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CA_6 impact on the corrosion behavior of cement-bonded spinel-containing refractory castables: An analysis based on thermodynamic simulations

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

[a]*Materials Science and Technology Research Institute (INTEMA), Ceramics Division, Av. Juan B. Justo 4302, 7600 Mar del Plata, Argentina*
[b]*Federal University of São Carlos – Materials Engineering Department, Rod. Washington Luiz, km 235, São Carlos, SP, C.P. 676 CEP 13565-905, Brazil*

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Abstract

This work focuses on the evaluation of the corrosion behavior of Al_2O_3–MgO cement-bonded castables based on thermodynamic calculations, in order to understand the reaction steps and some scientific and technological issues that still need to be better explained when such materials come into contact with basic industrial slags at high temperatures. Special attention was given to analyzing the role played by the calcium hexaluminate phase (CA_6) during the first heating stage of the samples and their further chemical attack. Experimental measurements (cup tests at 1500 °C) and thermodynamic simulations were carried out considering a basic slag ($CaO/SiO_2 = 4.2$) and four refractory castables with different spinel ($MgAl_2O_4$) sources (pre-formed or in situ) and with or without silica fume (0 or 1 wt%). Considering the attained results, a novel corrosion mechanism is proposed pointing out that a suitable design of the castable compositions can induce the formation of CA_6 at the border of the coarse aggregates, preventing their further dissolution and increasing the overall wear resistance of these refractories. In Addition, incorporating optimized contents of silica fume and cement to the spinel-containing castables helps to master the generation of the CA_6 and CA_2 protective layers, resulting in a lower chemical attack at high temperatures.

Keywords: C. Corrosion; D. Spinel; Castable; Thermodynamic simulation

1. Introduction

Calcium hexaluminate (CA_6, where C = CaO and A = Al_2O_3), generated during the first firing step of alumina–magnesia and alumina–spinel ($MgAl_2O_4$) castables bonded with calcium aluminate cements (CAC), presents a wide primary crystallization field in the CaO–Al_2O_3–Fe_2O_3 phase equilibrium diagram. As a result, refractory compositions containing this phase commonly present lower dissolution when in contact with molten iron-rich slags [1]. Besides that, the CA_6 formation can also increase the fracture energy of the designed refractories due to the platelet shape of these crystals, resulting in a mechanical barrier for the crack propagation derived from thermal stress [2].

As reported in the literature [3,4], the CA_6 formation mechanism, as well as the distribution and morphology of its crystals are extensively affected by the presence of microsilica (MS) and spinel (which can be added as pre-formed grains or by the in situ reaction between Al_2O_3 and MgO at high temperatures) in the formulation. The interaction of corundum [5–7] and Al_2O_3–MgO castables [8–13] with CaO-containing slags at high temperatures (CaO–Al_2O_3–SiO_2, CaO–MgO–Al_2O_3–SiO_2 and other more complex compositions) can also give rise to a dense and continuous layer of CA_6 at the border of the Al_2O_3 coarse grains (indirect corrosion), inhibiting the species diffusion and increasing the corrosion resistance of these materials [11,14]. However, this reaction is usually followed by high volumetric expansion, which can lead to the generation of cracks and flaws in the castable structure [5,6], favoring a greater liquid penetration and spoiling the overall performance of the refractory lining.

The CA_6 distribution in the matrix and/or the aggregate fractions of high-alumina CAC-bonded compositions (due to

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[*] Corresponding author.
E-mail addresses: agtomba@fi.mdp.edu.ar (A.G. Tomba Martinez), vicpando@ufscar.br (V.C. Pandolfelli).

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the reaction of CaO from the cement and the fine and coarse Al_2O_3 particles during firing) should influence the wear behavior and the compounds formed during the contact of molten slags and the castable constituents at high temperatures [13,15,16]. Sako et al. [16], for instance, recently proposed a mechanism to explain the corrosion of cement-bonded Al_2O_3–MgO formulations by basic slags, where the chemical wear degree of these products was directly related to the presence of CA_6 grains at the liquid–aggregates interface.

1.1. Al_2O_3–MgO cement-bonded castables' corrosion mechanism

Various studies concerning the chemical attack of alumina–spinel and alumina–magnesia castables (containing cement as binder source) by basic slags highlighted that the main reaction mechanism derives from the CaO interaction with solid or molten Al_2O_3, leading to CA_6 precipitation, as shown in the following equation:

$$6Al_2O_{3(s,\,l)} + CaO_{(l)} \rightarrow CaO \cdot 6Al_2O_{3(s)} \quad (1)$$

Some authors stated that the alumina is provided by the aggregates [8,17,18], whereas others did not mention whether the source of such oxide would be the coarse or fine grains of the formulation [10]. Nevertheless, in general, it is accepted that the corrosion process is initiated by the attack of the matrix components, followed by the dissolution of the aggregates [10,11,13].

Calcium dialuminate (CA_2) can also be formed as a continuous layer at the interface of the CA_6 grains. This former compound is associated with the reaction of calcium hexaluminate crystals with $CaO_{(l)}$, as presented in Eq. (2). In addition, other studies [5,6] pointed out that CA_2 might be generated before the CA_6 phase and at lower temperature (around 1200 °C) during the corrosion of polycrystalline alumina (Eq. (3)).

$$CaO \cdot 6Al_2O_{3(s)} + 2CaO_{(l)} \rightarrow 3[CaO \cdot 2Al_2O_3]_{(s)} \quad (2)$$

$$CaO \cdot 2Al_2O_{3(s)} + 4Al_2O_{3(s,l)} \rightarrow CaO \cdot 6Al_2O_{3(s)} \quad (3)$$

Berjonneau et al. [18] suggested that the features of these aluminate compounds, identified in cement-bonded Al_2O_3–MgO castable corroded samples indicated their precipitation from the molten slag. Based on experimental tests, Braulio et al. [13] also proposed that CA_6 formation might take place by solid state reactions. Another recent investigation [16] focused on the evaluation of alumina–spinel or alumina–magnesia refractory compositions (comprising pre-formed grains or in situ generation of $MgAl_2O_4$, respectively) containing CAC and with (1 wt%) or without microsilica (MS), after their interaction with a steel ladle basic slag. Fig. 1 shows SEM images that represents the refractory–liquid interface of each prepared formulation after corrosion cup tests carried out at 1500 °C for 3 h.

According to this work [16], the corrosion mechanism of these materials was directly related to the presence of calcium hexaluminate in the original microstructure, where their interaction with a molten liquid rich in CaO, FeO_x and SiO_2 at 1500 °C led to two distinct situations:

(a) The CA_6 crystals formed at the border of the tabular alumina coarse grains (during the pre-firing step of 0MS and 1MS alumina–magnesia castables, and 0MS alumina–spinel sample, Fig. 1) induced the generation of a dense layer of CA_2 (as described in Eq. (2)) that inhibited further infiltration.

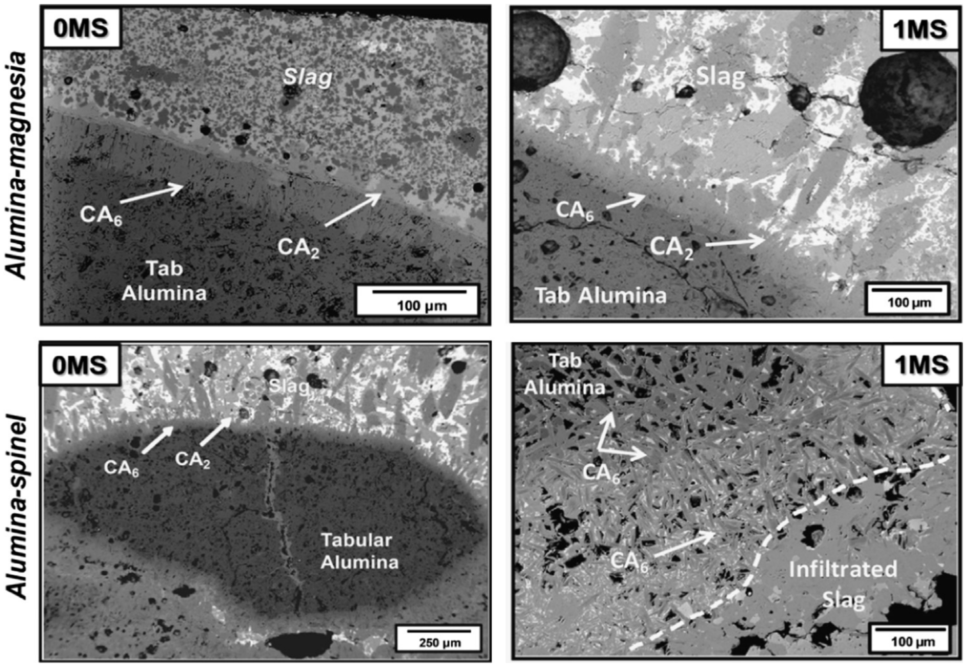

Fig. 1. SEM images of the refractory–slag interface for the Al_2O_3–MgO and Al_2O_3–$MgAl_2O_4$ castables' corroded samples attained after cup tests carried out at 1500 °C for 3 h. 0MS = microsilica-free; 1MS = 1 wt% of microsilica [16].