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Ceramics International 38 (2012) 6027–6033

CERAMICS INTERNATIONAL

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Short communication

Microstructural evolution of magnesia-based castables containing microsilica

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Received 19 March 2012; accepted 28 March 2012

Abstract

The higher performance of refractory materials applied in steelmaking vessels is mainly associated with the development of high-magnesia bricks. However, the same success has not yet been attained for the production of high-quality magnesia-based castables, due to the well-known magnesia hydration trend. In order to overcome this drawback, microsilica addition was tested as an anti-hydration additive in the present work. As it also leads to liquid formation at high temperatures in high-alumina CAC-containing castable compositions, the microstructural development of microsilica-containing magnesia-based castables was also analyzed by scanning electron microscopy, thermodynamics simulations and sintering assisted tests. According to the results, microsilica hindered the magnesia hydration and provided an additional bonding mechanism due to the reaction with MgO and water. Moreover, it helped to control the material's volumetric change by reducing the expansion associated with the spinel formation and also the shrinkage level afterwards.

Keywords: D. Spinels; Microsilica; Magnesia-based castables

1. Introduction

Nowadays, the benefits and drawbacks associated with the microsilica addition to alumina–magnesia refractory castables are well established. This submicrometric raw material induces good flowability during the castable processing and helps to control the *in situ* spinel ($MgAl_2O_4$) expansion at high temperatures [1–4]. Nevertheless, the mechanical performance at high temperatures of microsilica-containing castables is usually poor as a result of the low melting point phase generated in this system [5,6]. Due to these opposite roles, microsilica is considered a key component when designing high-alumina *in situ* spinel-forming castables for steel ladle lining.

In steelmaking workshops, however, the aggressive environment demands refractory materials with excellent corrosion resistance to basic slag (high CaO/SiO_2 ratio) [7]. Therefore, magnesia-based bricks have been successfully applied as working lining of BOF converters and of a steel ladle slag line [8–10]. Nonetheless, the production of pre-cast shapes based on high-MgO castables is still a challenge, mainly due to the well-known magnesia hydration feature [11,12]. Although the use of electrofused coarse grains may minimize this drawback [13], it is the high reactivity of finer grains which mostly draw the attention of the refractory producers at the present.

In order to overcome this problem, many researchers [14–17] have recently been attempting to find anti-hydration additives to act directly on the magnesia particle surface, avoiding the brucite ($Mg(OH)_2$) generation. Among all of them, microsilica seems to be one of the most effective, due to the protective layer build-up of silicic acid around the fine MgO particles after the SiO_2–water contact during mixing [17]. Some studies [18,19] even pointed out that microsilica combined with water and magnesia can also result in a suitable bonding system, providing a CaO-free alternative binder to replace the traditional calcium aluminate cement.

Regarding the microsilica role in magnesia-based castable compositions at high temperatures, Braulio et al. [20] reported that, as in the high-alumina systems, it also led to an initial liquid formation at roughly 1200 °C which counterbalanced the *in situ* spinel expansion. However, when the temperature is increased, the relationship between microsilica and the liquid present is not well established, as the microstructural evolution

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http://dx.doi.org/10.1016/j.ceramint.2012.03.070

of this system is substantially different from the usual one observed in alumina–magnesia castables. For the latter, silica remains a part of the permanent liquid during the whole heat treatment, whereas for the former, it is consumed during the belite ($CaO\cdot 2SiO_2$) formation, indicating that the liquid composition and its content is mainly ruled by the CaO presence. Consequently, the expansive behavior, which is an important characteristic of spinel castables and strongly depends on the phase formation during heating, is most likely differently affected by the microsilica content in magnesia-based compositions.

Thus, considering the microsilica importance to effectively inhibit the MgO hydration, a full understanding of the phase evolution in high-magnesia castables can be useful as a guideline for the production of basic refractory castables. It would also open up novel opportunities for processing pre-cast shapes for steelmaking plants with improved properties, such as steel ladle well blocks and tundish dams.

2. Experimental procedure

Different magnesia–alumina castables were designed according to the compositions presented in Table 1 to evaluate the microsilica's role in this system. In order to reduce the brucite formation, non-reactive electrofused magnesia (98 wt% of MgO, CaO/SiO_2 ratio = 3.5, Magnesita Refratários S.A., Brazil) was used as coarse aggregates ($d < 4.75$ mm). In the matrix, a fine dead-burnt source ($d < 45$ μm, 95 wt% of MgO, $CaO/SiO_2 = 0.36$, Magnesita Refratários S.A., Brazil) was added to react with calcined alumina (CL 370, Almatis, Germany) and fine tabular alumina particles (T60, $d < 200$ μm, Almatis, Germany) and, consequently, generate *in situ* spinel ($MgAl_2O_4$) during heating. The amount of alumina added to the compositions was calculated aiming at a total spinel content of 21 wt%, assuming a stoichiometric composition (72 wt%-Al_2O_3 and 28 wt%-MgO). Calcium aluminate cement (Secar 71, Kerneos, USA) was selected as the binder and the effect of different amounts (0, 0.25, 0.5 or 1.0 wt%) of microsilica (971 U, Elkem Materials, Norway) were analyzed for each CAC content (2, 4 or 6 wt%).

Table 1
Magnesia–alumina compositions with different calcium aluminate cement (C) and microsílica (M) contents. All of them comprised 8 wt% of tabular alumina < 200 μm, 7 wt% of reactive alumina CL 370 and 6 wt% of dead-burnt magnesia in their matrix.

	Composition (wt%)		
	Fused MgO ($d < 4.75$ mm)	CAC	Microsilica
6C 1M	72	6	1
6C 0.5M	72.5	6	0.5
6C 0.25M	72.75	6	0.25
6C 0M	73	6	0
4C 1M	74	4	1
4C 0.5M	74.5	4	0.5
4C 0.25M	74.75	4	0.25
4C 0M	75	4	0
2C 1M	76	2	1
2C 0.5M	76.5	2	0.5
2C 0.25M	76.25	2	0.25
2C 0M	77	2	0

After mixing the dry powder and the water content required for a suitable shaping (close to 4.2 wt% for all castables for vibratable applications), different samples were cast for the following tests:

- Splitting tensile strength during the curing time: the mechanical tests were conducted according to the ASTM C496-90 Standard on 5 cylindrical samples (40 mm × 40 mm) after 1, 3, 5 or 7 days of curing at 50 °C in a humid environment for 24 h, using universal mechanical testing equipment (MTS Systems, Model 819, USA). The same tests were also carried out in samples cured for one day at 50 °C and an extra day at 110 °C in order to verify whether brucite was formed during the drying stage.
- Assisted sintering technique: cylindrical samples of the castables containing 6 wt% CAC were produced following the 51053 DIN standard and the tests were conducted in refractoriness-under-load equipment (RUL, Neztsch, Germany), in which the dimensional linear change is measured as the sample is heated up to 1500 °C (3 °C/min), followed by a dwell time of 5 h at this temperature and under a compressive load of 0.02 MPa.

Thermodynamic simulations were carried out using FactSage^{TM} 6.2 (Thermfact and GTT-Technologies, Universidade Federal de São Carlos, FAI) in order to predict the phase evolution with temperature for the castables with 6 wt% of CAC, from 1250 °C to 1500 °C. Only the castable matrix composition was selected for the simulations and the calculated results were correlated with the materials expansive behavior. FToxid and Fact53 databases were used for these purposes.

Moreover, scanning electron microscopy (SEM) images of the samples containing 6 wt% of CAC and fired at 1500 °C/5 h were attained (JEOL JSM–5900 LV, the Netherlands) and EDS spot analyses (Point and Shoot, Noran NSS 2.2 analyzer, Thermo Fisher Scientific, Madison, USA) were also conducted. Thus, the phases which resulted from the thermodynamic simulations could be compared with those actually formed in the samples processed in lab conditions.

3. Results and discussion

The *in situ* magnesia hydration usually leads to a mechanical resistance decay as a function of time due to crack formation. In order to evaluate the microsilica role in this reaction, Fig. 1 shows the castable splitting tensile strength during the curing time for the magnesia–alumina castables containing different CAC and microsilica contents. Regardless of the binder content, the microsilica addition improved the mechanical behavior, pointing out not only its efficiency as an anti-hydration additive, but also as an additional binder by the reaction with MgO and water, as previously suggested in the literature [18,19]. This effect is even more evident in Fig. 1c, in

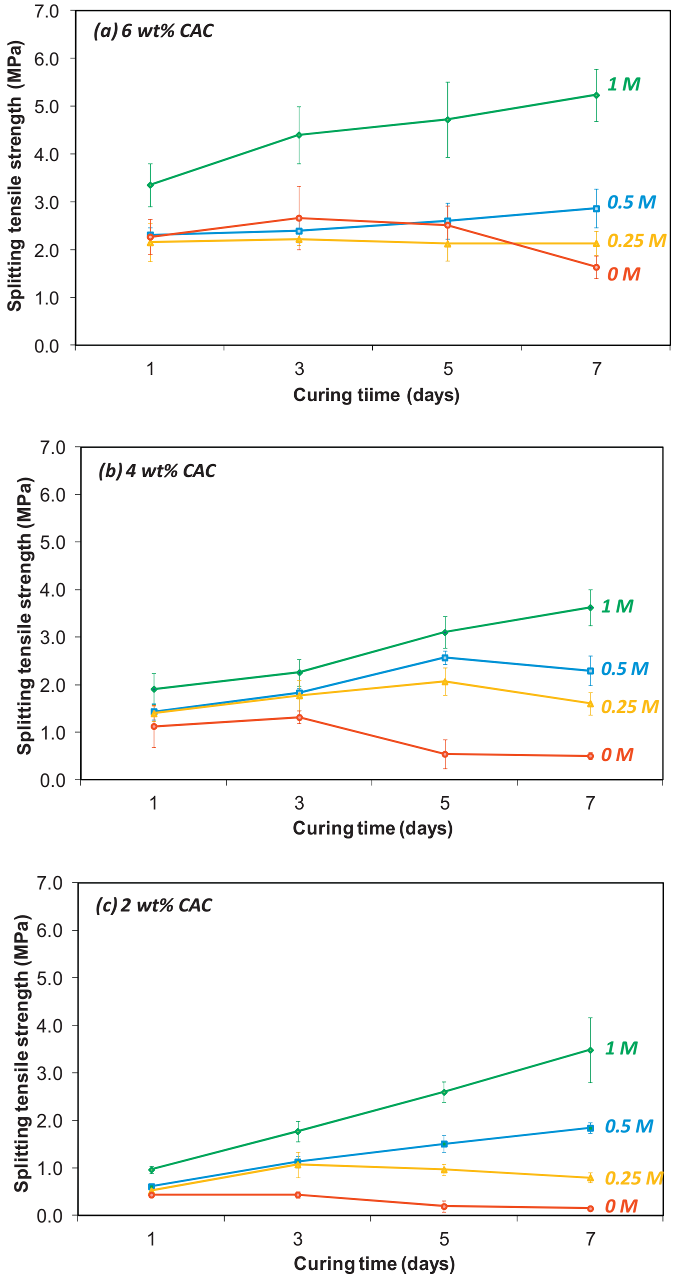

Fig. 1. Splitting tensile strength with the curing time for the castables containing (a) 6 wt%, (b) 4 wt% or (c) 2 wt% of CAC and different microsilica contents.

which the castables usually present low mechanical strength values, due to the reduced CAC content (2 wt%). It can be observed that, due to the microsilica presence, the 2C 1M composition showed values as high as the 6C 0.5M ones after curing for seven days (Fig. 1a).

Fig. 2 shows the mechanical resistance changes over time, calculated by comparing the strength values after one and seven days of curing for all evaluated castables. The results highlighted two important aspects related to CAC and microsilica effects. Firstly, it confirmed that the additional particles bonding provided by the reaction between microsilica, magnesia and water was more efficient when low CAC contents were added. Moreover, the microsilica addition was also important to inhibit the harmful effect of brucite formation, as a mechanical resistance drop was detected for all SiO_2-free castables. This negative consequence of magnesia hydration was more evident when lowering the CAC content, due to the reduced particle cohesion, which was not enough to withstand the stresses related to the brucite expansive formation.

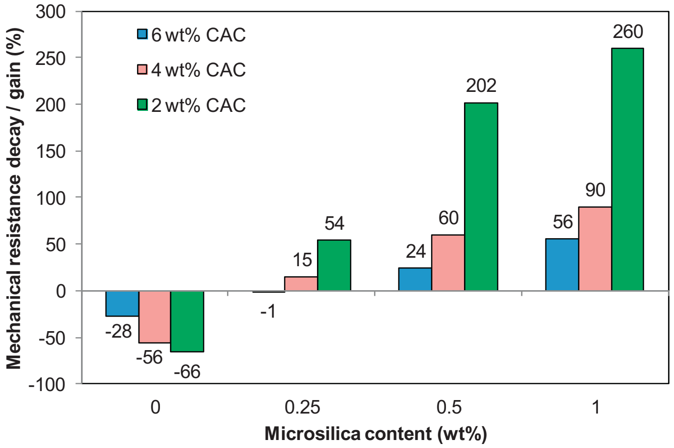

Fig. 2. Mechanical resistance changes after seven days of curing for the magnesia–alumina castables containing different microsilica and CAC contents.

However, one must bear in mind that the magnesia hydration effects were only observed after a long curing time (three or five days). As a splitting tensile strength of 1 MPa is considered suitable for demolding [21], one-day curing was suitable to provide for compositions containing 4 and 6 wt% CAC, a reasonable mechanical resistance value and no cracks due to brucite formation. For the castables containing 2 wt% CAC, a longer curing time and higher microsilica contents were required to be satisfactorily demolded (>1 MPa). Additionally, as the drying step is also critical for high-MgO castables, Fig. 3 presents the splitting tensile strength for the compositions after curing for one day at 50 °C and drying for another at 110 °C. No cracks were observed even for the castables without microsilica, confirming that the drawbacks related to brucite formation were successfully overcome.

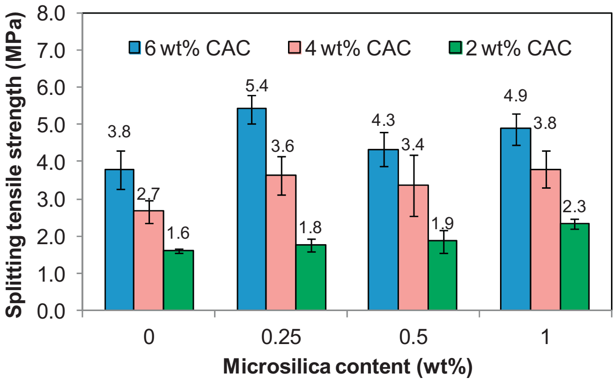

Fig. 3. Splitting tensile strength after curing at 50 °C for 24 h and drying at 110 °C for 24 h for the magnesia–alumina castables containing different microsilica and CAC contents.

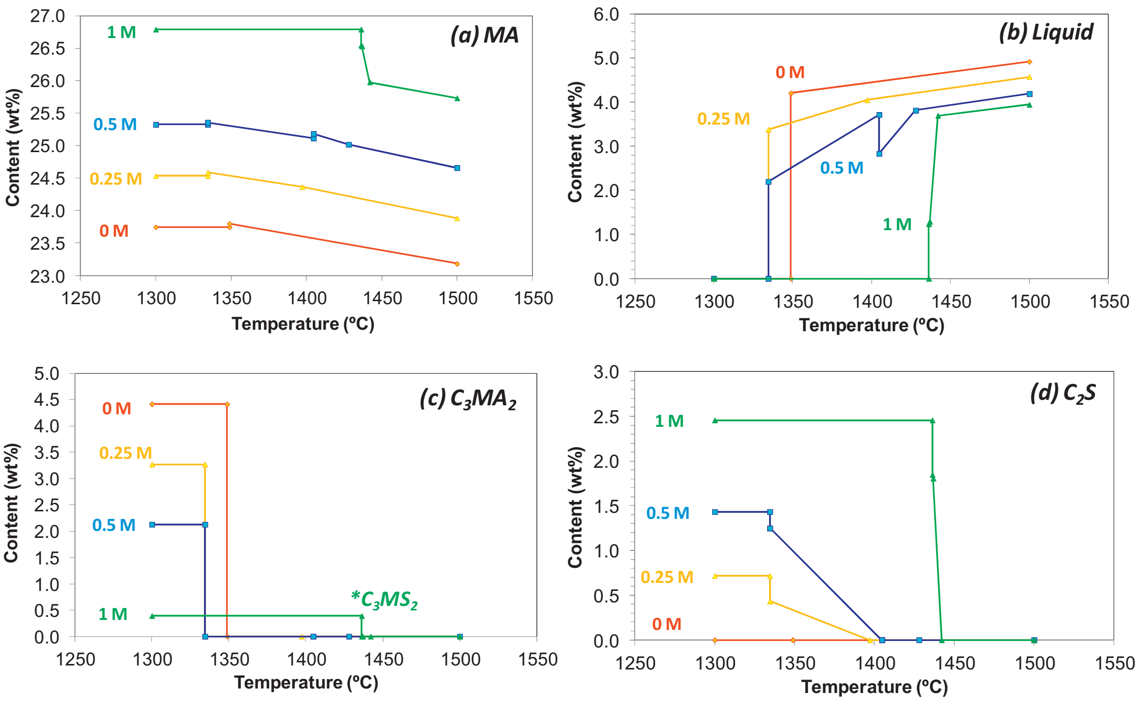

Fig. 4. Thermodynamics simulation of the phases present in the matrix of magnesia–alumina castables containing 6 wt% of CAC and different microsilica contents (0, 0.25, 0.5 and 1 wt%) at the 1300–1500 temperature range: (a) MA, (b) liquid phase, (c) C_3MA_2 (or C_3MS_2 for the 6C 1M composition) and (d) C_2S.

Regarding the microstructural development of magnesia–alumina castables with different microsilica content at high temperatures, Fig. 4 presents the thermodynamic simulation results for the matrix of the castables containing 6 wt% of CAC. In this figure, the following phases are predicted by the temperature: (a) spinel-MA, (b) liquid phase, (c) C_3MA_2 (except for the 6C 1M composition, which presented C_3MS_2 (merwinite) instead) and (d) C_2S (belite). In an equilibrium state, the castable matrix should be comprised by spinel, C_3MA_2 (or C_3MS_2) and C_2S (when SiO_2 is present) as the main phases at lower temperatures (~1300 °C). Then, with the temperature increase, the CaO-containing phases decompose at different temperatures, depending on the microsilica content, to give rise to a liquid phase (Fig. 4b).

The results in Fig. 4c and d show that when the microsilica content is higher, belite (C_2S) and merwinite (C_3MS_2) are preferentially formed, whereas C_3MA_2 is the main CaO-containing phase for the castables with none or little SiO_2 content (6C 0M and 6C 0.25M). Consequently, in Fig. 4a, a reduced spinel content was observed for lower microsilica addition, due to the MgO and Al_2O_3 consumption for the C_3MA_2 formation. Furthermore, as spinel is the only stable solid phase at 1500 °C, all C_3MA_2 is dissociated when the temperature is increased, resulting in higher amounts of liquid phase at 1500 °C for castables containing lower SiO_2 contents (Fig. 4b), which is also a relevant difference from the alumina–magnesia system. In high-Al_2O_3 castables, the liquid is silica-rich and, consequently, its content scaled with microsilica [3,5].

SEM images of the samples containing 6 wt% CAC and different microsilica content after firing at 1500 °C/5 h (Fig. 5) were attained in order to check whether the thermodynamic prediction is compatible with the results obtained in lab conditions. At this temperature, only spinel and liquid should be present in the castable matrix, according to the results in Fig. 4. However, when the samples were cooled down, the liquid phase crystallized into phases which were in total agreement with the thermodynamic simulation. C_2S was mainly found in the matrix of the 6C 1M composition; $C_2S + C_3MA_2$, for the 6C 0.5M one; and only C_3MA_2, for the compositions with low or no SiO_2 content (6C 0.25M and 6C 0M, respectively).

Based on the simulations and on lab results, it was possible to observe that although presenting basically the same matrix composition, the phase evolution predicted by thermodynamics for magnesia–alumina and alumina–magnesia castables are completely different. Considering the quaternary system Al_2O_3–CaO–SiO_2–MgO studied by Vázquez et al. [22], the composition of the high-alumina castable matrix is located inside the compatibility tetrahedron MA–CA_6–CAS_2–C_2AS, and, at 1500 °C, MA, CA_6 and liquid are the predicted phases in equilibrium. Hence, other silica-containing phases, such as belite or merwinite, were neither detected in practice nor in thermodynamic equilibrium calculations. Similar behavior was previously pointed out by other authors [20,23].

The above-mentioned results comprise a helpful tool to understand the expansive behavior of the magnesia–alumina castables with different microsilica contents shown in Fig. 6. The 6C 0MS composition presented the highest expansion at roughly 1300 °C when compared to the SiO_2-containing materials. This result is related to the better accommodation of the *in situ* spinel expansion provided by the presence of microsilica, which was already highlighted in the literature for

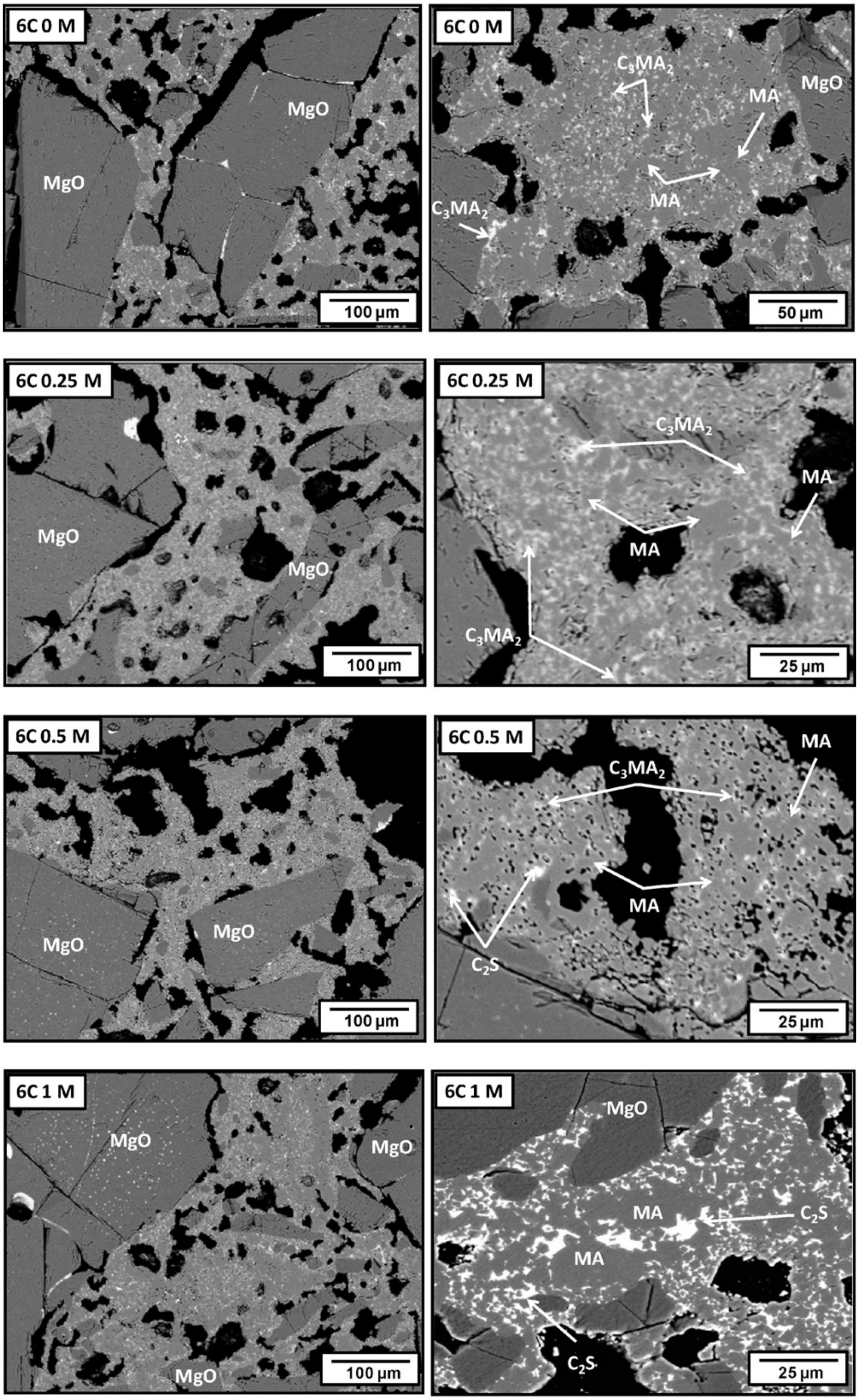

Fig. 5. Microstructure of magnesia–alumina castables containing 6 wt% of CAC and different microsilica contents (0, 0.25, 0.5 or 1 wt%) after firing at 1500 °C for 5 h.

high-alumina spinel-forming castables [3]. After the spinel formation ($T > 1400$ °C), a higher shrinkage level was detected for the 6C 0M composition, which is directly associated with the greater amount of liquid phase at this temperature range for this sample (Fig. 4b). Conversely to the alumina–magnesia system [3], the microsilica addition to high-MgO castables helped to control the material's excessive shrinkage level, providing a desirable volumetric stability after the heat treatment.

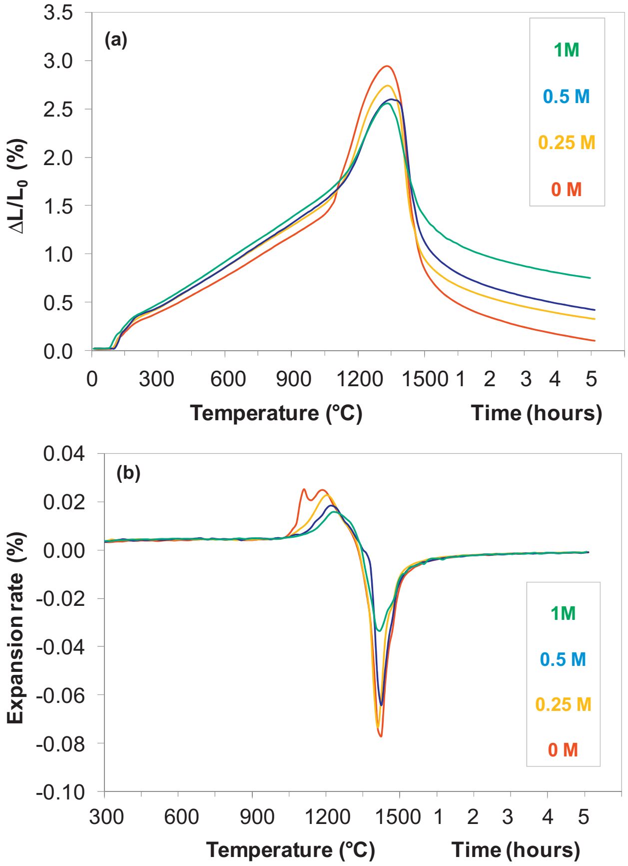

Fig. 6. (a) Expansion behavior and (b) expansion rate of the magnesia–alumina castables containing 6 wt% of CAC and different microsilica contents (0, 0.25, 0.5 or 1 wt%).

All the results pointed out that the microsilica addition was as important as the cement presence in the processing and microstructural development of high-magnesia refractory castables. Nevertheless, despite the above-mentioned microsilica's benefits, liquid phase is expected at high temperatures, according to the thermodynamic previsions. Therefore, some properties, such as the slag corrosion resistance, the hot modulus of ruptures and the creep resistance, must be evaluated in order to fully understand this complex refractory system.

4. Conclusions

Although still considered a challenge nowadays, no problem related to the brucite formation was detected during the processing of magnesia-based refractory castables, mainly due to the use of microsilica as an anti-hydration additive. Its role was even more relevant in castables containing low amounts of cement (2 wt%), which usually do not withstand the brucite formation stresses generated during curing or drying. For this composition, microsilica not only hindered the magnesia hydration, but it also provided an additional bonding mechanism, which improved the castable green mechanical strength to values basically as high as the one attained for the material containing 6 wt% of CAC.

The 6 wt% CAC results also showed that, despite the similar matrix chemical composition to the high-alumina one, the microstructural development of high-magnesia castables were quite different, involving other phases which are not usually detected in Al_2O_3-rich castables, such as C_3MA_2, merwinite (C_3MS_2) or belite (C_2S). In the presence of SiO_2, C_3MA_2 was not generated and, consequently, Al_2O_3 and MgO were consumed for the formation of a higher content of MA spinel. As MA is the only crystalline stable phase at 1500 °C, the amount of liquid phase in the castables containing 1 wt% of microsilica was lower than in the ones with 0.5, 0.25 or 0 wt%. Thus, the microsilica presence helped to control the material's excessive shrinkage level, providing a desirable volumetric stability after the heat treatment.

Acknowledgments

The authors are grateful to the Federation for International Refractory Research and Education (FIRE) and the Brazilian Research Funding CNPq for supporting this work, and D.H. Milanez for the sample preparation and for carrying out part of the tests.

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