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COMPARISON THE PHYSICO-CHEMICAL MODEL OF FERROSILICON SMELTING PROCESS WITH RESULTS OBSERVATIONS OF THE PROCESS UNDER THE INDUSTRIAL CONDITIONS

Based on the minimum Gibbs Free Enthalpy algorithm (FEM), model of the ferrosilicon smelting process has been presented. It is a system of two closed isothermal reactors: an upper one with a lower temperature T_1 , and a lower one with a higher temperature T_2 . Between the reactors and the environment as well as between the reactors inside the system, a periodical exchange of mass occurs at the moments when the equilibrium state is reached. The condensed products of chemical reactions move from the top to the bottom, and the gas phase components move in the opposite direction. It can be assumed that in the model, the Reactor 1 corresponds to the charge zone of submerged arc furnace where heat is released as a result of resistive heating, and the Reactor 2 corresponds to the zones of the furnace where heat is produced by electric arc. Using the model, a series of calculations was performed for the Fe-Si-O-C system and was determined the influence of temperatures T_1 , T_2 on the process. The calculation results show a good agreement model with the real ferrosilicon process. It allows for the determination of the effects of temperature conditions in charge zones and arc zones of the ferrosilicon furnace on the carbothermic silica reduction process. This allows for an explanation of many characteristic states in the ferrosilicon smelting process.

Keywords: ferrosilicon, model, equilibrium, FEM, submerged-arc furnace

1. Introduction

Ferrosilicon smelting is a continuous process carried out in the submerged arc furnaces with the Söderberg self-baking electrodes [1]. Respectively granulated raw materials are charged into the furnace from the top, in the form of the mixture batch consisting: quartzite, carbon reducers (coal, coke and wood chips), carriers of iron (mill scale or iron chips). Periodically, approximately at equal time intervals molten metal is tapped into the ladle, through one of the tap holes located near to the furnace hearth. Necessary heat for the highly endothermic reactions of silica reduction is generated direct in the furnace charge as a result of current flow by resistive heating, and by arc heating which burns in the gas chambers located near the electrodes tip. 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 on the principle of resistance heating and arc heating. One of the most important structural elements of the ferrosilicon furnaces are immersed in the charge self-baking Söderberg electrodes which bring electricity required for the process. Burning of electric arc and temperature conditions of the reaction zones have a close relationship with the position of electrodes tips in the furnace. The temperature distribution of reaction zones are not subject to direct measurements, but to provide the correct electrical and temperature conditions of the process it is necessary to systematically electrodes slipping. The optimal position of the electrodes leads to the minimization

of economic indicators of the process. In periods of good and stable operation of the ferrosilicon furnace in the reaction zones are conditions for the continuous evolution of new products of the silica reduction. This process has a cyclical nature and it is associated with melting and periodic penetration of liquid silica inside the arc chambers [1].

2. Model of the ferrosilicon process

For a fixed composition of the initial reaction mixture and set conditions of temperature and pressure ($T, P = const$), the equilibrium composition of the system is the most stable and corresponds to the minimum Gibbs Free Enthalpy. The non-stoichiometric algorithm of the Gibbs Free Energy Minimization Method (FEM) relies on solving the nonlinear optimization problem with constraints resulting from the mass balances of individual elements in which the objective function is:

$$\min_{\mathbf{n}} \frac{G(T, P, \mathbf{n})}{RT} \quad (1)$$

where:

$G(T, P, \mathbf{n})$ – Gibbs free enthalpy function,
 $\mathbf{n} = (\mathbf{n}^1, \mathbf{n}^2, \dots, \mathbf{n}^f)$, $\mathbf{n}^r = (n_{1r}^r, n_{2r}^r, \dots, n_{kr}^r)$

\mathbf{n}^r - vectors whose elements are numbers of moles of the various phase r components,

f - a number of phases constituting the system

R - gas const.

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This algorithm requires delivery of input data of the initial reaction mixture composition, parameters of the process (T, P) and a list of components that may appear in the equilibrium composition of the specific reaction system phases. This approach does not specify the chemical reactions or stoichiometric equations. Based on the FEM algorithm, a model of the reaction zones in the ferrosilicon submerged arc furnace was presented. The model is an extension of earlier models and concepts described in the publications [1] - [5]. It is a system of two closed isothermal reactors: an upper one with a lower temperature T_1 , and a lower one with a higher temperature T_2 (Fig. 1). Between the reactors and the environment as well as between the reactors inside the system, a periodical exchange of mass occurs at the moments when the equilibrium state is reached in the reactors. In each cycle, a reaction mixture with the molar composition corresponding approximately to the batch mixture of raw materials for the ferrosilicon smelting process is fed into the upper reactor:



At the same time, the condensed products of chemical reactions move from the top to the bottom, and the gas phase components move in the opposite direction. Simulation of the continuous ferrosilicon smelting process was implemented recursively. In cycle 1, a portion of the mixture (2) is fed into the Reactor 1 where the reactions take place until the equilibrium state at the temperature T_1 is reached. Then, the gas-phase products leave the Reactor 1 and after cooling to the temperature $T_w = 700^\circ\text{C}$, they do not participate in the further process. Simultaneously, the products of condensed phases of the Reactor 1 flow down and are introduced into the Reactor 2 where they react with each other until the equilibrium at the temperature T_2 is reached. Then, the condensed phase products leave the Reactor 2 and, after cooling to the temperature $T_s = 1650^\circ\text{C}$, form a metallic and slag phase and do not participate in the further process.

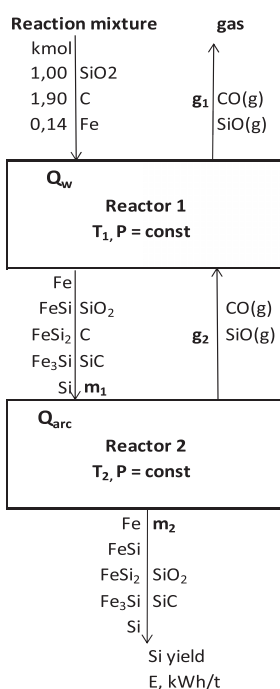


Fig. 1. Equilibrium model of the ferrosilicon smelting process with two reactors

The gas phase products with the equilibrium composition leave the Reactor 2 and, after cooling to temperature T_1 , they are introduced back into the Reactor 1 where they react to reach the equilibrium state again at the temperature T_1 . Once the Reactor 1 reaches the equilibrium, the gas phase products leave the reactor and after cooling to temperature T_w , they do not participate in the further process. The products of condensed phases remain in the Reactor 1 and take part in the reactions of the next cycle. Cycle 2 and each next cycle of the reaction system start with an introduction of a new portion of the reactants (2) to the Reactor 1. They react together with the other condensed components of the previous cycle until the equilibrium is reached at the temperature T_1 . In the subsequent cycles, the process is the same as in Cycle 1. In the real ferrosilicon process, the temperature T_w corresponds to the temperature of gases that are byproducts of the silica reduction process measured immediately after leaving the furnace charge surface. It can be assumed that in the model, the Reactor 1 corresponds to the charge zones of the submerged arc furnace where heat is released as a result of resistive heating, and the Reactor 2 corresponds to the zones where heat is produced by electric arc. The heat balance of the process includes the following components:

$$Q_w = \Delta H_{298}^{T_1} + \Delta H_{T_1}^{R1} + \Delta H_{T_1}^{T_2}(m_1) + \Delta H_{T_1}^{T_w}(g_1) + \Delta H_{T_2}^{T_1}(g_2) + \Delta H_{T_1}^{R1}(g_2) + \Delta H_{T_1}^{T_w}(g_2) \quad (3)$$

$$Q_{arc} = \Delta H_{T_2}^{R2} + \Delta H_{T_2}^{T_1}(m_2) \quad (4)$$

$$Q = Q_w + Q_{arc} \quad (5)$$

where:

- $\Delta H_{298}^{T_1}$ - enthalpy change of the substrates (2) during heating from the ambient temperature $T=298\text{K}$ to the temperature T_1 , (kJ/mol),
- $\Delta H_{T_1}^{R1}, \Delta H_{T_2}^{R2}$ - thermal effect of reactions in the reactor 1 and 2 respectively, (kJ/mol),
- $\Delta H_{T_1}^{T_2}(m_1)$ - enthalpy change of the condensed phases during heating while passing from the Reactor 1 to the Reactor 2, (kJ/mol),
- $\Delta H_{T_2}^{T_1}(g_2) + \Delta H_{T_1}^{R1}(g_2)$ - enthalpy change of the gas phase during cooling while passing from the Reactor 2 to the Reactor 1 and the thermal effect of the condensation reactions in the Reactor 1, (kJ/mol),

TABLE 1

The components of specific phases of the Fe-Si-O-C system

Phase 1	C(g)	C ₂ (g)	C ₃ (g)	C ₄ (g)	C ₅ O(g)	C ₆ O(g)	CO(g)
	CO ₂ (g)	C ₃ O ₂ (g)	Fe(g)	Fe ₂ (g)	Fe(CO) ₅ (g)	FeO(g)	FeO ₂ (g)
	O(g)	O ₂ (g)	C ₂ O(g)	O ₃ (g)	Si(g)	Si ₂ (g)	Si ₃ (g)
	Si ₄ (g)	SiC(g)	SiC ₂ (g)	Si ₂ C(g)	SiO(g)	SiO ₂ (g)	Si ₂ O ₂ (g)
Phase 2	FeCO ₃	Fe(CO) ₅	Fe ₂ (CO) ₉	Fe ₃ (CO) ₁₂	Fe _{0,945} O	Fe _{0,947} O	FeO
	FeO _{1,056}	Fe ₂ O ₃	Fe ₃ O ₄	Fe ₃ O ₄	FeO*SiO ₂	2FeO*SiO ₂	FeSiO ₃
	SiO ₂						
Phase 3	C						
Phase 4	SiC						
Phase 5	Fe ₃ C	Fe	FeSi	FeSi ₂	FeSi _{2,33}	FeSi _{2,43}	Fe ₃ Si
	Fe ₅ Si ₃	Si					

$\Delta H_{T_1}^{T_w}(g_1), \Delta H_{T_1}^{T_w}(g_2)$ - enthalpy change of the gas phase products after leaving the reactor 1 and cooling to the temperature by contact with a cold the charge leading down T_w , (kJ/mol),

$\Delta H_{T_2}^{T_1}(m_2)$ - enthalpy change of condensed phases after leaving the Reactor 2 and cooling from the temperature T_2 to $T_1 = 1650^\circ\text{C}$, (kJ/mol),

T_w - temperature of the gas-phase after leaving the Reactor 1 and cooling by heat exchange with the charge leading down, $T_w = 700^\circ\text{C}$,

Q_w, Q_{arc}, Q - components of the heat balance in Reactor 1 and Reactor 2, and a summary heat of the process, kJ/mol

The components Q_w, Q_{arc} of the heat balance characterize distribution of heat in the reaction zones of the ferrosilicon furnace. The component Q_w corresponds to the charge zones where heat release results from resistive heating and the Q_{arc} corresponds to gas chambers where heat is released as a result of arc heating.

3. Simulation of the ferrosilicon process with the model

The equilibrium composition was calculated using solver which is part of the equilibrium module of HSC 7.1 thermochemical software. This module enables to calculate multi-component equilibrium compositions in heterogeneous systems in isothermal and isobaric conditions by the FEM method. The HSC 7.1 software allows the use of a thermochemical database and solution of the FEM problem directly on Excel spreadsheet. Using the model (1)-(5), a series of simulation calculations was performed to determine the influence of temperatures T_1, T_2 on the process. In calculations was taken into account the initial composition of the reaction mixture (2) and it was found by means of the thermochemical database that in the temperature range of 1600 to 2200°C five phases with 53 components might occur in the Fe-Si-O-C system (Table 1). For each cycle, the equilibrium composition of

the reaction system as well as the mass and energy balances were determined. The relationships for the influence of temperature in the reactors 1 and 2 on the total mass fraction of Si in Reactor 2 (Si yield) and the number of moles of the main components of the Fe-Si-O-C in both reactors are presented graphically on Fig. 1,2. Using equations (3)-(5) in Table 2 has been presented calculation results of the process heat balance components Q_w, Q_{arc} and Q .

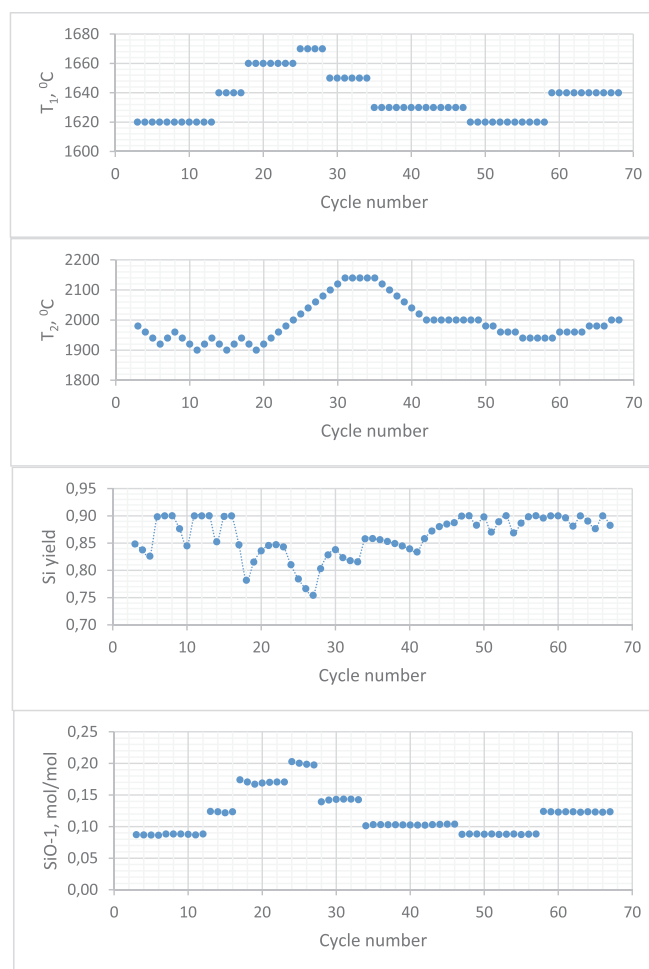


Fig. 2. Effects of the temperatures T_1, T_2 , on the Si yield in the Reactor 2 and the proportion of SiO(g) in the gas living Reactor 1 at equilibrium condition

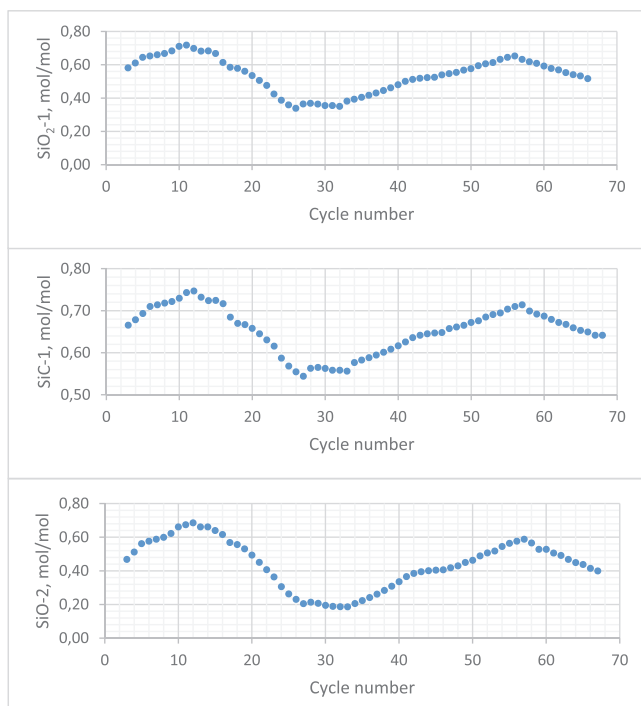


Fig. 3. Participation of SiO_2 and SiC in the Reactor 1 and the $\text{SiO}(\text{g})$ in gas-phase of Reactor 2 in subsequent cycles of operation the reaction system for the T_1, T_2 , as in Fig. 1.

TABLE 2

The heat balance of the process for the reaction mixture (2) and temperatures in the reactor : $T_1 = 1640^\circ\text{C}$, $T_2 = 1980^\circ\text{C}$

No.	Component of the heat balance	MJ/kmol	kWh/t	%
1	Heating of substrates (2) from temperature 25°C to T_1	192,99	1633,08	
2	Thermal effect of the processes in Reactor 1	443,40	3752,00	
3	Cooling gas from the Reactor 2 and its reaction in Reactor 1	-216,72	-1833,84	
4	Heating to a temperature T_2 condensed products of Reactor 1	35,96	304,30	
5	Cooling the gas to 700°C after leaving Reactor 1	-72,68	-615,02	
Component of the heat balance, Q_w		382,95	3240,52	44,26
6	Thermal effect of the processes in Reactor 2	494,54	4184,81	
7	Cooling products from Reactor 2 to the temperature $T_2=1650^\circ\text{C}$	-12,31	-104,13	
Component of the heat balance, Q_{arc}		482,24	4080,68	55,74
Summary energy consumption, $Q = Q_w + Q_{arc}$		865,19	7321,21	100
The energy consumption index, $E = Q/\eta$, $\eta = 0,89$		972,12	8226,08	

4. Comparison of the model with real process

Presented in Fig. 2,3 results of calculation allows for the determination of the effects of temperature conditions in charge zones and arc zones of the submerged arc furnace on the carbothermic silica reduction process and can be explained of its many characteristic states. It should be noted positive influence of lower temperature in Reactor 1, and a higher temperature in Reactor 2 on the process. This affects a higher Si yield, and increase of the process efficiency. In such conditions, mass transfer of SiO_2 and SiC between Reactors 1,2 is much higher as well as flow of $\text{SiO}(\text{g})$ in the opposite direction (Fig.3). Because of the kinetic conditions in real process not all of these products may fully react in the lower zones of the furnace when their quantity is large. The furnace operators usually believe that it

is a sign of a good ferrosilicon furnace operation when flows of a small amount of slag during metal tapping. However, when the amount of reduction products (SiO_2 , SiC , $\text{SiO}(\text{g})$) is too large, due to limitations in transportation of excessive weight of products between the upper and lower zones of the furnace it is the reason disturbances of the process. The results of calculations indicate that such conditions are related with too low temperature in the upper zones of the furnace. By furnace operators such state of the ferrosilicon process is identified with a carbon deficiency in the reaction zones, but this does not mean that it is contrary to the presented model. This follows from the low electrical resistivity of carbon-containing components and their significantly influence on distribution of current density in the furnace working space [1]. It makes that in the ferrosilicon furnace the metallurgical, thermal and electrical processes are mutually dependent from each other. To ensure a sufficiently high temperature in the reaction zones requires the presence of an electrical arc as a high temperature heat source. Therefore particularly important for the temperature conditions of the ferrosilicon process has got position of the electrodes in the furnace. Position of the electrodes is not only important for the stable burning of the electric arc and the temperature conditions in the lower zones of the furnace, but also affects the temperature distribution in charge of the upper zones in furnace. Location of the reaction zones and temperature distribution are highly affected by slipping of the electrodes. Carbon electrodes burning out and are shortened as a result of arcing erosion and chemical reactions of silica reduction process. For this reason, in order to prevent electrodes shortening and maintaining the correct temperature conditions of the reaction zones an appropriate strategy of electrodes slipping has a special significance. Obtained by the model calculation results show a satisfactory agreement with the statistical data of the 20 MVA ferrosilicon furnace. Confirmation of this are correlations shown in Fig. 4. between productivity of furnace, the amount of slag flowing out during metal tapping, and the size of the electrodes slipping. As deduced from the model, in the real process can be observed increased amount of slag flowing out during the metal tapping in periods characterized by a good performance of the furnace. Especially is clearly visible on Fig.4 the influence of too high temperature in the upper zones of the furnace on reduced amount of slag in the period from 22 June to 26 June. Increased intensity of the electrodes slipping in this period (Fig. 4) shows, that the reason of the high temperature in the charge of upper zones were "short" electrodes. Because of lack of space on Fig.4 are given statistics on slipping only one electrode, but identical data relate to the other electrodes.

5. Conclusion

The non-stoichiometric equilibrium model with two reactors allows for the explanation of many characteristic states of the ferrosilicon smelting process in the submerged arc furnace. It allows for the determination of the effects of temperature conditions and the heat distribution in charge zones and arc zones of the furnace on carbothermic silica reduction process. The calculation results for the Si yield and the specific energy consumption show a good agreement of the model and the industrial data for the ferrosilicon smelting.

REFERENCES

- [1] A.J. Schei, Kr.Tuset, H. Tveit, Production of High Silicon Alloys, Trondheim (1998).
- [2] N.K. Batra, Iron and Steelmaking **39**, 5, 399-404 (2003).
- [3] G. Eriksson, T. Johansson, Scandinavian Journal of Metallurgy **7**, 264-270 (1978).
- [4] B. Machulec, W. Bialik, Solid State Phenomena **212**, 183-186, (2013).
- [5] A.M. Valderhaug: Modelling and Control Submerged-Arc Ferrosilicon Furnace, dissertation, Department of Engineering Cybernetics, The Norwegian Institute Technology, Trondheim, Norway (1992).

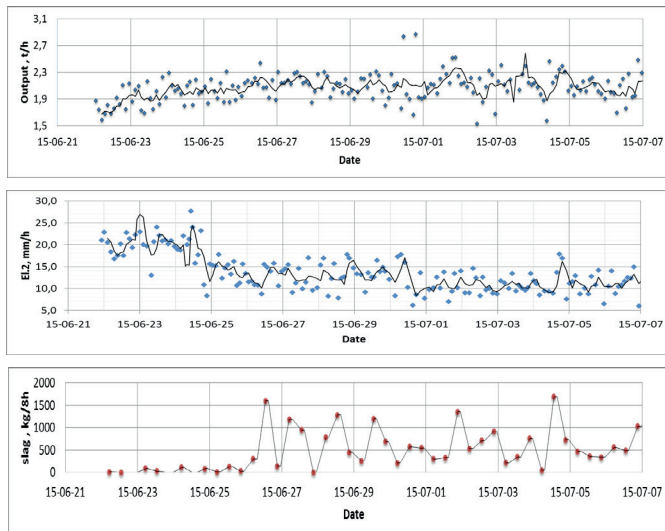


Fig. 4. Statistical data for the FeSi75 ferrosilicon furnace: efficiency of the furnace, slipping one of the electrodes (EI.2), and the weight of the slag flowing out during the metal tapping, (Open submerged arc furnace, 20 MVA, diameter of electrodes – 1.2 m)

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