CHEMISTRY & CHEMICAL TECHNOLOGY

Chem. Chem. Technol., 2017,
Vol. 11, No. 4, pp. 410–414

Chemistry

THERMODYNAMIC ANALYSIS OF OBTAINING FERROALLOY FROM SILICON-ALUMINUM-CONTAINING SILICA CLAY

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https://doi.org/10.23939/chcht11.04.410

Abstract. The article presents results of thermodynamic modeling of Fe-Si-Al complex containing alloy of the silica clay (77.8 % Al_2O_3, 11.6 % Al_2O_3). The modeling is based on the principle of minimum Gibbs energy and fulfilled by means of software complex HSC-5.1. It was found that the joint reduction of silicon and aluminum from an amorphous SiO_2 and Al_2O_3 is characterized by higher thermodynamic probability than from a mixture of a crystalline SiO_2 and Al_2O_3. At the silicon reduction there is the undesirable formation of a gaseous SiO; the transition degree of silicon in SiO can be reduced by means of decrease in temperature and increase in carbon content.

Keywords: Si-Al containing silica clay, thermodynamic modeling, carbothermic reduction, complex ferroalloy.

1. Introduction

In the production of siliceous ferro alloys, the initial components are quartzite, iron shavings and coke [1]. For the improvement of engineering and economical performance of complex ferroalloys production the researches on the coke replacement by various carbonaceous reducers [2-8] have been carried out. Also investigations connected with substitution of quartzite by cheap and effective siliceous material have been fulfilled [9, 10]. It is found that silica clay can be used as a raw component. Its distinctive feature is the presence of 90 % of silicon oxide not in a crystalline state, but in an amorphous one [11]. In accordance with [12] heat formation and Gibbs free energy of amorphous silica are less than those for quartz (for amorphous silica ΔH^0_{298} = – = – 901.56832 kJ; ΔG^0_{298} = –848.64072 kJ and for SiO_2(β-quartz) ΔH^0_{298} = –911.066 kJ; ΔG^0_{298} = –853.536 kJ). In this connection high reactivity of amorphous SiO_2 in comparison with crystalline SiO_2 can be expected.

A purpose of the given work is a research of a possibility of a complex silicon-aluminum-containing ferroalloy production from a silica clay of the Darbaza deposit located in the South Kazakhstan area.

2. Experimental

The silica clay chemical composition was (%): SiO_2 77.8; Al_2O_3 11.6; Fe_2O_3 3.4; CaO 1.6; MgO 1.5; TiO_2 0.5 and $CaSO_4$ 1.5. The research has been performed by means of a modeling technique on the basis of a complex HSC 5.1 program [13] in accordance with two subprograms. Equilibrium Compositions subprogram has been used for the Gibbs energy calculation, and the equilibrium element distribution has been determined by means of Reaction Equations subprogram using a principle of the Gibbs energy minimization.

Earlier this software package has been used by us at the research of equilibrium element distribution in iron-silicon-carbon-containing systems and for chloride sublimation processes [16].

3. Results and Discussion

At the first stage it has been found, that joint reduction of silicon and aluminum according to Eq. (1) from an amorphous SiO_2 is more preferable, than from a crystalline SiO_2 (Table 1).

$$2SiO_2 + Al_2O_3 + Fe + 7C = FeSi_2 + 2Al + 7CO \quad (1)$$

At the modeling of ferroalloy from the silica clay an amount of carbon has been calculated proceeding from a full reduction of silicon, aluminum and iron; and an iron amount – based on iron content in the ferroalloy – 55 %.

The curve of the temperature and carbon content influence on the equilibrium distribution of α silicon and aluminum is represented in Fig. 1. It follows from Fig. 1 that basic siliceous substances in the system “silica clay-carbon-iron” are SiO_2, $FeSiO_3$, Al_2SiO_3, $CaSiO_3$, $MgSiO_3$, Fe_3Si, FeSi, Si, $SiO_{(g)}$, and aluminum-containing compounds are Al_2SiO_5, Al and Al_2O_3. Besides the silicon in small amounts also passes into $FeSi_2$, Fe_3Si, CaSi. The silicon reduces at lower temperature in comparison with aluminum. It is connected with the fact that the temperature of silicon reduction beginning is 1941 K, and for aluminium – 2307 K.

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Table 1

Influence of temperature and SiO_2 form on ΔG (J) of silicon and aluminum reduction

SiO_2 form	1573 K	1673 K	1773 K	1873 K	1973 K	2073 K	2173 K	T_r, K
Crystalline	629.2	505	381.5	258.9	136.9	16.1	–104.0	2086.4
Amorphous	625.5	501.8	378.7	256.9	135.1	14.1	-106.3	2084.7

Note: T_r – temperature of the reduction beginning ($\Delta G = 0$)

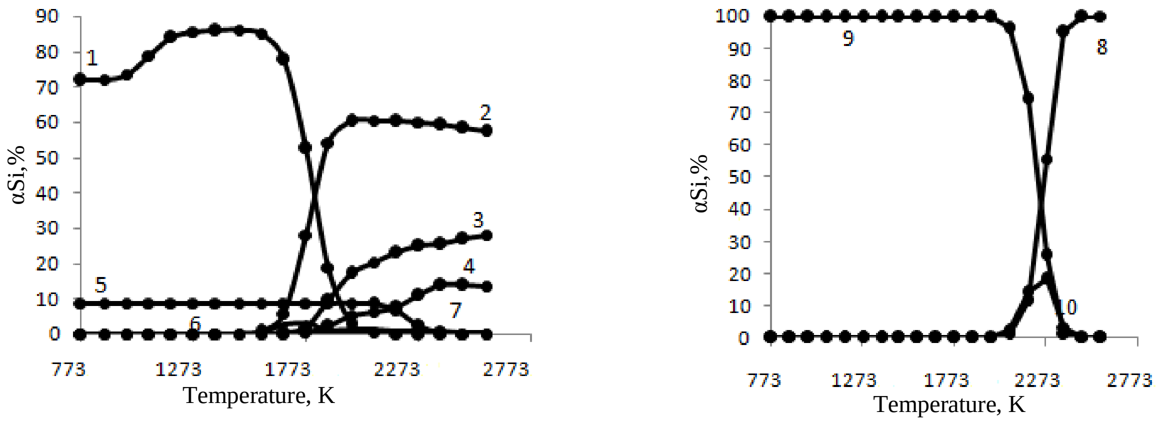


Fig. 1. Temperature effect on the α-Si and α-Al distribution in the system “silica clay-carbon-iron”: SiO_2 (1), FeSi (2), Al_2SiO_5 (3), Si (4), $SiO_{(g)}$ (5), Fe_3Si (6), FeSi (7), Al (8), Al_2SiO_5 (9) and Al_2O_3 (10)

Table 2

Influence of temperature and carbon content on the element silicon formation degree (%)

T, K	Carbon content, %			
	30	36	42	48
1473	$3.3 \cdot 10^{-4}$	$4.24 \cdot 10^{-4}$	$5.18 \cdot 10^{-4}$	$6.14 \cdot 10^{-4}$
1573	$9.42 \cdot 10^{-3}$	$12.1 \cdot 10^{-3}$	$14.91 \cdot 10^{-3}$	$17.168 \cdot 10^{-3}$
1673	0.13	0.17	0.21	0.25

Fig. 2 contains the information about the influence of temperature and carbon content on the equilibrium distribution degree of α-silicon in iron silicides. It follows from this figure that the silicon starts to turn into FeSi at $T \geq 1523$ K. The maximum αSi(FeSi) is observed at 1973–2273 K (60 %) and carbon content of 36–48 % relative to the silica clay weight. The silicon in an appreciable degree (>0.1 %) begins to reduce at $T \geq 1673$ K (Table 2).

Increase in the carbon amount from 30 to 48 % relative to the silica clay weight promotes the growth of silicon transition degree in element silicon; αSi(Si) increases from 12.92 to 33 %. In the process the dependence $\alpha Si(Si)_{max} = f(C)$ can be represented as follows:

$$\alpha Si(Si)_{max} = -131.01 + 44.289 \ln C \qquad (2)$$

The dependence of silicon transition degree in Fe_3Si and $FeSi_2$ on carbon content (C) has an extremal character (for Fe_3Si – at 1973 K, and for $FeSi_2$ – at 1773 K). The increase in carbon content from 30 to 42 % $\alpha Si(Fe_3Si)$ raises from 2.1 to 3.5 % and $\alpha Si(FeSi_2)$ changes from 1.15 to 1.37 %. Thus the carbon content influence on the values of αSi(FeSi) and $\alpha Si(FeSi_2)$ is described by Eqs. (3) and (4):

$$\alpha Si(Fe_3Si) = 33.309 - 1.4421C + 1.75 \cdot 10^{-2} \cdot C^2 \qquad (3)$$

$$\alpha Si(FeSi_2) = -157.9 + 13.164C - 0.36C^2 + 3.3 \cdot 10^{-3} \cdot C^3 \qquad (4)$$

The temperature and carbon content effect on the total silicon transition ($\alpha Si \sum$) in an alloy as FeSi, Fe_3Si, $FeSi_2$, CaSi, $CaSi_2$ and Si is represented in Fig. 2. It is obvious from the fidure that the appreciable (≥ 0.1 %) silicon transition in the ferroalloy is observed at 1473 K.

The increase in carbon amount leads to the increase of $\alpha Si\sum$. So, if carbon content is 30 % the maximum value of $\alpha Si\sum$ is 73 % at 2073–2273 K, and in the presence of 48 % of carbon $\alpha Si\sum$ increases to 91 % at 2373–2473 K. The dependence of $\alpha Si\sum_{max} = f(C)$ can be expressed by the equation:

$$\alpha Si\sum = -23.064 + 4.713C - 5.4 \cdot 10^{2} \cdot C^2 \qquad (5)$$

Because of the complex dependence of temperature and carbon amount influence on the extraction of silicon into the alloy, in further studies we used the method of the second order experimental design [16]. We found the following adequate regression equation: the effect of temperature (T, K) and the amount of carbon (C, % relative to the weight of the silica clay) on $\alpha\text{Si}\sum$.

$$\alpha\text{Si}\sum = 1.63\cdot10^{-10}\cdot T\cdot C - 9.51\cdot10^{-5}\cdot T^2 + 0.36T - -0.04C^2 + 0.93C - 378.42 \quad (6)$$

Using Eq. (6) and the methodology published in [17] we received three-dimensional image surface and its horizontal cuts as a dependence on temperatures and carbon amount (Fig. 3). Fig. 3 shows that high $\alpha\text{Si}\sum$ (85–87%) can be obtained in the technological field abc, that is takes place when the temperature is 2200–2470 K and 46–48 % carbon relative to the weight of the silica clay.

The temperature and carbon amount effect on aluminum content in the ferroalloy produced is represented in Table 3, and on silicon content and Al and Si sum in the ferroalloy – in Figs. 4 and 5.

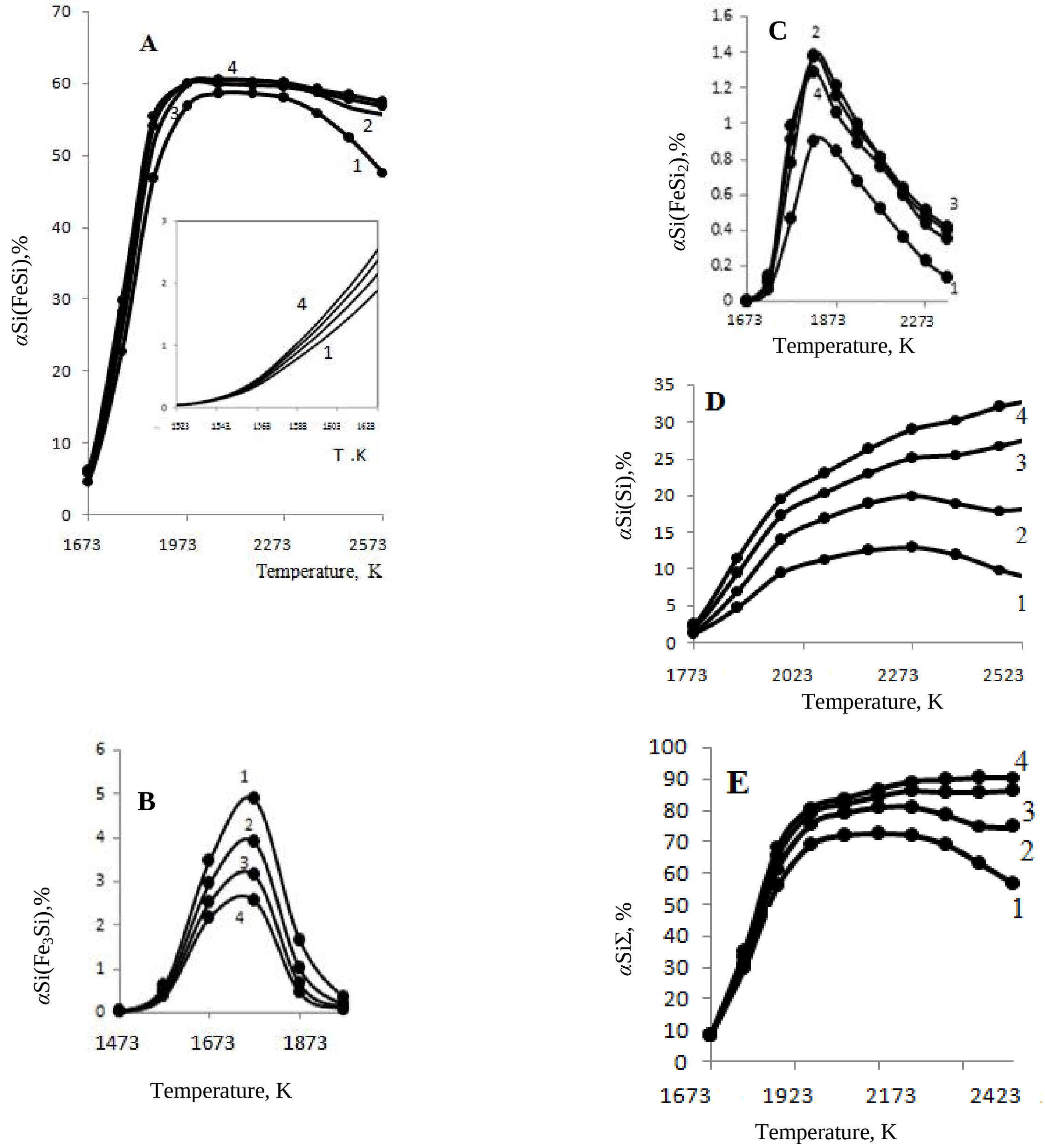
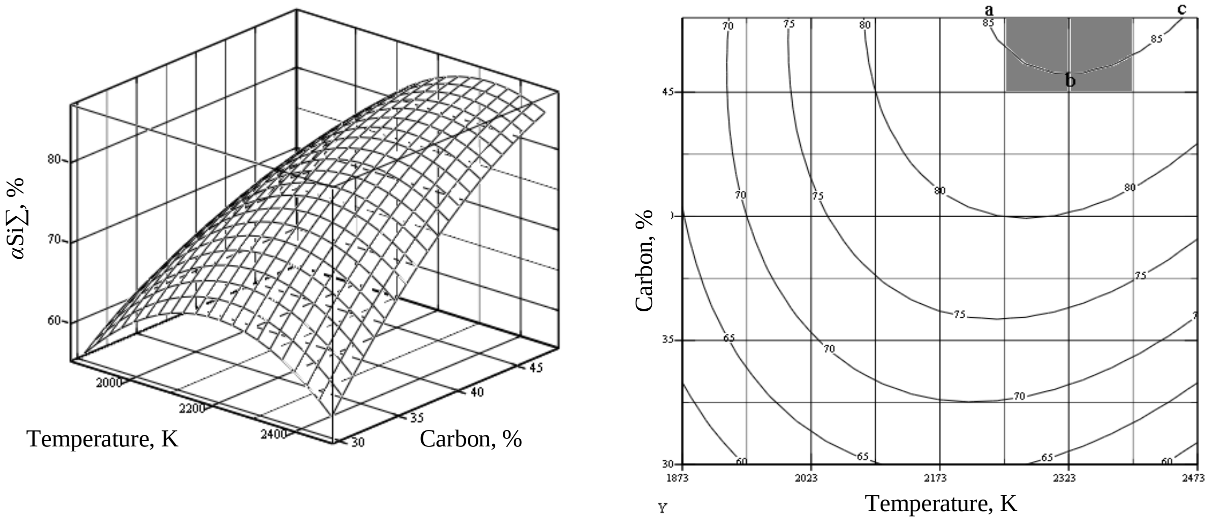


Fig. 2. Influence of temperature and carbon content on the silicon transition degree into iron silicides and element silicon in the system “silica clay-carbon-iron”. Silicon transition degree into FeSi (A), Fe_3Si (B), $FeSi_2$ (C), Si (D) and SiΣ (E). C, %: 30 (1); 36 (2); 42 (3) and 48 (4)



a) b)

Fig. 3. Influence of temperature and carbon on the degree of transition silicon in ferroalloy in the system "silica clay-carbon-iron": three-dimensional image of the response surface (a) and horizontal sections of the response surface (b). Digitals on the lines are $\alpha Si\sum$

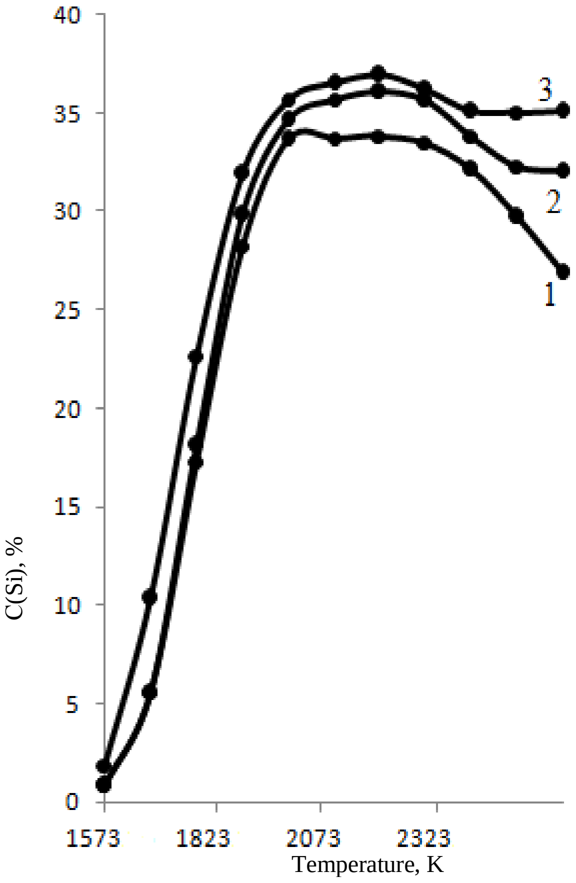


Fig. 4. Temperature and carbon amount effect on Si content in the ferroalloy with *C*, %: 30 (1); 36 (2) and 42 (3)

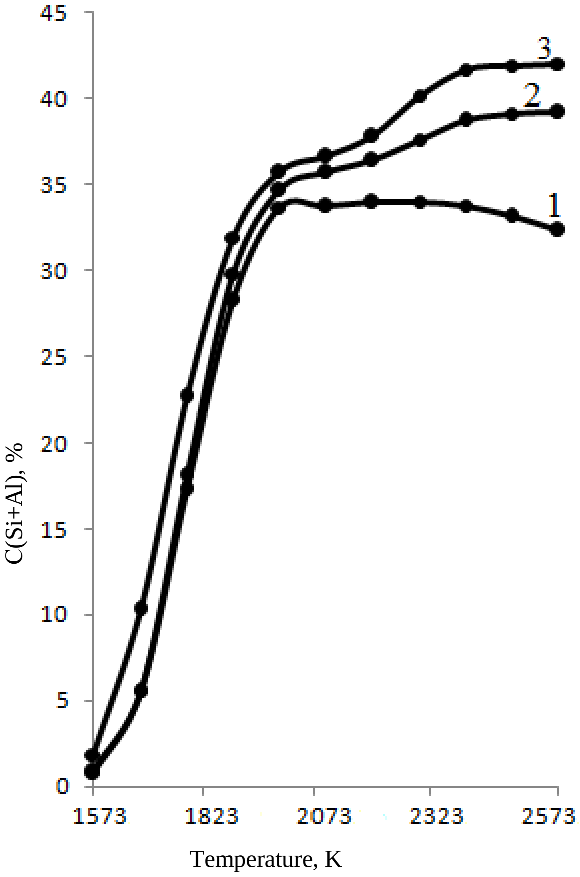


Fig. 5. Temperature and carbon amount effect on Si+Al content in the ferroalloy with *C*, %: 30 (1); 36 (2) and 42 (3)

Table 3

Temperature and carbon amount effect on aluminum content in the obtained ferroalloy

B, %	Temperature, K						
	1973	2073	2173	2273	2373	2473	2573
30	$6 \cdot 10^{-4}$	$6.5 \cdot 10^{-3}$	$6.9 \cdot 10^{-3}$	0.47	1.64	3.41	5.45
36	$2 \cdot 10^{-3}$	$3.1 \cdot 10^{-3}$	0.36	2.01	4.91	6.83	7.21
42	$4 \cdot 10^{-3}$	$7.9 \cdot 10^{-2}$	0.87	3.97	6.63	6.91	6.93

Note: B – carbon content relative to the silica clay weight

It follows from the data submitted in Table 2 that at 2373–2573 K the ferroalloy contains 6–7 % of aluminum.

The produced ferroalloy is a complex alloy; it represents ferrosilicoaluminum [14]. The content of the sum of silicon and aluminum in the alloy increases with increasing temperature and the amount of carbon (Fig. 5). Maximum Si+Al content in the alloy is 41 %. In accordance with Al/Si ratio in the obtained alloy (0.189–0.197) the given ferroalloy complex corresponds to ferrosilicoaluminum of FS45A10 grade [15].

4. Conclusions

On the basis of the results of thermodynamic modeling the interaction of silica clay with carbon and iron it is possible to draw the following conclusions:

– the joint reduction of silicon and aluminum from an amorphous SiO_2 and Al_2O_3 is characterized by higher thermodynamic probability than from a mixture of the crystalline SiO_2 and Al_2O_3;

– at the chemical interaction of an amorphous SiO_2-based silica clay with carbon in the presence of iron there is the reduction of silicon and aluminum and formation of Fe_3Si, FeSi, $FeSi_2$, Si, Al; in the process the silicon mainly converts into FeSi;

– at the silicon reduction there is the undesirable formation of the gaseous SiO; the transition degree of silicon in SiO can be reduced by means of decrease in temperature and increase in carbon content;

– a high (>85 %) degree of the silicon transition from the silica clay in the ferroalloy is observed at 2200–2470°K and 46 % of carbon (relative to the silica clay weight); the complex ferroalloy obtained – ferrosilicoaluminum – has the total silicon-aluminum content up to 42 %.

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Received: June 13, 2016 / Revised: August 28 2016 / Accepted: January 16, 2017

ТЕРМОДИНАМІЧНИЙ АНАЛІЗ ОДЕРЖАННЯ ФЕРОСПЛАВУ З КРЕМНІЙ-АЛЮМІНІЙ-ВМІСНОЇ ОПОКИ

Анотація. *Приведено результати термодинамічного моделювання процесу одержання комплексного Fe-Si-Al сплаву з опоки (77.8 % Al_2O_3, 11.6 % Al_2O_3). Термодинамічне моделювання проведено за допомогою програмного комплексу HSC-5.1. Визначено, що сумісне відновлення кремнію та алюмінію з аморфного SiO_2 та Al_2O_3 характеризується вищою реакційною здатністю, ніж із суміші кристалічного SiO_2 та Al_2O_3. Показано, що при відновленні кремнію відбувається небажане утворення газоподібного SiO; ступінь перетворення кремнію в SiO може бути зменшений за рахунок пониження температури і збільшення вмісту вуглецю.*

Ключові слова: *Si-Al-вмісна опока, термодинамічне моделювання, карботермічне відновлення, комплексний феросплав.*