IN SITU SPINELIZATION OF ZnO-CONTAINING Al_2O_3-BASED CASTABLES

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ABSTRACT

Although MgO-containing refractories have been extensively investigated during the latest decades, few studies evaluated the likelihood of using other chemical elements as inducers of spinel-like phase formation in refractory castables. In this regard, ZnO is a promising alternative as it can react to alumina at lower temperatures, giving rise to the spinel $ZnAl_2O_4$ (gahnite), which is nontoxic, has high refractoriness (> 1900 ºC), and suitable corrosion resistance. In this work, the addition of ZnO in alumina-based castables was assessed and compared with its MgO counterparts. Differential scanning calorimetry pointed out that gahnite formation takes place at lower temperatures (~ 1000 ºC) than the spinel $MgAl_2O_4$ (~ 1300 ºC). On one hand, this lower formation temperature induces anticipated mechanical strengthening, giving rise to the possibility of firing the ZnO-containing compositions at lower temperatures. On the other, scanning electron microscopy highlighted that this faster kinetics of $ZnAl_2O_4$ formation leads to remarkable changes in the morphology of the pores generated during the firing process, which is assigned to the Kirkendall effect. In contrast to MgO-containing compositions, the pores created by $ZnAl_2O_4$ formation are preferentially located at the interface of the alumina aggregates, inducing their partial detachment, which affects some key properties of the castable.

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1 INTRODUCTION

Since its beginning, the steelmaking industries have been leading technological breakthroughs due to the ever-increasing demand for higher productivity, performance and, more recently, sustainability. The continuous casting, RH degassing, direct reduction furnaces, application of bubbling-based methods to clean the steel and the partial replacement of chromite-containing refractories are just some examples. Regarding the latter, it is worth highlighting that since the 1970s, the system $MgO-Al_2O_3$ became extensively studied and applied as it is nontoxic and reacts at high temperatures (> 1300 ºC) forming the $MgAl_2O_4$ spinel, enhancing the mechanical behaviour and the slag corrosion resistance of the refractory[1].

Although its suitable thermo-mechanical and chemical properties, some aspects regarding $MgAl_2O_4$-containing castables remain unaddressed, such as the elevated formation temperature of $MgAl_2O_4$ in these systems (> 1300 ºC)[1], which implies high energy demand for its production, and the high carbon footprint related to MgO production (up to 7.5 kg CO_2 eq / kg MgO)[2]. In this sense, the introduction of alternative spinel-like phase inducers in alumina-based refractories may overcome these issues.

Having the same valence and almost the same ionic size as Mg^{2+}, zinc seems to be a promising alternative as it is harmless and reacts with alumina at intermediate temperatures (~ 1000 ºC), giving rise to the $ZnAl_2O_4$ spinel[3] (also referred to as gahnite). This crystalline phase has high refractoriness (> 1900 ºC), and good resistance to acids and alkali environments[3]. Additionally, its CO_2 footprint is estimated to be 30 % lower[4]. Although presenting these worthwhile features, few studies on using zinc sources in alumina-based refractory compositions were published. In this study, the addition of 11.4 wt% of ZnO (the amount required to generate 23 vol% of the spinel $ZnAl_2O_4$) in alumina-based castables bonded with calcium aluminate cement (CAC) or hydratable alumina (HA) was evaluated and compared with their MgO-counterparts, which characterizations were previously published by some of the authors[5].

2 MATERIALS AND METHODS

Tabular alumina (TA, d < 6 mm, Almatis, Germany) and reactive alumina (CL370, Almatis, Germany) were combined to obtain a vibrated castables (Alfred's particle packing, q = 0.26). Calcium aluminate cement (CAC, Secar 71, Imerys Aluminates, France) or hydratable alumina (HA, AlphaBond 300, Almatis, Germany) was used as binders, ensuring suitable mechanical strength at the pre-fired condition (green). For the compositions tested in this work, 11.4 wt% of ZnO (analytical grade, d_{50} = 0.65 µm, Basile Química, Brazil) was added to allow the formation of 23 vol% of $ZnAl_2O_4$, which is the same volume of $MgAl_2O_4$ attained in previously reported compositions (using MgO sinter, d_{50} < 212 µm, RHI Magnesita, Austria) taken as a reference. See Table I for details. All compositions were dispersed in a planetary rheometer with distilled water (3.8 wt% - 4.8 wt%) and 0.2 wt% of a polyethylene glycol-based dispersant additive (Castament FS60, BASF, Germany) to ensure suitable shaping according to ASTM C 1445 (vibrated flow ≈ 150%). After mixing, the castables were moulded, cured at 50 ºC for 24 h, and dried at 110 ºC for other 24 h. Additionally, some specimens were thermally treated at 1150 ºC, 1300 ºC, or 1500 ºC for 5 h.

Table I: Composition of castables.

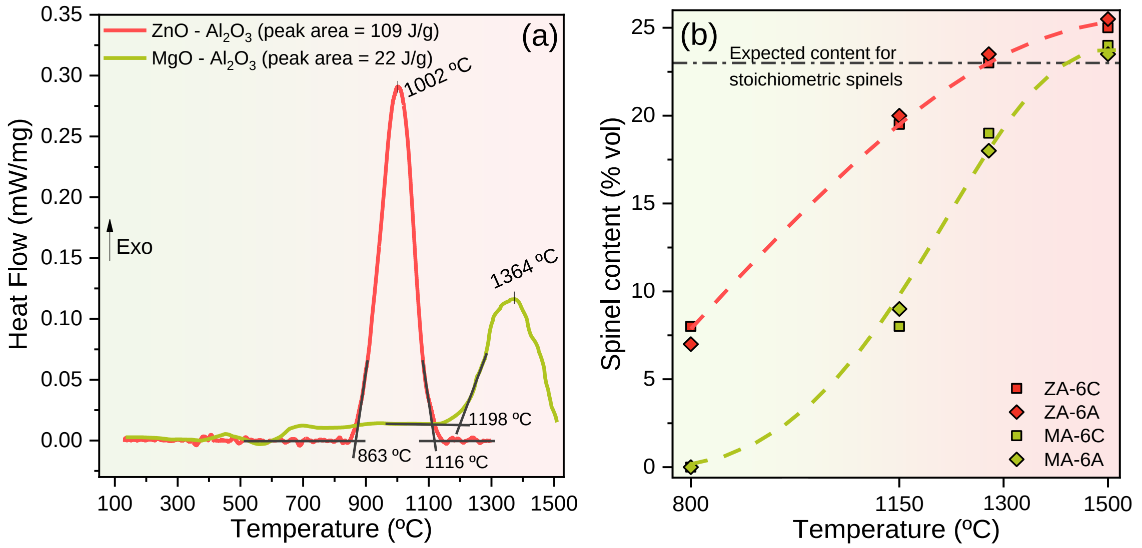
	TA	CL370	CAC	HA wt%	MgO	ZnO	SiO_2	Reference
MA-6C	80.0	7.0	6.0	-	6.0	-	1.0	Braulio *et al.*[5]
MA-6A	80.0	7.0	-	6.0	6.0	-	1.0	Braulio *et al.*[5]
ZA-6C	76.6	5.0	6.0	-	-	11.4	1.0	This study
ZA-6A	77.6	4.0	-	6.0	-	11.4	1.0	This study

Aiming at tracking down the kinetics of gahnite ($ZnAl_2O_4$) and spinel ($MgAl_2O_4$) formation, a stoichiometric amount of alumina and ZnO or MgO were analysed by differential scanning calorimetry (STA 449 F3 Jupiter, Netzsch, Germany) up to 1500°C (20 °Cmin^{-1}). Evaluating the formation of such phases in the castables, quantitative mineralogical content was assessed by applying Rietveld's refinement (Topas software, version 4.2, Bruker, USA) on X ray diffraction patterns (D8 Focus equipment, Bruker, Germany) of samples fired at different temperatures. *In situ* elastic modulus measurements up to 1400 ºC (Scanelastic equipment, ATCP Physical engineering, Brazil) were conducted in pre-fired samples to evaluate their strengthening behaviour during the sintering process. The dimensional change of fired samples was determined using the liquid immersion method (ASTM C20). Thermal shock damage resistance (ΔT = 1000 ºC) was conducted using multiple cycles for bars previously fired at 1500 ºC for 5 h. After every 2 cycles, the samples had their elastic modulus measured by the non-destructive resonance method (ASTM C-1198, Sonelastic equipment, ATCP Physical engineering, Brazil). Microstructure analysis by scanning electron microscopy (SEM) using the backscattered electron mode (BSE) was carried out using the Inspect S50 microscope (FEI Company, USA).

3 RESULTS AND DISCUSSION

Firstly, to assess the formation kinetics of the two spinel-like phases ($ZnAl_2O_4$ and $MgAl_2O_4$), equimolar mixtures of alumina and ZnO or MgO had their calorimetric profile assessed by differential scanning calorimetry (DSC) up to 1500 ºC [see Fig. 1(a)]. In tune with the literature, DSC analysis showed that gahnite started to form close to 850 ºC and had its maximum formation rate at 1002 ºC. For the magnesia spinel, these temperatures were 1198 ºC and 1364 ºC, respectively. Additionally, it could be confirmed that the peak of gahnite formation is narrower and results in a higher exothermic reaction than that of magnesia-spinel (109 gJ^{-1} and 22 gJ^{-1}, respectively), which indicates that the formation of MgO-spinel is carried out in a broader range of temperatures and with less energy release. This behavior can be assigned to the different mechanism of $ZnAl_2O_4$ and $MgAl_2O_4$ formation. The latter is formed by a counter-diffusional reaction, whereas $ZnAl_2O_4$ formation is carried out in a one-way transference of ZnO through Al_2O_3. Thus, this analysis pointed out a promising trend of anticipated formation of the Zn-spinel. However, the calorimetric analysis can only be run for small samples (up to 80 mg), which could not be representative of the whole castable. Therefore, ZnO- and MgO-containing compositions (MA-6C, MA-6A, ZA-6C, and ZA-6A) had their spinalization trend evaluated by quantitative X ray diffraction (XRD) after thermal treatment at several temperatures with a dwell time of 5 h [see Fig. 1(b)].

Figure 1: (a) Differential scanning calorimetry (DSC) of $ZnO-Al_2O_3$ (red) and $MgO-Al_2O_3$ (green) systems; and (b) spinel content assessed by quantitative X ray diffraction.

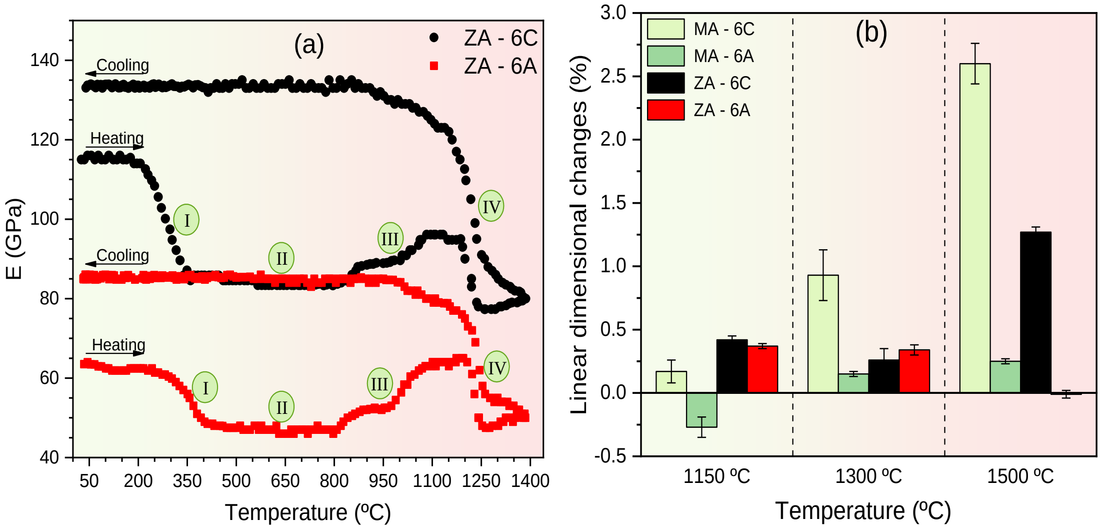


It could be seen that the binding system did not significantly affect the spinel content in all evaluated compositions. Conversely, the type of spinel-inducer additive showed a major influence. Accordantly to the DSC data, quantitative XRD confirmed that ZnO-containing compositions displayed spinel-like phase formation at lower temperatures. As indicated by DSC and XRD, the system $ZnO-Al_2O_3$ presented a higher reactivity than the $MgO-Al_2O_3$, which is expressed by the lower formation temperature of gahnite compared with the MgO-spinel. This trend raised the possibility of anticipated strengthening of ZnO-containing castables as the phase formation reaction can deliver an additional energy, favoring the sintering process. To investigate this hypothesis, *in situ* elastic modulus evaluation as a function of temperature up to 1400 ºC was performed [see Figure 2 (a)]. For both, CAC and HA bonded castables, a similar trend was observed. Above 200 ºC, the decomposition of hydrated phases took place (Region I), which is followed by a plateau (Region II) up to 800 ºC. Elastic modulus increases at intermediate temperatures (~ 800 ºC) was detected for both compositions (Region III), similarly as reported by Pinto *et al.*[6]. This behaviour is attributed to the high Zn^{2+} mobility[3], which favoured the formation of sintering necks and bridges at lower temperatures. After this first E increment, the elastic modulus continuously increased due to the sintering processes up to 1200 ºC. Above this temperature, a remarkable E decrease is noticed, which is assigned to the formation of a Si-rich liquid phase arising by the microsilica addition (Region V). Tracking down the cooling step, one can see that below 1200 ºC the previously formed liquid loses its mobility, resulting in a significant E increase. Below 1000 ºC, no significant E change was noticed, pointing out that no microcracking was induced by a mismatch of thermal expansion coefficients among the distinct phase formed. Therefore, CAC and HA were suitable to produce ZnO-containing castables that showed strengthening at intermediate (~ 800 ºC) temperatures, which is of high technological interest as lower firing temperature could be applied to produce this type of material.

Additionally, aiming at assessing the effects of phase formation on the dimensional stability, the distinct compositions were evaluated by their linear dimensional changes after firing at different temperatures for 5 h [Figure 2(b)]. At 1150 ºC, the ZnO-containing samples presented higher linear dimensional changes than their MgO counterparts due to the lower formation temperature of $ZnAl_2O_4$. Increasing the firing temperature (1300 ºC and 1500 ºC) resulted in a lower expansion of ZnO-containing samples, whereas it induced a higher expansion of the MgO-containing ones. This trend can be assigned to the densification process and $MgAl_2O_4$ formation, respectively. Moreover, due to the highly expansive formation of CA_6, CAC-bonded castables, no matter the spinel-inducer used, underwent a high expansion between 1300 ºC and 1500 ºC.

To enhance the interpretation of this results, the theoretical volumetric variation related to $ZnAl_2O_4$ and $MgAl_2O_4$ formation was indirectly estimated by calculating the density of the precursors (MgO, ZnO and Al_2O_3) and of the spinel-like phases using Rietveld's refinement to XRD profiles. This analysis showed that $MgAl_2O_4$ formation induces a high expansion (close to 8.4 vol%), which is in tune with previous published results[5]. However, for $ZnAl_2O_4$ the same trend was not attested as the formation of this phase was associated with a slight retraction of ~ 0.25 vol%. In other words, conversely to MgO-containing compositions, the expansion seen in ZnO-containing ones cannot be directly associated with an inherent expansion of the phases formed during the sintering process. In fact, the expansion in these ZnO-containing compositions occurs due to the more pronounced Kirkendall effect faced by these compositions.

Figure 2: (a) Young's modulus profile as a function of temperature up to 1400 ºC. Five regions are highlighted and described in the text; and (b) Linear dimensional changes of ZnO- and MgO-containing castables after firing at the indicated temperature for 5 h.



This effect, which is a well-known phenomenon resulting from the difference of the intrinsic diffusivities of atoms, can generate expansion of the material and located voids (pores) creation. Therefore, the distribution and morphology of the pores formed during the sintering of MgO- or ZnO- containing compositions can vary significantly, affecting the mechanical properties, as will be discussed in the results presented below.

Following the characterization of the castables, samples fired at 1500 ºC for 5 h had their thermal shock damage resistance evaluated (see Figure 3). After subsequent thermal cycles, the lower damage faced by the ZnO-containing castables is clear. This enhanced behaviour of ZnO-containing castables can be assigned to three features: (i) $ZnAl_2O_4$ presents a lower thermal expansion coefficient than $MgAl_2O_4$ (6.4×10^{-6} and 9.8×10^{-6} in the range of 600 ºC – 1200 ºC, respectively)[7]; (ii) this phase also presents higher thermal conductivity (27 $Wm^{-1}K^{-1}$ and 15 $Wm^{-1}K^{-1}$ at room temperature)[8]; and (iii) the distinct morphology of the pores created during $ZnAl_2O_4$, which could be act by branching the cracks. Aiming at evaluating the microstructural changes induced by using ZnO or MgO as spinel-like phase inducers, SEM/EDS analysis was conducted for MA-6A and ZA-6A compositions fired at 1500 ºC for 5 h (see Figure 4).

Figure 3: Thermal shock damage resistance (ΔT = 1000 ºC) for samples fired at 1500 ºC. Absolute values are depicted in (a), whereas (b) shows the % of retained elastic modulus.

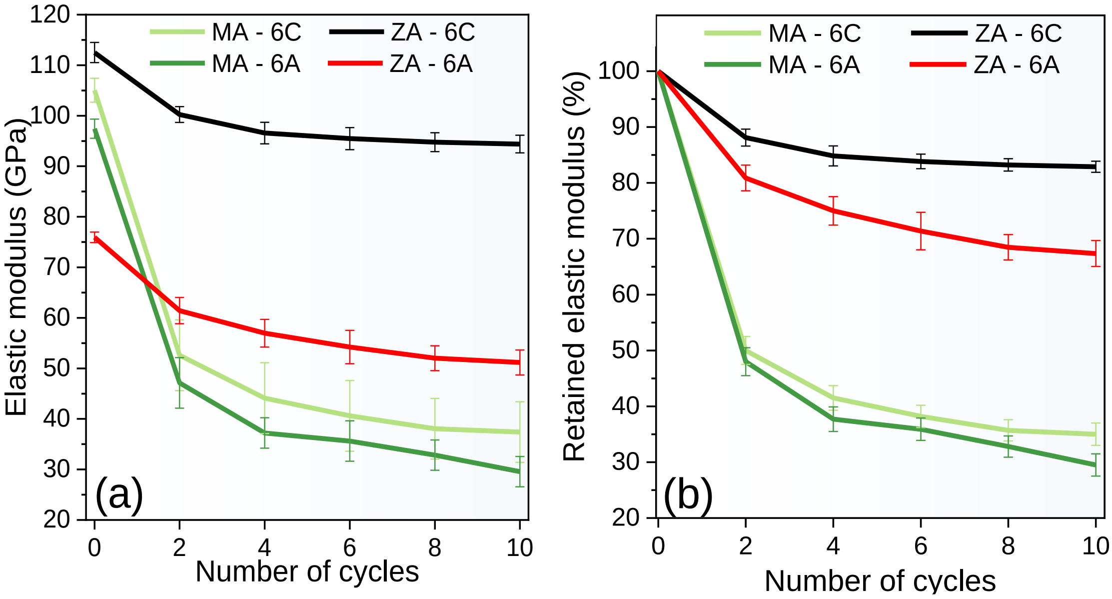
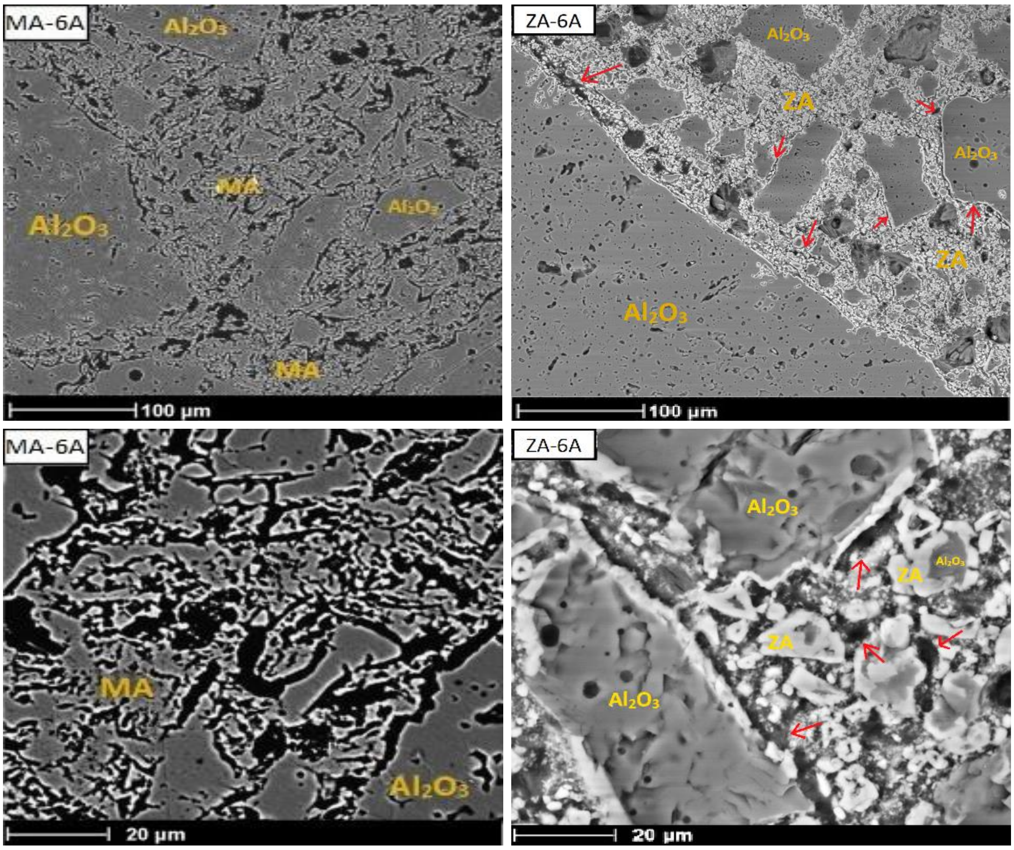


Figure 4: Microstructural evaluations (BSE) of castables bonded with HA after thermal treatment at 1500 ºC for 5 h. MA and ZA denote $MgAl_2O_4$ and $ZnAl_2O_4$, respectively.



It could be seen that only alumina and the spinel-like phases were detected. However, the main output of this analysis was the distinct morphological aspect of MgO-spinel and gahnite generation. Whereas the former was nucleated more uniformly in the castable microstructure, which could be assigned to the counter-diffusional aspect of the reaction between Al_2O_3 and MgO, the latter remained at the interface of alumina particles (forming a gahnite coating) due to the unidirectionality of ZnO in alumina[3]. In contrast to MgO-spinel, in which voids are formed more homogeneously along with the microstructure, the pores induced by gahnite formation are located preferentially at the interface of large alumina grains, leading to detachment of the aggregates.

4 CONCLUSIONS

The effects of replacing MgO with ZnO as spinel-inducing additives in castables bonded with calcium aluminate cement (CAC) or hydratable alumina (HA) were evaluated. Regardless of the binding system used, *in situ* E measurements attested an anticipated strengthening process at intermediate temperatures (~ 800 ºC) for ZnO-containing compositions. DSC and XRD analyses confirmed the lower formation temperature of gahnite ($ZnAl_2O_4$) compared with $MgAl_2O_4$. Although this fast kinetics of gahnite formation looks promising as lower temperatures will be required to produce spinel-based refractory castables, the quick unidimensional diffusion of ZnO may impact other key properties of the castable due to the significant Kirkendall effect that was confirmed by scanning electron microscopy (SEM/EDS) analysis. Thus, it was observed that MgO-spinel formation resulted in voids more uniformly distributed along with the castables microstructure, whereas the pores induced by gahnite formation are located preferentially at the interface of large alumina grains (alumina aggregates), causing their partial detachment from the matrix. Additionally, ZnO-containing compositions presented enhanced thermal shock damage resistance, which can be attributed to (i) its lower thermal expansion coefficient; (ii) the interfacial pores generated due to the Kirkendall effect; and (iii) the higher thermal conductivity.

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