INFLUENCE OF CAO AND MGO OXIDES ON THE FERROSILICON PROCESS IN THE SUBMERGED ARC FURNACES

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Abstract

Based on the equilibrium model with two isothermal reactors, the influence of CaO and MgO oxides on the ferrosilicon process in the submerged arc furnace was determined. The influence of addition of CaO and MgO oxides in the feed mixture on the SiC carbide phase formation, the contents of Ca and Mg elements in the chemical composition of the FeSi alloy as well as the efficiency of the carbothermal reduction process have been determined.

Keywords: Ferrosilicon process, equilibrium model, Gibbs Minimization Method, submerged arc furnace

1. INTRODUCTION

Ferrosilicon smelting in submerged arc furnaces is one of the most energy-consuming electrothermal processes [1,2]. Electrodes, immersed in the charge material, are ones of the most important structural components of the submerged arc furnace. They ensure a supply of the electric energy that is necessary for the process; moreover, the reaction zones are formed around the electrodes. The internal structure of the furnace and temperature distribution in the reaction zones have a close relationship with the proportions of the heat generated in the furnace by resistive heating and by arc heating. Technical and economic indicators of the ferrosilicon process are markedly affected by properties of raw materials, the composition of the batch mix and proper carbon balance in the furnace. Although the furnaces are equipped with modern computer systems for recording and visualization of measurement data, metallurgical parameters of the process are not directly measured. These assessments are still based to a large extent on intuition and experience of the operating staff of the furnaces and have a qualitative and subjective nature. Due to this, the working space inside the ferrosilicon furnace and reaction zones cannot be considered as the structure unchanging over time. Depending on a number of technological factors, SiC walls thickness of the gas chambers might increase or decrease, or may even completely disappear. One of the common reasons for disturbances in the ferrosilicon process is an accumulation of SiC carbide in the working space of ferrosilicon furnace, which is manifested by difficulties in the course of metal tapping. It is related both to excessive amounts of C_{fix} in the charge mixture and to inappropriate temperature conditions in the reaction zones. They lead to technological problems of metal tapping, including blocking the tap hole by thick slag and slow flow of metal from the furnace. Ferrosilicon smelting in the submerged arc furnaces is considered to be a slag-free process although small amounts of slag are always seen during the metal tapping. This is associated with the quality of raw materials and the presence of small amounts of Al_2O_3, CaO, MgO and TiO_2 oxides in the charge materials. Increased amounts of Al_2O_3 and deficiency of SiO_2, CaO, MgO oxides in the chemical composition of slag makes it dense and causes the process disturbances because of tapping problems. Therefore, some ferrosilicon manufacturers use limestone addition to the charge mixture (10 - 30 kg / 1000 kg of quartzite) [3], which results in more liquid slag, tapping improvement and better technical and economic indicators of the ferrosilicon smelting process. This particularly refers to processes where the main reducer is charcoal with small amounts of ash [3]. In processes with hard coal being applied as a main reducer, limestone additions are used only occasionally. This is related with higher amounts of ash in the hard coal with which the CaO, MgO and other oxide impurities are introduced into the ferrosilicon process.

2. EFFECTS OF PARAMETERS ON EFFICIENCY OF SILICA REDUCTION

Based on the recursive equilibrium model of the ferrosilicon smelting process with two closed isothermal reactors [4], a series of simulation calculations were performed to determine influence of CaO and MgO oxides on the ferrosilicon process in the submerged arc furnace. It is assumed that these oxides are applied in the process through the addition of $CaCO_3$ and $MgCO_3$ to the charge mixture. In industry, the CaO and MgO compounds are mainly applied in the process with the ash of coal reducers and with quartzite, similarly to other contaminants seen in the ferrosilicon smelting process: Al_2O_3, P_2O_5, TiO_2. As needed, $CaCO_3$ and $MgCO_3$ can be applied through the addition of limestone or raw dolomite with a regular batch mix. It is worth mentioning that contrary to limestone, additions of raw dolomite to the charge material for the ferrosilicon smelting are rather not used. In the equilibrium calculations for the Fe-Si-O-C-Al-Ca-Mg-Ti system, the non-stoichiometric Gibbs free enthalpy minimization algorithm (FEM) was used [5]. For the calculations, the HSC 7.1 software was applied, enabling the use of a thermochemical database and solution of FEM problems directly in the Excel spreadsheet [6]. In the equilibrium model of carbothermic silica reduction process, with two closed isothermal reactors, the basic parameters are T_1, T_2 temperatures of the upper and lower reactors as well as the reaction mixture composition where the basic parameter is the $\mathrm{C/SiO_2}$ molar ratio (**Table 1**) [4]. In addition, the calculation considers the effect of the $CaCO_3$ and $MgCO_3$ contribution in the reaction mixture on the ferrosilicon process. For the calculations, the following temperature ranges were taken into consideration: T_1: $1630-1650\ \mathrm{°C}$, T_2: $1920-2010\ \mathrm{°C}$. **Table 1** contains data on reaction mixture components. In **Figure 1**, examples of calculation results, obtained with the use of the physicochemical model for two various charge mixtures with different fractions of $CaCO_3$ and $MgCO_3$ in the reaction mixture, are presented schematically. The other process parameters are the same: the pressure *P* = 0.1 MPa, the temperatures of the upper and lower reactors T_1, T_2 as well as the molar ratio C/SiO_2 = 1.96 and fractions of the other parameters of the reaction mixture composition (**Table 1**).

Table 1 Molar composition of the equilibrium model for the ferrosilicon smelting process in the Fe-Si-O-C Al-Ca-Mg-Ti system

Component	(kg/kmol)	(kmol)
Al_2O_3	101.96	0.0005
Al_2O_3*SiO_2(A)	162.05	0.01
CaCO3	100.09	0.001 - 0.015
CaO	56.08	0.0001
FeO*SiO_2	131.93	0.01
MgO	40.3	0.001
$MgCO_3$	84.31	0.001 - 0.015
SiO_2	60.08	0.98
TiO_2	79.9	0.0006
Fe	55.85	0.13
C	12.01	1.92 - 2.00

Despite the same T_1, T_2 temperatures and the C/SiO_2 molar ratio and fraction of other components in the reaction mixture, the results presented in **Figure 1** shows that different fractions of $CaCO_3$ and $MgCO_3$ in the reaction mixture affect the fraction of SiC phase in the products that leave the Reactor 2 and efficiency of the silica reduction process (Si yield, energy consumption index *E*). The presence of $CaCO_3$ and $MgCO_3$ in the reaction mixture, in the amounts of approximately 0.006 mole/mole SiO_2 (respectively 19.6 and 14.0 kg/Mg of the alloy) results in considerable reduction of the SiC phase fraction in the products that leave the Reactor 2 and improvement of the technical and economic indicators of the process (**Figure 1**, on the left). In addition to the unfavorable effect on the Si yield, the SiC phase in the products that leave the Reactor 2 is a frequent reason disturbance of the ferrosilicon process under industrial conditions. This is related to technological difficulties with the metal tapping and accumulation of infusible SiC in the furnace working space. This leads to gradual worsening of the process temperature conditions and unfavorably affects SiO condensation in the upper zones of the furnace. It is related to electrical conductivity and the effects of SiC on electric and temperature field distributions inside the furnace. Based on the equilibrium model, relationships related to the effects of the $CaCO_3$ and $MgCO_3$ fractions in the reaction mixture on the SiC phase fraction in the products that leave the Reactor 2 and the energy consumption index were determined. (**Figure 2**). They show that $CaCO_3$ has a favorable effect only within a small range (0.0055 - 0.0065 mol/mol SiO_2) having regard to reduction of the carbide SiC phase fraction in the products that leave the Reactor 2. This corresponds to the fraction of $CaCO_3$ in the charge mixture at the level of approximately 10 kg / 1000 kg SiO_2 and about 19.6 kg/Mg of the alloy.

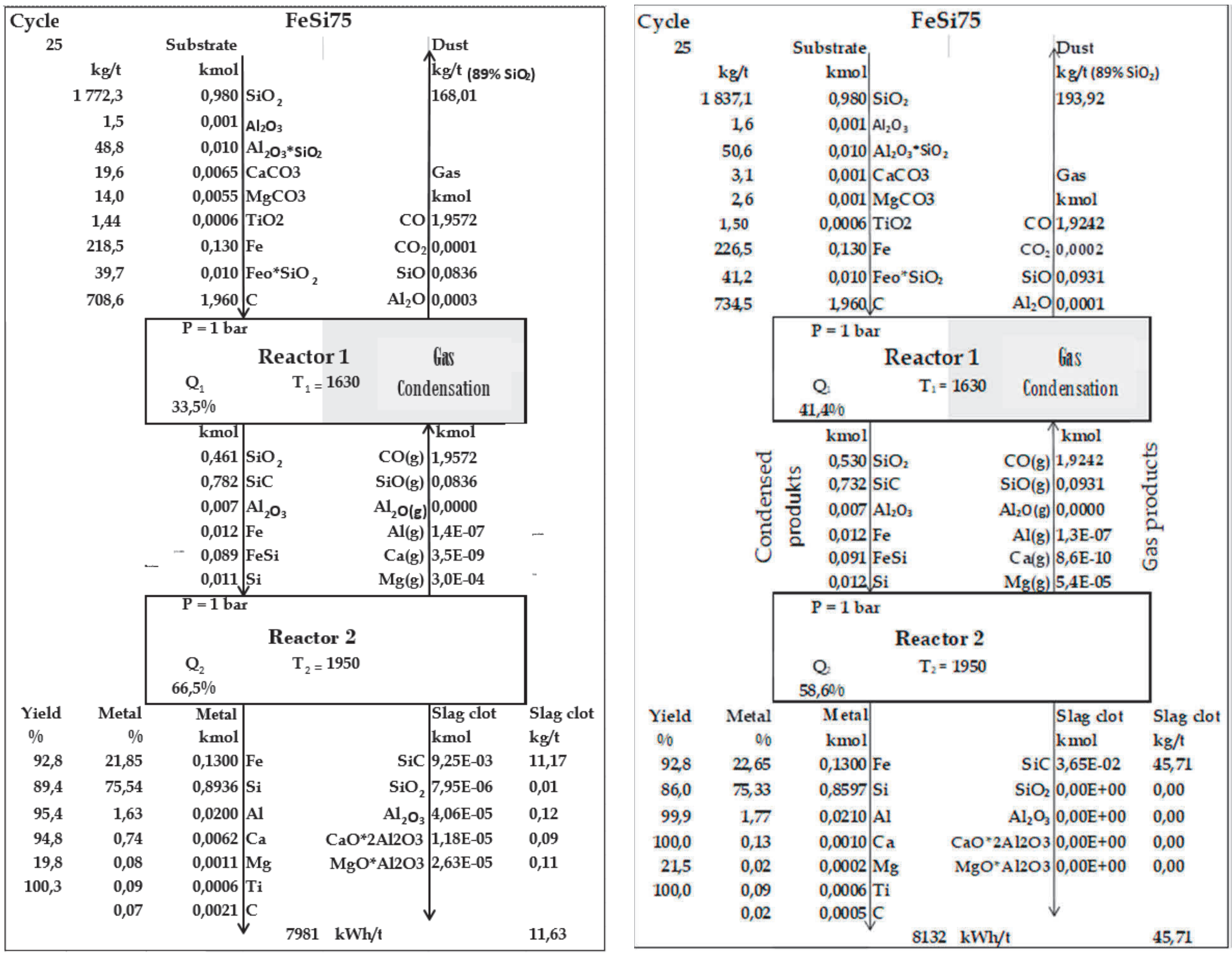

Figure 1 Examples of calculation results, obtained with the use of equilibrium model with two isothermal zones, for the FeSi75 ferrosilicon smelting following 25 cycles of the reactor operation. Basic components of the Fe-Si-O-C-Al-Ca-Mg-Ti system for two reaction mixtures with different $CaCO_3$ and $MgCO_3$ fractions (the main process parameters: $T_1 = 1630$ °C, $T_2 = 1950$ °C, $P = 0.1$ MPa, C/SiO_2 = 1.96 mol/mol)

It should be mentioned that neither higher nor lower $CaCO_3$ mole fractions than amounts within the above range have not a favorable effect on the metallurgical conditions of the process. In contrast to $CaCO_3$, an increasing fraction of $MgCO_3$ in the reaction mixture affects the reduction of SiC phase fraction in the products that leave Reactor 2 and improvement of the silica reduction process within almost entire investigated a range of 0.001 - 0.01 mole / mole SiO_2 (**Figure 2**). In Polish ferroalloy industry, the basic reducer in the ferrosilicon smelting process is the hard coal that introduces certain amounts of CaO and MgO with the ash to the process. Due to this, limestone addition to the charge material is not usually applied in the industrial practices. This type of addition is used only occasionally during the production of ferrosilicon with increased amounts of Ca in the alloy at a special order or in exceptional cases when big technological problems related to excessive amounts of SiC in the furnace are observed. A different situation is seen when the basic reducer in the ferrosilicon smelting process is charcoal. The amount of ash in charcoal is very small; therefore, the levels of CaO and MgO oxides in the process are low. Due to this, limestone additions of approximately 10 - 20 kg/Mg of the alloy (FeSi75) are applied in the charge material by some

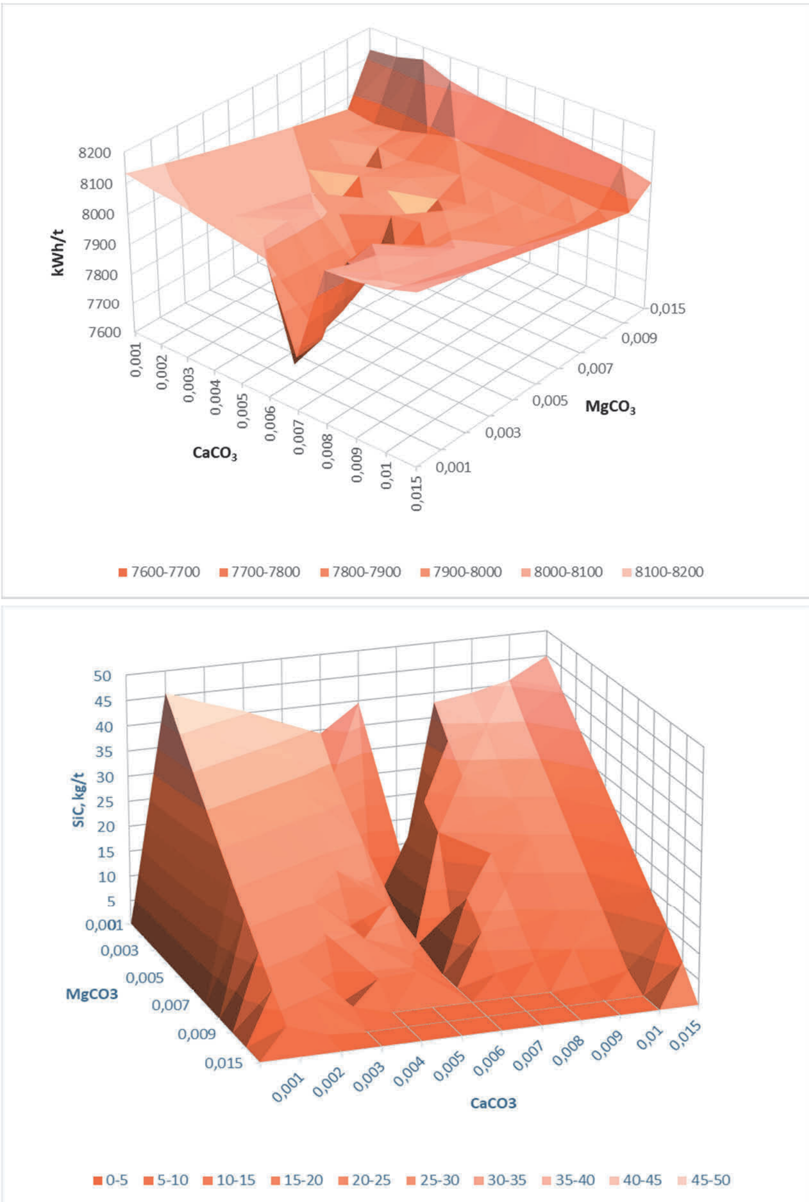

Figure 2 Effects of $CaCO_3$ and $MgCO_3$ fractions in the reaction mixture on the energy consumption index (upper graph) and of the SiC fraction in the products that leave the reactor (bottom graph). Process parameters: $T_1 = 1630$ °C, $T_2T_2 = 1950$°C, $P = 0.1\ MPa$, C/SiO_2 = 1.96 (the other details of the reaction mixture composition, see **Table 1**)

ferrosilicon manufacturers that use charcoal as the reducer to limit SiC formation and improve the stability of the metallurgical conditions [3]. **Table 2** presents data on technical and economic indicators of raw material consumption and simplified material balance for the FeSi75 smelting process in the 20 MVA furnace where the basic reducer is hard coal. The **Table 2** data show that CaO and MgO are applied in the process mainly with reducer ashes but their amounts are not sufficient and not within the optimal range based on calculations on the physicochemical model (**Figure 2**). To improve the metallurgical conditions of the ferrosilicon process, with reduction of SiC phase release in particular, as well as to improve technological conditions of metal tapping, small additions of CaO and MgO as raw dolomite [7] (~30 % CaO, ~20 % MgO) to the batch mix are suggested to be applied. The **Table 2** data show that the amounts of CaO and MgO to be applied in the process together with the charge material should be increased by about 100 % so that the ratio of CaO and MgO molar fractions was 0.0055 - 0.0065, respectively. This corresponds to the raw dolomite addition of approximately 10 kg / 1000 kg of quartzite to the charge mixture.

Table 2 Technical and economic indicators of raw material consumption and simplified materia balance facts for the process of FeSi75 smelting in the 20 MVA furnace

Raw material	Index	Chemical composition (wt %)										
	(kg/Mg)	W_t^r	A^r	V^r	C_{fix}	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	TiO_2	P_2O_5
Quartzite I	707,32					97,87	1,40	0,26	0,03	0,02	0,08	
Quartzite II	1,061,09					98,81	0,80	0,29	0,02	0,02	0,07	
Wood chips	422,04	46,00	1,03	41,00	11,97	15,20	2,65	3,80	32,50	8,60	0,26	17,69
Coal I	696,71	2,87	3,69	31,63	61,81	33,40	22,30	14,60	8,03	4,77	0,88	0,49
Coal II	353,67	7,09	5,94	33,47	53,50	26,70	18,6	21,30	6,50	8,60	0,80	1,10
Electrode paste	38,13	0	5	10	85,00	34,59	24,37	15,24	7,12	4,77	1,26	0,75
Scale	268,76	2,4				0,4		97,2				
Steel bars(1)	22,00											
Steel electrode jackets	2,76											
Energy, MWh/Mg	8,07											
Total mass of oxides (kg/Mg)						1756,27	28,27	328,52	5,42	3,76	1,78	1,14
Total mass of oxides (kg/Mg) SiO_2						1000,00	16,29	187,05	3,09	2,14	1,01	0,65
Total mass of oxides, mol/mol SiO_2						1	0,0082	0,0704	0,0033	0,0032	0,0008	
Produkt	(kg/Mg)					Chemical composition of metal (wt%)						
						Si	Al	Fe,	Ca,	Mg	Ti,	P,
Metal, FeSi75	1,000,00					75,02	1,49	22,83	0,36	0,11	0,10	0,03
Yield of elements	(%)					91,39	98,32	99,36	92,88	49,82	97,08	58,42

(1) - steel bars for the tap holes burn down by an electric arc,

[grey cell] - FeO (wt %).

3. CONCLUSIONS

1) Based on the equilibrium model with two isothermal reactors, effects of $CaCO_3$ and $MgCO_3$ additions to the reaction mixture on the SiC phase fraction in the products of ferrosilicon smelting process and efficiency of the silica reduction process were determined.

2) The model shows that within a small range, the $CaCO_3$ fraction has a favorable effect on the ferrosilicon smelting process (0.0055-0.0065 mol/mol SiO_2). This corresponds to the $CaCO_3$ fraction of approximately 10 kg / 1000 kg SiO_2. The addition of $CaCO_3$ results in reduction of the SiC phase fraction in the products that leave the process and improvement of its technical and economic indicators.
3) The fraction of $MgCO_3$ in the reaction mixture results in reduction of SiC phase and improvement of the silica reduction process efficiency within almost entire investigated range of 0.001-0.01 mol/mol SiO_2. The SiC phase fraction reduction increases with higher fractions of $MgCO_3$ in the reaction mixture.
4) The model shows that in Polish ferroalloy industry, amounts of CaO and MgO applied in the process with coal reducers are not sufficient compared to the optimal amounts determined with using the model. Addition of raw dolomite to the batch mix in the amount of 10 kg/Mg of quartzite is suggested so as to improve deficiency of the above oxides and improve the metallurgical conditions of the ferrosilicon process.

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