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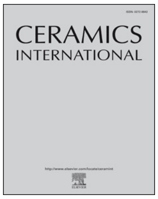

MgO fumes as a potential binder for in situ spinel containing refractory castables

A.P. Luz[a,*], L.B. Consoni[a], C. Pagliosa[b], C.G. Aneziris[c], 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] *RHI Magnesita, Research and Development Center, Praça Louis Ensch, 240, Contagem, MG 32210-902, Brazil*
[c] *Institute of Ceramic, Glass and Construction Materials, TU Bergakademie Freiberg, Agricolastrasse 17, 09599 Freiberg, Germany*

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ABSTRACT

MgO is pointed out as an alternative binder for refractory materials, mainly for systems where the presence of CaO might not be desired. Selecting the most suitable magnesia source is an important step as its purity and reactivity should influence the hydration reaction, leading to binding effect or cracks. This work investigated the design of vibratable high-alumina compositions bonded with MgO fumes [which is a very fine powdered oxide ($d < 3\,\mu m$) resulting from the production process of electrofused magnesia] and/or dead-burnt magnesia ($d < 212\,\mu m$). Acetic and formic acids were added to the castables during their processing steps in order to adjust the density of active sites for $Mg(OH)_2$ formation and control the crystal growth of this phase. The green mechanical strength and thermomechanical performance (cold and hot mechanical strength, thermal shock, refractoriness under load, corrosion, etc.) of designed MgO-bonded compositions were analyzed. Improved green mechanical strength and crack-free samples were obtained when adding up to 6 wt% of MgO fumes to the refractories and processing them with aqueous solutions with 3 wt% of formic acid. The compositions with 6 wt % of magnesia fumes resulted in samples with flexural strength in the range of 12.0 MPa after curing at 50 °C/ 24 h and similar green mechanical strength (12.9 MPa) as the ones bonded with 4.0 wt% of calcium aluminate cement after drying at 110 °C for 24 h, which highlights the great potential of this MgO source. Despite the enhanced green mechanical strength, alumina-based castables containing 6 wt% of MgO (fumes, dead-burnt or their blend) showed low mechanical strength at intermediate temperatures and high linear expansion, as a consequence of the the in situ spinel phase formation above 1200 °C. Thus, better densification, improved HMOR, thermal shock resistance and corrosion behavior were obtained for the castables prepared with less MgO fume contents.

1. Introduction

Recently some efforts have been made in the refractory field in order to develop CaO-free binders (i.e., based on alumina-silica, magnesia or magnesia-silica) that can replace the traditional calcium aluminate cement (CAC) in castable compositions [1–8]. Magnesia might be used as a hydraulic binder due to its reaction with water (Eq. (1)), resulting in brucite [$Mg(OH)_2$] precipitation in the refractory microstructure and, consequently, increasing its overall green mechanical strength when this reaction is properly controlled. Despite the challenges related to the expressive volumetric expansion associated with magnesium hydroxide formation (which can lead to crack generation and damage to the refractory structure during curing and drying steps [9]), the development of MgO-based binders would result in positive technological and economical advantages for refractory producers due to their performance and lower cost compared to CAC products.

$$MgO + H_2O \rightarrow Mg(OH)_2 \quad (1)$$

Selecting the most suitable magnesia source must take into account the purity and reactivity of this oxide, as the smaller the crystal size, the higher the specific surface area and its hydration likelihood [6,9]. Therefore, aiming to prevent the damage associated with the MgO hydration in refractory castables, one may choose to *(i)* induce faster brucite formation before the composition setting time, when the molded material still has enough freedom to accommodate stresses, and/or *(ii)* change the morphology of this hydrated phase by adjusting the pH solution, temperature and using hydrating agents [5,6,10–13].

Ammonium chloride, magnesium acetate, magnesium nitrate, nitric acid, acetic acid, magnesium chloride, sodium acetate, and others, are some examples of compounds that can affect the MgO hydration

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[*] Corresponding author.
E-mail address: anapaula@dema.ufscar.br (A.P. Luz).

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reaction rate [6,10–14]. Santos et al. [10] reported that carboxylic acids can adsorb onto MgO surface in aqueous medium leading to the formation of higher amounts of sites for brucite nucleation, hence, inducing faster hydration of this oxide. This process takes place by the heterolithic decomposition of these molecules on the magnesia surface, releasing H^+ cations and carboxylate anions that can be adsorbed at the sites occupied by O^{2-} or Mg^{2+}, respectively [10,15]. Besides that, the density of active sites on MgO surface is affected by the size of the selected carboxylic acid [10,16]. Therefore, based on the studies mentioned above, a limited growth of this hydrated phase can minimize crack and flaw generation in the refractories' structure.

In fact, magnesia should play two important roles when incorporated into high-alumina refractories, as (*i*) its controlled hydration can induce the binding effect among the castables' components and enhance their overall green mechanical strength and, (*ii*) the further heating of such materials should favor the Al_2O_3 and MgO reaction and, consequently, the spinel ($MgAl_2O_4$) phase formation (which usually takes place above 1000 °C and may also give rise to high volumetric expansion) [17]. The in situ generation of this latter compound is desired as it can increase the castables' slag corrosion resistance due to the spinel ability to trap Mn^{2+}, Fe^{2+} and Fe^{3+} ions in its structure via solid solutions. Thus, the resulting slag becomes silica-rich, leading to a more viscous liquid, which usually inhibits its penetration into the ceramic lining porosity [18]. Nevertheless, both transformations (brucite and spinel formation) can result in interfacial separation between aggregates and matrix or microcracks, depending on the overall expansion and microstructural features (such as the available porosity). This is the reason why the effects of these transformations on the refractory's properties should be monitored as a function of temperature to better understand such reactions and provide some insights that may lead to novel compositions with advanced performance.

Considering the promising results presented by Souza et al. [6] and Santos and colleagues [5,10] when adding formic, acetic or propionic acids to high-alumina refractory castables containing caustic or dead-burnt magnesia sources, this paper investigates the design of vibratable high-alumina compositions bonded with MgO fumes [powdered oxide ($d < 3$ μm) resulting from the production process of electrofused magnesia] and/or dead-burnt magnesia ($d < 212$ μm, which is traditionally added to MgO-containing castables due to its limited reactivity with water). Acetic and formic acids were added to the castables during their processing steps in order to adjust the density of active sites for $Mg(OH)_2$ formation and control the growth of their crystals. The most suitable amount of these acids to be incorporated into the dry-mixes was selected according to the different features of the used MgO powders (Table 1). Not only the green mechanical strength (which is directly related to the binding action derived from the magnesia hydration), but also the thermomechanical performance (cold and hot mechanical strength, thermal shock, refractoriness under load, etc.) of the designed MgO-bonded compositions were analyzed to highlight the benefits and drawbacks of this refractory system when exposed to a broad temperature range (30–1600 °C).

Table 1
Chemical composition and physical properties of the evaluated magnesia sources.

Oxides (wt%)	MgO fumes (MF)	Dead-burnt MgO (M)
CaO	0.61	0.80
MgO	97.34	98.12
SiO_2	0.64	0.34
Others	1.41	0.74
$CaO:SiO_2$ (molar ratio)	1.01	2.52
Properties		
Specific surface area (m^2/g)	5.60	0.56
Particle size (μm)		
d_{10}	0.25	1.77
d_{50}	0.80	15.22
d_{90}	2.96	50.49

2. Experimental

Two magnesia sources (MgO fumes = MF and dead-burnt = M) supplied by RHI Magnesita (Brazil) were evaluated in this work. MF is a very fine and reactive magnesia powder obtained during the production process of electrofused MgO, whereas the dead-burnt one resulted from $MgCO_3$ calcination. More details of MF and M features are shown in Table 1.

Vibratable castable formulations containing coarse and fine tabular alumina ($d < 6$ mm, Almatis, Germany), calcined and reactive Al_2O_3 (CL370 and CT3000SG, Almatis, Germany) and magnesia (MgO fumes and/or dead-burnt) were designed according to Alfred's particle packing model ($q = 0.26$ [19], Table 2). Firstly, castable compositions containing 0.5–6.0 wt% of MgO fumes were prepared in order to analyze the binding effect derived from the hydration process of this oxide. In a second moment, refractories presenting 6 wt% of MF and/or M (which should give rise to ~21 wt% of in situ $MgAl_2O_4$ formation at high temperatures) were also evaluated as, based on previous investigations [20–23], the optimal spinel content to improve the slag resistance and wear mechanisms of these high-alumina $MgAl_2O_4$-containing castables would be in the 20–25 wt% range. Less than 20 wt% of spinel content usually leads to a higher corrosion rate, whereas above 25 wt% it results in greater penetration [24].

Additionally, dos Santos et al. [5,10] pointed out that carboxylic acids can be added as agents to adjust the kinetic of MgO hydration in castable compositions, reducing the development of cracks even when using very reactive magnesia sources. Therefore, formic (molar mass: 46 g/mol, purity = 85%, Labsynth, Diadema, Brazil) and acetic (molar mass: 60 g/mol, purity = 99.7%, Labsynth, Diadema, Brazil) acids were selected as nucleation site activators for further brucite crystal formation and growth. Aqueous solutions containing 0.3–3.0 wt% of carboxylic acids (Table 2) were prepared and added to the castables' dry compositions during their mixing process.

A total of 0.1 or 0.2 wt% of the dispersant Castament® FS60 (Basf, Germany) was used during the preparation of the designed formulations. The dry-compositions were homogenized for 1 min and mixed with water for an additional 3 min in a rheometer [25]. The required liquid content and attained flow (ASTM C1445) are shown in Table 2. After that, prismatic samples (150 mm × 25 mm × 25 mm) were cast, cured at 50 °C for 24 h and dried at 110 °C for another 24 h. The curing temperature of 50 °C was selected in order to compare the developed mechanical strength of the prepared MgO-bonded castables with equivalent calcium alumina cement (CAC)-containing compositions.

The green mechanical strength of the cured and dried refractories was evaluated via 3-point bending tests (ASTM C133-97), whereas the apparent porosity was determined according to ASTM C380-00 using kerosene as the immersion liquid. A total of 5 samples were analyzed for each selected testing condition and the presented values consist of the average result as well as the calculated standard deviation.

After selecting the most promising castable compositions, additional samples were prepared and fired in the range of 300–1550 °C for 5 h. Cold flexural strength, apparent porosity, assisted sinterability, creep, refractoriness under load, permanent dimensional change, thermal shock resistance and hot modulus of rupture (HMOR) measurements were selected to evaluate the refractories' thermo-mechanical performance. The latter test was carried out at 300 °C, 600 °C, 900 °C, 1200 °C and 1450 °C (using five samples pre-fired for 5 h at the same testing temperature or at 1500 °C) in HBTS 422 equipment (3-point bending device, Netzsch, Germany).

Assisted sinterability, refractoriness under load and creep measurements were carried out in order to find out the linear dimensional change and thermal stability of the samples up to 1550 °C. Cylindrical specimens (height and external diameter = 50 mm and central inner diameter = 12.5 mm) were prepared according to 51053 DIN standard