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Slag attack evaluation of in situ spinel-containing refractory castables via experimental tests and thermodynamic simulations

A.P. Luz [a,*], M.A.L. Braulio [a], A.G. Tomba Martinez [b], V.C. Pandolfelli [a]

[a] *Federal University of São Carlos, Materials Engineering Department, Rod. Washington Luiz, km 235, São Carlos, SP 13565-905, Brazil*

[b] *Materials Science and Technology Research Institute (INTEMA), Ceramics Division, Av. Juan B. Justo 4302, 7600 Mar del Plata, Argentina*

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Abstract

Although the in situ spinel formation in alumina–magnesia refractory castables induces an expansive behavior, many investigations highlight its positive role in the corrosion resistance of such materials. Thus, this work addresses the slag attack evaluation of four designed in situ spinel-containing castables (containing hydratable alumina or calcium aluminate cement as a binder source and 0 or 1 wt% of silica fume) when in contact with a Fe_xO rich industrial slag. Corrosion cup-tests, microstructural characterization and a two-step thermodynamic simulation model were used in order to investigate the reactions taking place during the slag–refractory interactions. According to the attained results, hydratable alumina seems to be a suitable binder to improve the corrosion resistance of such castables, as it induces densification and the formation of an alumina-rich spinel phase at the slag–matrix interface. Moreover, the thermodynamic calculations matched to the experimental observations, attesting the efficiency of the proposed simulation model for the evaluation of the in situ spinel-containing castable corrosion behavior.

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

1. Introduction

Spinel ($MgAl_2O_4$) containing castables are widely used in steel ladles due to their outstanding thermo-mechanical properties, extended service life and chemical resistance [1]. Many investigations highlighted that fine and well distributed $MgAl_2O_4$ grains, formed in situ by the reaction of MgO and Al_2O_3 in the castable matrix, can increase slag corrosion resistance when compared to pre-formed spinel containing ones [2–5]. According to the proposed mechanism [2,4], CaO from the slag reacts with Al_2O_3 (available in the castable composition) forming calcium aluminate phases (CA_2 and CA_6), whereas Mn^{2+}, Fe^{2+} and Fe^{3+} ions can be trapped into the spinel structure via solid solutions. As a consequence, the slag becomes silica-rich, leading to a more viscous liquid and inhibits its penetration into the castable porosity. However, the in situ spinel generation is followed by a volumetric expansion and an exceeded reaction can lead to microcracking, giving rise to novel paths for further slag infiltration.

Some parameters (such as the MgO and alumina grain sizes [6,7], the binder system [8–10], the silica fume content [11–13] and the refractory aggregate sources [14]) influence the volumetric stability of the alumina–magnesia castables. The binder system can affect the in situ spinel formation and its expansive behavior due to its reactions and sinterability at high temperatures. Some authors [6] stated that the use of calcium aluminate cement (CAC) may lead to further expansion, which is mainly associated to CA_2 and CA_6 formation (where $C = CaO$ and $A = Al_2O_3$). Conversely, hydratable alumina (which is a binder based on the re-hydration ability of ρ-Al_2O_3) is an alternative material that can inhibit the CA_6 formation (due to the lack of CaO), resulting in a less porous microstructure containing finer spinel grains [6,7].

Regarding the silica fume role in the Al_2O_3–MgO castables properties, its addition to cement containing compositions can induce the presence of low melting temperature phases and a counterbalancing effect on the spinel disruptive expansion [11]. Moreover, this additive affects the calcium aluminates (CA_2 and CA_6) generation and speeds up $MgAl_2O_4$ formation, due to the ion diffusion increase in the presence of liquid phases [12,13]. Despite these advantages, high liquid contents result in

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* Corresponding author. Tel.: +55 16 33518253; fax: +55 16 33615404.
E-mail address: anapaula.light@gmail.com (A.P. Luz).

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shrinkage and decrease the castables refractoriness and corrosion resistance [14]. Conversely, the presence of silica fume in hydratable alumina bonded castables can also lead to a lower amount of a metastable SiO_2–Al_2O_3 liquid phase formation (~1250 °C), providing densification and reducing the overall in situ spinel expansion.

Based on these aspects, this work investigates the corrosion behavior of four designed alumina–magnesia castable compositions (containing hydratable alumina or calcium aluminate cement as a binder source and 0 or 1 wt% of silica fume) when in contact with high-iron oxide containing industrial slag at 1500 °C. Corrosion cup-tests, microstructural characterization (SEM–EDS) and thermodynamic calculations were carried out in order to evaluate and understand the possible reactions taking place during the slag–refractory interaction. An optimized thermodynamic simulation procedure [15] (where firstly the molten slag was placed in contact with the matrix components and later with the aggregates) was applied and the calculated results were presented, discussed and compared with the experimental ones.

2. Experimental and thermodynamic calculations

Four vibratable alumina–magnesia castables were designed according to the Alfred particle packing model ($q = 0.26$) [16]. The compositions comprised coarse tabular alumina as aggregates ($d \leq 6$ mm, Almatis, USA), dead-burnt magnesia ($d < 45$ μm, 95 wt% of MgO, $CaO/SiO_2 = 0.37$, Magnesita Refratários S.A., Brazil), reactive alumina (CL370, Almatis, USA), fine tabular alumina ($d < 200$ μm, Almatis, USA), silica fume (971U, Elkem, Norway) and calcium aluminate cement (CAC, Secar 71, Kerneos, France) or hydratable alumina (HA, AlphaBond 300, Almatis, USA) as binders. Table 1 presents the overall compositions evaluated in this work. A total of 6 wt% of MgO was added to the designed castables in order to result in 21 wt% of stoichiometric in situ spinel (72 wt% Al_2O_3–28 wt% MgO) after the reaction with calcined and fine tabular Al_2O_3 particles during the pre-firing step at 1500 °C.

The castable dispersion was carried out by adding 0.2 wt% of a polycarboxylate based dispersant (Bayer, Germany), leading to 3.9–4.1 wt% (CAC) or 5.3 wt% (HA) water content for a suitable vibratable shaping. After the mixing step, cylindrical samples with an external diameter of 10 cm, 10 cm in height, a central inner hole 5 cm in diameter and 5 cm deep were molded, cured at 50 °C for 24 h [in a humid environment (relative humidity = 100% for castables containing CAC – AM-6CAC0S and AM-6CAC1S) and at room conditions (relative humidity = 40% for the ones bonded with hydratable alumina – AM-6HA0S and AM-6HA1S)], dried at 110 °C for 24 h, calcined at 600 °C for 5 h and thermally treated at 1500 °C for 5 h (this last step was required in order to allow the in situ spinel and CA_6 formation).

Before the corrosion tests, the cup samples were filled in with 150 g of an industrial slag (Table 2). The corrosion cup tests were conducted in an electrical furnace (Lindberg Blue, Lindberg Corporation, USA) in an oxidizing atmosphere (oxygen partial pressure = 0.21 atm) at 1500 °C for 2 h.

After that, the corroded samples were cut and had their cross sections polished and prepared for scanning electron microscopy analysis (JEOL, JSM-7500F model, Germany). In addition, the slag penetration area was calculated using the Image J 1.42q software (Wayne Rasband, National Institutes of Health, USA), according to the procedure described by Braulio et al. [5] in order to quantify the corrosion damage.

Thermodynamic simulations were carried out using FactSage^{TM} version 6.2 [Thermfact/CRCT (Montreal) and GTT-Technologies (Aachen)]. Fact53, SGTE, FToxid databases and the Equilib and Viscosity modules were selected for this evaluation. All calculations were conducted considering a constant temperature of 1500 °C and pressure of 1 atm. Based on a two-step modeling calculation (previously developed by the authors [15]), initially 100 g of slag and 100 g of the castable matrix (Table 3) were reacted and the resulting liquid after each step was successively placed in contact with the original matrix, until the slag saturation was reached.

After that, 100 g of the resulting slag (liquid saturated with the matrix components) was used in the calculations involving 100 g of the aggregates. Due to the in situ $MgAl_2O_4$ and CA_6 formation (the latter taking place only for the CAC containing compositions) at the pre-firing step at 1500 °C, these formed phases were also considered for the matrix simulation (Table 3). In order to define the matrix composition for the thermodynamic simulations, not only the amount of the initial raw materials of the designed castables was considered, but also the results attained by quantitative X ray diffraction (XRD) and scanning electron microscopy (SEM–EDS) evaluations of the fired samples [5] were used.

3. Results and discussion

3.1. Corrosion cup-tests and microstructural analysis

Fig. 1 presents the corroded sample images and the calculated penetration area after the slag infiltration. The

Table 1
General information related to the castable compositions.

Raw materials (wt%)	AM-6CAC0S	AM-6CAC1S	AM-6HA0S	AM-6HA1S
Tabular and calcined alumina	88	87	88	87
Dead-burnt magnesia	6	6	6	6
Calcium aluminate cement	6	6	–	–
Hydratable alumina	–	–	6	6
Silica fume	–	1	–	1

AM: alumina magnesia; CAC: calcium aluminate cement; S: silica fume.