ENGINEERED EXPANSION ROUTES FOR ALUMINA-MAGNESIA REFRACTORY CASTABLES[1]

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Abstract

Alumina-magnesia refractory castables present an expansive behavior usually associated to the *in situ* spinel formation at temperatures above 1.000°C. As these castables are commonly bonded with calcium aluminate cement, expansive reactions involving CA_2 and CA_6 generation must also be taken into account in the engineering expansion design. Additionally, as the refractory aggregates comprise mostly of a castable formulation, it is important to consider their effect on the volumetric stability. Therefore, this work addresses, based on the assisted sintering technique and microstructural evaluation (SEM and XRD), an overall analysis concerning the effect of raw materials on the expansion behavior of *in situ* spinel castables, in order to attain a designed expansion based on previously engineered microstructure. One route to achieve this aim was to evaluate the effect of the cement content, which affected the CA_6 formation. Furthermore, as microsilica influences spinel, CA_2 and CA_6 formation, its amount was another way to forecast castable expansion. Changing the magnesia grain size was an additional possibility for the engineered expansion control, as its particle size reduction resulted in a lower overall expansion. The results also pointed out that refractory aggregates can be active partners in the castables' reactions. Finally, various expansion routes were attained and presented, resulting a greater flexibility design and optimization of the thermal-mechanical benefits when *in situ* spinels are applied to steel ladles.

Key words: Spinel; Cement; Expansion.

ROTAS DE EXPANSÃO ENGENHEIRADA PARA CONCRETOS REFRATÁRIOS ALUMINA-MAGNÉSIA

Resumo

Concretos refratários alumina-magnésia apresentam usualmente um comportamento expansivo, em decorrência da formação de espinélio *in situ* em temperaturas superiores a 1000ºC. Como estes concretos são normalmente ligados com cimento de aluminato de cálcio, as reações expansivas que envolvem a formação de CA_2 e CA_6 também devem ser consideradas no projeto de expansão engenheirada. Adicionalmente, uma vez que os agregados refratários constituem a maior parcela da composição, é importante também considerar seu efeito sobre a estabilidade volumétrica. Sendo assim, este trabalho consiste, baseado na técnica de sinterabilidade assistida e na avaliação microestrutural (MEV e DRX), em uma análise global do efeito das matérias-primas sobre o comportamento expansivo de concretos espinelizados *in situ*, visando-se obter um projeto de expansão baseado na prévia engenharia de microestrutura. Uma rota para atingir esta meta foi a avaliação do teor de cimento, o que afetou à formação de CA_6. Além disso, como a microssílica influencia a formação de espinélio, CA_2 e CA_6, o seu teor foi uma outra forma de se prever a expansão do concreto. A alteração do tamanho de grão da magnésia foi uma possibilidade adicional para o controle da expansão engenheirada, já que a redução do tamanho de partícula resultou em menor expansão final. Os resultados destacaram ainda que os agregados refratários podem ser parceiros ativos nas reações dos concretos. Por fim, várias rotas de expansão foram obtidas e apresentadas, resultando em maior flexibilidade de projeto e para otimização dos benefícios termo-mecânicos quando espinélios *in situ* são aplicados em panelas de siderurgia.

Palavras-chave: Espinélio; Cimento; Expansão.

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1 INTRODUCTION

Microsilica and magnesia are two important raw materials, playing special roles for *in situ* spinel formation of alumina-magnesia castables. Adding microsilica compensates the *in situ* disruptive expansion by forming low-melting temperature phases, such as gehlenite and anorthite.(1,2) As a result of this counterbalance effect, the microsilica content control can be used to design alumina-magnesia castable expansions. Concerning magnesia and its grain size, Nakagawa et al.(3) indicated that a major contribution to spinel expansion is the one way diffusion from magnesia to alumina grains, based on the solid state spinel formation mechanism proposed by Wagner.(4) In addition to this study, Kiyota(5) suggested that spinel expansion is related not only with the density difference between reactants and products, but also with the pores left after MgO diffusion. Consequently, controlling the magnesia grain size is another way to attain different expansion levels.

As calcium aluminate cement is the most common binder applied to these sorts of castables, CA_2 and CA_6 formation must also be considered, as they are also followed by expansion. Concerning calcium dialuminate (CA_2), its formation is carried out at temperatures close to 1000℃ and involves a volumetric change of +13.6%.(6) At higher temperatures (roughly 1400℃), calcium hexaluminate (CA_6) is developed and leads to an additional +3% of volumetric change.(7) Therefore, the CAC content must also be taken into account when controlling the expansive behavior of this system.

As spinel, CA_2 and CA_6 phases are generally detected in the alumina-magnesia castables' matrix, is commonly found in the literature studies involving only fine particles and not the castable as a whole.(6,8,9) However, to understand which particle size range of the castable's raw materials are reacting during sintering is not so straightforward. One typical example is the CA_6 formation, which is frequently found embedded on the surface of tabular alumina grains. Thus, as refractory aggregates mostly consist of a castable composition, their effect must also be analyzed in order to make clear their role to the overall volumetric stability behavior and to validate whether matrix studies are meaningful to represent the overall castable composition.

Considering the effect of these raw materials on the expansion behavior of cement-bonded alumina-magnesia refractory castables, the objective of this study is to provide a systemic approach by considering the cement and microsilica content, the magnesia grain size and the refractory aggregate nature (tabular alumina and fused magnesia). As a result, different expansion controlling routes are provided, assuring flexibility to select alumina-magnesia castables, aiming to attain the best thermal-mechanical performance and cleaner steels.

2 MATERIALS AND TECHNIQUES

Various *in situ* spinel castables were analyzed with different cement contents (6, 4 and 2 wt%), microsilica amounts (0, 0.25, 0.5, 1 and 1.25 wt%), MgO grain sizes (< 13 µm, < 45 µm and < 100 µm) and refractory aggregates (tabular alumina or fused magnesia). Table 1 presents the compositions evaluated, except for the MgO grain size effect, where the dead-burnt MgO < 45 µm of the main composition was substituted by others magnesia sources (< 13 µm and < 100 µm). All the dead-burnt magnesia presented the same purity (95 wt% MgO) and CaO/SiO_2 ratio (0.36). For the aggregate evaluation, the castables were prepared with the same matrix, in order to generate 21wt% spinel.

Table 1. Castables compositions.

	Main composition	**CAC evaluation**	**Microsilica evaluation**	**Fused MgO effect**
Tabular alumina (d ≤ 6 mm)º (wt%)	**80**	**82 / 84**	**79.75 / 80.5 / 80.75 / 81**	**8**
Reactive aluminaº (wt%)	**7**	**7**	**7**	**7**
Dead burnt MgO (< 45 µm)Δ (wt%)	**6**	**6**	**6**	**6**
Microsilica 971U• (wt%)	**1**	**1**	**1.25 / 0.5 / 0.25 / 0**	**1 / 0**
Calcium aluminate cement (Secar71)□ (wt%)	**6**	**4 / 2**	**6**	**6**
Fused magnesia (d ≤ 4.75 mm)Δ (wt%)	**0**	**0**	**0**	**72 / 73**

ºAlmatis, Germany / ΔMagnesita S.A., Brazil / •Elkem, Norway / □Kerneos, France

The assisted sintering technique was carried out on a refractoriness-under-load equipment (Model RUL 421 E, Netzch, Germany). Cylindrical samples were prepared according to the 51053 DIN standard. For thermal expansion evaluation, samples were heated up to 1500°C under a rate of 3°C/min and kept at this temperature for 5 hours. The compression load applied was 0.02 MPa. Microstructural evaluations were performed by XRD quantitative analyses and by scanning electron microscopy (SEM), in order to detect the amount and distribution of the developed phases after sintering at high temperatures.

3 RESULTS AND DISCUSSION

In previous work of the authors,(10) the expansive behavior of alumina-magnesia castables was shown to be affected by the calcium aluminate cement content, pointing out that spinel is not the only expansion source in this system. Figure 1a indicates the effect of CAC content on the expansion of alumina-magnesia castables and Figure 1b their respective expansion rate, highlighting the mechanisms developed during the materials' thermal treatment, due to spinel and CA_6 formation. Therefore, in order to attain different expansion levels, one solution is to control the cement content, if the spinel amount, distribution and size should be kept constant.

Nevertheless, this route affects the microstructures developed at high temperatures (Figure 2) and consequently the castables' properties. The sample with the lower CAC content (2 wt%) densified and presented a smaller amount of CA_6. On the other hand, increasing the cement amount to 6 wt% resulted in well developed CA_6 crystals and a microstructure containing a large amount of pores. Concerning the CA_6 content, the sample with 6 wt % CAC presented 14 wt% of this phase, whereas the one containing 4 wt% CAC attained 8 wt% of CA_6. The amount of CA_6 in the sample containing 2 wt % CAC was below the XRD detection range. Then, as CA_6 is a desired refractory phase due to its needle-like shape and chemical stability, some amount of cement must be incorporated, in order to take advantage of the benefits associated to this phase (i. e., improvements on thermal shock and corrosion resistance). Therefore, adding 4 wt% CAC appears to be a good balance, as the expansion is not very high, even with a suitable CA_6 content.

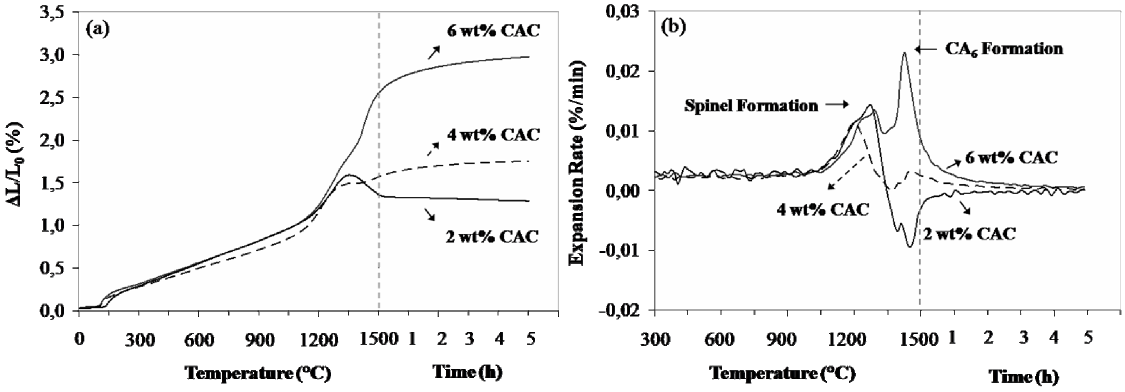

Figure 1. (a) Expansion behavior and (b) expansion rate of alumina-magnesia castables containing different calcium aluminate cement content (2, 4 or 6 wt%).(10)

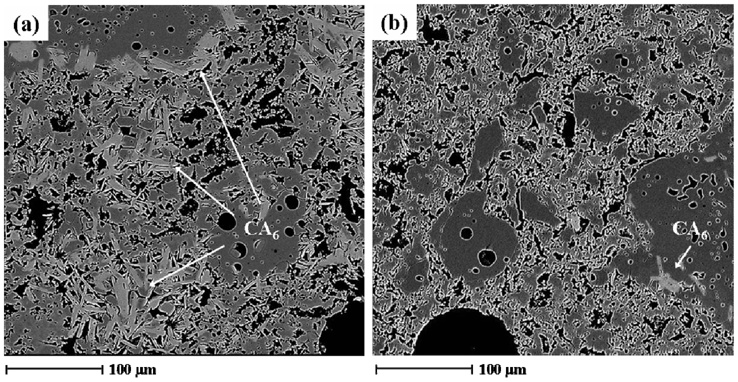

Figure 2. CA_6 crystals in alumina-magnesia castables containing (a) 6 or (b) 2 wt% CAC, after firing at 1500°C for 5 hours.(10)

Another way to design the expansion is by controlling the microsilica content of this class of castables, as shown in Figure 3.(11) Considering the assisted sintering curves (Figure 3a), the samples containing 0.25 wt% and 0.5 wt% silica resulted in a large expansion compared to the 0 wt% one. However, an additional increase in the microsilica content (1 wt%and 1.25 wt%) resulted in a lower expansion than for those containing 0.25 wt% and 0.5 wt% SiO_2. This reduction in the expansion can be associated to a higher glassy phase formation, counterbalancing the expansion phenomena associated to CA_2, spinel and CA_6 formations.

The expansion rate (Figure 3b) shows that different mechanisms were triggered when changing the silica content. The first peak can be attributed to CA_2 formation, due to the temperature range (900°C-1.100°C). This peak was observed for the samples containing no silica (0 wt%) or a low silica content (0.25 wt%), because in these compositions there was no competition between silica and alumina to react with calcia, increasing the likelihood of CA_2 formation. Conversely, higher amounts of silica (> 0.5 wt%) induced interactions in the CaO-SiO_2-Al_2O_3 system, reducing the CA_2 expansive reaction. The second peak observed was related with *in situ* spinel formation and the higher silica contents (0.5, 1 wt% and 1.25 wt%) led to a lower expansion rate. This result is in tune with the literature,(1,2) which indicates the silica related phases ability to accommodate the spinel expansion.

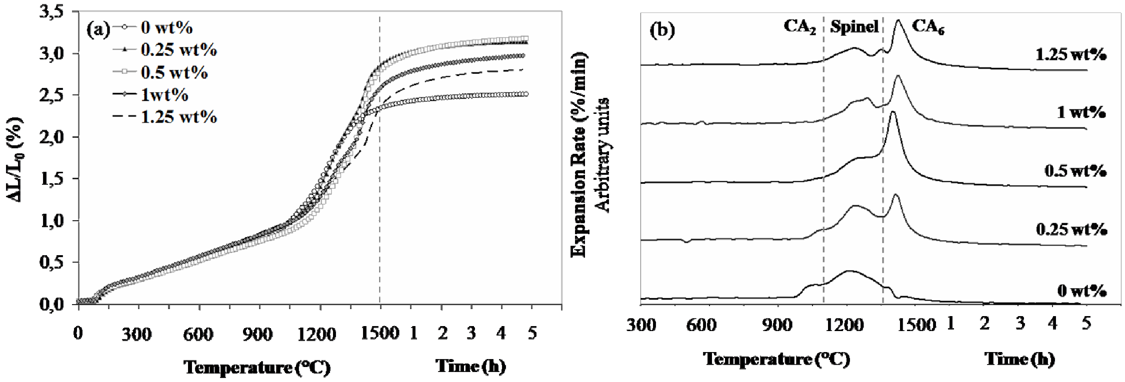

Figure 3. (a) Expansion behavior and (b) expansion rate of alumina-magnesia castables containing different microsilica content (0 wt%, 0.25 wt%, 0.5, 1 wt% or 1.25 wt%).(11)

On the other hand, silica played an opposite role during CA_6 formation, increasing the expansion peak rate when added up to 0.5 wt% of SiO_2 addition. According to De Jonghe, Schmid e Chang,(12) the presence of calcium and aluminum silicates eases CA_6 formation by generating faster paths for ion transportation. However, there is a limited silica content (0.5 wt%) that helps to speed up the CA_6 formation. For higher silica content (1 wt% and 1.25 wt%), the amount of CA_6 is reduced, as the interaction between SiO_2 and CaO increases.

In addition, the presence of silica affected the morphology of the CA_6 crystals (Figure 4). The sample containing no silica (0 wt%) showed an equiaxed crystal growth around tabular alumina grains, whereas the castable with 0.5 wt% SiO_2 (which resulted in the highest CA_6 peak) presented CA_6 in a needle-like morphology, not only around tabular alumina grains, but also in the castable matrix. An and colleagues(13) indicated in a previous work that a solid state reaction or a solution precipitation reaction (absence or presence of silica and glassy phases) leads to different CA_6 shapes. These differences in the morphology and the CA_6 distribution are also responsible for the higher expansion peak for the samples containing up to 0.5 wt% of silica.

The MgO grain size control is also another alternative for designing the expansion of alumina-magnesia. Figure 5a presents the expansion as a function of magnesia grain size.(14) For the coarsest grains (< 100 μm), the expansion was high due to the huge pores left after spinel formation and the greater CA_6 content, as higher amounts of fine alumina was available for its formation.(15) For smaller grain sizes (< 45 μm and < 13 μm), the linear expansion was reduced from 6% to values close to 2%, indicating that the pores left after MgO diffusion plays a special role in the expansive behavior. For the finest MgO grain size (< 13 μm), it was even possible to detect that spinel formation reaction ended up before the CA_6 formation beginning. This aspect can be clearly analyzed by the expansion rate in Figure 5b, where the spinel and CA_6 peaks were well defined for this MgO grain size. On the other hand, increasing the MgO grain size led to a delay in spinel formation and then the two reactions occurred simultaneously.

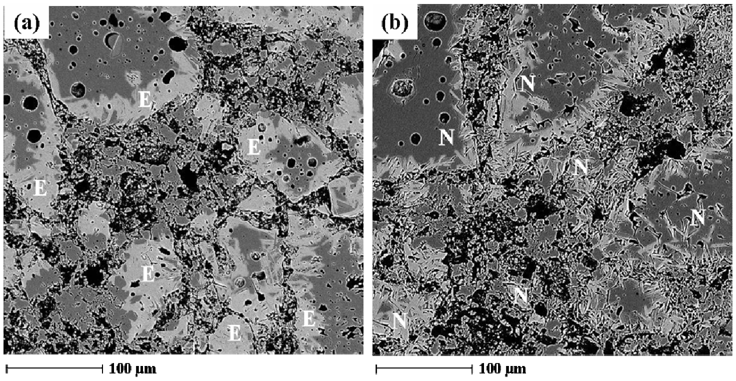

Figure 4. CA_6 crystal morphology and distribution in alumina-magnesia castables after firing at 1.500°C for 5 hours, containing (a) 0 wt% silica (E = equiaxed) and (b) 0.5 wt% silica (N = needles).(11)

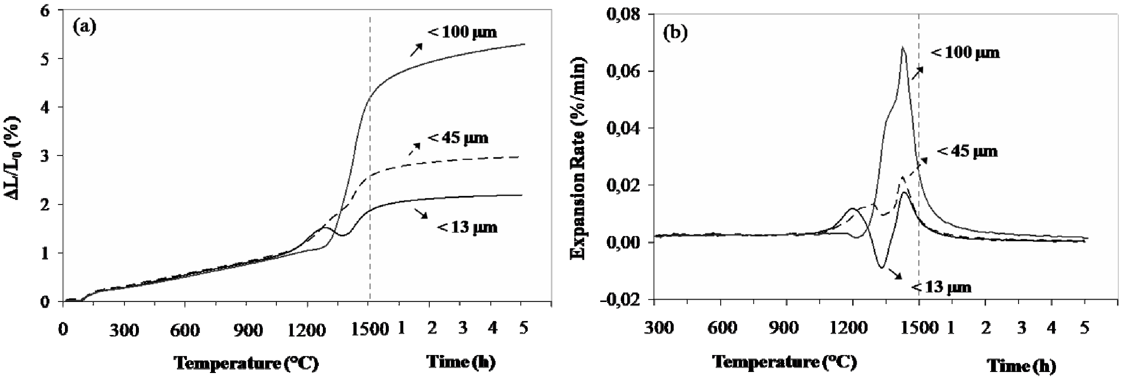

Figure 5. (a) Expansion behavior and (b) expansion rate of alumina-magnesia castables containing different MgO grain sizes (< 13, < 45 and < 100 µm)(14).

The slower kinetics for the coarsest MgO grains also affected the phases developed after firing at 1500°C. For the finest MgO grain sizes (< 13 and < 45 µm), the microstructure was constituted by alumina, spinel and CA_6, as commonly observed in this class of castables. However, the composition containing the MgO < 100 µm presented not only these phases, but also forsterite (Mg_2SiO_4) and most likely monticellite ($CaMgSiO_4$).(16) To better understand these different microstructures, three aspects must be analyzed:

(i) for fine MgO addition there was almost no magnesia left after firing at 1.300°C for 5 hours (spinel was almost completely formed), whereas for the coarse MgO, most of the magnesia was not reacted (there was practically no spinel);

(ii) according to Simonin et al.,(17) a high amount of glassy phases is present in the system CaO-Al_2O_3-MgO up to 1.300°C, which is reduced with the CA_6 formation;

(iii) from a thermodynamics point of view, monticellite and forsterite are more favorable than spinel formation at temperatures higher than 1.300°C. Therefore, as the dissolution was lower for the coarsest MgO grain size, when CA_6 started to be formed, magnesia could interact with silica, calcia and alumina, forming forsterite and monticellite.

A final feature that must be pointed out is the effect of refractory aggregates on the volumetric stability of *in situ* spinel castables. To analyze it, two castables were prepared with different aggregates (tabular alumina or fused magnesia-rich), with the same matrix (6 wt% of dead-burnt <45 µm MgO, 15 wt% of fine alumina, 6 wt% CAC and 1 wt% microsilica) in order to attain 21 wt% spinel.(18) These two compositions presented opposite trends during the assisted sintering technique test (Figure 6a): expansion for the alumina-magnesia castable and shrinkage for the magnesia-alumina one. This latter behavior could be associated to: (a) the formation of a transient liquid phase ($C_{12}A_7$ melting), as no CA_6 peak was evident for the magnesia-rich castable (Fig. 6b), and, (b) due to the reaction between silica and calcia at 1500ºC, leading to bellite (C_2S) formation. Therefore, as no calcium aluminate phase was detected in this sort of castable, it was assumed that alumina presented in the CAC reacted with MgO aggregates, increasing the spinel formation in this system.

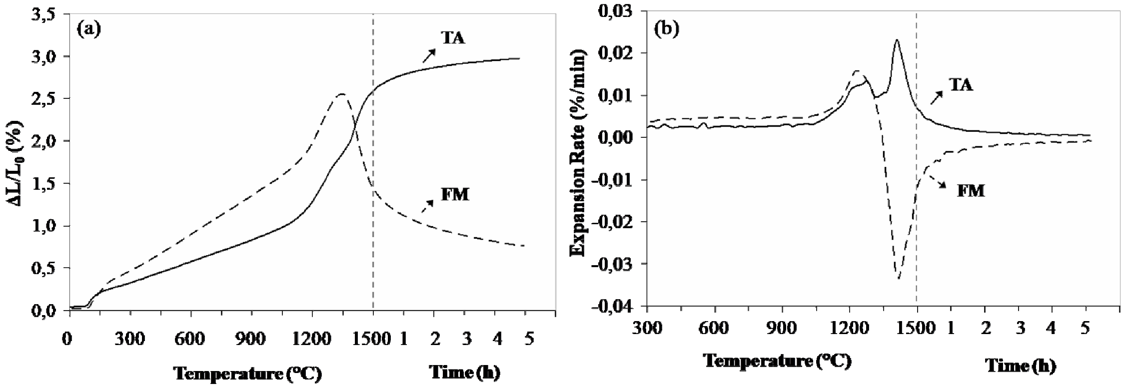

Figure 6. (a) Expansion behavior and (b) expansion rate of alumina-rich (TA = tabular alumina) or magnesia-rich (FM = fused magnesia) castables.(18)

As shown in Figure 7, a greater interaction between aggregates and matrix components was detected in both systems. For the alumina-rich composition, it was possible to analyze the reaction between tabular alumina and CaO, resulting in the CA_6 formation. In an analogous manner, spinel was formed around fused MgO, indicating a reaction between these aggregates and alumina. Considering these aspects, aggregates must not be disregarded in castable studies as they are active partners in the reactions at high temperatures. Thus, studies considering only the castable matrix components might lead to unrealistic interpretations, as it may not represent the castable as a whole.

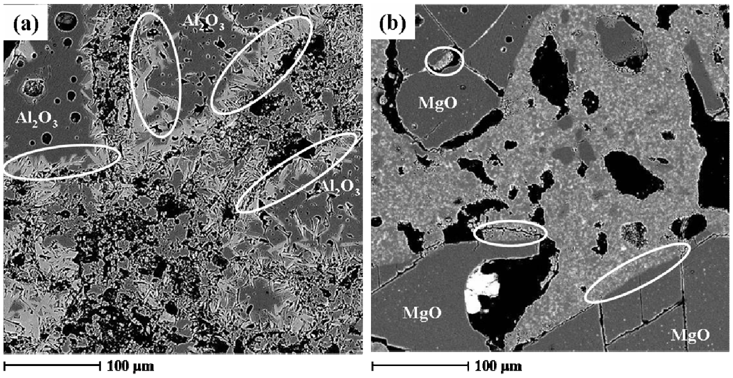

Figure 7. Aggregates reaction: (a) CA_6 formation in tabular alumina grains and (b) spinel formation in fused magnesia, after firing at 1.500°C for 5 hours.(18)

4 CONCLUSIONS

Considering the effect of cement and microsilica content and the MgO grain size, various compositions were analyzed attaining different expansion levels and providing alternative designs. Fig. 8 summarizes the influence of these raw materials and variables on the expansion behavior of alumina-magnesia castables.

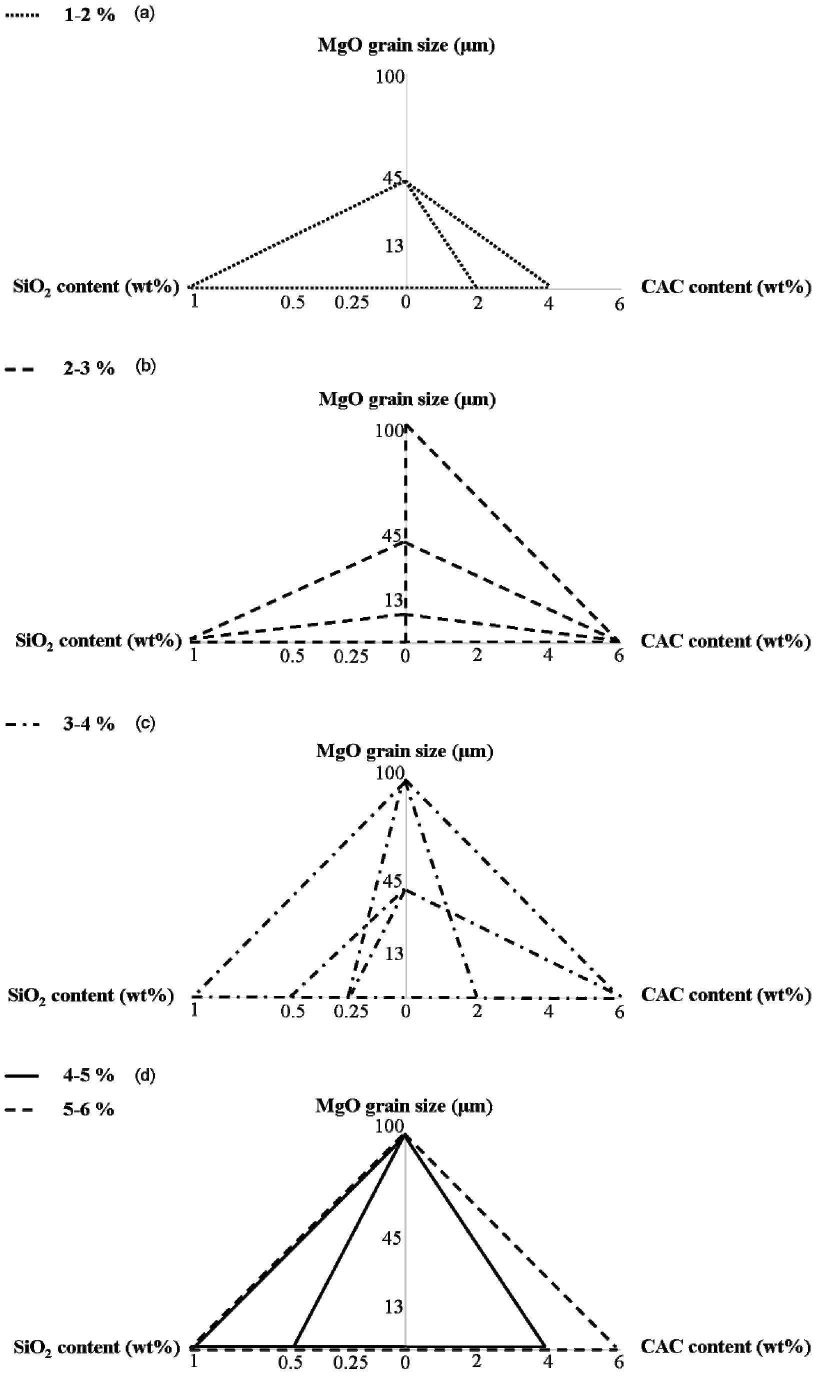

Figure 8. Expansion routes for castables fired at 1500°C for 5 hours, containing different combinations among calcium aluminate cement, microsilica and MgO grain sizes: (a) 1-2%, (b) 2-3%, (c) 3-4% and (d) 4-5 and 5-6% of linear expansion.

1-2% Expansion range: Figure 8a indicates that the best way to attain low expansion levels is by reducing the cement content in castables containing MgO lower than 45 µm, even with high silica content.

2-3% Expansion range: the absence of silica (for the samples with MgO < 45 µm or < 100 µm) is another route to lower expansions (Figure 8b). Additionally, smaller MgO grain sizes (< 45 µm or < 13 µm) associated with a high CAC (6 wt%) and silica (1 wt%) contents provided expansions in this same range.

3-4% Expansion range: intermediate silica contents (0.25 wt% and 0.5 wt%) combined with small MgO grain size and 6 wt % CAC led to a higher expansion (Figure 8c). Furthermore, small CAC content (2 wt%) with 1 wt% silica was not enough to control the expansion for coarse MgO grains, resulting in linear expansion higher than 3%.

4-5 and 5-6% Expansion ranges (Figure 8d): the associations of high silica content (1 wt%) with 4 wt% CAC or lower silica content (0.5 wt%) with 6 wt% CAC for the coarse MgO, resulted in expansions in the range of 4-5 % (Figure 8d). Finally, using coarse MgO and high CAC and microsilica contents led to an expansion in the range of 5-6 %.

Therefore, this study showed that the design of alumina-magnesia expansion must be attained by a systemic approach, as the interactions among cement, microsilica and MgO grain size could provide alternative routes to the expansion target, maintaining the desired costs, thermal-mechanical performance and, consequently, cleaner steel.

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