Magnesium fluoride role on alumina–magnesia cement-bonded castables

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Abstract

Mineralizing agents can be a suitable alternative to speed up and anticipate ($T < 1200\ ^{\circ}C$) spinel ($MgAl_2O_4$) generation, improving the overall performance of refractory castables at high temperatures. Nevertheless, only a few studies have investigated the impact of magnesium fluoride on the properties of such materials. Considering this aspect, aqueous suspensions and alumina–magnesia cement-bonded compositions with and without MgF_2 were evaluated in order to better understand its effect on the castable's phase evolution. Thermogravimetric tests, X-ray diffraction, thermodynamic analysis, apparent porosity, hot elastic modulus and sintering assisted measurements were carried out to evaluate the compositions. The mineralizing agent reacted with calcium aluminate cement in the initial processing steps giving rise to CaF_2. Additionally, the prepared suspensions also revealed that solid state reactions between reactive alumina and MgF_2 induced spinel formation at relatively low temperatures ($800\ ^{\circ}C$). Due to the presence of these two fluorides (MgF_2 and CaF_2), a liquid phase was formed at temperatures close to $1000\ ^{\circ}C$, increasing the $MgAl_2O_4$ generation rate. The transformations identified in the suspension compositions were in tune with the castables' *in situ* hot elastic modulus results. These later measurements also revealed that the liquid phase presented a transient feature, as it was completely consumed during transformations at high temperatures. Nevertheless, the samples showed a marked thermal expansion due to spinel formation, indicating that an additional component to counterbalance this volumetric expansion (such as small amounts of fumed silica) must be simultaneously added to this castable material.

1. Introduction

It is already well stated that the solid state reaction between alumina and magnesia, to generate $MgAl_2O_4$, is controlled by an inter-diffusion mechanism of Mg^{2+} and Al^{3+} ions [1–3]. Based on that, to maintain the electroneutrality, three Mg^{2+} ions difuse from the magnesia particles to the alumina ones, whereas two Al^{3+} ions migrate in the opposite direction, leading to spinel formation at the interface area between them. In order to carry on the reaction, Mg^{2+} and Al^{3+} cations need to diffuse through the generated $MgAl_2O_4$ thin layer [1], which slows down the overall reaction rate.

The expansive behavior of this phase transformation is associated with the different densities among the reactants (MgO: 3.58 g/cm^3 and Al_2O_3: 3.98 g/cm^3) and the product ($MgAl_2O_4$: 3.60 g/cm^3). Nevertheless, experimental tests usually lead to expansion levels greater than the theoretical one, indicating that other factors must account for this phenomenon. According to Nakagawa et al. [4], different expansion values can be attained depending on the R parameter, which represents the spinel thickness ratio showing the amount of $MgAl_2O_4$ generated at the alumina side.

Due to the distinct diffusion rate of the involved species, pore formation may also result in the site previously occupied by the higher mobility component (MgO). Therefore, as pointed out in the schematic mechanism shown in Fig. 1, the spinel layer growth leads to a local linear change (ΔX), whereas the counter-flux of vacancies induce the Kirkendall porosity (P) generation at the original magnesia location [5].

Over the last years, various publications in the scientific literature have investigated parameters that influence *in situ* spinel

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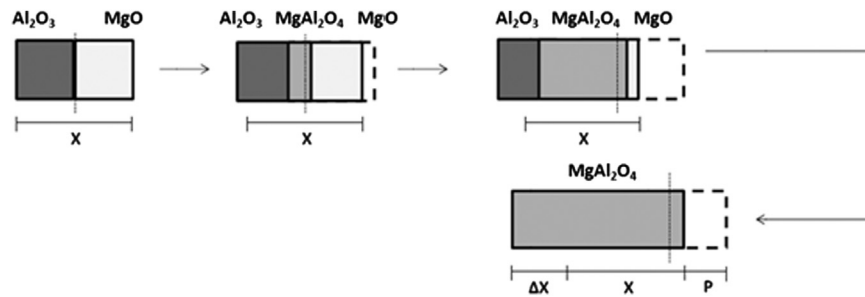*E-mail address:* uaitiago@gmail.com (T.M. Souza).

Fig. 1. Spinel formation process based on the Mg^{2+} and Al^{3+} ions diffusion and Kinkendall porosity generation (where *X*: initial length; ΔX: local linear change and *P*: porosity) [5].

formation. Regarding the MgO sources, coarser particles present lower reactivity, delaying their reaction with alumina [6]. On the other hand, magnesias and aluminas with higher specific surface areas induce the generation of a greater amount of spinel at lower temperatures [7–9]. When dispersed, the use of nanoscaled particle suspensions further enhances the diffusion driving force, speeding up sintering. Based on that, the addition of colloidal alumina suspensions results in materials with lower overall expansion [10,11].

Mineralizing agents can be added to refractory castable compositions aiming to induce *in situ* $MgAl_2O_4$ formation. Different compounds can be used for this purpose in Al_2O_3–MgO based systems such as AlF_3, $MgCl_2$, MgF_2, LiF, B_2O_3, CaF_2, TiO_2, ZnO, etc. [12,13]. These additives act by [12] (i) increasing the solid state reaction rate; (ii) reducing the spinel generation starting temperature; and (iii) changing the liquid phase viscosity or its surface tension, affecting both crystal growth and morphology.

It is reported that the addition of AlF_3 and CaF_2 mineralizers to Al_2O_3–MgO compositions may lead to F^- ions incorporation in the anion sublattice, as its ionic radius is smaller than the oxygen one ($r_{F^-} = 0.136$ nm and $r_{O^{2-}} = 0.176$ nm) [14]. The replacement of O^{2-} ions by F^- ones results in an increase of the cation vacancy concentration, enhancing Mg^{2+} and Al^{3+} diffusion through alumina and spinel lattices.

Although most of the published work was based on the evaluation of fluorides in Al_2O_3–MgO binary mixtures, the presence of different raw-materials can significantly change the mineralizing mechanism. Braulio et al. [15,16], for instance, pointed out that liquid phase formation was the main parameter speeding up spinel generation in the Al_2O_3–MgO–CaO–SiO_2 castables containing 1 wt% of MgF_2. As MgF_2 is an inorganic salt with a relatively high melting point (1255 ± 3 °C [17]), this result highlighted that this additive most likely reacted with other components of the composition.

Considering this scenario, the main objective of this work was to evaluate the addition of magnesium fluoride to Al_2O_3–MgO–CAC refractory castables and its influence on the phase transformations involving the matrix's components. In order to understand the correlation between the *in situ* reactions and the materials' performance, aqueous suspensions containing magnesium fluoride [MgF_2–Al_2O_3, MgF_2–CAC (calcium aluminate cement) or MgF_2–Al_2O_3–CAC] and refractory castable compositions with or without MgF_2 were analyzed. Despite

the promising features of this mineralizing compound, such aspects have not been explored in previous studies.

2. Materials and techniques

2.1. Aqueous suspensions

Firstly, the effect of magnesium fluoride (Sigma-Aldrich, technical grade) on aqueous suspensions (80 wt% of solids) containing MgO–Al_2O_3, MgF_2–Al_2O_3, MgF_2–CAC (calcium aluminate cement) (mass ratio of 1:1 for all of them) and MgF_2–CAC–Al_2O_3 (mass ratio of 1:1:1) was investigated. It is important to highlight that, based on the molar ratio [MgO–Al_2O_3 (1:0.4); MgF_2–Al_2O_3 (1:0.6); MgF_2–CAC (1:0.7); MgF_2–Al_2O_3–CAC (1:0.6:0.7)], all samples comprised an excess of magnesium when compared with the spinel stoichiometric composition ($MgAl_2O_4$).

Suspensions were prepared using dead burnt magnesia (Magnesita Refratários S.A., Brazil; Table 1), reactive alumina (CL370 C, Almatis, USA) and calcium aluminate cement (Secar 71, Kerneos, France). The dispersion was carried out by adding 0.1 wt% of citric acid (Synth, Brazil). Following the mixing step, cylindrical samples (diameter=20 mm × height=20 mm) were cast under vibration, cured at 50 °C for 24 h in an environment with relative humidity close to 80% and dried at 110 °C for another 24 h. Samples were also thermally treated in an electrical furnace (Lindberg Blue, Lindberg Corporation, USA), under a heating rate of 1 °C/min, up to 600, 800, 1000 and 1200 °C with a dwell time of 5 h.

After the thermal treatment, the samples were ground (dp < 45 μm) in a tungsten carbide mill (AMEF, model AMP1-M, Brazil) and analyzed using an X-ray diffraction technique (Bruker equipment, model D8 Focus, Germany) and the EVA software. TG and DSC (differential scanning calorimetry) measurements of the dried materials were carried out in Netzsch STA 449 equipment, under a heating rate of 10 °C/min with synthetic air (80% N_2–20% O_2) flow of 50 cm^3/min and α-Al_2O_3 as a correction standard.

Thermodynamic simulations were also performed using FactSage™ software [version 6.3.1, Thermofact/CRCT (Montreal) and GTT-Technologies (Aachen)] in order to predict the phase transformation evolution and equilibrium phase diagrams of the evaluated systems, under a total pressure of 1 atm and different temperatures. FactPS and FToxid databases and