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The impact of pre-formed and *in situ* spinel formation on the physical properties of cement-bonded high alumina refractory castables

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Abstract

Alumina–magnesia and alumina–spinel castables present some unique characteristics. Whereas the *in situ* spinel ($MgAl_2O_4$) formation provides an enhanced corrosion and thermal-shock resistance to the castable, the composition with pre-formed grains shows higher volumetric stability and do not have the inherent MgO hydration problems. As these distinct ways of spinel incorporation result in particular properties to the refractory material, a castable containing both *in situ* and pre-formed spinel might present balanced properties and a suitable performance in steel ladle applications. Considering these aspects, cement-bonded high alumina castables containing both pre-formed and *in situ* spinel were developed and evaluated by means of assisted sintering tests, microstructural analyses, thermodynamics simulation and mechanical and thermal-mechanical properties evaluation. The CA_6 formation presented different features according to the content of *in situ* spinel generation in the matrix, which affected the castable properties. Additionally, compositions containing both *in situ* and pre-formed spinel seemed to be a feasible way of attaining a designed linear dimensional change without affecting the spinel and CA_6 contents.

Keywords: B. Microstructure; D. Spinel; E. Refractories

1. Introduction

Alumina–magnesia castables have been increasingly used as lining materials for steel ladles below the slag line, mainly due to their chemical properties and better thermomechanical behavior when compared to the alumina–spinel ones [1]. Lee and Zhang [2] have shown that the ideal spinel ($MgAl_2O_4$) content to ensure an optimized corrosion and penetration resistance is close to 21 wt%. However, according to the selected raw materials and the different reaction mechanisms, the residual expansion due to the formation of 21 wt% of *in situ* spinel may be excessive, and could then spoil the material's structural integrity as a result of crack generation [3–5].

As some important properties of the alumina–magnesia castable could be affected by the microcrack coalescence resulting from excessive residual expansion due to spinel formation [6], pre-formed spinel additions would be a better path to control it. Nevertheless, the severe thermal cycles and the constant chemical attack of the refractory lining in the steel ladle environment could easily decrease the castable working life if pre-formed spinel is used [2]. Besides this, when using pre-shaped products, a designed expansion is desirable to inhibit slag and molten steel penetration at the lining joints [7,8]. Considering these aspects, castables containing only pre-formed spinel do not satisfy all requirements.

Furthermore, both alumina–magnesia and alumina–spinel castables are commonly bonded with calcium aluminate cement (CAC) owing to the fast curing time and high green mechanical strength [9–11]. Adding CAC to spinel compositions leads to calcium hexaluminate [$CaO{\cdot}6Al_2O_3$ (CA_6)] formation at roughly 1400 °C [12,13]. The most significant advantage of this phase is its needle-like morphology growth, which typically occurs when it is formed through a liquid-phase diffusion mechanism [14,15]. However, although the acicular CA_6 grains could increase the castable's thermal-shock resistance, this reaction, similarly to the *in situ* spinel formation, is followed by a residual expansion ($\Delta V \sim 3.01\%$)

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[16]. For these reasons, attaining a cement-bonded spinel castable with desirable properties and a controlled overall expansion is not a straightforward task.

In this paper, castables with optimized spinel content (21 wt%) and CAC content were developed with a goal of attaining cement-bonded castables containing CA_6 and both pre-formed and *in situ* spinel with low residual expansion. In such a composition, the *in situ* spinel phase could enhance the thermal-shock and molten slag resistance, whereas the pre-formed grains would ensure suitable volumetric stability.

2. Experimental procedures

2.1. Materials

Four compositions were formulated to evaluate the simultaneous addition of pre-formed and *in situ* spinel into cement-bonded refractory castables. The vibratable castables were formulated based on the Alfred packing model [17] with a particle size distribution coefficient $q = 0.26$. All compositions contained tabular alumina ($d \leq 6$ mm, Almatis, Ludwigshafen, Germany) as aggregates, 6 wt% calcium aluminate cement (Secar 71, Kerneos, Chesapeake, USA) as the binder, and 1 wt% of microsilica (971 U, Elkem, Kristiansand, Norway). Four high alumina compositions were evaluated, with a total spinel content target of 21 wt%. Magnesia was the limiting reactant for the *in situ* spinel formation, with its content varied from 0 to 6 wt%.

The alumina–magnesia castables were prepared with 6 wt% dead-burnt MgO (95 wt% MgO, $CaO/SiO_2 = 0.36$, $d \leq 45$ μm, Magnesita Refratários S.A., Contagem, Brazil), producing 21 wt% of stoichiometric *in situ* spinel during the heat treatment. Magnesia reacted with the 7 wt% of calcined alumina (CL 370, Almatis, Ludwigshafen, Germany) and the finest particles of the tabular alumina ($d < 0.2$ mm). Conversely, 21 wt% of pre-formed spinel (AR78, 78 wt% of alumina, Almatis, Ludwigshafen, Germany) in three granulometric fraction grades ($d \leq 0.5$ mm, $d \leq 45$ μm and $d \leq 20$ μm) were added to produce an alumina–spinel castable.

Based on these compositions, two intermediate castables were prepared with both pre-formed and *in situ* spinel by changing the MgO/pre-formed spinel ratio (2 wt% of MgO/14 wt% of AR78 spinel or 4 wt% of MgO/7 wt% of AR78 spinel). The castable compositions are shown in Table 1.

Besides the MgO and the pre-formed spinel content, the fine alumina amounts (calcined alumina and tabular alumina ≤ 0.2 mm) are also different in the compositions. This change was carried out to assure that after the *in situ* spinel formation, the fine alumina available for the CA_6 formation (10 wt%) would be the same for the four castables.

2.2. Castables' preparation and characterization

The castables were mixed for 5 min in a rheometer developed in the authors' research group [18] following a two-step water-addition procedure used by Pileggi et al. [19,20]. The water content required for suitable casting varied from 4.0 to 4.2 wt%. After mixing, the samples were cured at 50 °C for 24 h in a humid environment, dried at 110 °C for 24 h, and pre-fired at 600 °C for 5 h (1 °C/min).

In order to analyze the castables' expansive behavior, all samples were fired in an refractoriness under load equipment (Model RUL 421E, Netzsch, Selb, Germany) using cylindrical samples ($D = 50$ mm, $H = 50$ mm) with an internal hole of 12.4 mm, prepared according to the 51,503 DIN standard. Linear dimensional changes were measured while the samples were heated to 1500 °C (3 °C/min), followed by a dwell time of 5 h under a compressive load of 0.02 MPa.

Microstructural analyses were carried out using a scanning electron microscopy (JEOL JSM–5900 LV) for samples fired at 1500 °C for 5 h, while the phase content was determined by X-ray diffraction quantitative analysis (TOPAS 4.1, Bruker) for samples fired at 1150 °C, 1300 °C and 1500 °C for 5 h. The objective of the analysis was to determine the spinel and CA_6 content and morphology in order to correlate the castable properties with their phase development. Thermodynamics simulations were also conducted to predict the liquid-phase content and its composition at 1500 °C (FactSage, Thermfact and GTT-Technologies, Universidade Federal de São Carlos, FAI). The composition used for these calculations was the fine grain matrix with an alumina excess to consider part of the coarse alumina grains, whose surface also participate in phase reactions.

Cold and hot modulus of rupture (CMOR and HMOR) measurements were carried out under three-point bending tests (ASTM C 133-94 for CMOR and ASTM C 583 for HMOR) using 150 mm × 25 mm × 25 mm samples. CMOR tests were conducted at room temperature using Universal Materials Test Equipment (Model 810, MTS System, Eden Prairie, MN, USA) for samples pre-fired at 1150 °C, 1300 °C and 1500 °C for 5 h. HMOR measurements were made at 1150 °C, 1250 °C and

Table 1
Composition of castables evaluated with different MgO and pre-formed spinel content.

Raw materials	Content (wt%)			
	0 wt% MgO	2 wt% MgO	4 wt% MgO	6 wt% MgO
Tabular alumina ($d \leq 6$ mm)	62	62	62	62
Tabular alumina ($d \leq 0.2$ mm)	10	12.7	15.3	18
Reactive alumina	–	2.3	4.7	7
Dead-burnt magnesia ($d \leq 45$ μm)	–	2	4	6
Pre-formed spinel ($d \leq 0.5$ mm)	21	14	7	–
CAC	6	6	6	6
Microsilica	1	1	1	1

1450 °C using Netzsch 414/3 HMOR Equipment (Netzsch, Selb, Germany) for samples pre-fired at 1150 °C, 1300 °C and 1500 °C for 5 h, cooled at room temperature and then reheated for testing.

Thermal-shock resistance tests were run to analyze the influence of the *in situ* spinel content and the CA_6 characteristics on the castables' thermal-mechanical properties. The tests consisted of 10 heating/cooling cycles ($\Delta T = 1000$ °C). Samples pre-fired at 1500 °C completed one thermal cycle after a holding time of 15 min inside the furnace, followed by another 15 min of cooling in air at room temperature. The castables' room temperature elastic modulus decrease was evaluated every 2 cycles using the resonance technique (ASTM C-1198) performed by a TRZ-02 Ultrasonic Transducer Analyzer (ATCP, São Carlos, Brazil).

3. Results and discussion

Fig. 1 presents the assisted sintering profiles and the expansion rate of the castables with different MgO and pre-formed spinel contents. Three different mechanisms took place during the castables' linear change behavior when increasing the temperature: (1) sintering shrinkage, (2) *in situ* spinel formation and (3) CA_6 generation. In Fig. 1a, the increase in the magnesia content led to a higher overall expansion due to the greater *in situ* spinel formation at the 1100–1300 °C temperature range. This increase is indicated by the increasing spinel expansion peak in Fig. 1b [13]. Moreover, the sintering shrinkage, which was totally hidden by the spinel expansion in the castable with the highest MgO content (6 wt%), was progressively highlighted as the magnesia and, consequently, the *in situ* spinel content decreased.

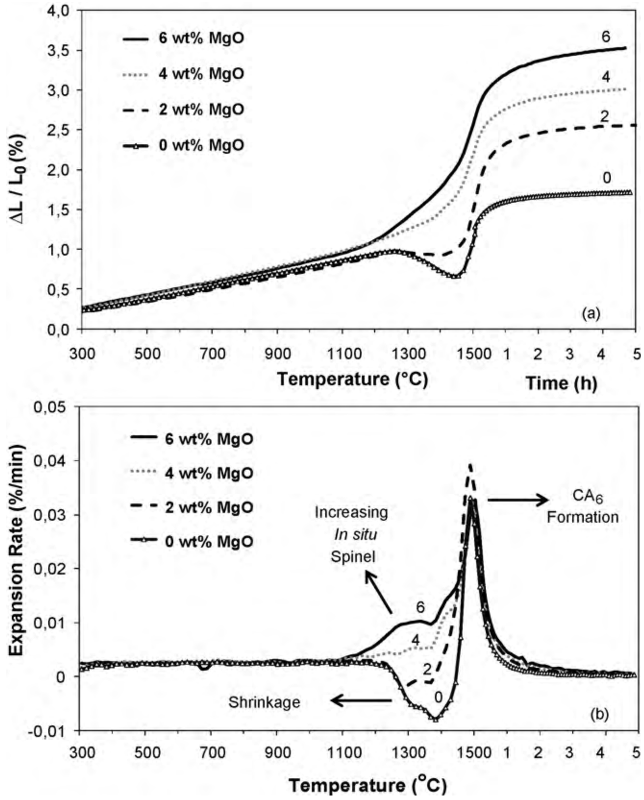

Fig. 1. Expansion behavior (a) and expansion rate (b) of the castables containing different MgO and pre-formed spinel content.

Furthermore, despite the fact that the alumina content available for the CA_6 formation was adjusted to be the same for all compositions, the expansive rate peak in Fig. 1b at roughly 1400 °C for the four compositions did not have the same shape and intensity. The peak intensity was considered to be the difference between its minimum point at roughly 1400 °C and its maximum value at nearly 1500 °C. Therefore, the castables without or with minor *in situ* spinel formation (0 and 2 wt% of MgO) had a higher CA_6 expansion peak intensity, especially taking into account the previous sintering shrinkage characteristic of the low MgO containing compositions. The peak height could be indicative of the amount of CA_6 formed during heating or the way that the CA_6 reaction occurred and was accommodated in the castable microstructure. Concerning the CA_6 content, Table 2 presents the X-ray diffraction quantitative analysis of the castables containing different MgO and pre-formed spinel contents after firing for 5 h at three temperatures: 1150 °C, 1300 °C and 1500 °C. Despite the sort of spinel used (*in situ*, pre-formed or both), the total CA_6 amount after firing at 1500 °C was nearly the same for all compositions.

This result indicates that the calcium hexaluminate grain physical characteristics, such as its morphology and distribution throughout the microstructure, may account for the different expansive behavior. In order to confirm this aspect, Fig. 2 presents the SEM images of the castables' microstructure after firing at 1500 °C for 5 h.

As all castables comprised microsilica in their compositions, the CA_6 crystals presented an acicular morphology due to an ion diffusion mechanism controlled by a molten liquid, as already discussed by Braulio et al. [14]. Nonetheless, the CA_6 grains were located in different regions of the castables' microstructure, depending on the amount of MgO added. The location of CA_6 is closely related to the alumina availability in the microstructure (matrix and/or grain) in this research, and not to the mixing step. For the magnesia free castable (0 wt% MgO), CA_6 grains were detected mainly in the matrix, whereas in the alumina–magnesia sample (6 wt% MgO), very little was found in the matrix, with considerably more at the edges of the tabular alumina (TA) aggregates. For the samples with 2 and 4 wt% of MgO, intermediate situations were detected. When only 2 wt% of MgO was added, the CA_6 formation was almost entirely found in the castable matrix, with some needles being formed in the TA aggregates; whereas in the sample with 4 wt% MgO, the presence of crystallized CA_6 was mainly found in the alumina coarse grains, which led to a microstructure closer to the 6 wt% MgO castable sample. The TA aggregates without any CA_6 in them (0 and 2 wt% of MgO) are highlighted in Fig. 2, pointing out the higher likelihood of finding this phase only in the matrix, where there is little or no *in situ* spinel.

Considering the microstructural changing shown in Fig. 2, the different CA_6 expansion rate peak profiles of the castables with distinct *in situ* and pre-formed spinel content are likely

Table 2
XRD quantitative analysis of the castables' after firing at 1150 °C, 1300 °C and 1500 °C for 5 h.

	Temp. (°C)	Total spinel (wt%)	*In situ* spinel (wt%)	MgO (wt%)	CA6 (wt%)
0 wt% MgO	1150	21	–	–	–
	1300	21	–	–	–
	1500	21	–	–	18
2 wt% MgO	1150	17	3	0.6	–
	1300	18	4	0.1	–
	1500	22	8	–	18
4 wt% MgO	1150	12	5	2	–
	1300	18	11	0.3	–
	1500	23	16	–	18
6 wt% MgO	1150	10	10	3.1	–
	1300	16	16	1.4	–
	1500	22	22	–	16

associated with the CA_6 growth mechanism. According to previous work [21], the CA_6 expansion depends mainly on its crystal growth mechanism. Conversely, the spinel expansion mechanism is related to the intrinsic volumetric change due to the difference in density between product and reactants. Thus, when the acicular CA_6 phase was formed in the matrix, it resulted in higher values of linear change, as observed for the samples with lower MgO content (0 and 2 wt%). On the other hand, for castables containing 4 and 6 wt% MgO, the CA_6 expansion was accommodated by the CA_6 growing towards the internal part of the tabular alumina grains.

The CA_6 generation in the alumina aggregates of the high magnesia containing castables (4 or 6 wt% MgO) could also be related to the *in situ* spinel Al_2O_3–MgO composition. For these

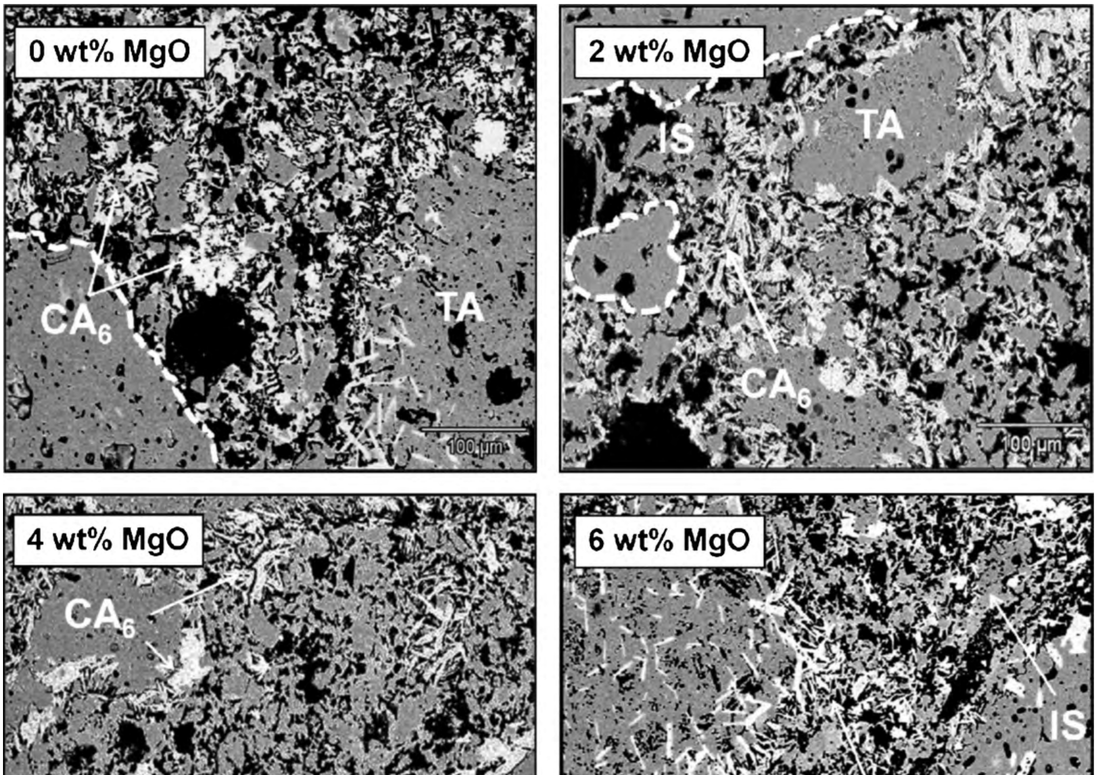

Fig. 2. Microstructure of the castables containing distinct MgO and pre-formed spinel content after firing at 1500 °C for 5 h. TA: tabular alumina; and IS: *in situ* spinel. The dotted line in the micrograph with 0 and 2 wt% MgO points out the higher likelihood of finding CA_6 only in the matrix in these compositions.

castables, the MgO content was selected according to the desired *in situ* spinel content, targeting a stoichiometric spinel formation (72 wt% Al_2O_3–28 wt% MgO). However, based on SEM-EDAX analysis, the *in situ* spinel Al_2O_3–MgO composition obtained for the three magnesia containing castables was 77 wt% Al_2O_3–23 wt% MgO, indicating an alumina-rich solid solution. This alumina enrichment of the spinel phase led to a lack of fine alumina availability in the matrix for additional CA_6 formation, limiting its growth to the border of tabular alumina coarse grains. Therefore, an increase in the *in situ* spinel content resulted in greater CA_6 generation in the castable's aggregates. Conversely, in the absence of magnesia, the calcium hexaluminate was predominately formed in the matrix, as there was no previous *in situ* spinel formation, and no further consumption of fine alumina.

In order to help clarify the influence of the spinel used (*in situ*, pre-formed or both) and of the CA_6 location on the mechanical properties of the castables, cold modulus of rupture tests (CMOR) were conducted at room temperature on samples fired at 1150 °C, 1300 °C and 1500 °C for 5 h. The results are presented in Fig. 3.

The castables with higher magnesia content (4 and 6 wt%) showed higher CMOR after firing at 1150 °C and 1300 °C, which is the temperature range where the *in situ* spinel formation takes place. Note that, at 1500 °C, the mechanical strength values dropped for the samples with 0 and 2 wt% of MgO, whereas they continuously increased for the castables with 4 and 6 wt% of MgO. The lower strength results attained for the higher pre-formed spinel containing compositions (0 and 2 wt% MgO) could be attributed to the higher CA_6 formation in the matrix, which led to microcracks generation. Conversely, the preferential CA_6 formation at or in the tabular alumina aggregates for the 4 and 6 wt% MgO compositions seemed to be in agreement with the increase in the CMOR due to the lower expansion rate associated to this phase and due to enhanced microstructural bridging between the tabular coarse grains and the castable matrix. Additionally, as shown in Table 2, the *in situ* spinel reaction was still taking place in the 1300–1500 °C temperature range, which may be correlated to the higher cold modulus of rupture after firing at 1500 °C for 5 h for the castables containing 4 and 6 wt% MgO. The *in situ* spinel network formation in the matrix could also contribute to the higher mechanical strength.

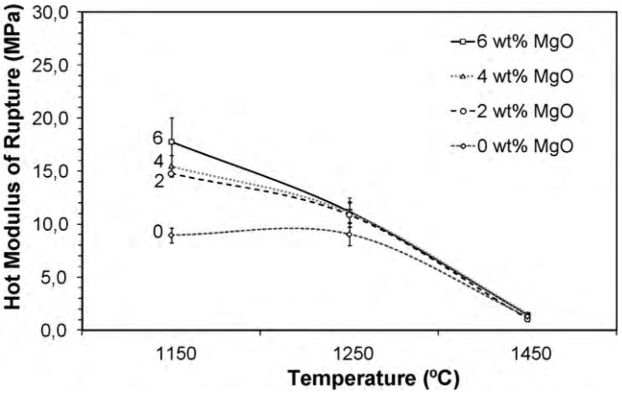

Fig. 4. Hot modulus of rupture at 1150 °C, 1250 °C and 1450 °C of the castables with different MgO and pre-formed spinel content. The samples were previously fired at 1150 °C, 1300 °C and 1500 °C for 5 h, cooled at room temperature and then reheated for testing.

Besides observed microstructure changes, the liquid-phase formation predicted from the thermodynamic simulation for the Al_2O_3–MgO–CaO–SiO_2 system at high temperatures may also explain the cold modulus of rupture behavior, contributing to higher values at room temperature. Hot modulus of rupture (HMOR) tests were carried out at 1150 °C, 1250 °C and 1450 °C, for the samples previously fired at 1150 °C, 1300 °C and 1500 °C for 5 h, as shown in Fig. 4, to evaluate predicted liquid formation.

As detected in the CMOR, the castables' HMOR at 1150 °C scaled with the magnesia content, mainly due to the increase of the matrix reactivity and, consequently, the occurrence of reactions at lower temperatures, as noted in Table 2. At 1250 °C and above, the liquid-phase formation due to the presence of microsilica became more significant, drastically affecting the castables' hot modulus of rupture. Therefore, the liquid content might have prevailed over the possible benefits related to the needle-like CA_6 generation and its location in the microstructure. Fig. 5 shows the results obtained from the thermodynamic simulation, indicating the liquid-phase amount for the four castables. Although the liquid content of the

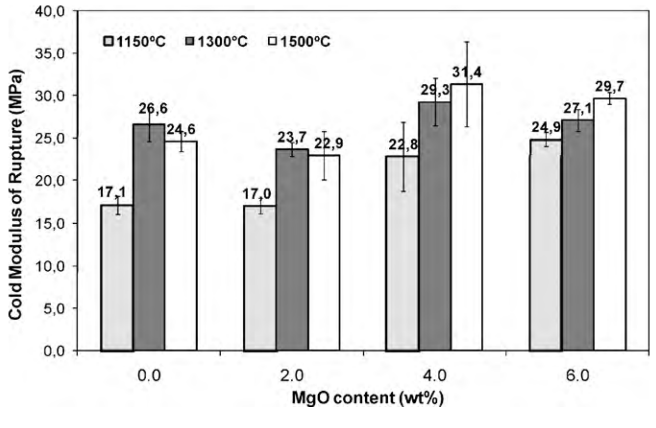

Fig. 3. Cold modulus for rupture of the castables with different MgO and pre-formed spinel content after firing for 5 h at 1150 °C, 1300 °C and 1500 °C.

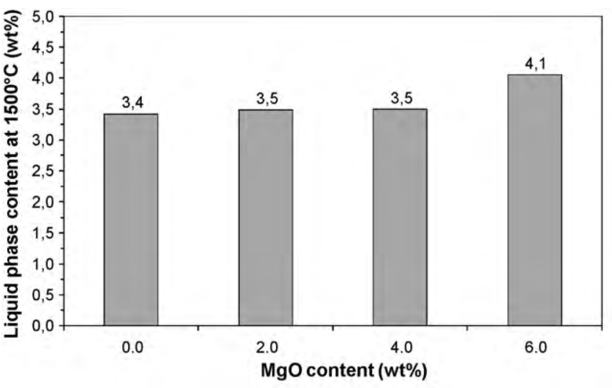

Fig. 5. Thermodynamics estimations of liquid-phase content for different MgO contents at 1500 °C predicted using thermodynamic simulation.

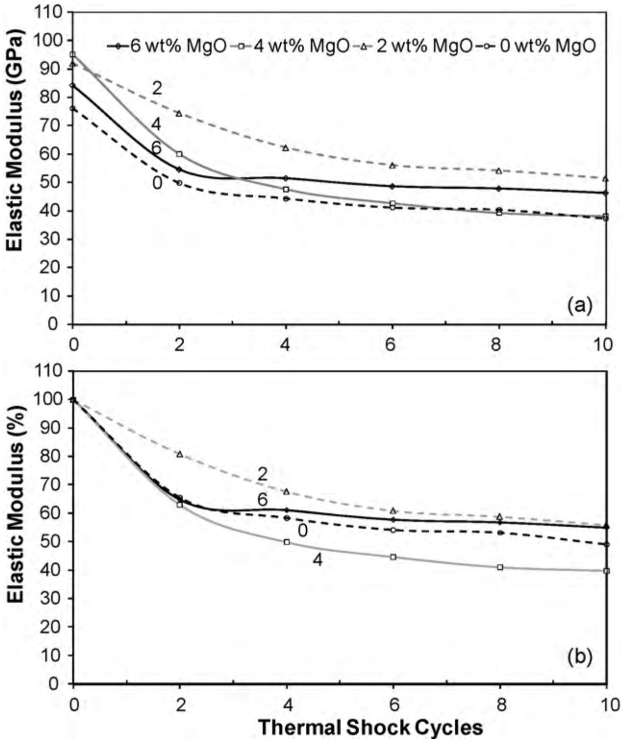

Fig. 6. Thermal-shock resistance of the samples with different MgO and pre-formed spinel content in absolute values (a) and in percent change (b).

castable with 6 wt% of MgO differed from the others, all of them seemed to present enough liquid formation to impact the mechanical strength at high temperatures, explaining the similar decrease in the HMOR values (Fig. 4).

Fig. 6 presents the room temperature elastic modulus loss as a function of thermal-shock cycles for the castables with different MgO and pre-formed spinel content pre-fired at 1500 °C for 5 h. It can be observed that there was no discernable relationship between the castable behavior considering only the *in situ* spinel content or the CA_6 characteristics. Besides these phases, thermodynamic simulation also predicted the formation of anorthite ($CaAl_2Si_2O_8$), gehlenite ($Ca_2Al_2SiO_7$) and a glassy phase during sintering, which, in fact, were not detected by XRD due to the low amount of each phase (<5 wt%) in the castable microstructure. As these phases contents are likely different for distinct compositions and would directly affect the castables thermal shock resistance, a better understanding of the thermal-mechanical properties of such cement-bonded spinel containing compositions would be attained by evaluating microsilica free castables. These castables would not form these additional phases (anorthite and gehlenite), and the thermal shock and the hot mechanical properties analysis could be directly related to the actual role of the *in situ* spinel and the calcium hexaluminate phases and their location (grain or matrix).

4. Conclusions

The main aspects obtained by evaluating castables containing different *in situ* and pre-formed spinel content can be summarized as follows:

- The reduction of the MgO content led to lower overall linear expansion, due to the decrease of the *in situ* spinel content and to a higher sintering shrinkage effect.
- Due to alumina enrichment of the *in situ* spinel, the calcium hexaluminate crystals distribution throughout the castable microstructure was impacted by the type of spinel (*in situ*, pre-formed or both). For the castables containing 4 and 6 wt% magnesia, higher amounts of alumina-rich spinel were formed, leading to a lack of fine alumina and, thus, to greater CA_6 formation at the boundaries of tabular alumina aggregates. For the castables containing 0 and 2 wt% of MgO, none or minor *in situ* spinel was formed, and the CA_6 was prone to be generated in the matrix.
- When the *in situ*/pre-formed spinel ratio decreased, the CA_6 caused the overall expansion above 1400 °C to be higher, and the sintering shrinkage at roughly 1300 °C to be greater. This balanced expansive behavior suggested that the simultaneous use of pre-formed and *in situ* spinel was an interesting alternative to attain a suitable linear change without affecting the spinel and CA_6 content, when corrosion performance is the aim.
- Regarding the mechanical properties, the castables' CMOR and HMOR at 1150 °C generally increased with the magnesia content, mainly due to the beginning of the spinel formation. Nonetheless, at the highest firing temperature (1500 °C) it was not possible to evaluate the possible benefits related to the spinel and CA_6 in the mechanical strength, owing to the presence of liquid phases. According to the thermodynamic predictions, the liquid contents of all compositions seemed to be high enough to impact the hot properties, and to result in higher strength at room temperature.
- Similarly to the mechanical strength, the thermal-shock analysis could have been affected by the presence of additional phases, such as gehlenite, anorthite and/or a glassy phase. Thus, a better understanding of the mechanical and thermal-mechanical properties of the cement-bonded spinel castables could be attained by evaluating microsilica free compositions.

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References

[1] S. Mukhopadhyay, P.K. Das Poddar, Effect of preformed and *in situ* spinels on microstructure and properties of a low cement refractory castable, Ceramics International 30 (3) (2004) 369–380.

[2] S. Zhang, W.E. Lee, Spinel-containing refractories, in: S. Zhang, W.E. Lee (Eds.), Refractories Handbook, Marcel Dekker Inc, USA, 2004, pp. 215–257.

[3] M.A.L. Braulio, L.R.M. Bittencourt, V.C. Pandolfelli, Magnesia grain size effect on *in situ* spinel refractory castables, Journal of European Ceramic Society 28 (2008) 2845–2852.

[4] H. Sarpoorlaky, K.G. Ahari, W.E. Lee, Influence of *in situ* phase formation on microstructural evolution and properties of castable refractories, Ceramics International 28 (5) (2002) 487–493.

[5] Y. Kiyota, Reducion of permanent linear change of Al_2O_3–MgO castable, in: Proceedings of UNITECR 07, 2007, pp. 546–549.

[6] G.B. Cintra, M.A.L. Braulio, M.A.M. Brito, L.R.M. Bittencourt, V.C. Pandolfelli, *In-situ* spinelization and thermal-shock performance of refractory castables, Cerâmica 54 (2008) 287–295 (in Portuguese).

[7] A. Agarwal, The development of Al_2O_3–MgO castables for precast shapes in ladle application, in: Proceedings of the UNITECR 05, 2005, p. 366.

[8] H. Tomiya, H. Tada, E. Iida, Development of unburned Al_2O_3–MgO brick for steel ladle, in: Proceedings of UNITECR 07, 2007, pp. 470–473.

[9] W.E. Lee, W. Vieira, S. Zhang, A. Ghanbari, H. Sarpoolaky, C. Parr, Castable refractory concretes, International Materials Reviews 46 (3) (2001) 145–167.

[10] K.M. Parker, J.H. Sharp, Refractory calcium aluminate cements, Transactions of the British Ceramic Society 82 (1) (1982) 35–42.

[11] C. Parr, L. Bin, B. Valdelievre, C. Wöhrmayer, B. Touzo, The advantages of calcium aluminate cement containing castables for steel ladle applications, in: Proceedings of ALAFAR 2004, 2004, p. 10.

[12] B. Touzo, F. Somonin, C. Wöhrmeyer, C. Parr, Microstructural changes in calcium aluminates cement bonded castables system, in: Proceedings of UNITECR 05, 2005, pp. 35–39.

[13] M.A.L. Braulio, D.H. Milanez, E.Y. Sako, L.R.M. Bittencourt, V.C. Pandolfelli, Expansion behavior of cement-bonded alumina–magnesia refractory castables, American Ceramic Society Bulletin 86 (12) (2007) 9201–9206.

[14] M.A.L. Braulio, L.R.M. Bittencourt, J. Poirier, V.C. Pandolfelli, Microsilica effects on cement bonded alumina–magnesia refractory castables, Journal of the Technical Association of Refractories (Japan) 28 (3) (2008) 180–184.

[15] C. Dominguez, J. Chevalier, R. Torrecillas, L. Gremillard, G. Fantozzi, Thermomechanical properties and fracture mechanism of calcium hexaluminate, Journal of European Ceramic Society 21 (2001) 907–917.

[16] J.M. Auvray, C. Gault, M. Huger, Evolution of elastic properties and microstructural changes versus temperature in bonding phases of alumina and alumina–magnesia refractory castables, Journal of European Ceramic Society 27 (2007) 3489–3496.

[17] J.E. Funk, D.R. Dinger, Particle packing: Part III. Discrete versus continuous particles sizes, Interceram 41 (5) (1992) 332–333.

[18] R.G. Pileggi, A.E. Paiva, J. Gallo, V.C. Pandolfelli, Novel rheometer for refractory castables, The American Ceramic Society Bulletin 79 (1) (2000) 54–58.

[19] R.G. Pileggi, A.R. Studart, J. Gallo, V.C. Pandolfelli, How mixing affects the rheology of refractory castables: Part I, The American Ceramic Society Bulletin 80 (6) (2001) 27–31.

[20] R.G. Pileggi, A.R. Studart, J. Gallo, V.C. Pandolfelli, How mixing affects the rheology of refractory castables: Part II, The American Ceramic Society Bulletin 80 (7) (2001) 38–42.

[21] E.Y. Sako, M.A.L. Braulio, D.H. Milanez, P.O. Brant, V.C. Pandolfelli, Microsilica role in the CA_6 formation in cement-bonded spinel refractory castables, Journal of Materials Processing Technology 209 (2009) 5552–5557.