 – and 10 wt% of Fe_2O_3) were considered in the first reaction stage between these two materials. All calculations were made for a constant temperature of 1550 °C and pressure of 1 atm. After the first reaction step, the resulting liquid slag (S_1) was again put in contact with the same amount (100 g) of the original castable composition used before and a further thermodynamic calculation was carried out. This procedure was constantly repeated until the calculated amount of the main solid phases (after all the possible reactions) attained a constant value. After that, the changes in the amount of the phases (predicted by the thermodynamic simulations) formed during the interaction of the liquid with the castables were compared with those attained in experimental corrosion cup-tests.

Nevertheless, it is well known that the matrix portion of the castables (comprised by the binder and other components with finer average particle size, $d < 100$ μm) is very reactive and can be easily incorporated by the slag. Thus, a further route to analyze the castable corrosion consists of the following simulation steps: (1) the contact between the slag and the matrix and after the liquid saturation, (2) the interaction between the resulting slag and the aggregates. In this case, the same procedure described before were applied, where initially

Table 2
Chemical composition of the industrial secondary metallurgy slag.

Composition	Al_2O_3	MgO	CaO	SiO_2	MnO	Fe_2O_3
Wt%	29.6	3.1	44.9	5.3	2.2	4.9