Original Article

Metallurgical silicon carbide for steelmaking: a thermodynamic simulation

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Abstract

Silicon carbide is a unique material produced by the Acheson process, obtaining two main grades: crystal and metallurgical. SIKA® MET, the metallurgical silicon carbide, has gained prominence for steel sectors due to its unique properties, being used as agent for deoxidation and exothermic purposes in steelmaking routes. It has been presented as an alternative to the FeSi75 usage. FeSi75HP and SIKA® MET were agents added to the bath at 298K and the hot metal was at 1873K. The FactSage® simulation studied the deoxidizing effect varying the agent quantity until 10kg added to the bath. The Thermo-Calc® simulation studied the exothermic effect in a fixed proportion of 3kg of agent per ton of steel, using TCOX10 database and EERZ for a kinetic approximation in a ladle. The deoxidation effect between both agents were similar after 3kg of addition. The exothermic effect obtained a small temperature difference of approximately 10 °C between them, associated to the effect of interaction coefficients of Si or heat generation from carbon content. Due to the similarity of deoxidizing and exothermic properties between both agents and high prices usually obtained for FeSi75, silicon carbide could be considered a cost saving agent to be used for steelmaking routes.

Keywords: Silicon Carbide; Agent; Deoxidation; Exothermic.

1 Introduction

Silicon carbide (SiC) is a unique material mostly produced through carbothermic reduction of silica sand and petroleum coke in Acheson furnaces, obtained in two main forms: crystal SiC and metallurgical SiC [1].

The diverse properties of silicon carbide, such as hardness, high temperature and oxidation resistance, high mechanical strength, chemical inertness, and semiconductivity have allowed its applicability in different industrial markets. Abrasive, refractory, electronics, technical ceramics, and metallurgy fields are among them [1].

One of the main forms of SiC, the metallurgical grade, has gained prominence in the foundry and steel sectors due to its ability to optimize processes and improve the quality of the final products. It has been constantly used in induction furnaces, cupolas, LD converters, ladle for distinct purposes. According to the aim, Fiven's metallurgical silicon carbide product (SIKA® MET) can be supplied in various forms and purity levels [1].

1.1 Deoxidizing effect

One of the purposes of SIKA MET for steelmaking routes is related to its silicon and carbon deoxidizing properties, as described by the equation 1 and equation 3 below, when added for chemical adjustments in secondary refining. Their strong oxygen affinity is related to their standard free energies, and more deeply related to their activity-composition relation in a metallic solution, being represented below by equation 2 and equation 4 below [2,3].

$$[\mathrm{Si}]+2[\mathrm{O}] \leftrightarrow (\mathbf{SiO_2}) \tag{1}$$

$$\Delta G° = -\,RT\,\ln K = -\,RT\ln\left[\frac{\left(a_{SiO_2}\right)}{\left[h_{Si}\right]\times[h_O]^2}\right] \tag{2}$$

$$[\mathrm{C}]+[\mathrm{O}] \leftrightarrow (\mathrm{CO})_g \tag{3}$$

$$\Delta G° = -\,RT\,\ln K = -\,RT\ln\left[\frac{p_{CO}}{\left[h_C\right]\times\left[h_O\right]}\right] \tag{4}$$

Ferrosilicon alloys, e.g., FeSi75, and other carburizing agents can be substitutes for silicon carbide for this same purpose, but they usually contain a higher content of impurities such as aluminum, hydrogen, and sulfur in their chemical compositions, which may promote steel contamination and the formation of metallic inclusions [2,4]. According to Leont'ev *et al.* [4], SiC has a better affinity for oxygen compared to silicon and carbon individually, a complex deoxidizing agent activity close to aluminum and a more stable assimilation of silicon than ferrosilicon.

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1.2 Exothermic effect

A second purpose of SIKA® MET for steelmaking routes is related to the exothermic effect through silicon and carbon oxidation reactions. As silicon is the main element to generate heat for the metallic bath during first period of converter blowing, when there is lack of heat reserve some silicon-based agents are usually added to the charge [5-7].

Low silicon content in hot metal, low temperature of hot metal or usage of a higher scrap amount are common associated reasons. Consequently, this addition allows the heat to achieve the target condition for the blowing end period [6-8].

Ferrosilicon alloys are the usual choice for this objective, especially FeSi75 with expressive content of silicon. Due to FeSi75 high prices in recent years, new silicon-based agents, with contents normally lower than 75%wt of Si, has been developed as an alternative to replace it in primary refining applications, such as FeSi40 alloy and briquettes containing silicon [9].

SIKA® MET has showed to be a great alternative for FeSi75 for distinct reasons such as a considerable content of silicon, after Si oxidation stage its carbon content is oxidized exothermically, heat cost-effective, lower impurity levels, and no need to add a carburizing agent along with the agent [2,5].

According to Ferreira *et al.*, one adopted strategy to evaluate the thermal effect of additions to a metallic bath is calculating three heat parcels: dissociation of the existing compounds at 298K, heating of the pure elements from 298K to bath temperature, and the dissolution of the elements in the bath to bath temperature [10]. As the heat of reaction depends only on the initial and final states, softwares make a sum-up calculation of all contributions sketched as it follows in Figure 1 and Equation 5 [8,11], The oxidation reactions and their entalphies were also described by Equations 6-9 below [11,12].

$$\Delta H_1 + \Delta H_R + \Delta H_2 + \text{Heat losses} = 0 \qquad (5)$$

$$\left(H_T - H_{298}\right)_{agent} = \sum_{i=1}^{n} n_i \times (H_T - H_{298}) \qquad (6)$$

$$\text{At 1873K: } \text{Fe75\%Si} + (O_2)_g \leftrightarrow [Fe] + (SiO_2) \quad \Delta H = -20{,}844 \frac{kJ}{\text{kg of furnace charge}} \qquad (7)$$

$$\text{At 1873K: } SiC + \frac{3}{2}(O_2)_g \leftrightarrow (SiO_2) + (CO)_g \quad \Delta H = -19{,}420 \frac{\mathbf{kJ}}{\textbf{kg of furnace charge}} \qquad (8)$$

$$\text{At 1873K: } (CO)_g + \frac{1}{2}(O_2)_g \leftrightarrow (CO_2)_g \quad \Delta H = -22{,}420 \frac{kJ}{Nm^3 \text{ of } O_2} \qquad (9)$$

This work aimed to study through software thermodynamic simulation the different effects between using FeSi75HP and SIKA® MET as agents for steelmaking. The softwares calculated the final temperature obtained for the metallic bath, as well as the final composition for the steel and slag, and steel oxygen content with different agent quantities.

2 Material and methods

The thermodynamic simulation was developed in two distinct softwares: FactSage® and Thermo-Calc®. Both used as an input information the chemical compositions of metallurgical silicon carbide SIKA® MET 85% 0x10 mm and high purity ferrosilicon alloy FeSi75HP. The initial temperature considered for the agents was 298K and it was considered a temperature of 1873K for the metallic bath.

2.1 Chemical compositions

Silicon carbide sample was supplied by Fiven Brazil and then prepared by the following steps: grinding, screening, quartering and then pulverization. The contents were analyzed by XRF from Malvern Panalytical Model Magic. The free carbon content was analyzed by gravimetry after calcination. The free silicon content was analyzed by eudiometry in sodium hydroxide solution. The silicon

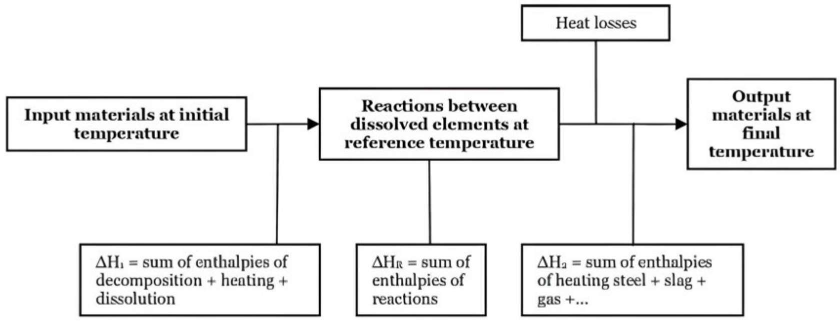

Figure 1. Enthalpy contributions. Reproduced from Kumar et al. [11].

oxide was gravimetrically measured after reacted with hydrofluoric acid. All the mentioned procedures followed the FEPA Standard resolutions [13]. The complete SIKA® MET composition was described in Table 1 below.

The FeSi75HP sample and its composition was supplied by a partner company. The composition was described in Table 2 below.

Also, the initial composition for the residual steel was chosen and it was described in Table 3 below.

Based on the agent compositions, it was noticeable that the silicon content was found to be sixteen percent lower in silicon carbide than in FeSi75HP, as was already expected. Otherwise, the total carbon content in the silicon carbide considering the free carbon contribution reached thirty percent, which means an important source of heat and deoxidation for the bath. All individual elements were obtained in oxide form for SIKA® MET composition, that would be easily flotated and incorporated to the slag. Standard FeSi75 compositions usually have a higher content of Al than obtained for this specific sample.

2.2 FactSage® simulation conditions

The FactSage® simulation was developed using FactPS, FToxid and FSstel as database and as sub-database FToxid-SLAGA e FSstel-Liquid. The agent mass at 298K, parameter <A>, was varied individually in increments of 0.5 from 0 to 10 kg/ton at a constant temperature of 1873K, according to the selected conditions in Figure 2.

2.3 Thermo-Calc® simulation conditions

In order to obtain the agents reacting at the initial time with the bath while varying the temperature during a certain period of ten minutes, the thermodynamic equilibria were calculated using the CALPHAD database TCOX10, and the reaction kinetics were simulated using the Effective Equilibrium Reaction Zone (EERZ) at Thermo-Calc® software.

It was used a fixed proportion of 3kg of agent at 298K per one ton of steel at 1873K. The parameters such as mass transfer in the reaction zone, densities, oxide transfer velocity to the slag, heat transfer, and cooling constant of steel were selected as shown in the Figure 3 below, based on ladle process described by Graham and Irons [14].

The kinetic model assumed a local equilibrium was reached at the interface between the liquid slag, but the kinetics of the reaction were limited by the mass and heat transfer into and out of this reaction interface along compositional and thermal gradients. The conditions stablished above made possible to consider that all agents added were melted or dissolved in the steel zone, with the aid of Ar purged from a porous plug on the ladle bottom to promote inclusion flotation and temperature homogenization, except for cases with non-metallic phase formation [14-16].

3 Results and discussion

3.1 FactSage® simulation results

The oxygen content dissolved on steel composition tends to decrease with the agent addition due to oxides formation, following the thermodynamic principles, as observed in Figure 4 below.

The deoxidizing behavior for silicon carbide and FeSi75HP was showed to be very similar to each other with the gradual increase of agent quantity, according to Figure 3. Li et al. [17] have calculated the theorical deoxidation ability for using silicon and silicon carbide and obtained 0.875 and 0.833, respectively.

For 0.5 kg of agent, SiC SIKA® MET presented slightly better performance compared to FeSi75HP, which switched between them when it reached 1.5 kg of addition. After 3 kg of agent, both have showed to obtain the same deoxidizing effect for the bath. However, it has been tested previously that if used a FeSi75 with higher aluminum

Table 1. Chemical composition (at %wt.) for Silicon carbide SIKA® MET 85% 0x10 mm

Agent	SiC	Si*	C*	SiO2	C_{free**}	Si_{free**}	Al	Ti	Mg	Ca	Fe
SIKA® MET 85%	86.436	60.505	25.931	6.212	4.908	0.198	0.731	0.032	0.147	0.229	0.173

*Si and C contents were calculated values based on SiC content, considering SiC stoichiometry composed by 70% of silicon and 30% of carbon; **C_{free} and Si_{free} are residual elements that were measured by gravimetry and eudiometry, respectively.

Table 2. Chemical composition (at %wt.) for FeSi75HP

Agent	Si	Fe	Al	Ca	P	Mn	Ti	Cr	Cu	Ni
FeSi75 HP	76.629	22.916	0.164	0.029	0.008	0.207	0.021	0.011	0.011	0.007

Table 3. Initial chemical composition (at %wt.) of the residual steel

Fe	C	Si	Mn	S	P	O
99.8275	0.03	0.001	0.05	0.0045	0.011	0.076

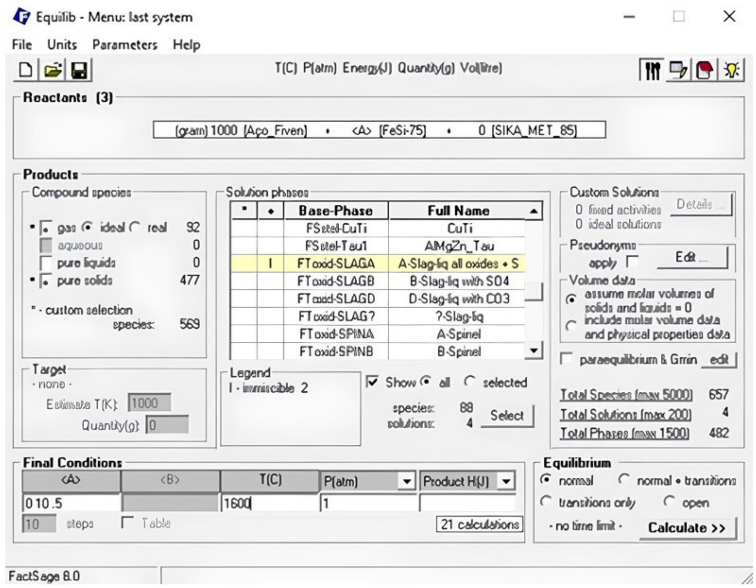

Figure 2. FactSage® selected conditions.

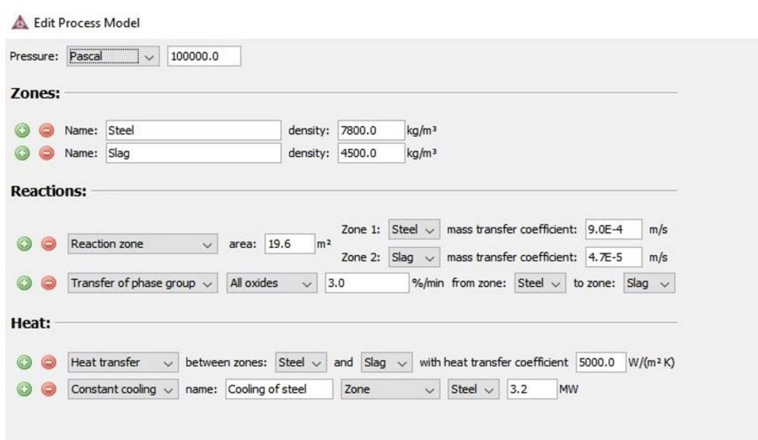

Figure 3. Kinetics Parameters selected based on *Graham and Irons* conditions [14].

contents, i.e., standard compositions, can slow down the rate of total oxygen removal in the bath [2].

The composition of the deoxidized steel using 2kg of agent can be seen in Table 4 below.

As noticed previously, between 1.5 kg and 3kg of agent FeSi75HP addition reached lower oxygen levels than SiC SIKA® MET. The highest silicon percentage was found for FeSi75HP following the mass balance of a high content of silicon for this agent. However, only approximately sixty-five percent of the total silicon introduced by FeSi75HP sample was incorporated to the steel composition, compared to fifty-nine percent for SiC SIKA® MET sample, the rest of silicon was used for deoxidation floating to the slag. This could be related to the interaction coefficients of the silicon's activity in a metal solution containing other elements, such as carbon [3].

The carburizing effect in steel composition was pronounceable, SiC SIKA® MET had three times higher carbon content than for FeSi75HP, keeping low impurities levels for phosphorus and sulfur. This result confirmed that SiC SIKA® MET is an important asset to replace a carburizer added along with the agent, if necessary, since SiC SIKA® MET did not slow down the deoxidation kinetics and did not contaminate the bath with impurities, differently from the result obtained when for the usage of FeSi75 along with graphite in a previous work [2].

Additionally, at the deoxidation equilibrium point for using agent, the composition of the deoxidized steel was obtained for 3 kg of agent and described in Table 5 below.

It was recognizable that the difference between the dissolved oxygen between SiC SIKA® MET and FeSi75HP decreased increasingly. Nonetheless, the sulfur and phosphorus removals showed to be ineffective as expected, only the silicon and carbon contents continued to increase even more, the latter two being limited depending on the target final steel composition. To this end, if necessary, a new strategy should be implemented, for example an injection of CaC_2 to achieve ultra-low-sulfur steel compositions [3].

A complex deoxidation for a distinct purpose using CaC_2 and SiC has already been developed to reduce nonmetal inclusions such as aluminosilicate, calcium sulfides and coarse alumina inclusion [4].

The silicon incorporation to steel composition increased continuously more, compared to 2kg addition, seventy-five percent of its total for FeSi75HP sample and seventy-one percent of its total for SiC SIKA® MET, increasing the possible effect of the interaction coefficients on silicon available for deoxidation, which was reduced even more for FeSi75HP [3].

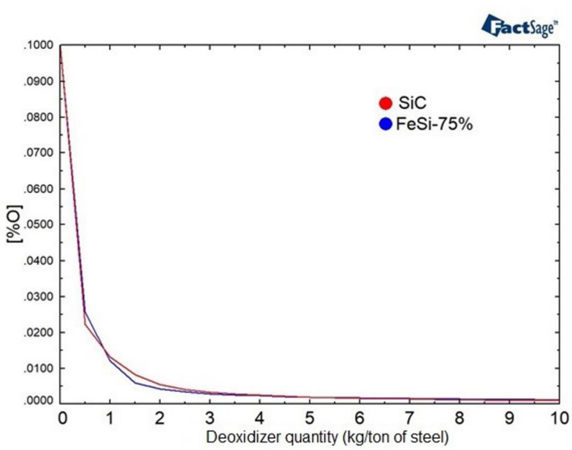

Figure 4. Deoxidation of steel according to each deoxidizer quantity.

The slag compositions with 2 and 3 kg of agent were informed in Table 6 below.

For all represented cases above, it would be necessary to add lime to control slag basicity and refractory degradation due their extreme acid behavior saturated with silica, however for FeSi75HP would be needed a slightly greater usage of lime. However, this additional increase of CaO can decrease the temperature by reducing the thermal effect of the insert of FeSi75HP.

Therefore, if it is necessary to add different amounts of lime, the same addition of FeSi and SiC should not be considered, but rather the necessary addition of each one to have the same thermal effect. Regarding SiC, one must consider the impact that may have in the incorporation of carbon into the steel. [12].

For both agents, the higher amount of 3kg decreased the FeO concentration in the slag, which could be explained by the change in its activity coefficient due to the reduction in the slag basicity. In addition, the FeO content could be reduced by two different reactions, a first one with dissolved silicon and second one with dissolved carbon, both forming liquid iron [8].

According to the mass balance of both agents, the alumina content was already a formed oxide in SiC SIKA® MET composition and increased with a higher addition. In the case of FeSi75HP, the aluminum element content in its composition could be partially incorporated into the slag as alumina and part of this remained as inclusions in the steel with increasing addition [4].

Table 4. Composition of deoxidized steel (at %wt.) with 2kg of agent

Agent	O	C	P	S	Mn	Si
No add	0.0760	0.0300	0.0110	0.0045	0.0500	0.0010
SiC	0.0168	0.0900	0.0110	0.0045	0.0481	0.0715
FeSi75HP	0.0124	0.0300	0.0110	0.0045	0.0501	0.0988

Table 5. Composition of deoxidized steel (at %wt.) with 3kg of agent

Agent	O	C	P	S	Mn	Si
No add	0.0760	0.0300	0.0110	0.0045	0.0500	0.0010
SiC	0.0121	0.1200	0.0110	0.0045	0.0481	0.1279
FeSi75HP	0.0091	0.0300	0.0110	0.0045	0.0503	0.1724

Table 6. Composition of the slag (at %wt.) with 2kg and 3 kg of agent addition

Agent	Al_2O_3	SiO_2	CaO	FeO	Fe_2O_3	MnO	TiO_2
SiC (2kg)	9.15	67.83	2.14	11.40	0.0034	1.63	7.8565
FeSi75HP (2kg)	10.64	71.32	1.56	9.15	0.0019	6.75	0.5796
SiC (3kg)	10.21	71.27	2.40	8.31	0.0017	1.83	5.9772
FeSi75HP (3kg)	10.90	75.15	1.68	6.75	0.0010	5.01	0.5056

3.2 Thermo-Calc® simulation results

The exothermic behavior for both agent additions can be observed in the Figure 5 below.

The exothermic reactions were developed at two minutes of simulation, which it was possible to notice following the peak temperature for both agents. The highest temperature of approximately 1617 °C was obtained for FeSi75HP due to its higher Si content, as it is the most exothermic reaction, compared to SiC SIKA® MET with lower Si which obtained approximately 1607 °C [8].

Nonetheless, even with a sixteen percent less silicon content, SiC SIKA® MET presented a small temperature difference of approximately ten degrees to FeSi75HP, which could be justified by the aid of heat generated from carbon oxidation, according to Turkdogan [12].

In cases where carbon content was totally incorporated to the steel composition, as obtained in Table 5, the small temperature difference could be justified for the effect of the interaction coefficients on silicon's activity reducing its Si available for deoxidation for FeSi75HP usage, representing a small difference of Si content used for deoxidation of approximately 1.2%wt compared to SiC SIKA® MET addition [3].

After reached peak temperature, the cooling rate had association to the heat transfer between slag-metal and the environment [13].

FeSi75 has showed to be expensive agent, inversely for SiC which tended to be cheaper than ferrosilicon alloys throughout the years. Thus, considering the obtained temperature difference, silicon carbide could be a more heat cost-effective option for exothermic applications [4,9,17]. According to Asian Metals [18], between 2008 and 2018, fluctuations in price differences between FeSi and SiC were observed, resulting in price increases of 55% to 5% for FeSi, making it possible to consider an average of FeSi 30% more expensive than SiC for the same agent quantity. However, it is also necessary to consider the updated price quotations.

Furthermore, according to Li et al. [17], the monoxide carbon gas generated by using SiC in converters could promote better purification of molten steel due to the easier combination of silica to other oxides to be flotated.

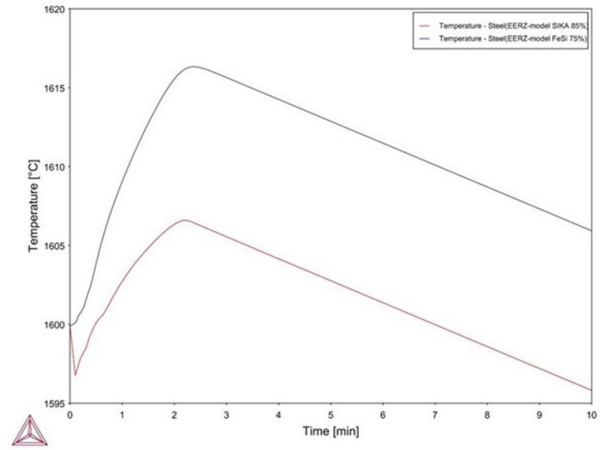

Figure 5. Thermal behavior after agent addition period.

4 Conclusion

It was presented through thermodynamic simulations that SiC SIKA® MET is a great alternative for FeSi75 alloy as an agent for steelmaking routes, either for deoxidizing or exothermic purposes, due to its similar deoxidation property to FeSi75HP after 3kg of agent addition and small temperature difference obtained for the bath between them, being a heat cost-effective option for an agent. But also, silicon carbide presented to be a purer source of silicon and carbon for the metallic bath, avoiding inserting elements that would promote the formation of nonmetallic inclusions. The SiC SIKA® MET for deoxidation in ladle and for converters to control the thermal balance and oxygen content has been industrially used and continuously studied by different authors.

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