Towards a Better Understanding of the Chemical Reactions Between Iron Carbide and Silicon Carbide

Serzhanov G.M.* and Shevko V.M.

M. Auezov South Kazakhstan State University, Shymkent, Kazakhstan

Abstract

This article contains the research results of the equilibrium interaction of iron carbide (Fe_3C) with silicon carbide (SiC) in a temperature interval of 700-2000 K with the formation of iron silicides (Fe_3Si, Fe_5Si_3, FeSi, $FeSi_2$), by using the program of the Finnish metallurgical company Outokumpy HSC Chemistryj-5.1 for Windows with regard to the electrothermal production of ferrosilicium from siliceous and carbon-containing raw materials.

On the basis of the received regression equations connecting the Gibbs energy change with the temperature and the silicon content in a ferroalloy, the response surfaces (change of the Gibbs free energy - ΔG_T^0) and their horizontal sections for three groups of ferroalloys were constructed with the program Mathcad. The silicon content in the first group of alloys is 14.3-23 %, in the second group of alloys – 23-33.3 % and in the third group of alloys – 33.3-42.8 %. It was established, that the reactions between Fe_3C and SiC with the formation of iron silicides in the range of temperatures 700-2000 K are possible, and the probability of these reactions increases with increasing the mole ratio Fe_3C/SiC from 0.166 to 1.0. As a result of the reactions the low-silicon ferrosilicium can be obtained, answering to a grade FS20 with Si content from 19 to 27 % and consisting of a mixture of Fe_3Si and Fe_5Si_3, and also the ferrosilicium corresponding to a grade FS25 with a Si content from 23 to 29 % and consisting of a mixture of Fe_5Si_3 and FeSi. It was found, that at the technological temperature of 1900-2000 K the maximum Si content in the received ferrosilicium can't be more than 37.7-38.8 %. Production of the medium-silicon and the high-silicon ferrosilicium answering to grades FS45- FS90 from the Fe_3C-SiC mixture is impossible from a thermodynamic point of view.

The received information extends our knowledge about the iron silicides formation during the electrothermal production of ferrosilicium with a silicon content in the alloy from 19 to 90 %.

Introduction

At the ferrosilicon melting from the quartzite, coke and steel cuttings mixture in an electric furnace bath a SiC crucible is formed which reacts with the steel cuttings and forms Fe_3C. It is known [1-3] that Fe_3C takes part in the ferrosilicon formation, reacting with SiO_2, SiO and Si (for example with the formation of FeSi) according to the reactions:

$$2Fe_3C + SiO_2 = FeSi + 5Fe + 2CO \quad (1)$$

$$Fe_3C + SiO = FeSi + 2Fe + CO \quad (2)$$

$$Fe_3C + 3Si = 3FeSi + C \quad (3)$$

However, the literature information concerning the iron carbide behaviour in a furnace bath at the ferrosilicon production is limited. This article contains results of the research into the equilibrium reactions between Fe_3C and SiC with formation of Fe_3Si, Fe_5Si_3, FeSi, $FeSi_2$ and their mixtures, leading to ferrosilicon with a silicon content from 14.3 to 50 %. This research was supported by the software program of the Finnish metallurgical company Outokumpy HSC-5.1 [4].

Reactions Modeling

Thermodynamic research was carried out with 3 groups of Fe-Si alloys with a different Si content: 1 group – from 14.3 to 23 % and composed of Fe_3Si and Fe_5Si_3; 2 group – 23-33.3 % and composed of Fe_5Si_3 and FeSi; 3 group – 33.3-50 % and composed of FeSi and $FeSi_2$. The research goals included the study of the influence of the tempera-

* Corresponding author. E-mail: gsm_ask@mail.ru

ture and the Fe_3C/SiC mole ratio on the probability of iron-silicon alloys formation. Tables 1-3 contain the data about the influence of the Fe_3C/SiC mole ratio on the Si content in the formed ferroalloys.

The Gibbs energy (ΔG_T^0) dependence on temperature for the 3 groups of reactions is represented in Fig. 1.

Table 1
Influence of the Fe_3C/SiC mole ratio in the initial mixture (β) on the Si content for the first group of alloys

# mixture	β	Si content in the alloy, %
1.	1.0	14.3
2.	0.90	15.5
3.	0.83	16.7
4.	0.75	18.8
5.	0.66	20.0
6.	0.625	21.05
7.	0.61	21.4
8.	0.60	21.7
9.	0.55	23

Table 2
Influence of the Fe_3C/SiC mole ratio in the initial mixture (β) on the Si content for the second group of alloys

# mixture	β	Si content in the alloy, %
10.	0.55	23
11.	0.53	23.8
12.	0.5	25
13.	0.44	27.2
14.	0.4	29.4
15.	0.33	33.3

Table 3
Influence of the Fe_3C/SiC mole ratio in the initial mixture (β) on the Si content for the third group of alloys

# mix-ture	β	Si content in the alloy, %
16	0.33	33.3
17	0.31	34.5
18	0.29	36
19	0.28	37.2
20	0.26	38.5
21	0.22	42.8
22	0.16	50

Results and Discussion

Figure 1 shows that obtaining an alloy containing 14.3-23 % of Si and composed of Fe_3Si, Fe_5Si_3 and their mixtures, is possible in a wide temperature range. From a thermodynamic point of view, the formation of an alloy with a low Si content (14.3%) is more probable than with a high Si content (23%). It is related to the various durabilities of iron silicides. So, the heat of Fe_3Si formation from Fe and Si at 1573 K, reduced to 1 gram atom of Si, is equal − 105.3 kJ, and the analogous value for Fe_5Si_3 is – 87.6 kJ.

It is also noticed that an increase of the Fe_3C/SiC mole ratio from 0.55 to 0.9 increases the probability of a Fe-Si alloy formation.

The formation of a ferroalloy with a Si content of 23-33.3 % and composed of Fe_5Si_3 and FeSi and their mixtures from a mixture of Fe_3C and SiC is possible in a temperature interval of 700-1800 K (the sudden change in the shape of the curve of $\Delta G_T^0=f(T)$ is contributed to the melting of the FeSi). It follows from Fig. 1, that in a temperature interval of 700-1800 K the formation of alloys containing more than 38.8% of Si from a Fe_3C and SiC mixture is impossible.

Using the second order method of planning an experiment [5] we received the following adequate regression equations for the 3 types of reactions:

For the first group
(Si content in the alloys from 14.3% to 23%)

$$\Delta G_T^0\,(I) = -71.298-0.0189\cdot T+4.268\cdot Si+4.1\cdot 10^{-6}\cdot T^2-0.077\cdot Si^2-2.347\cdot 10^{-4}\cdot T\cdot Si \quad (4)$$

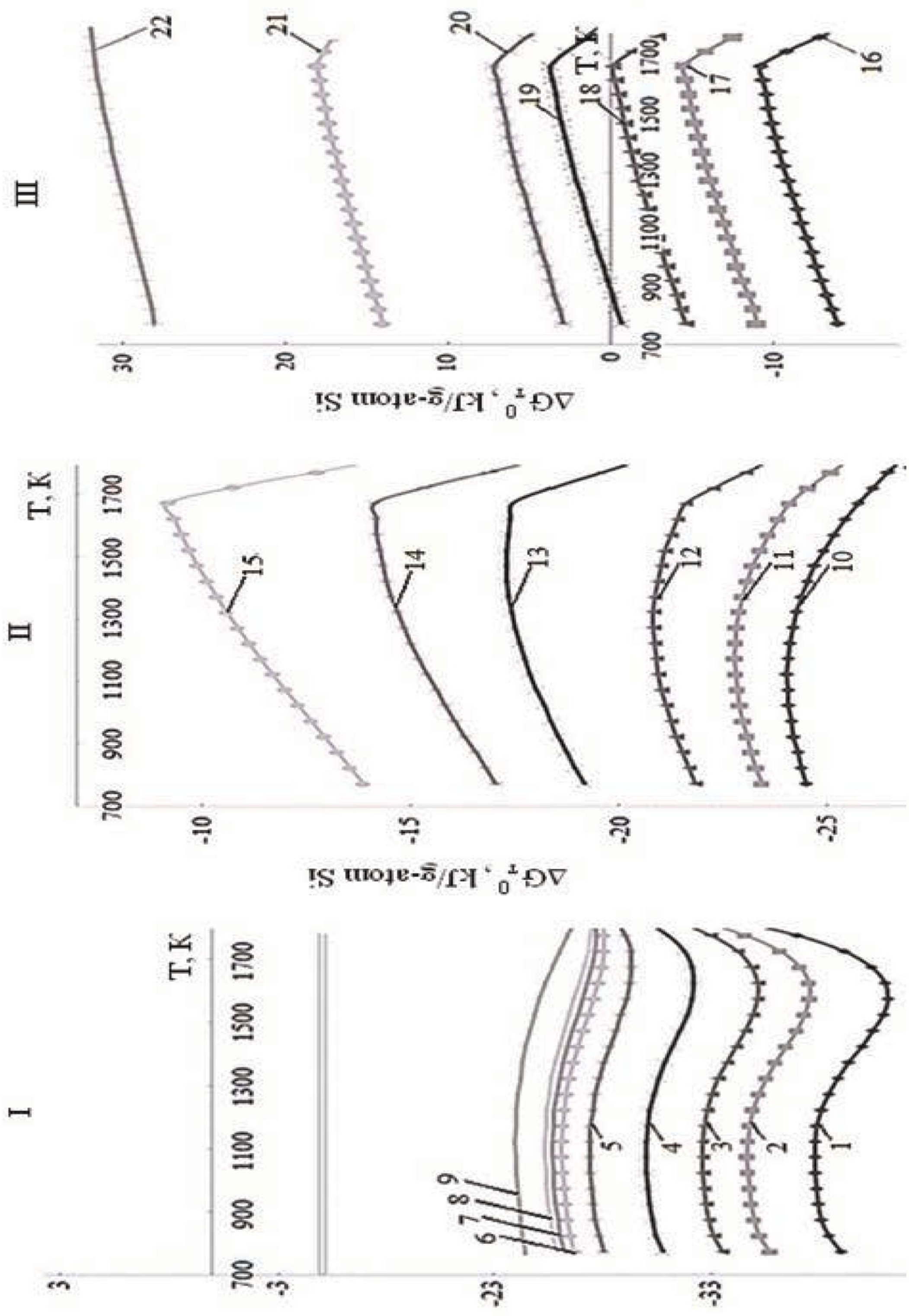
For the second group
(Si content in the alloys from 23% to 33,3%)

$$\Delta G_T^0\,(II) = -101.991-0.034\cdot T+3.298\cdot Si+2.075\cdot 10^{-5}\cdot T^2-0.0585\cdot Si^2-8.852\cdot 10^{-4}\cdot T\cdot Si \quad (5)$$

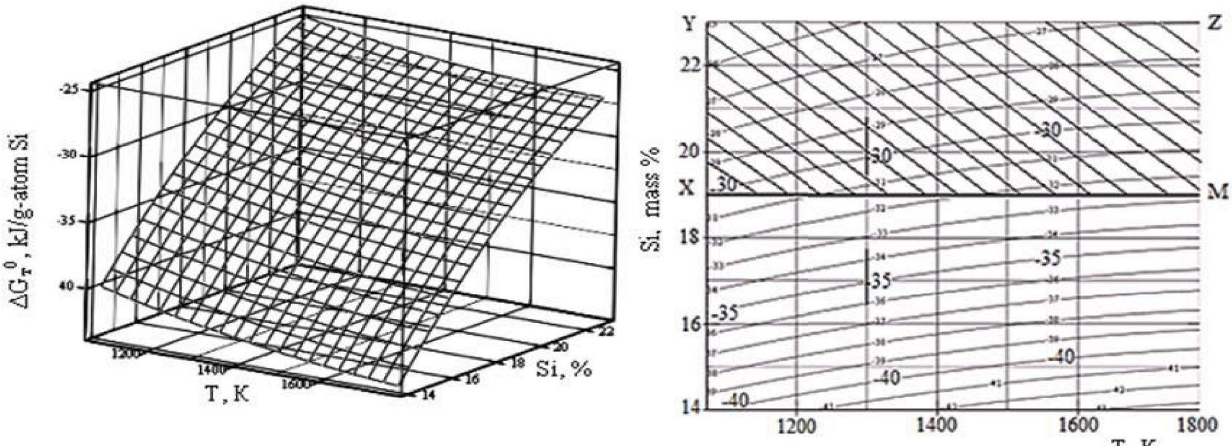
For the third group
(Si content in the alloys from 33,3% to 50%)

$$\Delta G_T^0\,(III) = -369.37-0.1155\cdot T+12.224\cdot Si+2.6\cdot 10^{-5}\cdot T^2-0.0994\cdot Si^2-1.057\cdot 10^{-3}\cdot T\cdot Si \quad (6)$$

where ΔG_T^0 – Gibbs energy change on 1 gram atom of Si, kJ; T – temperature, K; Si – mass content of Si in the formed ferroalloy, %. On the basis of the equations (4-6) using the Mathcad program [6] we constructed the response surfaces (ΔG_T^0) and their horizontal sections (Figs. 2-4). For the first group of alloys (Si content from 14.3% to 23%) (Fig. 2) the greatest probability of formation is observed for alloys with a low Si content. And the low-silicon ferrosilicon corresponding to the grade FS20 can be found in the field XYZM. Ferrosilicon with a lower Si content is formed below the line XM. From Figs. 3-4 follows that the form of a response surface (ΔG_T^0) in the alloys containing 23-33.3% and 33.3-42.8% of Si has an identical (slightly convex) character.

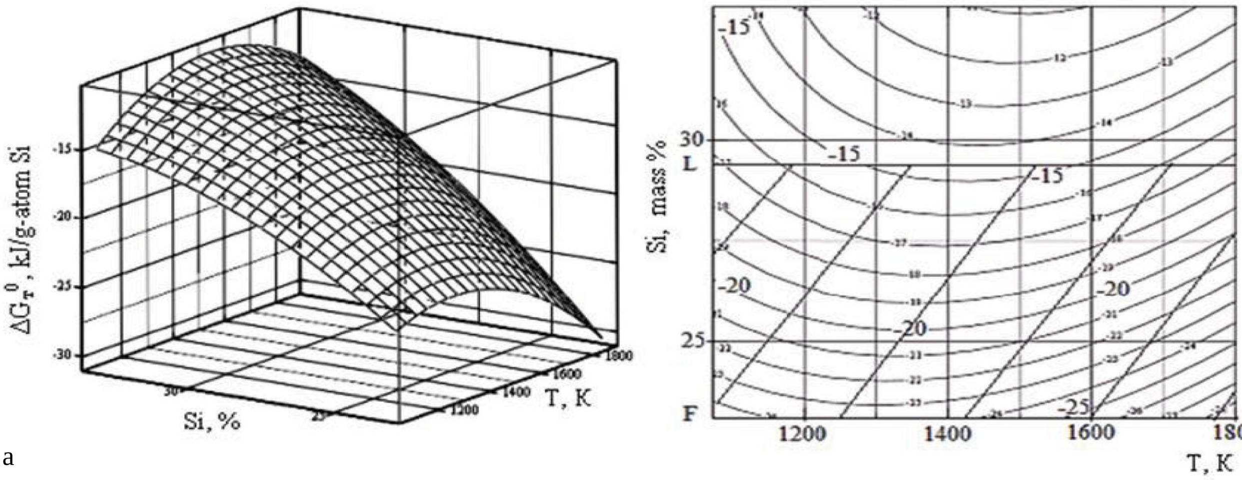


Si content in products: I-14.3-23%; II-23-33,3%; III-33,3-50%
The numbers of the lines correspond to the mixtures numbers, presented in the tables 1-3
Fig. 1. Temperature influence on ΔGт0 of chemical reactions between Fe_3C and Si.



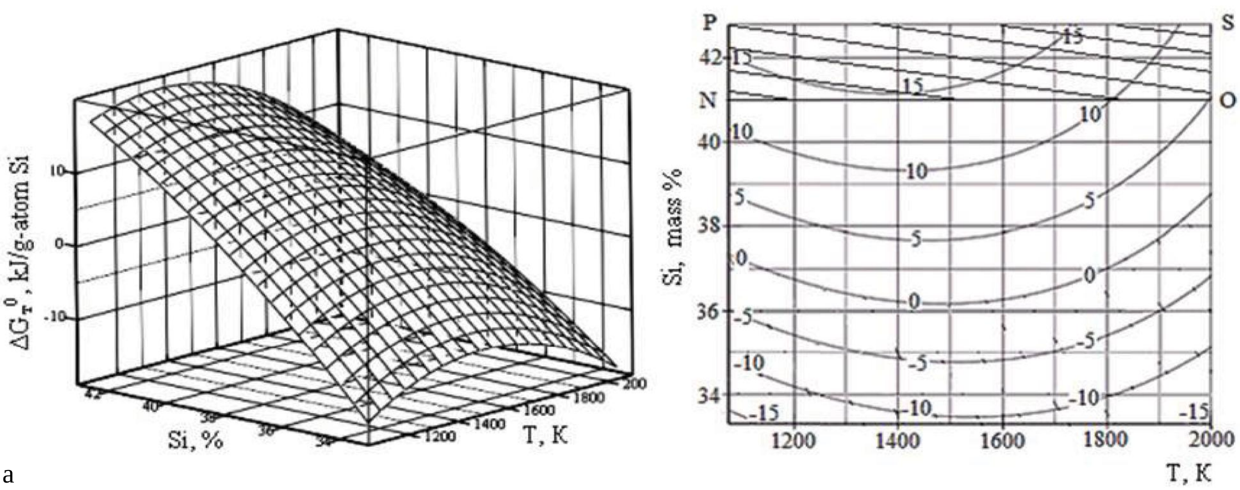
a b

A – a response surface form, B – horizontal sections of response surfaces (numbers on lines – ΔG_T^0)
Fig. 2. Influence of temperature and Si content in a ferroalloy on a response surface form and its horizontal sections at forming a ferroalloy containing 14.3-23% of Si.



a b

A – a response surface form, B – horizontal sections of response surfaces (numbers on lines – ΔG_T^0)
Fig. 3. Influence of temperature and Si content in a ferroaloy on a response surface form and its horizontal sections at forming a ferroalloy containing 23-33.3 % of Si.



a b

A – a response surface form, B – horizontal sections of response surfaces (numbers on lines – ΔG_T^0)
Fig. 4. Influence of temperature and Si content in a ferroalloy on a response surface form and its horizontal sections at forming a ferroalloy containing 33.3-42.8 % of Si.

From a thermodynamic point of view, the formation of low-silicon ferrosilicon of the FS25 grade with a Si content from 23% to 29% from Fe_3C and SiC in a temperature interval of 1100-1800 K is limited by the area FLCD (Fig. 3). In a temperature interval of 1100-2000 K the formation of medium-silicon and high-silicon ferrosilicon corresponding to the grade FS45 with a Si content from 41% to 47% (the area NPSO on Fig. 4) from a Fe_3C and SiC mixture is impossible. The formation of medium-silicon and high-silicon ferrosilicon corresponding to grades FS50- FS90 from a Fe_3C and SiC mixture is impossible for the same reason.

Thus, during the ferrosilicon melting, Fe_3C and SiC present in the furnace can influence the formation of ferrosilicon of grades FS20 and FS25. There is no expected influence of iron and silicon carbides on the formation of medium-silicon and high-silicon ferrosilicon of grades FS45- FS90.

Conclusion

The research carried out on the nFe_3C-mSiC systems allowed us to establish, that:

- in a temperature interval of 700-2000 K chemical reactions between iron carbide and silicon carbide with the formation of iron silicides are possible;
- the probability of the formation of iron silicides increases with an increasing Fe_3C/SiC mole ratio in the initial mixture from 0.166 to 1.0 and the Si content reduction in formed ferroalloy;
- the low-silicon ferrosilicon, corresponding to grades FS20 (19-27% of Si and composed of a Fe_3Si and Fe_5Si_3 mixture) and FS25 (23-29% of Si and composed of a mixture of Fe_5Si_3 and FeSi) can be obtained from Fe_3C and SiC;
- at the technological temperature of 1900-2000 K, the maximum Si content in the formed ferrosilicon cannot exceed 37.7-38.8 %;
- from a thermodynamic point of view the formation of ferrosilicon of FS45 grade with a Si content from 41 to 47% from a mixture of Fe_3C and SiC is impossible, therefore it should not be expected that Fe_3C and SiC influence the melting of medium-silicon and high-silicon ferrosilicon of grades FS45-FS90 in an electric furnace.

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