IN-SITU Al_2O_3-MgO AND Al_2O_3-ZnO SPINEL FORMATION: THE KINKERDALL EFFECT ON PHYSICAL AND THERMOMECHANICAL PROPERTIES

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ABSTRACT

The ever-increasing demand for cleaner steels is the driving force for the development of zero-carbon bricks. These refractories have some advantages such as lower thermal conductivity and no direct CO_2 emissions during the operation, reducing thermal losses and environmental impacts related to their use. Differently from the materials technology currently used, which addresses the thermal shock and corrosion resistance by carbon additions, engineered C-free bricks with *in-situ* spinalization in their microstructure emerge as an alternative to fulfill the existing demand for performance and for producing steels with lower carbon contents. Another way to remove carbon from the matrix of bricks for steel ladles applications, is to replace the binder with a C-free system. To enhance some properties of this type of refractory, the addition of spinel-like inducers (MgO or ZnO) has been studied. These oxides react with alumina forming $MgAl_2O_4$ and $ZnAl_2O_4$, respectively. $MgAl_2O_4$ formation is well-known to be a counter-diffusional solid-state reaction, in which the Kirkendall effect leads to a residual porosity. However, few studies evaluated the kinetic aspects of gahnite formation in refractories. This work compares the diffusion mechanisms in the Al_2O_3-MgO and Al_2O_3-ZnO systems, addressing the role played by the Kinkerdall effect on the physical and thermomechanical properties of refractory bricks.

1 INTRODUCTION

The development of the steelmaking industry, which accounts for the largest worldwide refractories consumption, induces the current request for increasingly cleaner steels. In this regard, the refractory industry needs to be innovative adapting its products and processes to improve refractory properties, especially during their applications at high temperatures. This scenario leads to new global refractories demands: produce eco-friendly and easily recyclable products, presenting low CO_2 footprint and lower thermal conductivity. Consequently, the refractory industry needs to pursue novel solutions based on engineered microstructures with the objective of a lifetime increase of refractory bricks, expanding the attaining equipment availability at the customer's site and increasing energy savings during the production process. Unlike the existing technology (Al_2O_3-MgO-Carbon bricks or AMC bricks), which provides enhanced thermal shock and corrosion resistance by the carbon sources addition, tempered bricks with intentional carbon-free microstructure[1], that takes advantage of the first steel ladle heating for the *in-situ* spinelization

emerge as an alternative to fulfill the current requirements for performance and joint closing. Additionally, it induces to the development of ultralow carbon (ULC) steels with lower than 20 ppm of C-content[2].

Among the commercially available minerals, only chrome ore presents spinel in its geological formation and can be directly applied in refractory compositions. All other spinel-like phases used for refractory applications need to be produced by two main routes: *in-situ* formation during the sintering of the material or *ex-situ* syntheses that can be carried out by solid-state reactions or electrofusion processes. *In-situ* spinelization reduces the cost and carbon footprint compared with the pre-formed spinel additions, especially because the electrofusion step is avoided. Nowadays, the most studied and applied spinel-like phase in the refractory industry is the magnesium aluminate ($MgAl_2O_4$) as it presents a suitable balance of physical, chemical, and thermomechanical properties[3]. However, *in-situ* reaction induced by MgO-containing in alumina-based refractories implies some challenges such as hindering [$Mg(OH)_2$] formation and controlling the remarkable expansion associated with the expansion of $MgAl_2O_4$ (6.0-8.0%)[4]. Based on the suitable properties', according to the literature, the optimal %MgO-content for a proper balance between thermal shock damage and corrosion resistance is 6 wt.% (23.1 vol.% of spinel) for non-shaped refractories[5].

Refractory brick properties are evolved as a function of temperature through sintering phenomena, however, there are mechanisms, for example, Wagner and Kinkerdall effects that interfere in this process. According to Wagner's mechanism[6,7], solid-state spinel formation occurs via counter diffusion of Al^{3+} and Mg^{2+} ions at the MgO-$MgAl_2O_4$ and Al_2O_3-$MgAl_2O_4$ interfaces. Because of these reactions, solubility occurs more intensely in the Al_2O_3-$MgAl_2O_4$ layer and as a result, a thicker layer of spinel in the Al_2O_3 aggregate is formed when compared to that of MgO in a theoretical 3:1 ratio. However, Wagner´s mechanisms overlook the residual porosity induced in the microstructure due to the differences in ions diffusion coefficient (Kinkerdall effect)[8]. For shaped bricks, neither the optimum MgO content nor the effects generated by the Wagner´s mechanisms and Kinkerdall effect on the refractory´s properties were clearly mentioned in the literature.

Although the rich literature regarding spinelizing reaction between MgO and Al_2O_3, several other oxides with the same valence of Mg^{2+} can react with alumina to form spinel-like phases, e.g., Mn^{2+}, Fe^{2+}, Co^{2+}, Zn^{2+}, and are interesting alternatives for spinel refractory applications. Each oxide has a specific diffusion speed, with different reaction kinetics and earlier spinelization will occur based on the oxide diffusion rate parameters. To achieve spinelization at lower temperatures and joint closure, zinc oxide stands out as a promising oxide to assist these goals. The presence of $ZnAl_2O_4$ is justified by its high melting temperature (1950 °C), lower thermal expansion coefficient ($7x10^{-6}$; 25-900 °C) and good resistance to acid and alkali attack[6,7]. However, the reaction and kinetics mechanism in the ZnO-Al_2O_3 system, in contrast to the Al_2O_3-MgO system, was not fully addressed, yet. Branson[6] reported that the reaction between zincite and alumina occurs by the solid-state mechanism, in which the diffusion of Zn^{2+} ions to Al_2O_3 and to the $ZnAl_2O_4$ interface is extremally fast, being considered a one-sided diffusion. Due to the lack of studies addressing the spinelization kinetics in MgO- or ZnO-containing shaped refractories, the impacts on expansion, sintering behavior, and mechanical properties remain unexplored. In this work, the comparison of the same volumetric amount (23.1 vol.%) of each spinel ($MgAl_2O_4$ or $ZnAl_2O_4$) *in-situ* produced in alumina-based bricks was conducted and their influence on the physical and mechanical properties was evaluated.

2 MATERIALS AND METHODS

High-alumina shaped bricks were produced by using Alfred´s model with a particle size distribution coefficient of q = 0.37. To compare the Al_2O_3-MgO and Al_2O_3-ZnO systems avoiding interference in the *in-situ* reactions, no mineralizing agent or sintering additives were added, and the same water-based binder system was used for both compositions. As previously mentioned, the addition of 6 wt.% of magnesium oxide (DBM, 98% purity, RHI Magnesita, Brazil) was established as a reference because this is the optimum amount of MgO to obtain a good balance of properties for non-shaped refractories[5]. This magnesia addition induces 23.1 vol.% of $MgAl_2O_4$ in the refractory matrix after firing. To enable a fair comparison, the ZnO-containing composition were produced using 11.4 wt.% of zinc oxide (Zincite, 99,5% purity, Brasoxidos, Brazil), leading to the same volumetric amount of spinel-like phase formed at the thermodynamic equilibrium (23.1 vol.% of spinel). The details of each composition are presented in Table 1, which shows the use of White Fused Alumina (WFA, d > 4,75mm, Elfusa, Brazil) and reactive alumina (RG 400, Almatis, Germany) as Al_2O_3 sources.

All formulations were homogenized in roller mixers and hydraulic presses were used to shape the bricks into 160 x 85 x 63 mm^3. All bricks were tempered at 200 °C / 6 h and then fired for 5 hours at 800 °C, 1000 °C, 1200 °C, 1400 °C and 1600 °C for evaluation. Samples dimensions were measured before and after all heat treatments with digital calipers for linear dimensional changes evaluation. Density and apparent porosity were evaluated by Archimedes' principle (liquid immersion method using kerosene as the liquid medium (NBR-6220)), Cold crushing strength (CSS) were performed in a Kratos ECC (100 kN load cell) (JIS (R-2206)) using 50 mm^3 specimens and hot modulus of rupture (HMOR) tested at 1400°C after 3 hours in an electric furnace with a continuous samples (150 x 25 x 25 mm^3) feeding system and coupled to a mechanical press (Kratos K500/2000). To compare the progress of formed phases after all thermal treatments, quantitative mineralogical content was calculated by applying Rietveld's refinement (Topas software, version 4.2, Bruker, USA) on X ray diffraction patterns (X'Pert PRO equipment, Bruker, USA) obtained from milled samples of each composition. Microstructure analysis by field scanning electron microscopy (SEM) using the backscattered electron mode (BSE) was carried out using the JSM-7100FLV (JEOL, JAPAN) with energy dispersive X-ray spectroscope (EDS) coupled on gold-coated samples. In order to evaluate the damage caused by thermal cycling, the thermal shock resistance test was conducted on a refrigerated copper plate on pre-fired samples at 1600 °C / 5 hrs, where the drop in the elastic modulus was followed during 20 thermal shock cycles with 1000 °C of temperature variation. The elastic modulus was obtained by the ultrasound method, using bars (160 x 40 x 40 mm^3). Based on the ultrasound velocity obtained and measuring the geometric density of the material, the value of the elastic modulus E was calculated.

Table 1: Shaped bricks formulations.

Raw materials	A-23.1M (wt%)	A-23.1Z (wt%)
WFA < 4,75 mm	87.0	81.6
RG 4000 < 75 µm	7.0	7.0
DBM (MgO)	6.0	-
Zincite (ZnO)	-	11.4
Water-based binder system	+	+

3 RESULTS AND DISCUSSIONS

To evaluate the spinelization trend induced by MgO or ZnO, quantitative mineralogical phases content was evaluated by X-ray diffraction. The patterns of the phases formed are presented in Figure 1.

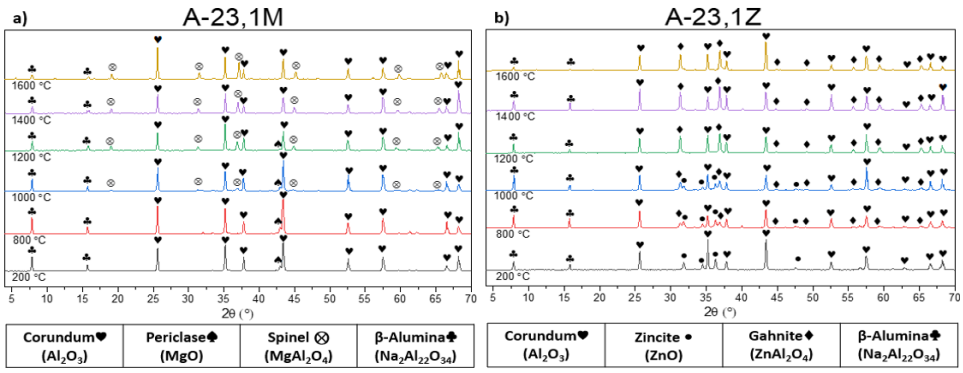

Figure 1: Qualitative X-ray diffraction evolution for Al_2O_3-MgO (a) and Al_2O_3-ZnO (b) systems.

These results confirm the higher reactivity and, thus, earlier spinelization of the Al_2O_3-ZnO compared with the Al_2O_3-MgO system. The former started the spinelization reaction below 800 °C (see the gahnite peak) whereas no $MgAl_2O_4$ was detected for the MgO-containing composition. Additionally, these analyses show full $ZnAl_2O_4$ generation at 1200 °C, which could be attested both for the formation of the expected amount of this spinel phase and for the extinction of the zincite peak in the XRD-diffractogram.

Related to the AB_2O_4 spinel phase evolution and their impact on microstructure, the influence of the expansive spinel phase on the porosity for refractory concretes by Wagner's mechanisms and the Kinkerdall effect are stressed in the literature for magnesia aluminate. However, Wagner's mechanisms do not consider the share of the residual porosity in the microstructure voids, and it has been reported that the Kinkerdall effect has more influence on the expansion than on the diffusional process and spinelization[5]. Additionally, the theoretical calculation shows that $MgAl_2O_4$ formation induces an expansion of approximately 8.1%[4]. The comparative physical properties of Al_2O_3-MgO (A-23.1M) and Al_2O_3-ZnO (A-23.1Z) systems as a function of the different heat treatments are presented in Figure 2.

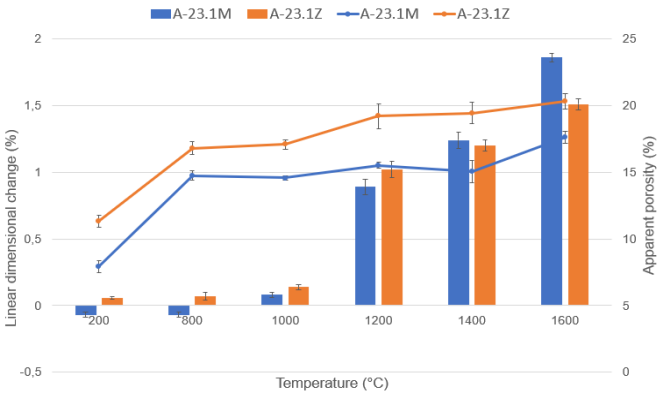

Figure 2: Apparent porosity and linear dimensional change after different firing temperatures.

For all firing temperatures tested, the apparent porosity of the ZnO-containing system showed superior values compared to the MgO-containing system. At 200 °C, this behavior can be explained by MgO-hydration that, in the presence of water, forms brucite [$Mg(OH_2)$], which is not observed for the ZnO-containing system[9]. Between 200 °C and 800 °C, composition A-23.1M presents an apparent porosity increase due to the brucite decomposition and volatiles released from the binder system. However, for A-23.1Z, as the zinc oxide does not hydrate in the processing conditions applied in this work, the porosity trend is assigned to the volatiles exit and may be indicative of the contribution of the early $ZnAl_2O_4$ reaction. Above 1000 °C, all the brucite has been decomposed and no longer influences the porosity, but voids were generated in the microstructure because of its decomposition. Li *et al*.[7], reported the early spinelization capacity of the Al_2O_3-ZnO system and the benefits that this expansion brings to the thermomechanical properties in non-shaped materials, but limited information is found for shaped ones.

In this work, no significant differences were found in the open porosity between the temperatures between 1000 and 1200 °C, and it can be concluded that the early spinelization did not influence the porosity in this temperature range, but above 1200 °C its increase was observed, which could be related to pore coalescence or/and matrix sintering, increasing the distance between the matrix and the medium and coarse aggregates. For the MgO-containing systems, the porosity remains constant after 1000 °C and the influence of the spinelization was only observed above 1400 °C, which is an indicative that the microstructure is no longer able to accommodate the expansive $MgAl_2O_4$ phase, likely affecting the mechanical strength of the refractory brick due to the generation of microstructural defects.

For the Al_2O_3-ZnO system in shaped bricks, the expansion due to $ZnAl_2O_4$ formation and the influence of the Kinkerdall effect on the microstructure were not fully addressed in the literature[4]. Therefore, the same approach applied by Braulio *et al*.[10] to estimate the volumetric expansion related to $MgAl_2O_4$ formation was carried out by using the densities (measured by Helium pycnometer for the raw materials used in this study) and mass percentages of the reacting oxides to form a stoichiometric $ZnAl_2O_4$, according to equation 1. The theoretical variation was obtained by the ratio of the calculated density divided by the experimentally measured density of a stoichiometric spinel (stoichiometric $ZnAl_2O_4$ produced and measured by the authors of this work), represented by equation 2:

$$\frac{1}{\rho} = \frac{Al_2O_3\ \%p}{\rho\ Al_2O_3} + \frac{ZnO\ \%p}{\rho\ ZnO} = \frac{0.56}{3.99} + \frac{0.44}{5.66} \rightarrow \rho \sim 4.59\ \frac{g}{cm^3} \qquad (1)$$

$$\Delta V = \left(\frac{4.59}{4.65} - 1\right) x\ 100 \sim -1.26\% \qquad (2)$$

Analyzing the obtained result, it is concluded that the $ZnAl_2O_4$ formation does not directly imply expansion, in fact, a shrinkage of 1.26 vol.% is expected. However, this was not the trend seen by measuring the linear dimensional changes of the composition after firing at different temperatures, which could be attributed to expansive behavior due to Kinkerdall induced porosity creation (see Figure 2). This result agrees with that found by Braulio *et al.*[10] for MgO-containing refractory castables, showing that the share of the expansion to the porosity has less influence when compared to the residual porosity due to the MgO-diffusion to alumina by the solid-state mechanism. To check how the increase in apparent porosity affects the dimensional variations on *in-situ* gahnite- and spinel-like shaped bricks, linear dimensional changes were carried out. Figure 2 shows the variation in the dimensions of the samples as a function of temperature.

Comparatively evaluating the calculated volumetric differences, 8.1%[4] for $MgAl_2O_4$ and -1.26% for $ZnAl_2O_4$, it is possible to conclude that for the commonly studied system, the combination of spinel expansion together with the residual porosity caused by the Kinkerdall effect resulted in the linear changes and consequently, in the apparent porosity. For the Zn-spinel-like system, based on these results, the porosity values can be related to the linear variation, only generated by the Kinkerdall effect, confirming the mechanism cited by Blanson[6,11]. The expansion at 1600 °C for the MgO-containing system is considered high for steel ladles applications, as each brick can compress its surroundings neighbors resulting in cracks. Therefore, for using the *in-situ* spinelization in refractories bricks, it is necessary to identify the ideal content oxide-addition to ensure that the expansion and properties are suitable for linings applications. To evaluate the behavior of the changes generated in the microstructure by the Wagner´s mechanism and Kinkerdall effect caused by *in-situ* spinelization of ZnO and MgO with alumina after heat treatment at 1600 °C for 5 hours, SEM/EDS analyses were performed and are presented in Figure 3.

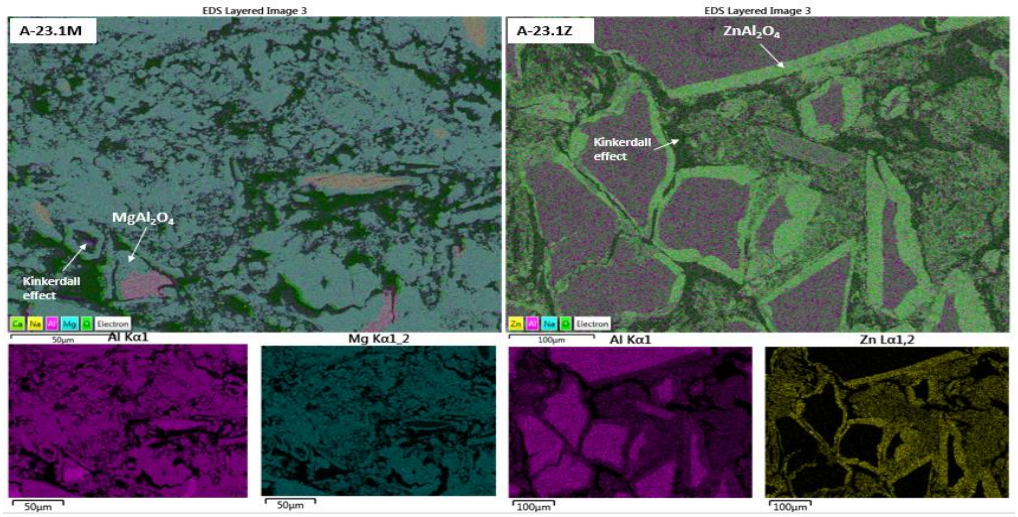

Figure 3: Comparative microstructure evaluation of the samples after firing at 1600 °C / 5 hours analyzed by SEM/EDS.

For A-23.1M, homogeneous reaction sites and a good sinterability between the coarse aggregates and the fine particles were observed. The interdiffusion effect is also seen in this system via the residual porosity due to MgO diffusion surrounded by a spinel ring, presenting periclase scattered out to the entire microstructure. For the A-23.1Z system, the Kinkerdall effect is again more evidenced, with porous networks separating the matrix from the aggregates, hindering sintering and the properties development caused by unilateral diffusion. It was observed that a Zn-diffusion to coarse alumina created a uniform and homogeneous $ZnAl_2O_4$-coating, and it can also be seen a highly reacted and densified matrix, resulting in the increase of this porosity at temperatures above 1300 °C, because of the increased gap between the matrix and aggregates. Aiming at verifying the effect of these two diffusion systems and different degrees of residual porosity, the mechanical compressive strength test was evaluated (Figure 4).

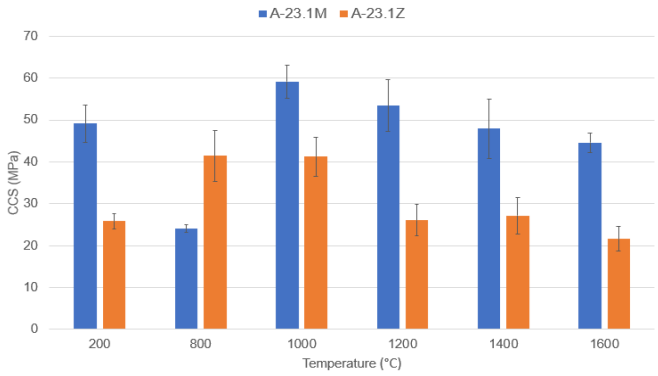

Figure 4: Cold crushing strength (CCS) for high alumina bricks with MgO- or ZnO-addition as a function of temperature.

For the A-23.1M system it is observed that the mechanical strength increases as the spinelization process starts (~1000 °C) and that as the spinelization evolves, the defects in the microstructure led to the decrease of the mechanical strength. Possibly, this behavior in the MgO-containing system may be related to the excessive expansion coming from $MgAl_2O_4$, indicating that for shaped bricks, the 6 wt.% MgO added is above the ideal content for steel ladle applications. An explanation for this drop in mechanical strength is related to the increased porosity and expansive effect of the $MgAl_2O_4$ phase damaging the microstructure. The same effect of increased compressive strength with the spinelization is observed for A-23.1Z up to 200 °C to 800 °C and keeping the same level at 1000 °C caused by the early forming of $ZnAl_2O_4$. However, with the evolution of temperature, it is noted that the Kinkerdall effect starts to govern the mechanical properties, and the high residual porosity practically nullifies the sintering process. This behavior differs from results presented in the literature[12], in which using up to 0.2 wt.% ZnO as an additive increased mechanical property by acting as a mineralizing agent in systems containing $MgAl_2O_4$[12]. In order to evaluate the effect of ZnO and MgO addition on *in-situ* spinelization, the HMOR test was carried out with samples socked at 1400 °C for 3 hours (Figure 5).

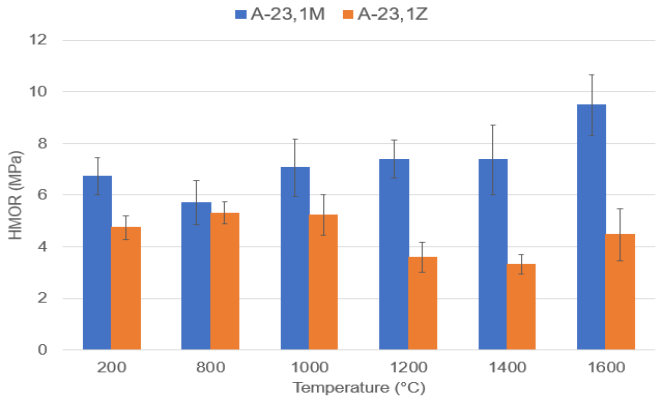

Figure 5: Hot modulus of rupture (HMOR) carried out at 1400 °C / 3 hours of the high alumina bricks with MgO- or ZnO-addition as a function of temperature.

At 200 °C, it is observed that composition A-23.1M presents an improved result compared with A-23.1Z. This fact can be correlated with the apparent porosity values obtained at this same temperature (Figure 2) in which the MgO-containing composition presented a packed microstructure and, thus, fewer

defects in the matrix. At 800 °C it is observed that both compositions presented similar results, and this can be addressed due to the early spinelization of the Al_2O_3-ZnO system. However, at 1000 °C, the spinelization evolves and the Kinkerdall effect starts to govern the microstructural transformations, and above 1200 °C, with the complete formation of $ZnAl_2O_4$ phase, the damage caused by residual porosity directly influences the HMOR values. On the other hand, the composition containing MgO presented increased HMOR values with the firing temperature increased. Such result can be related to the evolution of spinel formation in the Al_2O_3-MgO system (see Figure 1), and it can be concluded that the increase of $MgAl_2O_4$ spinel-like phase formation contributes to the mechanical strength improvement. Looking forward to understanding the effects of $MgAl_2O_4$ and $ZnAl_2O_4$ phases to the thermomechanical properties, the multi-cycle thermal shock damage test was carried out (Figure 6).

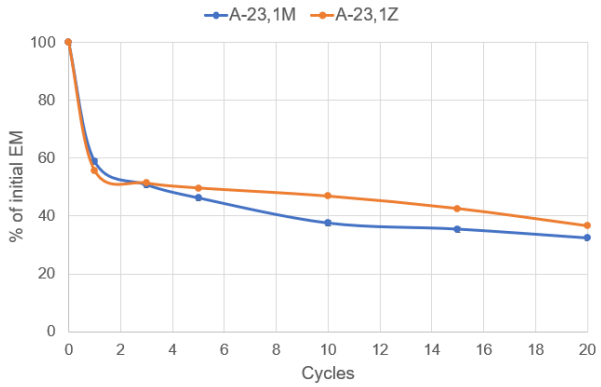

Figure 6: Elastic modulus damage as a function of thermal shock cycling for bricks fired at 1600 °C with 1000 °C of temperature variation.

Both elastic modulus (EM) curves presented comparable behavior, in which the most intense decay occurred for the first cycles, followed by the stabilization of the values after 3 cycles. According to the literature[13], the *in-situ* spinelization or the pre-formed spinel in the composition contributes to the increase in resistance to thermal shock through the microcracks formation and the increase in apparent porosity. In this work, we can insert the Kinkerdall effect might be acting as a toughening mechanism, because it was observed that composition A-23.1Z showed improved resistance to thermal cycling compared to A-23,1M, and the residual porosity present in this Al_2O_3-ZnO system, may reinforce this behavior. Therefore, a new tool for thermal shock improvement emerges as promising, in systems where the controlled Kinkerdall effect becomes an ally for thermo-mechanical properties. The impact of *in-situ* spinelization of the Al_2O_3-ZnO system without MgO additions in shaped bricks, has never been mentioned in the consulted literature, so this study helps to enhance the understanding of the effects of this spinelization on the mechanical properties of this type of material.

4 CONCLUSIONS

Al_2O_3-MgO and Al_2O_3-ZnO systems where ZnO replaces MgO as *in-situ* spinel-forming in shaped bricks, were evaluated. To enable fair comparisons, magnesia and zincite were added to induce the same volumetric amount (23.1 vol.%) of spinel-like phase formed at the thermodynamic equilibrium. Supported by the qualitative and quantitative XRD analyses, the early gahnite formation at temperature just above 800 °C

was confirmed. Additionally, it was entirely reacted at 1200 °C, conversely to the 1300 °C for $MgAl_2O_4$ formation. These results are in line with the literature, proving that the fast diffusion of Zn^{2+} compared to Mg^{2+}, and especially focusing on the difference caused in the residual porosity due to this unilateral ZnO-reaction with alumina in the microstructure. Even though this fast kinetics of gahnite formation seems hopeful for join closings at lower temperatures for shaped bricks, unilateral migration of Zn causes a significant Kirkendall effect attested by scanning electron microscopy (SEM/EDS) analysis.

According to the microstructure, it is possible to observe a homogeneous sintering reaction between MgO and Al_2O_3 raw materials whereas for the ZnO-containing formulation, voids between the matrix and aggregates caused by the substantial Kinkerdall effect directly inhibited the sintering behaviour. An interesting coating was formed at the alumina-coarse boundaries attesting the high quantity of ZnO diffused from the matrix to the aggregates. This outstanding porosity was reflected on the mechanical properties making the A-23.1Z composition with values below those required for applications such as steel ladle linings, however, this same residual porosity when formed in a controlled way, helps the thermal shock performance.

This work corroborated to illustrate the unilaterality of the diffusion of Zn ion in alumina, adding additional information on the impact of the quick diffusion on some mechanical properties. Additionally, also confirmed the challenge between expansion spinel-like phases *versus* sintering degree in the Al_2O_3-MgO system and also highlighted that, in the Al_2O_3-ZnO counterpart system, the densification competition is between the residual porosity by the Kinkerdall effect *versus* sintering degree, because the residual porosity affects the microstructural voids more than the formation of the $ZnAl_2O_4$ phase. Nevertheless, it is concluded that the properties development is directly affected by the diffusion kinects of the bi-valent ion into alumina, in other words, by the unilateral diffusion. Hence, these results indicate that the addition of ZnO replacing MgO for refractory applications is not suitable due to the decrease in mechanical properties caused by the Kinkerdall effect. However, the ZnO-addition can be useful as an *in-situ* spinelizing additive, or as pre-formed synthetised spinel-like $ZnAl_2O_4$ raw material.

5 ACKNOWLEDGMENTS

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