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CERAMICS INTERNATIONAL

Ceramics International 41 (2015) 4714-4725

www.elsevier.com/locate/ceramint

CA₆ impact on the corrosion behavior of cement-bonded spinel-containing refractory castables: An analysis based on thermodynamic simulations

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> Received 16 October 2014; accepted 3 December 2014 Available online 11 December 2014

Abstract

This work focuses on the evaluation of the corrosion behavior of Al_2O_3 –MgO cement-bonded castables based on thermodynamic calculations, in order to understand the reaction steps and some scientific and technological issues that still need to be better explained when such materials come into contact with basic industrial slags at high temperatures. Special attention was given to analyzing the role played by the calcium hexaluminate phase (CA₆) during the first heating stage of the samples and their further chemical attack. Experimental measurements (cup tests at 1500 °C) and thermodynamic simulations were carried out considering a basic slag (CaO/SiO₂=4.2) and four refractory castables with different spinel (MgAl₂O₄) sources (pre-formed or in situ) and with or without silica fume (0 or 1 wt%). Considering the attained results, a novel corrosion mechanism is proposed pointing out that a suitable design of the castable compositions can induce the formation of CA₆ at the border of the coarse aggregates, preventing their further dissolution and increasing the overall wear resistance of these refractories. In Addition, incorporating optimized contents of silica fume and cement to the spinel-containing castables helps to master the generation of the CA₆ and CA₂ protective layers, resulting in a lower chemical attack at high temperatures.

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Keywords: C. Corrosion; D. Spinel; Castable; Thermodynamic simulation

1. Introduction

Calcium hexaluminate (CA₆, where C=CaO and A=Al₂O₃), generated during the first firing step of alumina–magnesia and alumina–spinel (MgAl₂O₄) castables bonded with calcium aluminate cements (CAC), presents a wide primary crystallization field in the CaO–Al₂O₃–Fe₂O₃ phase equilibrium diagram. As a result, refractory compositions containing this phase commonly present lower dissolution when in contact with molten iron-rich slags [1]. Besides that, the CA₆ formation can also increase the fracture energy of the designed refractories due to the platelet shape of these crystals, resulting in a mechanical barrier for the crack propagation derived from thermal stress [2]. ism, as well as the distribution and morphology of its crystals are extensively affected by the presence of microsilica (MS) and spinel (which can be added as pre-formed grains or by the in situ reaction between Al_2O_3 and MgO at high temperatures) in the formulation. The interaction of corundum [5–7] and Al_2O_3 –MgO castables [8–13] with CaO-containing slags at high temperatures (CaO– Al_2O_3 –SiO₂, CaO–MgO– Al_2O_3 –SiO₂ and other more complex compositions) can also give rise to a dense and continuous layer of CA₆ at the border of the Al_2O_3 coarse grains (indirect corrosion), inhibiting the species diffusion and increasing the corrosion resistance of these materials [11,14]. However, this reaction is usually followed by high volumetric expansion, which can lead to the generation of cracks and flaws in the castable structure [5,6], favoring a greater liquid penetration and spoiling the overall performance of the refractory lining.

As reported in the literature [3,4], the CA₆ formation mechan-

The CA_6 distribution in the matrix and/or the aggregate fractions of high-alumina CAC-bonded compositions (due to

http://dx.doi.org/10.1016/j.ceramint.2014.12.020

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the reaction of CaO from the cement and the fine and coarse Al_2O_3 particles during firing) should influence the wear behavior and the compounds formed during the contact of molten slags and the castable constituents at high temperatures [13,15,16]. Sako et al. [16], for instance, recently proposed a mechanism to explain the corrosion of cement-bonded Al_2O_3 -MgO formulations by basic slags, where the chemical wear degree of these products was directly related to the presence of CA₆ grains at the liquid–aggregates interface.

1.1. Al_2O_3 -MgO cement-bonded castables' corrosion mechanism

Various studies concerning the chemical attack of alumina– spinel and alumina–magnesia castables (containing cement as binder source) by basic slags highlighted that the main reaction mechanism derives from the CaO interaction with solid or molten Al_2O_3 , leading to CA_6 precipitation, as shown in the following equation:

$$6Al_2O_{3(s,l)} + CaO_{(l)} \rightarrow CaO \cdot 6Al_2O_{3(s)}$$

$$\tag{1}$$

Some authors stated that the alumina is provided by the aggregates [8,17,18], whereas others did not mention whether the source of such oxide would be the coarse or fine grains of the formulation [10]. Nevertheless, in general, it is accepted that the corrosion process is initiated by the attack of the matrix components, followed by the dissolution of the aggregates [10,11,13].

Calcium dialuminate (CA_2) can also be formed as a continuous layer at the interface of the CA_6 grains. This former compound is associated with the reaction of calcium hexaluminate crystals with $CaO_{(l)}$, as presented in Eq. (2). In

addition, other studies [5,6] pointed out that CA_2 might be generated before the CA_6 phase and at lower temperature (around 1200 °C) during the corrosion of polycrystalline alumina (Eq. (3)).

$$CaO \cdot 6Al_2O_{3(s)} + 2CaO_{(l)} \rightarrow 3[CaO \cdot 2Al_2O_3]_{(s)}$$
(2)

$$CaO \cdot 2Al_2O_{3(s)} + 4Al_2O_{3(s,l)} \rightarrow CaO \cdot 6Al_2O_{3(s)}$$
(3)

Berjonneau et al. [18] suggested that the features of these aluminate compounds, identified in cement-bonded Al_2O_3 -MgO castable corroded samples indicated their precipitation from the molten slag. Based on experimental tests, Braulio et al. [13] also proposed that CA₆ formation might take place by solid state reactions. Another recent investigation [16] focused on the evaluation of alumina–spinel or alumina–magnesia refractory compositions (comprising pre-formed grains or in situ generation of MgAl₂O₄, respectively) containing CAC and with (1 wt%) or without microsilica (MS), after their interaction with a steel ladle basic slag. Fig. 1 shows SEM images that represents the refractory–liquid interface of each prepared formulation after corrosion cup tests carried out at 1500 °C for 3 h.

According to this work [16], the corrosion mechanism of these materials was directly related to the presence of calcium hexaluminate in the original microstructure, where their interaction with a molten liquid rich in CaO, FeO_x and SiO₂ at 1500 °C led to two distinct situations:

(a) The CA₆ crystals formed at the border of the tabular alumina coarse grains (during the pre-firing step of 0MS and 1MS alumina–magnesia castables, and 0MS alumina–spinel sample, Fig. 1) induced the generation of a dense layer of CA₂ (as described in Eq. (2)) that inhibited further infiltration.



Fig. 1. SEM images of the refractory-slag interface for the Al_2O_3 -MgO and Al_2O_3 -MgAl_2O₄ castables' corroded samples attained after cup tests carried out at 1500 °C for 3 h. 0MS = microsilica-free; 1MS = 1 wt% of microsilica [16].

(b) The higher alumina availability in the formulation containing pre-formed spinel and 1 wt% MS (due to the formation of CA₆ mainly at the refractories' matrix region before the cup tests) resulted in the presence of a greater content of the calcium hexaluminate phase in the corroded microstructure, as the liquid should attack the fine, as well as the coarse components of this refractory (Fig. 1).

Additional aspects related to the performance of the castables evaluated by Sako et al. [16] are presented in Table 1. The lower corrosion resistance (high corrosion index) of the AS1MS composition (alumina-spinel with 1 wt% MS), containing CA₆ which was mainly generated in the matrix fraction of the samples was associated with the overall volumetric expansion derived from the marked formation of this aluminate phase. This transformation led to crack formation in the resulting microstructure, increasing the liquid infiltration at high temperatures. SEM analyses of the corroded AS1MS samples also showed that the coarse grains were exposed to the contact with the molten slag (favoring the higher chemical attack), as the generation of a dense CA₂ layer at the border of the aggregates was not observed (Fig. 1). Other important factors that induced the alumina-spinel castables' wear behavior were related to: (1) the liquid formed in the AM1MS (alumina-magnesia composition with 1 wt% MS) and AS1MS refractory microstructures due to the presence of microsilica in these formulations, as this phase should be incorporated by the molten slag during the corrosion process, and (2) the lower amount (Table 1) and the reduced size of the pores contained in the AMOMS (alumina-magnesia, 0 wt% MS) and ASOMS (aluminaspinel, 0 wt% MS) samples, which halted the further slag penetration at high temperatures.

The slag attack of the castables' matrix was not reported in the most recently published work by Sako et al. [16]. However, a previous study by these authors [15] indicated that the infiltrated region of the prepared microsilica-containing refractories showed CA₂ and CA₆ (AM1MS) or only this latter phase (AS1MS), as well as MgAl₂O₄ with iron and manganese dissolved in its structure, and C₂AS (where, $S=SiO_2$). These results were in agreement with other investigations presented in the literature [13,18,19].

1.2. Further important aspects to be evaluated

Based on the CA_6 distribution in the generated microstructure, the proposed mechanisms help to explain the distinct corrosion behavior of cement-bonded castable compositions [presenting different spinel sources (in situ or pre-formed) and with or without microsilica] when in contact with basic slags. Nevertheless, there are still some aspects to be better discussed, such as:

- (1) The matrix role in the overall corrosion process, as this is the most reactive portion of the formulation and the dissolution of the fine refractory components in the molten liquid should change the slag composition.
- (2) The alumina sources and their availability, considering that

a higher amount of this oxide in the composition might lead to CA_6 formation instead of CA_2 . For instance, preformed spinel-containing castables should incorporate a higher amount of alumina in the slag, as their tabular Al_2O_3 grains are usually not coated by CA_6 (formed after pre-firing treatment and before a chemical attack) [16]. Other formulations, presenting a dense calcium hexaluminate layer at the border of the coarse particles, show a physical barrier that prevents further alumina dissolution. However, regardless of the aggregate corrosion, other alternative Al_2O_3 sources (i.e., fine spinel and CA_6 particles contained in the matrix) have not been considered.

- (3) The role of CaO (derived from the refractory materials) in the precipitation/formation of calcium aluminate compounds during the solid–liquid interaction needs also to be further analyzed. The main calcia source in the evaluated castables is the CA₆ crystals generated during the samples' pre-firing step. However, the vitreous phase formed in the matrix of the formulations with silica fume (MS) which contains a small amount of oxide phases (CaO, Al₂O₃ and SiO₂ in AS1MS and these components plus MgO in AM1MS) and the remaining CA₂ of the AM0MS system [13] could also provide CaO to the melt.
- (4) The distinct morphology and texture of CA_6 crystals formed around the tabular alumina particles during the chemical attack of the spinel-containing castables (Fig. 1), as there are marked differences between them and those generated during the first thermal treatment of the samples (pre-firing step). Based on this evaluation, most likely, it would better explain the CA_2 formation and whether this phase should be generated in the presence of the preexistent CA_6 layer.

Therefore, considering the aspects presented above, the following questions could arise: (a) What is the calcium hexaluminate (formed in the microstructure during firing) impact on the castables' corrosion behavior? (b) Which factor is the most important for improving the corrosion resistance: CA_6 crystals at the border of the aggregates or their absence in the matrix fraction? (c) Which calcium aluminate is firstly formed by the slag– refractory reaction, CA_2 or CA_6 ? (d) What is the CA_6 (derived from the corrosion reactions) effect in suppressing the refractory wear?

In order to answer these questions, this work focused on thermodynamic simulations of the corrosion resistance of the four cement-bonded spinel-containing refractory castables reported by Sako et al. [16]. Additional data were also attained by the re-evaluation of the corroded samples' microstructure. The main objective of this study was to better understand the CA_6 impact on the spinel-containing castables' chemical resistance.

Theoretical calculations can be successfully applied to the analysis of such phenomenon due to the complexity of the selected systems and the various reactions that can take place at high temperatures. However, it must be pointed out that some aspects are not considered in this method (i.e., distribution of the phases in the microstructure, presence of pores, etc.), which might lead to differences between the calculated and practical results. According to previous studies, the procedure proposed by Luz et al. [20], considering first the matrix corrosion, followed by the aggregate–slag interaction in a further step, can be used for this purpose. Although these simulations can overestimate the matrix role in the refractory wear process, this model describes the phase transformations more accurately when compared to calculations based on the overall components (fine and coarse ones) of the castable formulation [21].

2. Thermodynamic calculations

The data related to the corrosion behavior of the castables AM1MS, AM0MS, AS1MS and AS0MS at 1500 °C (Table 1 and Fig. 1) were reported by Sako et al. [16]. The chemical composition of the industrial slag selected for these experiments (cup test, 2 h at 1500 °C) is presented in Table 2 (CaO/SiO₂ basicity=4.2).

Thermodynamic simulations were carried out using Fact-Sage software [version 6.3.1, Thermfact/CRCT (Montreal) and GTT-Technologies (Aachen)], which comprises a series of modules that access and cross link thermodynamic databases and allow for various calculations. For this study, the following databases: FactPS, SGTE and FToxid, and the Equilib, Viscosity and Reaction moduli were selected.

The castable corrosion simulation method consisted of [20,21]: (1) evaluating the contact between the slag and the matrix and, after the liquid saturation, (2) analyzing the interaction between the resulting slag and the aggregates. Hence, first 100 g of slag and 100 g of the castable matrix were reacted and the resulting liquid

Table 1

Physico-chemical properties of the spinel-containing castables designed by Sako et al. [16].

Composition	Phase content (wt%)		CA ₆ location after pre-firing step (1500 °C/5 h)		Apparent porosity (%)	Slag corrosion index ^b (%)	
	CA ₆	MgAl ₂ O ₄	Particle boundaries ^a	Matrix			
AM0MS AM1MS AS0MS AS1MS	21.3 22.4 21.3 21.8	27.6 32.6 20.8 22.3	High Medium High –	– Low – High	$\begin{array}{c} 17.4 \pm 0.4 \\ 23.1 \pm 0.9 \\ 15.2 \pm 0.5 \\ 20.0 \pm 0.3 \end{array}$	$\begin{array}{c} 6.3 \pm 0.2 \\ 8.5 \pm 0.3 \\ 7.9 \pm 0.3 \\ 34.0 \pm 1.2 \end{array}$	

AM=alumina-magnesia, AS=alumina-pre-formed spinel, 0MS=without microsilica, 1MS=with 1 wt% of microsilica.

^aCA₆ located at the border of tabular alumina coarse particles.

^bBased on cup-tests carried out at 1500 °C for 3 h in air.

Table 2	
Chemical composition of the industrial slag used in the corrosion tests.	
	-

Oxide	Al_2O_3	MgO	CaO	SiO_2	MnO	FeO_x	P_2O_5	TiO ₂	Cr_2O_3	SO ₃
wt%	1.6	8.5	34.2	8.7	4.1	40.8	1.4	0.4	0.2	0.1

of each step was successively placed in contact with the original matrix, until the slag saturation was reached. After that, 100 g of the resulting slag (liquid saturated with the matrix components) was used in the calculations involving 100 g of the aggregates [20,21]. All calculations were made at a constant temperature of 1500 °C, 1425 °C and 1350 °C and total pressure of 1 atm.

In order to define the matrix composition for the thermodynamic simulations (Table 3): (a) the particle size of the raw materials contained in the refractory formulations ($d < 200 \mu$ m) [16], and (b) the results attained from quantitative X-ray diffraction (XRD, partially presented in Table 1) and scanning electron microscopy (SEM-EDS) evaluations of the samples fired at 1500 °C for 5 h [16] were considered.

Besides the pictures presented in Fig. 1, additional micrographs and EDS results provided by Sako et al. [16] were also re-analyzed in order to attain further microstructural details of the phases derived from the interaction of the refractories and molten liquid.

3. Results and discussion

The phase evolution predicted for the castable's matrix and molten slag contact is presented in Fig. 2. In each graph, *S* represents the original slag composition (located on the left side) and *M* the phases generated at 1500 °C in the castable matrix (calculations based on the data previously presented in Table 3). Solid phases were only generated after a marked interaction of the molten liquid with the fine components of the refractories (Fig. 2), in which various calculations steps (from 8 to 20) were required to attain the equilibrium state. The number of calculated interactions indicates the likelihood of the chemical attack of the samples, and this information can be used to define which formulation would have the highest corrosion resistance [20].

Besides that, a second round of simulations involving the aggregate oxides (Table 3) and the resulting molten slag (derived from the liquid–matrix interaction and saturated in the castables' fine components) was also carried out. However, as pointed out in Fig. 3, further slag–aggregate contact does not give rise to significant changes in the evaluated systems, except for castable AM1MS.

A similar trend between the number of calculation steps derived from the slag-matrix interaction (Fig. 2) and the

Table 3

Chemical composition of the castables matrix and aggregates used for the thermodynamic calculations.

Fraction	Oxide	(wt%)						
		AM1MS	AM0MS	AS1MS	AS0MS			
Matrix	Al ₂ O ₃	29.20	29.43	31.12	26.22			
	CaO	0.44	0.42	1.76	0.42			
	SiO ₂	1.00	_	1.00	-			
	MgO	6.00	6.00	4.62	4.62			
Aggregates	Al_2O_3	62.00	62.77	60.12	66.02			
	CaO	1.32	1.34	_	1.34			
	MgO	-	-	1.38	1.38			



Fig. 2. Phase evolution predicted by the thermodynamic simulations based on the interaction among the slag-matrix components of castables (a) AM1MS, (b) AM0MS, (c) AS1MS, and (d) AS0MS at 1500 $^{\circ}$ C. The solid lines connecting the points are used only as a guide.

samples' of liquid infiltration (obtained via experimental corrosion cup-tests [16]) was observed (Fig. 4). Due to the major role and faster dissolution of the fine raw materials during the castables' chemical attack, these theoretical results were better correlated to the relative infiltrated area (penetration index) of the refractories, when compared to those for plain coarse aggregates or the blend of matrix + aggregates.

As the slag penetration advances into the four designed castables, the reactions involving the molten slag and solid phases should give rise to different components (CA₂, CA₆, spinel, as shown in Fig. 2) according to the following reaction sequence:

matrix + slag \rightarrow spinel \rightarrow spinel + CA₂ \rightarrow spinel + CA₂ + CA₆ \rightarrow spinel + CA₆ + corundum

In addition to these compounds, liquid generation and spinelcontaining Fe^{+2/+3} ions in the solution are also expected to be found at high temperatures. Based on the predicted phase transformations, CA₂ would be the first calcium aluminate formed after being in contact with the slag–castables' matrix. Fig. 2 points out that the increase in the CA₆ content is followed by a proportional decrease in the CA₂, indicating that the latter would be precipitated in an earlier stage. As a consequence, these changes in the calcium aluminate amount would result in a final layered microstructure for all evaluated compositions. Spinel dissolution in the molten liquid is also expected to take place in the first contact of the castables with the slag at 1500 °C, inducing the decrease in the MgAl₂O₄ content in the first calculation step (except for the AS1MS material, Fig. 2).

Fig. 1 shows that continuous and dense layers of calcium aluminate phases were detected at the border of the coarse tabular alumina grains, according to the same sequence suggested by the simulations: CA_6 around the corundum particles and CA_2 in contact with the slag. Only the AS1MS sample did not present the calcium dialuminate phase in the corroded interface and this aspect will be better discussed later. The new phases generated between the slag and the castable confirm that corrosion was carried out via an indirect mechanism, which corresponds to the dissolution of the refractory matrix and precipitation of the solid phases close to the less reactive grains (aggregates). The amount of the calcium aluminate compounds attained via thermodynamic simulations (sum of the total mass, in grams, of CA_2 and CA_6 content



Fig. 3. Phase evolution for the interaction between the slag-aggregates of castables (a) AM1MS, (b) AM0MS, (c) AS1MS, and (d) AS0MS at 1500 $^{\circ}$ C. *L* represents the liquid saturated in the matrix components (after the first round of calculations – Fig. 2) and *A* is the predicted aggregate composition at 1500 $^{\circ}$ C. The solid lines connecting the points are used only as a guide.



Fig. 4. Correlation between the number of calculation steps attained for the slag-matrix interactions at 1500 $^{\circ}$ C and the slag penetration index (SCI, based on experimental cup-tests carried out at 1500 $^{\circ}$ C for 3 h [16]).

identified in each calculation step) after analyzing the matrix fraction shows a suitable correlation with the total thickness of the CA_2+CA_6 layer measured in the SEM images (Fig. 5).

Composition of AS1MS presented the highest content and the thickest layer of calcium hexaluminate, resulting in a distinct behavior when compared to the other systems. According to Figs. 2 and 3, all calcium aluminates should mainly be derived from the dissolution of the refractory's fine grains and their further precipitation at the solid–liquid interface, confirming the important role played by the matrix components in the chemical corrosion process. This interpretation differs from the one proposed by Sako et al. [16], as they stated that the final distribution of the precipitated phases is determined by the reaction of the corrosive liquid with the aggregates. In addition, most likely the partial dissolution of the external surface of the coarse grains, as well as their reactions in a solid state should also take place as highlighted by Braulio et al. [13].

Some authors [16] reported that the Al_2O_3 availability in the refractory structure is the main factor that affects the generation of calcium aluminates (CA₆ in AS1MS, and CA₂ and CA₆ in the other compositions) during the samples' corrosion. Fig. 6 presents the amount (in grams) of Al_2O_3 and CaO contained in 100 g of the selected castables (Table 3) as a function of the total content of CA₂ and CA₆ predicted by the thermodynamic

calculations carried out for the slag-matrix interaction at 1500 °C. Taking into account the fitting lines, the CaO content in the castable matrix fraction seems to show a better correlation than Al_2O_3 with the new phases precipitated at high temperatures. Therefore, the main crystalline phases formed during the corrosion process should also directly depend on the calcia amount.

As mentioned before, the CA_6 crystals generated in the castables' matrix during their pre-firing step were the major CaO source of the evaluated systems. Thus, the presence of this phase in the most reactive fraction of the compositions (matrix region) seems to control the overall corrosion reactions. Castable AS1MS (which only contains calcium hexaluminate crystals in the matrix) is the refractory that presents the highest amount of calcia available for the generation of calcium aluminates when in contact with the selected slag.



Fig. 5. Correlation between the thickness of the CA_2+CA_6 dense layer formed at the slag-refratory interface during the corrosion cup-tests carried out at 1500 °C and the total mass of these calcium aluminate phases predicted by the thermodynamic simulation (slag-matrix interaction) at the same temperature.



Fig. 6. Correlation between the CA_2+CA_6 content predicted by the thermodynamic calculations during the slag-matrix interaction at 1500 °C and the original amount of CaO or Al₂O₃ in the castable matrix fraction (considering a total of 100 g).

For the other evaluated formulations [where CA_6 was mainly located at the border of the coarse tabular alumina grains (Table 1)], the lower CaO content derived from the matrix dissolution in the molten liquid affected the CA_2 and CA_6 formations and, consequently, the slag corrosion index (Table 1).

As predicted by the thermodynamic simulations (Fig. 2) and reported in other work [11,13], CA₂ is the first compound generated due to the interaction of spinel-containing cementbonded castables with the slag, whereas further CA₆ formation (related to CA₂ and Al₂O₃ reaction) is also expected to take place due to the incompatibility between calcium dialuminate and alumina [20]. However, based on SEM results of the corroded samples, no CA₂ layer was identified in the AS1MS composition at the solid–liquid interface. In order to clarify this aspect, a new analysis of the SEM images collected by Sako et al. [16] was made.

In the AS1MS corroded region, the CA₆ crystals were identified as long platelets (aspect ratio \sim 7) with random orientation, forming a dense layer presenting large thickness $(\sim 250 \ \mu m)$. These features indicate that their crystallization process should take place in a non-uniform and fast manner in the presence of the liquid phase. In Addition, voids or other solid phases close to the CA₆ crystals were observed. These defects consisted mainly of round (similar to the ones contained in the tabular alumina aggregates) or irregular pores. According to the corrosion mechanism proposed by Sako et al. [16], calcium hexaluminate crystals were generated due to the slag attack of the unprotected coarse tabular Al₂O₃ grains, as pointed out in Eq. (1). The high negative ΔG value (-261,1 kJ/mol) of this reaction represents its driving force, which may explain why this transformation is the most effective one detected during the samples' corrosion at 1500 °C.

Nevertheless, based on Eq. (1), it is not possible to infer (1) why pores were formed inside the CA₆ layer at the corroded interface, or (2) what the CA₂ role in this process was, as this phase should be generated before the calcium hexaluminate. A reasonable explanation concerning the latter aspect is that the initial interaction between refractory and slag led to calcium dialuminate formation, which was almost totally converted to CA₆ when the castables were kept at 1500 °C for 2 h during the corrosion cup-tests. As a consequence, only isolated and few CA₂ crystals (without forming a continuous and visible layer) were roughly identified in the SEM/EDS images.

Considering that the slag melting point is close to 1350 °C (based on experimental measurements), the calcium dialuminate phase could also be formed before reaching the selected holding time at 1500 °C. Thus, most likely the molten liquid must infiltrate and react with the refractories even during the corrosion test heating stage, favoring the consumption of the CA₂ phase. However, what was the reason for the main difference between AS1MS corroded samples and the other castables that contained CA₆ and CA₂ layers at their solid– liquid interface (Fig. 1)? Further thermodynamic calculations were carried out, considering the refractory corrosion (slag– matriz and slag–aggregates) at intermediate temperatures (1350 and 1425 °C), in order to shed some light on this remaining question. The attained results pointed out that there will be a matrix attack in such conditions, resulting mainly from the formation of spinel, CA₂, CA₆ and more liquid. Furthermore, lower amounts of mellilita (Ca₂AlSiO₂O₇–Ca₂Al₃O₇) or anorthite (CaAl₂Si₂O₈) in the silica-containing formulations, or galaxite (MnAl₂O₄) in the silica-free castables were also detected. As previously highlighted in the simulations performed at 1500 °C, the coarse aggregate corrosion has a lower relevance in the overall degradation behavior of the refractories.

Fig. 7 shows the total mass of the CA₂, CA₆ and resultant liquid derived from the thermodynamic calculations of the slag-matrix corrosion as a function of the temperature. Fig. 8 also presents the liquid phase viscosity evolution with the calculation step for each evaluated temperature (1350, 1450 and 1500 °C). In general, at 1350 and 1425 °C, the predicted CA₂ total content is higher than CA₆, except for AS1MS samples kept at 1350 °C. The major differences between this latter castable and the other compositions are mainly related to the calculation hexaluminate amount generated at the three selected temperatures and the resulting liquid detected at 1500 °C during the corrosion of the matrix fine components. It is believed that neither the total CA₂ content nor the slag

viscosity changes would justify the different performance of AS1MS (lower corrosion resistance and absence of a CA_2 dense layer at the solid–liquid interface) when compared to the other castables.

Therefore, the additional simulations carried out below 1500 °C confirmed the CA_2 transformation into CA_6 for all designed compositions, but a more intense reaction of the calcium dialuminate should take place in the AS1MS microstructure. Based on the features of the evaluated refractory systems and the theoretical calculation results, the corrosion behavior of the castable containing pre-formed spinel and 1 wt % of silica fume is associated with the following aspects:

- (a) The higher CaO content in its matrix fraction (found as CA_6 crystals, which were generated during the samples pre-firing at 1500 °C for 5 h) seems to be the main factor that affects the refractory dissolution and further formation of calcium aluminates at the solid–liquid interface (Fig. 5). The extensive CA_6 formation (expansive reaction) also favored the higher slag penetration in the AS1MS samples, due to the resultant larger pore size and intermediate pore content of this material.
- (b) The aggregates (which will not present a CA_6 protective coating, as observed for the other evaluated pre-fired



Fig. 7. Total mass content of (a) CA₂, (b) CA₆ and (c) resultant liquid predicted to be formed during the slag-castable matrix interaction at 1350, 1425 and 1500 °C.



Fig. 8. Evolution of the liquid viscosity with the number of calculation steps during the thermodynamic calculations of the slag-matrix corrosion at 1350, 1425 and 1500 $^{\circ}$ C.

castables) will be more prone to be attacked by the slag, leading to higher Al_2O_3 dissolution into the liquid and, consequently, giving rise to a more viscous molten phase.

(c) The lower spinel dissolution pointed out in the thermodynamic simulations (for the temperatures of 1350 °C and 1500 °C) for the AS1MS composition should reduce the MgO and increase the CaO concentration in the slag.

Thus, it is expected that the same reaction sequence should be observed for AS1MS and the other castable systems, where the main differences are only related to the advance degree of these transformations due to a combination of physical (pores content and size) and chemical (CaO and Al₂O₃ availability) aspects. As reported by Braulio et al. [13], the generation of a protective CA₆ dense layer (derived from the CA₂ crystals formed in a previous step) at the refractory interface can take place according to two mechanisms, comprising: (i) liquid (Eq. (4)), or (ii) solid state (Eqs. (5) and (6)) reactions.

$$6Al_2O_{3(l)} + CaO_{(l)} \rightarrow CaO \cdot 6Al_2O_{3(s)}$$

$$\tag{4}$$

$$CaO \cdot 2Al_2O_{3(s)} + 4Al_2O_{3(s)} \rightarrow CaO \cdot 6Al_2O_{3(s)}$$
(5)

$$CaO_{(s)} + 6Al_2O_{3(s)} \rightarrow CaO \cdot 6Al_2O_{3(s)}$$
(6)

These different routes can explain the features of the CA₆ phase found in the AS1MS corroded samples (Fig. 1). The first alternative (liquid state transformation) for the calcium hexaluminate generation is equivalent to the proposal by Sako et al. [16], which highlighted that the second phase filling in the voids located among the CA₆ crystals should be derived from the presence of a liquid phase at high temperatures. On the other hand, the second route (solid state reactions) explains the presence of pores with similar features as the ones contained in the original tabular alumina aggregates. In this latter case, the presence of platelet crystals with sharp corners indicates that a liquid phase with high viscosity might have been formed at the CA₂ and CA₆ crystalization temperatures, inhibiting its fast movement and preventing the complete filling of the voids contained in the microstructure. Therefore, this approach seems to be in tune with the hypothesis of the CA2 formation at lower temperatures in the AS1MS system and, therefore, the CA₆ formation should occur as pointed out

in Eq. (5). Moreover, Fig. 8 confirms that at 1350 $^{\circ}$ C and 1425 $^{\circ}$ C, the liquid viscosity contained in the samples of this castable was four fold higher than the one predicted to be attained at 1500 $^{\circ}$ C.

Regarding the AM0MS, AM1MS and AS0MS refractories, no significant difference was identified in the texture of the CA₆ crystals generated in these materials during the corrosion process (Fig. 1). There was a preferential orientation of this phase and the resultant layer thickness was smaller, compared to the AS1MS. In addition, the morphology of the CA₆ crystals (derived from the slag attack) was not the same as the original ones formed during the pre-firing step, especially for the AM1MS samples. This aspect points out that there was a partial or total dissolution of CA₆ at high temperatures, inducing its further re-precipitation in the presence of the molten liquid. The higher density of the calcium aluminates layers (due to the lower amount of pores in these regions when compared to the AS1MS composition) indicates that these phases were generated in a controlled process in the presence of liquid, and this latter should have also favored a better accommodation of the CA₆ and CA₂ crystals in the microstructure.

The formation of the new calcium hexaluminate crystals in the AM1MS, AM0MS and AS0MS castables can take place according to Eqs. (4)-(6), where the following Gibbs free energy values were calculated: $\Delta G_{(4)} = -275.8 \text{ kJ/mol},$ $\Delta G_{(5)} = -7,5$ kJ/mol and $\Delta G_{(6)} = -109,2$ kJ/mol. The lower ΔG results for the reactions (5) and (6) can be associated to the higher control of the CA₆ crystallization process. Besides that, Eqs. (5) and (6) represent the interaction of solid and liquid phases, as expected during the contact of the molten slag and AM1MS, AM0MS and AS0MS refractories (as presented in Fig. 1). On the other hand, the predicted liquid viscosity (Fig. 8) was kept at reduced values even at temperatures lower than 1500 °C, mainly for the compositions without silica fume (MS), which is in tune with the route proposed for the generation of the calcium aluminate crystals in these castables (i.e., in the presence of a liquid with lower viscosity).

Therefore, when considering the generation of CA₂ and CA₆ due to the interaction of the castables and the selected basic slag, the main difference between the AS1MS system and the other refractories is not related to the reaction mechanisms, but to the conditions where they took place. The formation of a less viscous liquid phase during the corrosion of the AM (0MS and 1MS) and ASOMS materials most likely induced a better homogeneization of the ions concentration in the medium, favoring a more controlled generation of the calcium aluminate dense layers at the solid-liquid interface. Nevertheless, it is important to highlight that the slag corrosion index (SCI, shown in Table 1) of the evaluated compositions did not present a good correlation with the amount of calcium aluminates predicted by the thermodynamic simulations. This fact indicates that other aspects besides the overall content of CaO of the refractories (i.e., presence of SiO₂, leading to a higher generation of liquid phase at high temperature, and others) affected their corrosion behavior.

Due to the similar CaO content in the matrix portion of the AMOMS and ASOMS compositions, only a minor difference in the SCI results could be detected. Nevertheless, based on the

thermodynamic simulations, the slag penetration in this latter system should be less significant according to the lower number of calculation steps required to reach the liquid saturation and the amount of CA_2 and CA_6 formed at high temperatures. As dense, continuous and thicker calcium aluminate layers were formed at the border to the corroded aggregates of the AMOMS castable (Fig. 1), most likely they acted as a physical barrier to protect their coarse particles more effectively. This fact can explain the higher corrosion resistance of these samples. In Addition, the distinct size of the preformed spinel particles contained in the ASOMS composition and the generated in situ spinel phase in the AMOMS should also play a role in the corrosion behavior of these materials.

3.1. Additional insights related to the corrosion mechanism

According to the analysis of the data derived from the thermodynamic simulations and the re-evaluation of the SEM images of the corroded Al₂O₃–MgO castable samples, some of the questions initially raised in this work could be clarified. For instance, considering the studied castables and the selected basic slag:

- An important aspect is the presence of CA_6 in the refractory matrix, as this phase is generated during the pre-firing step of the castable due to the reaction of alumina and the calcium aluminate cement (binder additive). Besides that, other factors also affect the corrosion behavior of these systems, such as: (a) the presence of other additives (i.e., silica fume), and (b) the pore sizes, the apparent porosity level, and others.
- The generation of the CA₆ phase at the border of the tabular alumina grains during the heating process does not seem to have a major effect on the final corrosion resistance of the castables, as this compound should be partially or totally dissolved in the molten slag at high temperatures.
- The CA₂ phase should be formed before the CA₆ one. The absence of calcium dialuminate in the AS1MS system is associated with its complete conversion to calcium hexaluminate compound.
- The crystallization of a greater amount of CA₆ as a result of the slag–refractory interaction can also lead to some side effects, not only due to the crack generation related to the volumetric expansion and fair accommodation of this phase in the resultant microstructure, but also to the random distribution of the newly formed crystals.

Based on that, a more accurate corrosion mechanism can be proposed for the Al₂O₃–MgO CAC-bonded castables when in contact with a basic industrial slag (CaO/SiO₂=4.2), presenting low content of Al₂O₃ (1.6 wt%) and high amount of FeO_x (40.8 wt%) at 1500 °C:

 As the slag melts at temperatures lower than 1500 °C, the formed liquid penetrates into the open pores of the castable's microstructure and readily reacts with its matrix (fine) components;

- (2) the dissolution of spinel, alumina and CA₆ (if the latter is contained in the matrix portion) should take place in a further moment, increasing the liquid ionic concentration with Ca⁺², Mg⁺² and Al⁺³. After the slag saturation in these components, the precipitarion of solid phases (such as CA₂ and spinel at a first stage) is expected to be observed;
- (3) with the advance of this process, the CA₂ phase should react with Al₂O₃ giving rise to CA₆ crystals and generating a dense layer (indirect corrosion) on the surface of the coarse and less reactive tabular alumina particles. The aggregates can also undergo partial or total dissolution (depending on their size), leading to a greater incorporation of ions (Al³⁺) into the molten medium and favoring the precipitation of CA₂ and CA₆ at the solid–liquid interface.

The calcium hexaluminate crystallization derived from the slag attack can occur according to the following steps: (a) coating the coarse alumina grains, that react with $CA_{2(s)}$ or $CaO_{(l)}$, and/or (b) by the interaction of $CaO_{(l)}$ and $Al_2O_{3(l)}$ incorporated into the molten medium. When a high amount of CaO is contained in the castable's matrix composition, the $CA_2 \rightarrow CA_6$ transformation can take place even before reaching the maximum temperature (1500 °C) selected for the experimental corrosion tests. In this case, the higher content of CA₆ crystals generated may lead to a crack formation in the castable's structure due to the volumetric expansion associated with this reaction. Thus, new channels for the liquid infiltration should be formed, favoring the advance of the refractory corrosion.

The presence of silica fume or the spinel source (pre-formed or in situ) will mainly affect the content of the phase generated due to the solid–slag contact: liquid, calcium aluminates and spinel. Regarding the molten liquid, a high amount of this phase indicates that the castable was readily attacked and a greater dissolution of its solid components took place at high temperatures. Considering the calcium aluminates, the higher resulting content of CA₂ and CA₆ is not directly associated with a better protection of the coarse aggregates (indirect corrosion) due to the formation of denser and continuous coating layers of these phases. In fact, if the crystallization of CA₂ and CA₆ is carried out in a random and nonorganized manner (leading to the generation of a porous structure), then, no further contribution of these phases to improve the castables' corrosion resistance should be observed.

4. Conclusions

This work presented and discussed the most recent understanding regarding the high temperature corrosion of CACbonded Al_2O_3 -MgO refractory castables, pointing out the main role of the CA₆ phase and the other components located at the matrix of these materials. Considering the thermodynamic simulation results and the re-evaluation of the SEM images of the corroded interface of the samples, some remaining questions could be better explained, as highlighted below:

• A better slag corrosion resistance is not only attained by the formation of a dense CA₆ layer at the border of the coarse

aggregates, but castable compositions containing a reduced or absence of CaO content in the matrix fraction should also show an improved performance.

- CA₂ is expected to be formed in the castable microstructure before the CA₆ and also help the formation of the latter phase at higher temperatures during the slag attack.
- Considering that the location of the CA₆ grains in the resulting refractory microstructure (after the pre-firing step) plays an important role in the slag corrosion resistance of these materials, a proper design of the castable compositions should be carried out in order to induce the formation of this phase mainly coating the aggregates' surface and preventing their dissolution. By selecting an optimized content of silica fume in addition to a suitable fraction of pre-formed and in situ spinel grains, improved control of the generation of the CA₂ and CA₆ protective layers is expected to result in a reduced chemical attack. Replacing calcium aluminate cement by an alternative binder (i.e., hydratable alumina, colloidal alumina) can also be another route for enhancing the corrosion behavior of this refractory system.
- Silica-free castable containing alumina and magnesia (for the in situ spinel generation, AMOMS) presented the best corrosion resistance, which is associated to the formation of CA₆ crystals mainly at the border of the coarse tabular alumina grains. This feature led to the reduction of CaO availability in the matrix fraction of the refractory and resulted in a lower increase of the liquid amount due to the fine components dissolution. In this sense, the thermodynamic simulation results were able to predict the spinel dissolution and its effect on the precipitation of solid phases that act forming dense layers (i.e., calcium aluminates) preventing the corrosion advance. Nevertheless, further investigations are still necessary in order to better explore the effect of different spinel sources as an alternative route to induce the generation of dense and protective layers at the solid-liquid interface.

Acknowledgments

The authors would like to thank CNPq, FIPAI and Magnesita for supporting this work.

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