

# Thermodynamic evaluation of SiC oxidation in $\text{Al}_2\text{O}_3$ – $\text{MgAl}_2\text{O}_4$ –SiC–C refractory castables

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Received 3 December 2009; received in revised form 22 January 2010; accepted 17 March 2010

Available online 28 April 2010

## Abstract

The literature suggests that  $\text{MgAl}_2\text{O}_4$  can accelerate SiC oxidation in  $\text{Al}_2\text{O}_3$ – $\text{MgAl}_2\text{O}_4$ –SiC–C refractory castables. Thus, in this work thermodynamic calculations have been carried out using FactSage<sup>®</sup> software in order to explore, search for and understand the role of  $\text{MgAl}_2\text{O}_4$  on the SiC oxidation. According to the thermodynamic predictions, at 1500 °C and under a reducing atmosphere, there is no evidence that spinel might directly affect SiC oxidation. The increase of SiC content in an  $\text{Al}_2\text{O}_3$ –SiC–C (AL) castable composition was mainly related to the reaction between mullite and carbon. On the other hand, the SiC generation in the  $\text{Al}_2\text{O}_3$ – $\text{MgAl}_2\text{O}_4$ –SiC–C (SP) composition was a result of the reaction involving liquid  $\text{SiO}_2$  and carbon from the refractory. Therefore, the lower SiC content in the SP castable resulted from the refractory's phase transformations. It was also suggested that the samples thermally treated 15 times at 1500 °C did not reach the equilibrium condition, which explains the differences between experimental and thermodynamic results.

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**Keywords:** Oxidation; Carbon containing refractories; Thermodynamic calculations; FactSage<sup>®</sup>

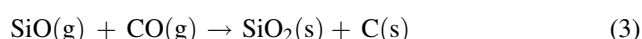
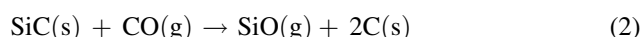
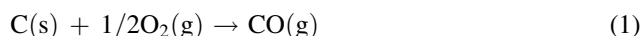
## 1. Introduction

$\text{Al}_2\text{O}_3$ –SiC–C and  $\text{Al}_2\text{O}_3$ – $\text{MgAl}_2\text{O}_4$ –SiC–C refractory castables are mainly used in main blast furnace troughs due to their superior thermal shock and corrosion resistance, when in contact with liquid slags and metals [1,2]. The main trough is usually designed with a zone lining, which implies that the composition of the refractories in the slag line and metal line could be distinct.  $\text{Al}_2\text{O}_3$ –SiC–C castables usually contain a high amount of SiC (15–20 wt%) in order to improve their corrosion and thermal shock resistance. However, the high oxidation of SiC by FeO is the main cause of refractory wearing when they are applied to the metal zone. Thus, one alternative to reduce this effect consists of adding MgO or  $\text{MgAl}_2\text{O}_4$  as a component of trough castables, which could provide a higher FeO corrosion resistance [3–6].  $\text{Al}_2\text{O}_3$ – $\text{MgAl}_2\text{O}_4$ –SiC–C castables show a lower wear rate during their working time

because FeO can be incorporated as a solid solution in the spinel phase.

On the other hand, a drawback for the  $\text{MgAl}_2\text{O}_4$  addition is its possible influence on the silicon carbide oxidation [1,3,4,7]. According to the literature, a few reactions could be used to explain how spinel accelerates SiC oxidation. Kageyama et al. [1] estimate that the oxidation mechanism can be described as follows:

- (1) Active SiC oxidation under a reducing atmosphere:



- (2) Mg(g) release from the spinel grains in a reducing atmosphere.



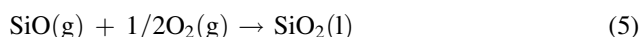
- (3) Acceleration of SiC oxidation.

- (a) The oxygen released (Eq. (4)) will induce  $\text{CO(g)}$  generation and, consequently, SiC oxidation.

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(b) SiO(g) can also react with oxygen and increase the SiO<sub>2</sub>(l) amount.



Furthermore, Iida et al. [4] suggested that the partial pressure of SiO(g) from SiC and Mg(g) from spinel (presented in the reacting environment) could affect the oxidation rate of the trough castable. The hypothesis discussed by these quoted authors is described as follows [4]: (1) Mg(g) generates liquid in the refractory pores by reacting with the matrix of the solid (liquid phase comprised by MgO–CaO–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub>). (2) SiO<sub>2</sub> has some solubility in the liquid so SiO(g) can also be dissolved in the liquid phase. (3) The consumption of SiO(g) lowers its partial pressure and to keep the equilibrium of the system more SiC is oxidized (Eq. (2)).

Other studies also stated that after the formation of a SiO<sub>2</sub> film on the SiC grains, the O<sub>2</sub> diffusion rate in this region is the determining step of further oxidation [3,7,8]. In the case of refractories containing spinel, MgO migrates into the SiO<sub>2</sub> and the diffusion rate of O<sub>2</sub> increases, resulting in the advance of SiC oxidation.

As quoted before, some hypotheses are presented in the scientific literature, but all studies are only based on experimental results and there is no general agreement among them. Thus, this work aims to carry out some thermodynamic calculations using the FactSage<sup>®</sup> software in order to further explore, search for and understand the MgAl<sub>2</sub>O<sub>4</sub> role in the SiC oxidation.

## 2. Thermodynamic calculations

These calculations are based on the minimization of free energy of the system, making it possible to find out the nature of the solid, liquid and gaseous phases, as well as their chemical composition and reaction rate at the thermodynamic equilibrium [9–11]. Simulations have been carried out using FactSage<sup>®</sup> (version 6.0), a fully integrated database and software jointly developed between Thermfact/CRCT (Montreal) and GTT-Technologies (Aachen). It consists of a series of modules that access, manipulate thermodynamic databases and perform various calculations.

The databases used in this study are: Fact53 (gas species, solid and liquid compound thermodynamic database) and FToxid (compounds and solutions for oxide databases). The equilibrium phases were predicted using the “Equilibrium” module, considering the following as possible phases: gas, slag or liquid and various solid solutions (including spinel, mullite, etc.).

The compositions used in this work were based on the refractories studied by Kageyama et al. [1] (see Table 1). Other castable formulations were also evaluated [3–5], but the obtained results followed the same trends observed in the investigation presented as follows.

Firstly, the oxidation behavior of SiC and C contained in the castable compositions were evaluated at 1500 °C (isothermal condition) and as a function of the CO(g) content. After that, the phase evolution of the AL and SP castables was explored in the

Table 1

Castable compositions evaluated in the thermodynamic simulations (wt%) [1].

Materials	AL	SP
MgAl <sub>2</sub> O <sub>4</sub>	–	65
Al <sub>2</sub> O <sub>3</sub>	81	16
SiC	15	15
C	2	2
CaO	2	2

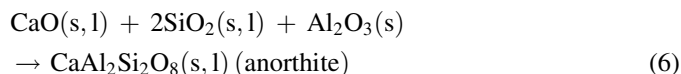
1100–1600 °C temperature range, in the presence of distinct CO(g) amounts. Additionally, the resulting amount of SiC, SiO<sub>2</sub> and C based on the calculations and the experimental testing were compared.

### 2.1. SiC oxidation behavior in the presence of CO(g)

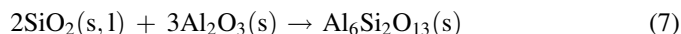
Some papers present experimental investigations of the role of MgAl<sub>2</sub>O<sub>4</sub> on the SiC oxidation under a reducing atmosphere at 1400 °C and 1500 °C [1,3,4,7]. Therefore, the chemical phase evolution of the AL and SP castables at 1500 °C and under a reducing atmosphere were evaluated using the thermodynamic calculations. It was considered that 0.1 moles of CO for each 100 moles of solid material was sufficient to provide a reducing atmosphere [12]. However, in order to check which condition fits the experimental tests, the effect of the CO(g) content in the calculations was investigated and the amount of gas phase added to the system ranged from  $\langle A \rangle = 1$  g to 10 g (which is equivalent to 0.04–0.4 moles of CO(g)).

Fig. 1a shows the phase evolution for the AL castable at 1500 °C as a function of CO(g) content. In this case, when a small amount of CO is in the reacting environment (about 1 g or 0.04 moles), Al<sub>2</sub>O<sub>3</sub>, CA<sub>6</sub> (CaAl<sub>12</sub>O<sub>19</sub>), SiC, C and liquid (comprised by CaO, SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>) are present in the thermodynamic equilibrium. According to Eqs. (2) and (3), the reactions between SiC and CO induce the silicon carbide consumption and carbon deposition as the oxidation progresses (see Fig. 1).

When a higher amount of CO(g) is added to the system, CaAl<sub>12</sub>O<sub>19</sub> is decomposed and a liquid phase is formed. This liquid might also be consumed according to the following equation:



Moreover, the mullite generation (Al<sub>6</sub>Si<sub>2</sub>O<sub>13</sub> – Eq. (7)) only occurs when the oxidation of SiC by CO(g) is increased.



On the other hand, Fig. 1b shows the results for the composition containing pre-formed MgAl<sub>2</sub>O<sub>4</sub>. When  $\langle A \rangle = 1$  g, phases CA<sub>2</sub> (CaAl<sub>4</sub>O<sub>7</sub>), MgAl<sub>2</sub>O<sub>4</sub>, SiC, C and liquid are present in the thermodynamic equilibrium. Depending on the CO(g) content in the environment, some transformations might be carried out, such as: SiC oxidation, carbon deposition, CA<sub>2</sub> dissolution into the liquid phase and an increase in the liquid

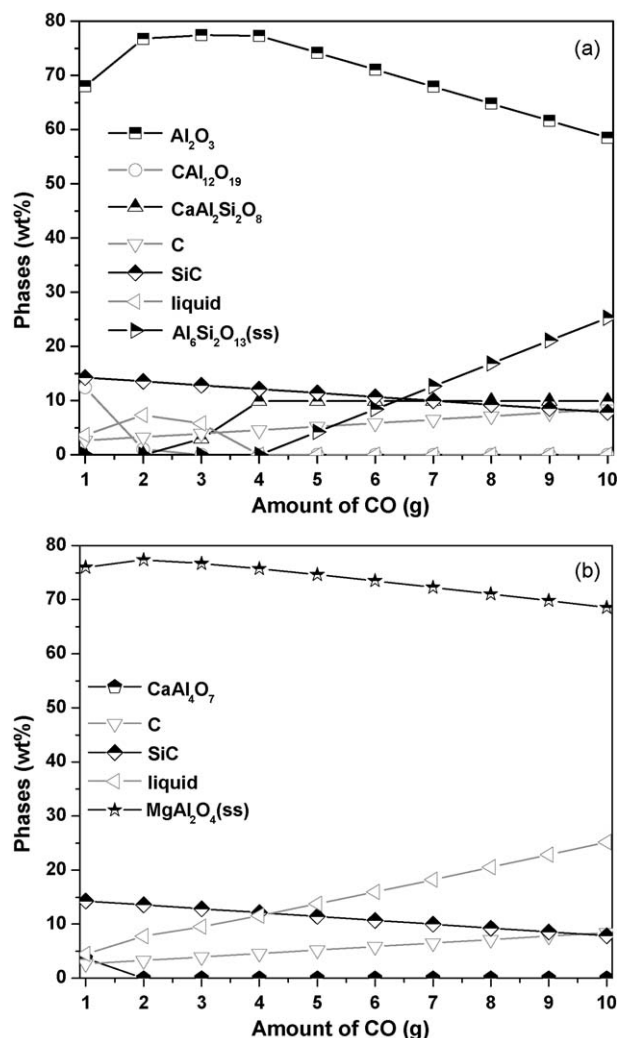


Fig. 1. Phase evolution of the castables (a) AL and (b) SP at 1500 °C as a function of the CO(g).

content. The partial dissolution of the MgO and  $\text{Al}_2\text{O}_3$  from spinel and of the  $\text{SiO}_2$  generated from SiC oxidation are the main causes for the liquid phase content increase. Additionally, the 16 wt% of alumina initially added to the SP composition is partially incorporated into the  $\text{MgAl}_2\text{O}_4$  solid solution, which explains why the spinel amount is higher than the original 65 wt%.

Comparing the results shown in Fig. 1, the same values of SiC and C were obtained for both tested materials. Therefore, it can be concluded that the addition of  $\text{MgAl}_2\text{O}_4$  to the SP castable does not seem to affect the silicon carbide oxidation. For the evaluated conditions, there was no evidence that reaction (4) and Mg(g) formation occurred due to the lower values of the gas phase activity in this system (gas activity < 1). Thus, according to the thermodynamic results, the mechanisms proposed by Kageyama et al. [1] are not applied in this case.

At this point, the results of the thermodynamic predictions did not confirm the influence of Mg(g) on the SiC oxidation at 1500 °C. Therefore, the next step of the investigation was to evaluate the chemical phase changes for the AL and SP castables in the 1100–1600 °C temperature range and in the

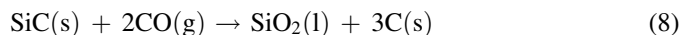
presence of distinct CO(g) contents (Figs. 2 and 3). The aim of this evaluation was to observe whether some of the transformations in the castable compositions might consume or generate SiC at high temperatures.

The addition of 2 g (0.08 moles), 4 g (0.16 moles), 7 g (0.28 moles) or 10 g (0.4 moles) of CO to the environment and its influence on the phase evolution of the castables was investigated. The thermodynamic predictions were further compared with the experimental results of some castable samples, which were previously thermally treated 15 times at 1500 °C with a dwelling time of 3 h at this maximum temperature [1]. During the experimental tests, AL and SP refractories were fired inside a sealed box, where the samples were embedded in coke, to assure that CO would be present and to avoid the castable's oxidation by  $\text{O}_2$ .

The amount of CO(g) available in the reducing atmosphere and the temperature act directly in the phase transformations of the castables, as can be seen in the following discussions and in Figs. 2 and 3.

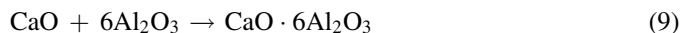
#### 2.1.1. Reducing atmosphere containing 2 g (0.08 moles) of CO(g)

When only 0.08 moles of CO are added, the predicted phases in the equilibrium for the composition containing a high  $\text{Al}_2\text{O}_3$  content (AL), at 1100 °C, are:  $\text{Al}_2\text{O}_3$ ,  $\text{CA}_6$  ( $\text{CaAl}_{12}\text{O}_{19}$ ), anorthite ( $\text{CaAl}_2\text{Si}_2\text{O}_8$ ), SiC and C (Fig. 2a). The amount of  $\text{SiO}_2$  was estimated using Eq. (8) and considering that all gases of the environment would be involved in this reaction.



About 2.1 wt% of  $\text{SiO}_2$  will be available to react and form anorthite at 1100 °C. From the original 15 wt% of SiC, 1.4 wt% reacted with CO, leaving 13.6 wt% (see Fig. 2a). Furthermore, the resulting carbon amount based on Eq. (8), as well as the 2 wt% initially present in the AL composition makes a total of 3.3 wt% of C. The increase in carbon content was also observed in the experimental results for samples treated at 1500 °C under a reducing atmosphere, i.e., changing from 2 wt% to 3 wt% in the AL castable [1].

On the other hand, SiC and C values (predicted by the thermodynamic calculations) were constant up to 1600 °C in the evaluated condition and Eq. (8) is the only reaction that consumes SiC and generates C, over the temperature range of 1100 °C and 1600 °C. Moreover, 4.9 wt% of anorthite (Eq. (6)) and 11.9 wt% of  $\text{CA}_6$  (Eq. (9)) are expected to be formed at 1100–1400 °C (Fig. 2a).



After all these reactions, the alumina content in the AL composition is reduced from 81 wt% to 68 wt%, following reactions (6) and (9).

However, at temperatures higher than 1400 °C, some phase changes such as anorthite and  $\text{CA}_6$  decomposition lead to the liquid phase generation. This liquid is comprised by CaO,  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  and a total amount of 8.7 wt% is formed at 1600 °C (Fig. 2a). SiC and C contents are kept constant and no gas formation is observed when only 0.08 moles of CO(g) are

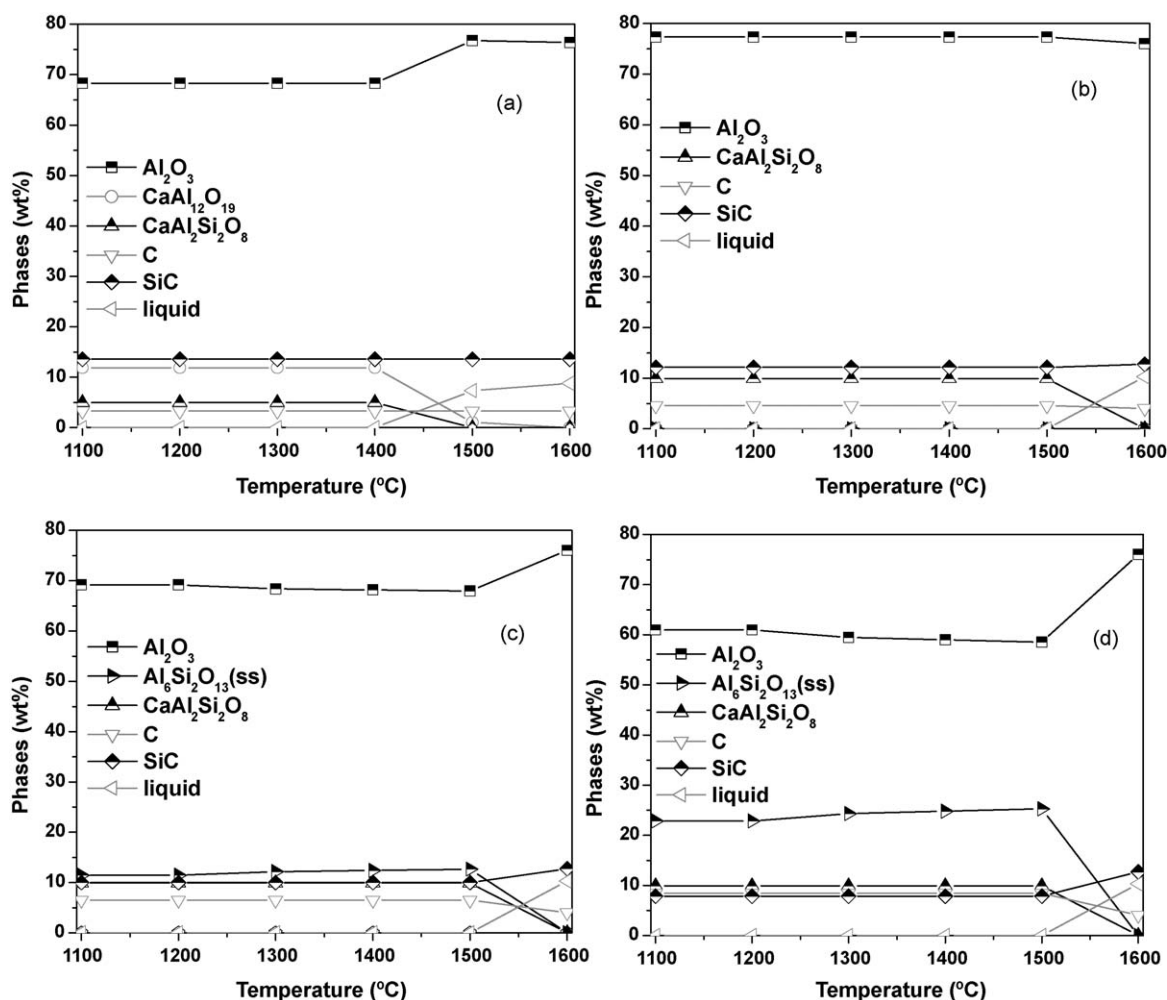


Fig. 2. AL castable phase evolution as a function of temperature under reducing atmosphere: (a) 2 g or 0.08 moles, (b) 4 g or 0.16 moles, (c) 7 g or 0.28 moles and (d) 10 g or 0.4 moles of  $\text{CO}(\text{g})$ .

added to the firing environment of the AL castable samples at the temperature range of 1100 °C to 1600 °C.

The presence of a small amount of melilite (which is a solid solution between guelenite ( $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ ) and akermanite ( $2\text{CaO} \cdot \text{MgO} \cdot \text{SiO}_2$ )) at 1300 °C, is the main difference between the AL (Fig. 2a) and SP (Fig. 3a) results. The same  $\text{SiO}_2$ , anorthite and  $\text{CA}_6$  contents quoted before in the analysis of the AL castable results are attained again for the SP composition between 1100 °C and 1200 °C (according to reactions (6), (8) and (9)). The liquid phase is detected at a lower temperature (1300 °C) and a total of 8.9 wt% of liquid is expected to be formed at 1600 °C with the following composition: 2 wt%  $\text{CaO}$ , 0.5 wt%  $\text{MgO}$ , 2.1 wt%  $\text{SiO}_2$  and 4.3 wt%  $\text{Al}_2\text{O}_3$ . Moreover, the  $\text{MgAl}_2\text{O}_4$  content increase (changing from the original 65 wt% to 76 wt% at 1600 °C) is related to the alumina incorporation into the spinel solid solution.

The same amounts of SiC (13.6 wt%) and C (3.3 wt%) were observed for the AL and SP thermodynamic calculations in the 1100–1600 °C temperature range. These results confirm that the SiC content was only affected by its reaction with  $\text{CO}(\text{g})$  (Eq. (8)), which is the gas phase initially added to the system.

Thus, the alumina–magnesia spinel did not play a role in the SiC oxidation when 0.08 moles of  $\text{CO}(\text{g})$  are present in the environment. This result is not compatible with the chemical composition of the samples obtained in the experimental tests, which was 3 wt% and 4.3 wt% of C and 9.5 wt% and 8 wt% of SiC for AL and SP castables, respectively [1].

Therefore, aiming to evaluate whether the experimental results and thermodynamic predictions differences are due to the reducing atmosphere, further calculations involving higher amounts of  $\text{CO}(\text{g})$  were performed as follows.

#### 2.1.2. Reducing atmosphere containing 4 g (0.16 moles) of $\text{CO}(\text{g})$

The addition of 0.16 moles of  $\text{CO}(\text{g})$  increases the SiC oxidation of the AL and SP castables and 4.3 wt% of  $\text{SiO}_2$  and 2.6 wt% of C can be generated at 1100 °C. After this reaction, 12.1 wt% of SiC remains in the castable composition and all  $\text{CaO}$  reacts with alumina and silica forming anorthite (Eq. (6)) at this temperature, as shown in Figs. 2b and 3b.

Anorthite decomposition and liquid formation will only occur above 1500 °C and the  $\text{SiO}_2$  and C interaction might also



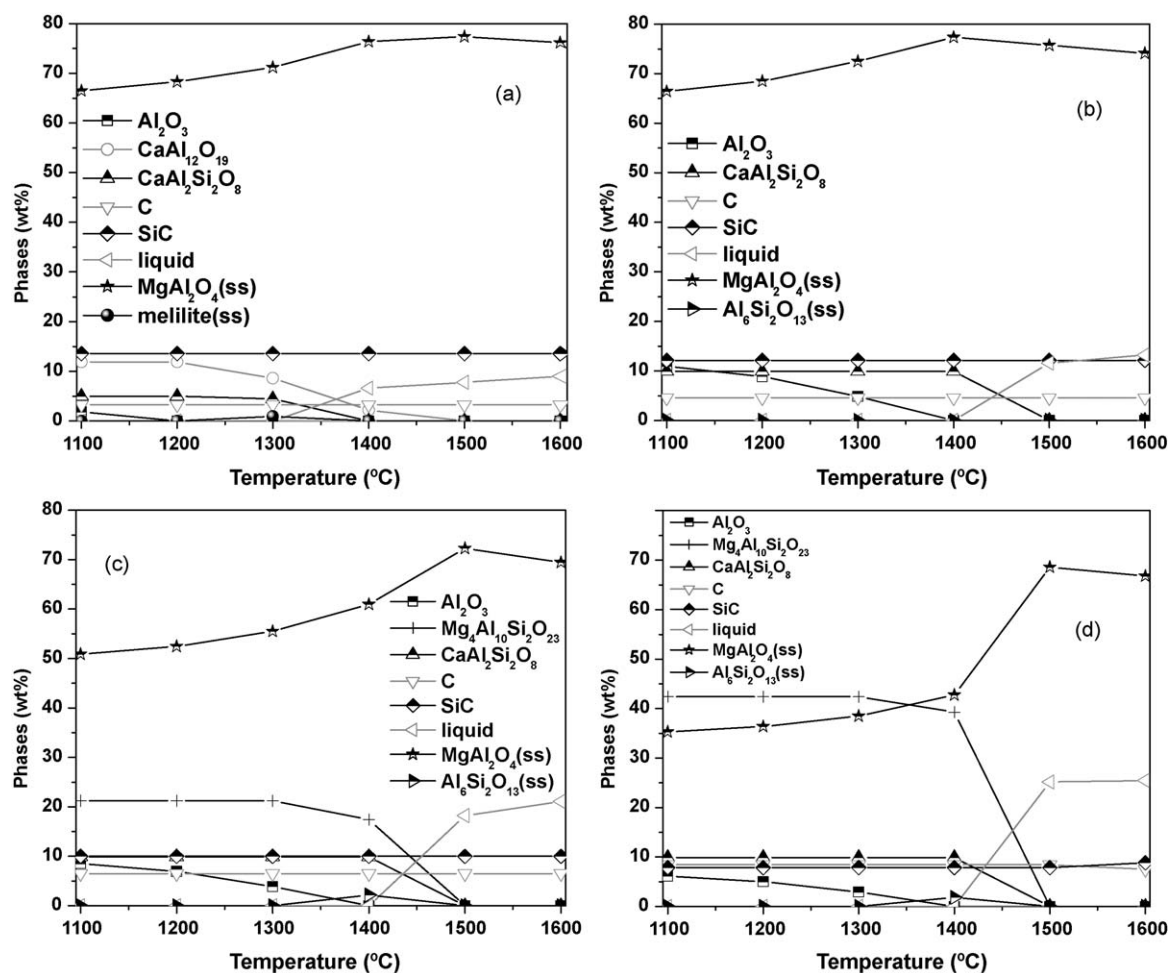


Fig. 3. SP castable phase evolution as a function of the temperature under reducing atmosphere: (a) 2 g or 0.08 moles, (b) 4 g or 0.16 moles, (c) 7 g or 0.28 moles and (d) 10 g or 0.4 moles of CO(g).

increase the SiC amount at the maximum temperature evaluated –1600 °C, according to Eq. (10).



Therefore, the SiC and C final values in the AL castable composition, are 12.7 wt% and 4 wt%, respectively, at 1600 °C (see Fig. 2b).

The presence of  $\text{MgAl}_2\text{O}_4$  can cause some changes in the SP castable results. As quoted before for Eqs. (6) and (8), approximately 9.9 wt% of anorthite and 4.3 wt% of  $\text{SiO}_2$  are obtained at 1100 °C. The spinel chemical composition is modified due to the incorporation of  $\text{Al}_2\text{O}_3$  into this solid solution, as the temperature is increased (Fig. 3b). Anorthite decomposition is carried out above 1400 °C and the spinel phase partially induces the increase of the liquid up to 1600 °C. Although the AL castable presented a small increase of SiC at high temperatures, the amount of SiC and C did not change between 1500 °C and 1600 °C, for the SP composition. Thus, a small difference in SiC and C contents in both studied materials was detected at the maximum temperature evaluated. AL and SP castables showed similar values of SiC and C at 1500 °C based on the thermodynamic analyses, but these results are not compatible with the experimental tests.

### 2.1.3. Reducing atmosphere containing 7 g (0.28 moles) of CO(g)

When exposed to a reducing atmosphere with 0.28 moles of CO(g), the AL castable faced the same transformations described before. The main difference was the higher amount of mullite formed at 1100 °C due to the 7.5 wt% of  $\text{SiO}_2$  generated from the SiC oxidation by CO(g). Thus, 4.3 wt% of  $\text{SiO}_2$  is expected to be consumed to produce anorthite (Eq. (6)) and the remaining 3.2 wt% can also react with  $\text{Al}_2\text{O}_3$  forming 11.4 wt% of mullite (Eq. (7)).

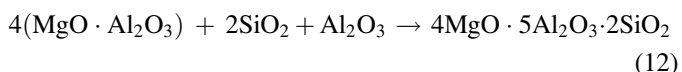
After these transformations, 69 wt% of alumina still remains in the AL castable at 1100 °C (Fig. 2c). The mullite phase is not a stoichiometric compound and alumina might be incorporated into solid solution at high temperatures [13]. The results obtained in the FactSage® considers that 12.6 wt% of mullite is available in the AL castable composition at 1500 °C. This increase in the mullite amount (changing from 11.4 wt% to 12.6 wt%) is associated to the extra alumina content solubilized into this solid solution at this temperature. There is no other transformation in the AL castable composition in the 1100–1500 °C temperature range, as can be seen in Fig. 2c. Nevertheless, anorthite and mullite decompositions induce the increase of  $\text{Al}_2\text{O}_3$ , SiC and liquid phases above 1500 °C. In fact, the reaction between

mullite and carbon from the refractory material leads to the formation of  $\text{Al}_2\text{O}_3$ , SiC and CO (Eq. (11)) [14].

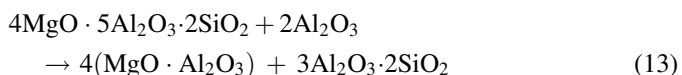


As a result, 2.4 wt% of SiC is generated and a total of 12.7 wt% of this carbide is found in the castable composition at 1600 °C. The amount of CO(g) generated in Eq. (11) is 3.3 g, which is equivalent to 0.14 moles of gas. According to the thermodynamic calculations, this gas phase mainly consists of CO ( $p_{\text{CO}} = 0.991$  atm), SiO ( $p_{\text{SiO}} = 8.07 \times 10^{-3}$  atm) and  $\text{CO}_2$  ( $p_{\text{CO}_2} = 4.97 \times 10^{-5}$  atm).

Castable SP, which contains spinel in its composition, presents a high content of saphirine ( $4\text{MgO} \cdot 5\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ) derived from the reaction between spinel, alumina and silica at 1100 °C (Fig. 3c). After the anorthite formation, the remaining  $\text{SiO}_2$  of the castable is consumed on the saphirine formation (Eq. (12)).



The incorporation of alumina into the spinel solid solution (about 5.8 wt% in the 1100–1300 °C temperature range) displaces the equilibrium to the  $\text{MgAl}_2\text{O}_4(\text{ss})$ –mullite–saphirine compatibility triangle and induces mullite formation at 1400 °C (Eq. (13) and Fig. 3c).



The spinel and liquid amount increases due to the anorthite, mullite and saphirine decomposition between 1400 °C and 1500 °C. Furthermore, no changes to the SiC and C contents were detected between 1100 °C and 1600 °C (Fig. 3c) in the SP castable composition and the SiC content derived from its initial oxidation by CO(g).

#### 2.1.4. Reducing atmosphere containing 10 g or 0.40 moles of CO(g)

In this case, the high amount of mullite and saphirine formed after the SiC oxidation was the main change in the

studied castables at 1100 °C. SiC content did not change in the range from 1100 °C to 1500 °C and above this temperature, SiC generation and C consumption mechanisms for each castable composition are distinct. As quoted before, the increase of SiC content in the AL castable composition is carried out by the reaction between mullite and carbon (Eq. (11)). On the other hand, the SP castable does not present mullite in its composition above 1500 °C and the SiC generation is only related to the reaction involving liquid  $\text{SiO}_2$  and carbon from the refractory (Eq. (10)). At 1600 °C, about 4.1 wt% of  $\text{SiO}_2$  is required to form SiC in the spinel containing castable.

According to Eq. (10) and the thermodynamic predictions, the SiC content increases from 7.8 wt% to 8.8 wt% (Fig. 3d) and 3.8 wt% of CO is equivalent to 0.16 moles of gas ( $p_{\text{CO}} = 0.992$  atm,  $p_{\text{SiO}} = 6.73 \times 10^{-3}$  atm,  $p_{\text{Mg}} = 7.26 \times 10^{-4}$  atm and  $p_{\text{CO}_2} = 4.98 \times 10^{-5}$  atm). At 1600 °C, the castable SP presents a lower gas phase and SiC formation than the AL one, but the presence of Mg(g) indicates that spinel decomposition (Eq. (4)) and/or the reaction between  $\text{MgO}(\text{l})$  and C(s) (Eq. (14)) might occur.



It is believed that role of Mg(g) on the SiC oxidation at high temperatures is negligible, due to the low amount of this phase in the equilibrium condition. The SiC content in the AL and SP castables (as a function of temperature and up to 1500 °C) are very similar (Figs. 2 and 3), but the reaction between mullite and carbon is the main cause for the increase in the SiC content (from 7.8 wt% to 12.7 wt%) in the composition without spinel. Moreover, the  $\text{SiO}_2$  content as a liquid in the AL and SP castable at 1600 °C, are: 3.4 wt% and 6.7 wt%, respectively. Therefore, the lower SiC content in the SP castable results from the refractory's transformations and reactions involving  $\text{SiO}_2$  and C. There was no evidence that the spinel sped up SiC oxidation and based on the calculations carried out using the FactSage<sup>®</sup> software, the spinel addition to  $\text{Al}_2\text{O}_3$ –SiC–C castables did not affect SiC oxidation.

Table 2  
Summary and comparison between experimental and thermodynamic results.

Castable's component		SiC (wt%)		SiO <sub>2</sub> (wt%)		C (wt%)	
		AL	SP	AL	SP	AL	SP
Compositions							
Experimental values [1]	1500 °C	9.5	8	4.5	7.5	3	4.3
Temperature (1500 °C)							
Thermodynamic results	0.08 moles CO(g)	13.6	13.6	2.1	2.1	3.3	3.3
	0.16 moles CO(g)	12.1	12.1	0	4.3	4.6	4.6
	0.28 moles CO(g)	10.0	10.0	0	7.5	6.5	6.5
	0.40 moles CO(g)	7.8	7.8	0	10.7	8.4	8.4
Temperature (1600 °C)							
Thermodynamic results	0.08 moles CO(g)	13.6	13.6	2.1	2.1	3.3	3.3
	0.16 moles CO(g)	12.7	12.1	3.3	4.3	4.0	4.6
	0.28 moles CO(g)	12.7	10.0	3.3	7.5	4.0	6.5
	0.40 moles CO(g)	12.7	8.8	3.3	9.2	4.0	7.5

### 3. Comparison between the experimental results and thermodynamic calculations

Although the experimental results showed that the AL and SP samples have different SiC and C contents after thermal treatment at 1500 °C, in the thermodynamic equilibrium these values are similar, even when distinct CO(g) contents are presented in the environment. Table 2 shows a summary of the experimental and thermodynamic results. According to the thermodynamic predictions, SiC and C values in the AL and SP castables will only be distinct above 1500 °C, due to the reactions involving mullite (Eq. (11)) and SiO<sub>2</sub> (Eq. (10)) with the carbon from the refractory.

Nevertheless, it is believed that the equilibrium condition was not attained in the tests performed by Kageyama et al. [1], due to the remaining 4.5 wt% of SiO<sub>2</sub> in the AL castable sample. This fact indicates that the reaction between Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> to form mullite was not completed and silica was still present in the refractory.

Spinel addition did not accelerate SiC oxidation under the thermodynamic equilibrium condition at 1500 °C. Most likely, the higher liquid phase amount generated in the SP castable composition, at high temperatures, may affect its working performance over time.

The amount of CO(g) added to the reacting system induces SiC oxidation at temperatures higher than 1100 °C. Moreover, in the same conditions and in the thermodynamic equilibrium, AL and SP castables must present the same values as SiC and C at 1500 °C.

### 4. Concluding remarks

Although, the SiC content in the Al<sub>2</sub>O<sub>3</sub>–MgAl<sub>2</sub>O<sub>4</sub>–SiC–C (SP) castable samples fired at 1500 °C and in a reducing atmosphere was lower than the Al<sub>2</sub>O<sub>3</sub>–SiC–C (AL) ones, the same trend was not observed in the thermodynamic predictions conducted using the FactSage<sup>®</sup> software. According to the calculations, the amount of SiC, SiO<sub>2</sub> and C might change due to some transformations at temperatures higher than 1500 °C.

Mullite formation and its presence in the castable composition at high temperatures induces the SiC generation due to the mullite reaction with the carbon in the AL castable samples. On the other hand, the addition of spinel to the SP castable allows saphirine's formation and in the temperature range of 1300–1500 °C, only a small amount of mullite might be formed in the refractory castable. At temperatures higher than 1500 °C, the reaction involving SiO<sub>2</sub> from the liquid phase and C from the solid, increases the SiC amount. In addition,

spinel addition might also help forming a high amount of liquid phase, which could affect the refractory performance. Thus, according to the thermodynamic predictions, the lower SiC amount is not associated to the spinel addition, but to the reaction transformations of the AL and SP castables.

### Acknowledgments

The authors are grateful to the Brazilian research funding institution FAPESP for its financial support of this work.

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