серебра в штейн при оптимальных условиях плавки и оптимальном составе шлака составило 98,7-99,1 % и 79,9-98,3 %, соответственно.

Ключевые слова: коренная упорная руда золота, сульфидный медный концентрат, флюс, плавка на штейн, шлак.

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COMPLEX FERROALLOY OBTAINING from SILICON- and ALUMINUM-CONTAINING SILICA CLAY

Abstract. For increase of technological efficiency of raw materials in manufacture of silicon-containing alloys it is necessary to raise reactivity of SiO_2 in the raw materials. The silica clay, which contains to 90 % of SiO_2 in amorphous, high active state, can be used as such the raw material. The given article contains the research results of thermodynamic modelling and electrosmelting the Darbaza deposit silica clay with obtaining a complex ferroalloy. The thermodynamic modelling has been performed by means of a software package Outokumpu, and the electrosmelting – in an arc furnace. Temperature (from 500 to 2500°C) and iron amount (from 20 to 120 % from the silica clay weight) effect on Si and Al distribution degree in a system silica clay-C-Fe has been determined. It has been found the positive influence of iron on silicon extraction in an alloy (as FeSi, Fe_3Si, Fe_5Si_3, Si) and reduction of silicon loss as SiO(g). From the thermodynamic point of view the Darbaza silica clay can be applied for obtaining a ferroalloy FS45A10 (40 % of Si, 7.5-10 % of Al) at 2048-2100°C in the presence of 20-45 % of iron and 36 % of carbon from the silica clay weight. At the experimental electrosmelting a charge contained 54 % of the silica clay, 22 % of coke and 24 % of steel shavings in an arc ore-thermal furnace the formation of a complex ferroalloy contained 46-52.8 % of ∑Si+Al has been observed. In accordance with this parameter the ferroalloy obtained corresponds to ferrosilicoaluminum of a grade of FS45A10.

Keywords: silica clay, silicon, aluminum, reduction, thermodynamic modelling, electrosmelting, ferrosilicoaluminum.

Introduction. Ferrosilicoaluminum applies to the complex ferroalloys [1], which are used for steel deoxidation and reduction of content of nonmetallic inclusions in it. The ferrosilicoaluminum requirement in the CIS countries in the beginning of XXI century made 200 ths t a year [2]. Ferrosilicoaluminum is produced from bauxites, high-ash coal, ash of thermal power stations, carbonaceous rock [1-3]. In these raw materials silicon is in a crystalline state. Increase of intensity of smelting silicon-containing alloys including ferrosilicoaluminum is possible at use of the siliceous raw materials, which have raised reactivity. Silica clay, which contains to 90 % of silicon in the amorphous, high reactionary state (in comparison with crystalline SiO_2) can be used as such the raw material. The basis of this statement is the fact that $\Delta G^\circ_{298}(SiO_{2\ amorph}) = -849.8$ kJ/mol, and for SiO_2(β-quartz) ΔG°_{298} is more negative: -854.7 kJ/mol [4]. Presence of Al_2O_3 in silica clay expands its possibilities as the raw material; in particular silica clay can become a potential material for ferrosilicoaluminum manufacture. The given article contains the research results on obtaining ferrosilicoaluminum from the silica clay of the Darbaza deposit (South Kazakhstan area).

Experimental Part. The researches have been performed by means of a thermodynamic modelling method and electrosmelting the silica clay in a mixture with coke and iron shavings. The thermodynamic modelling of interaction of the silica clay with carbon and iron has been carried out with use of a software package HSC-5.1, developed by the Finnish metallurgical company Outokumpu [5]. This program allows describing in detail the processes of ferroalloy manufacture [6-8]. The modelling has been fulfilled in a temperature interval of 500-2500°C. The carbon amount has made 100 % from the amount theoretically necessary for the full reduction of silicon, aluminium and iron (36 % from the silica clay weight), and the iron amount – from 20 to 120 % from the silica clay weight. The equilibrium distribution of silicon and aluminium between the initial substances and reaction products has been determined.

Electrosmelting a charge contained the silica clay has been carried out in a single-phase furnace with controlled capacity (from 5 to 25 kW). A diameter of a graphite electrode is 3.0 cm, an internal diameter of a graphite crucible is 6 cm. Weight of the charge is 0.7-0.8 kg. After the electrosmelting the crucible with the charge has been cooled within 5-6 hours. Then the crucible has been broken, and the melt products have been weighed and analyzed for determination of content of basic components. The alloy density has been determined by a bottle method. Used the information [9] about connection of the total silicon and aluminum content (C_{Si+Al}, %) with the alloy density (D, g/cm^3) we have obtained the following equations $C_{Si+Al} = f(D)$:

for D = 2.33-3.52 g/cm^3:

$$C_{Si+Al} = 690.679 – 545.783D + 166.151D^2 - 17.467D^3; \quad (1)$$

for D = 3.52-6.09 g/cm^3:

$$C_{Si+Al} = 130.878 – 21.232D + 0.859D^2: \quad (2)$$

for D = 6.09-7.859 g/cm^3:

$$C_{Si+Al} = +3755.875 - 1524.918D^2 + 208D^3 – 9.515D^3: \quad (3)$$

These equations have been used for calculation of the total content of silicon and aluminum. Several samples of the ferroalloy have been analyzed with use of a scanning electron microscope (JSM-6490LV Japan). The silicon content has been determined in certain samples by means of decomposition with a mixture of hydrofluoric and nitric acids. At determination of optimum technological parametres in some cases a rototable second-order planning method has been used [10].

The researches have been performed with the silica clay with the following chemical composition: 77.8 % of SiO_2, 11.6 % of Al_2O_3, 1.5 % of CaO, 1.5 % of MgO, 3.4 % of Fe_2O_3, 1.8 % of K_2O, 0.7 % of Na_2O, 1.7 % - other. The coke contained 87.8 % of carbon and the steel shavings – 98.4 % of Fe.

Results Discussion. The information about temperature effect on equilibrium silicon distribution degree (α, %) in a system *silica clay-carbon-iron* at small iron amount (20 % from weight of the silica clay) is represented in figure 1. It follows from the figure that the silicon turns generally in the following compounds: SiO_2, $FeSiO_3$, Al_2SiO_3, SiC, Si, FeSi, SiO, $MgSiO_2$. And the FeSi formation is observed at T≥1300 °C, and the Si formation – at 1400 °C at that. Undesirable formation of gaseous SiO begins at 1500 °C. The increase in the iron amount to 120 % from the silica clay mass leads to the disappearance of SiC. In addition the iron content in the charge essentially influences on equilibrium silicon distribution degree (αSi) in the compounds FeSi, SiO(g) and Si.

The in-depth information about influence of temperature and iron amount on silicon distribution in silicon-containing substances is represented in figure 3.

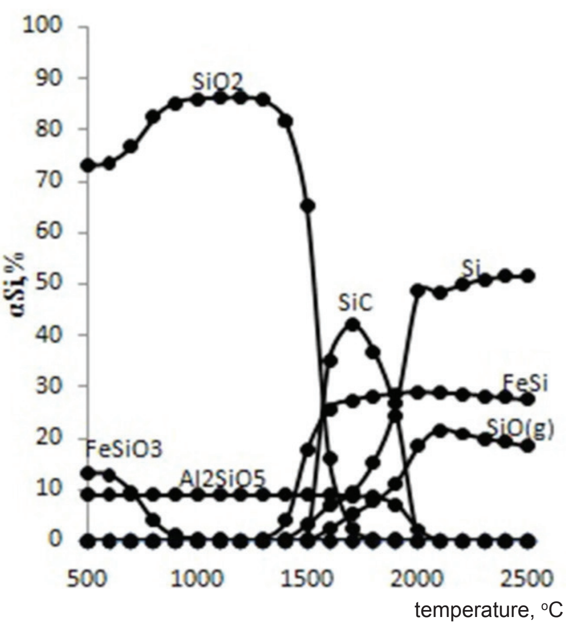


Figure 1 – Temperature effect on αSi in a system *silica clay-C-20%Fe*

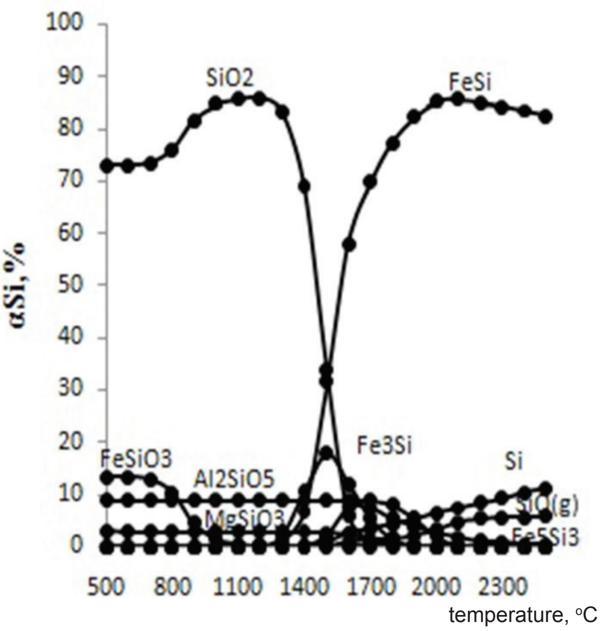
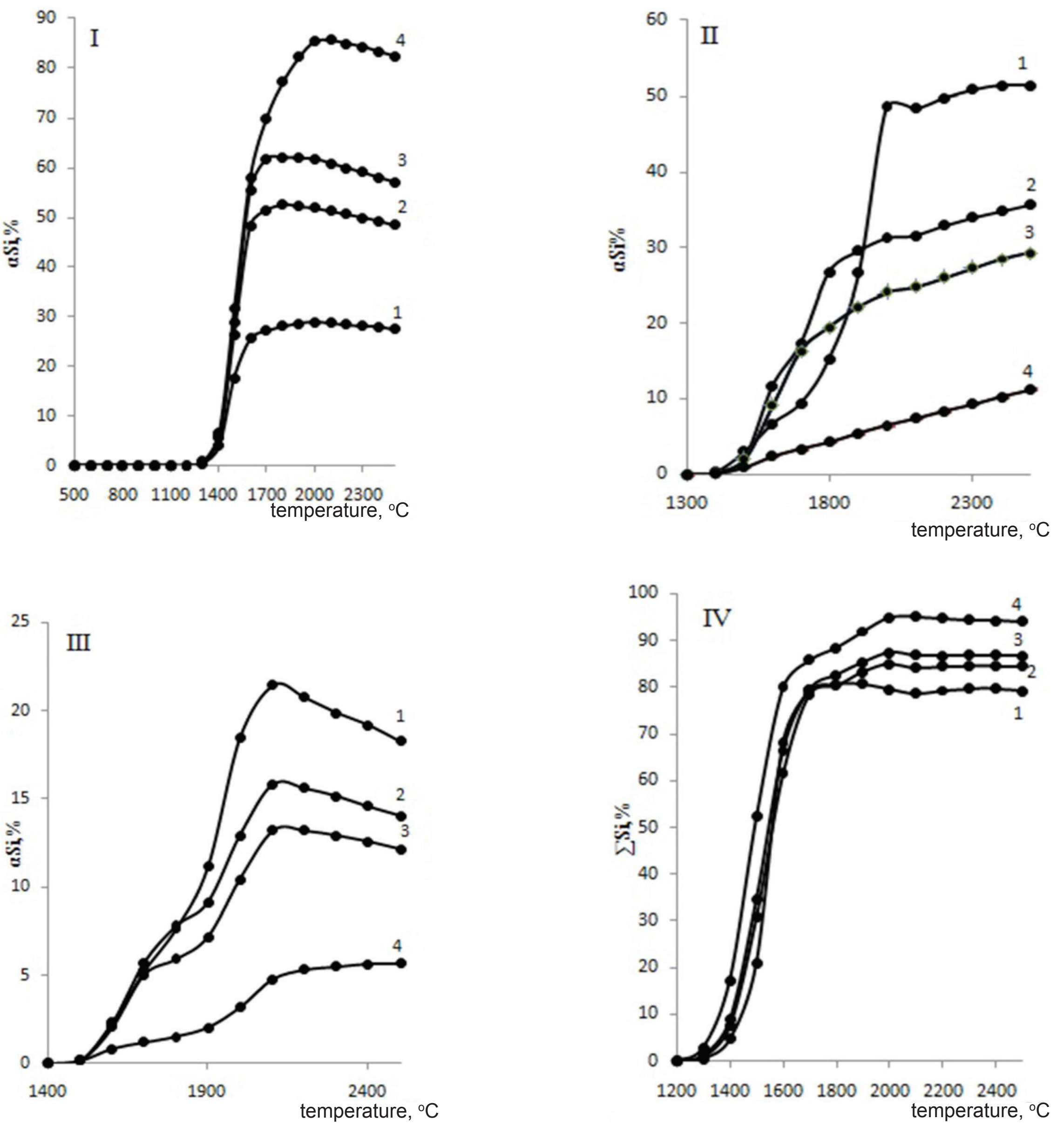


Figure 2 – Temperature effect on αSi in a system *silica clay-C-120%Fe*



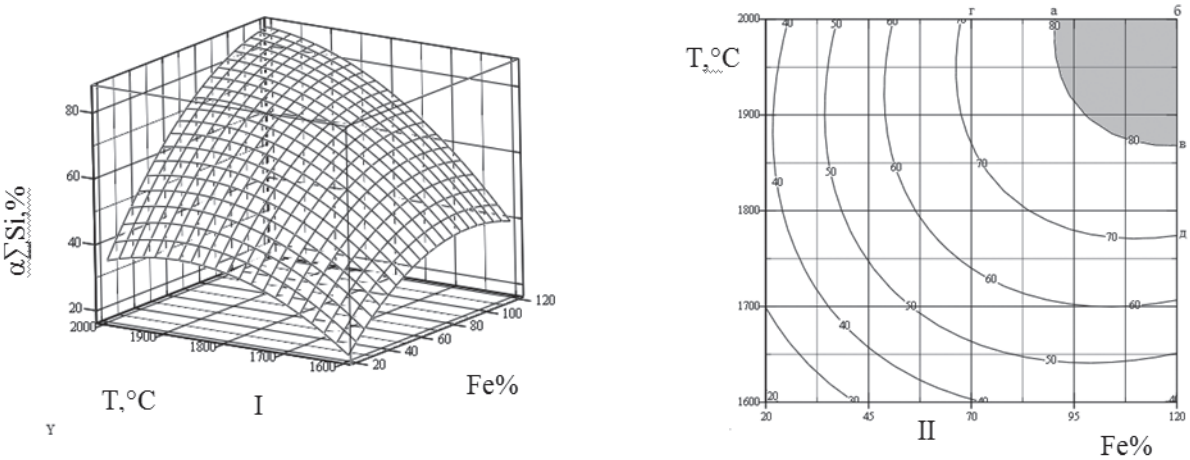
Extraction of silicon: I – in FeSi, II – in Si, III – in SiO(g), IV – the total extraction in an alloy
1 – 20 % of Fe, 2 – 40 % of Fe, 3 – 50 % of Fe, 4 – 120 % of Fe

Figure 3 – Influence of temperature and iron amount on αSi in silicon-containing substances in a system *silica clay-C-mFe*

It follows from the figure 3, that the increase in iron amount from 20 % to 120 % from the silica clay weight leads to the increase in αSi in FeSi from 29.2 to 86.2 %, reduction of αSi in SiO(g) from 23.1 to 5.4 %, decrease of αSi in element silicon from 50.6 % to 11.8 % and increase in silicon transition degree from the silica clay in an alloy (as iron and silicon silicides) from 80.6 to 95.4 %. The adequate regression equation of temperature and iron amount effect on the total transition degree of silicon in an alloy (αSi∑) looks like:

$$\alpha Si\sum = -866.981 + 0.958\cdot T - 2.58\cdot 10^{-4}\cdot T - 0.397\cdot Fe - 4.25\cdot 10^{-3}\cdot Fe^2 + 7.548\cdot 10^{-4}\cdot Fe\cdot T \quad (4)$$

A 3D picture of the dependence αSi∑ = f(T, Fe) and horizontal sections of a response surface have allowed to establish, that it is possible to reach αSi∑ from 80 to 89.3 % in a temperature area of 1860-2000°C and iron amount from 93 to 120 % from the silica clay weight (area *абв*, fig.4), and αSi∑ from 70 to 89 % - in a temperature interval of 1775-2000°C and iron amount of 68-120 % (in area *гбд*, figure.4).

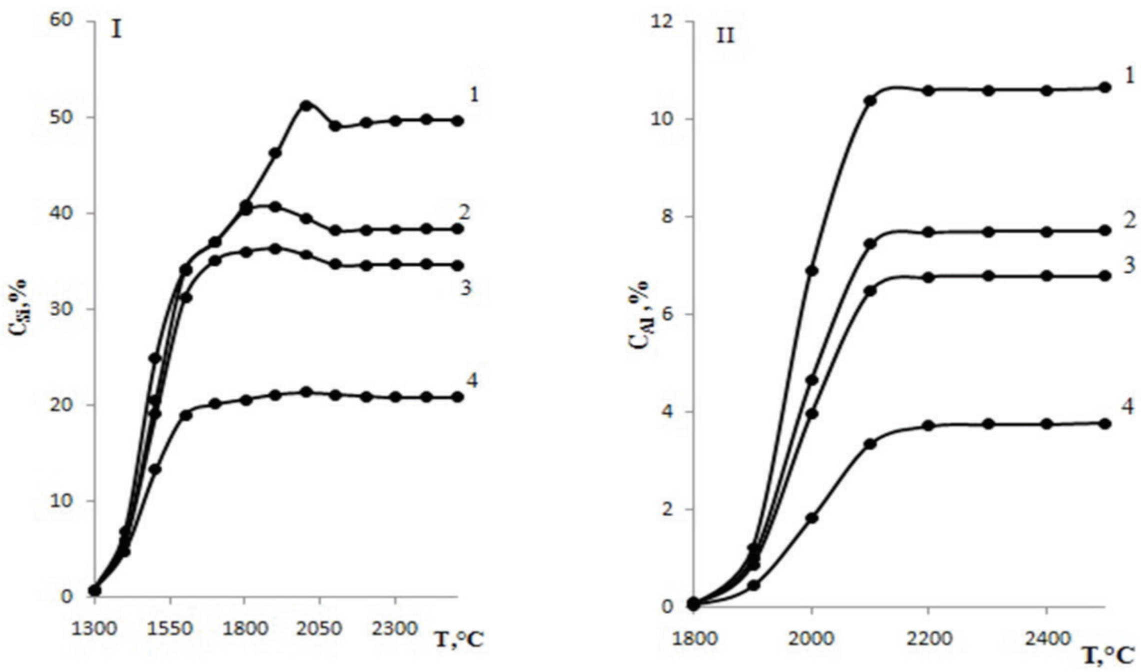


I – 3D picture II – Horizontal sections of a response surface

Figure 4 – Influence of temperature and iron amount on αSi∑

Iron in the charge influences not only on the transition degree of silicon in the alloy, but also on the silicon and aluminium content in the alloy (figure 5). The increase of iron amount leads to the reduction of silicon content in the alloy from 51.7 % to 20.8 % and aluminium content from 10.4 to 3.8 %.

At the comparison of figures 3 and 5 it is evident, that at constant temperature influence of the iron amount in the charge on αSi∑ and C_{Si} has opposite character; at the increase of iron amount the silicon extraction degree in the alloy increases, and silicon and aluminium concentration in the alloy decreases. It is obvious from figure 6.

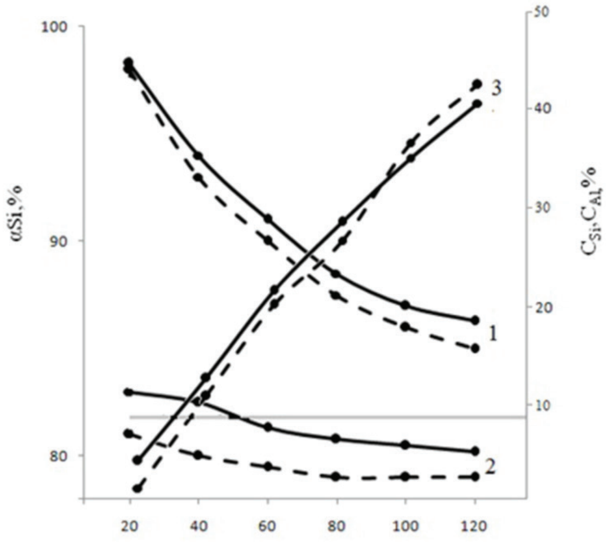


I – Si content

II – Al content

1 – 20 % of Fe, 2 – 40 % of Fe, 3 – 50 % of Fe, 4 – 120 % of Fe

Figure 5 – Influence of temperature and iron amount on silicon and aluminium content in the alloy



Fe, % from the silica clay weight
(--) – 2000 °C , (–) – 2100 °C
1 – C_{Si}, 2 – C_{Al}, 3 – αSi∑

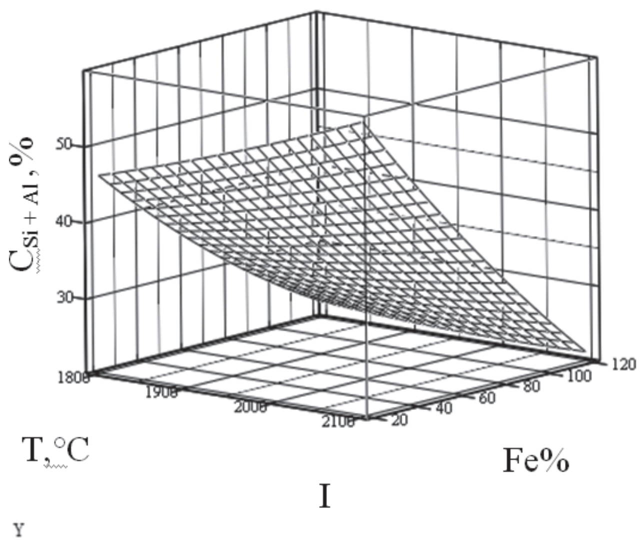
Figure 6 – Influence of temperature and iron amount on silicon extraction degree in the alloy and silicon and aluminium content in it

The alloy obtained is referred to the complex compounds contained silicon and aluminium; therefore it is important to know the iron amount and temperature effect on the total content of silicon and aluminium in the alloy (C_{Si+Al}). At the use of the rototable second-order planning method [10] the adequate equation C_{Si+Al} = f (Fe, T) has been found:

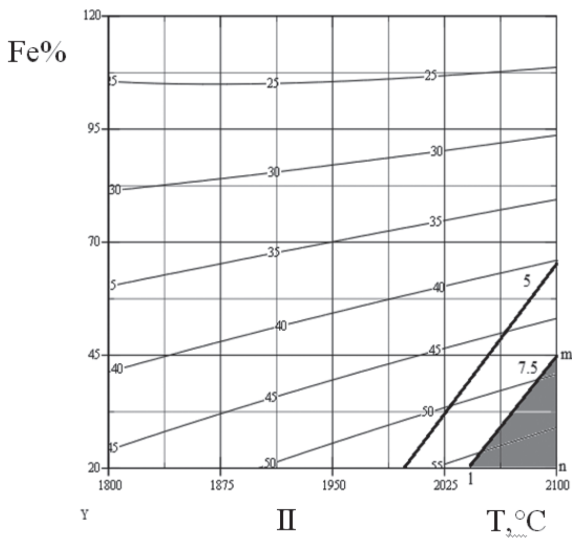
$$C_{Si+Al} = 46.18-3.757\cdot10^{-2}\cdot T+0.488\cdot Fe+2.28\cdot \cdot10^{-5}\cdot T+6.81\cdot10^{-4}\cdot Fe^{2}-4.57\cdot10^{-4}\cdot T\cdot Fe \quad (5)$$

On the basis of the equation a solid response surface and its horizontal sections have been constructed (figure 7). It is follows from this figure, that an alloy of a grade of FS45F10 (40 % of Si, 7.5-12.5 % of Al, ∑Si+Al = 47.5-52.5 % [2]) can be produced in a technological area *lmn* (T = 2048-2100°C and Fe = 20-45 % from the silica clay weight). In so doing the αSi in the alloy is 60-65 %.

At the electrosmelting a charge (54 % of the silica clay, 22 % of coke, 24 % of steel shavings) within 60 minutes a ferroalloy contained 46-52.8 % of ∑Si+Al has been obtained. The electron microscopic analysis of a surface of the ferroalloy sample is represented in figure 8. It is follows from this figure, that the alloy contains 48.92 % of ∑Si+Al (41.83 % of Si and 7.09 % of Al). The bottle method has been used for determination of the ferroalloy density, and then – the total silicon and aluminum content $\sum_{Si+Al}$ in it. The alloy produced according to the sum of silicon and aluminium (46-52.8 %) corresponds to ferrosilicoaluminum of a grade of FS45A10 [2].

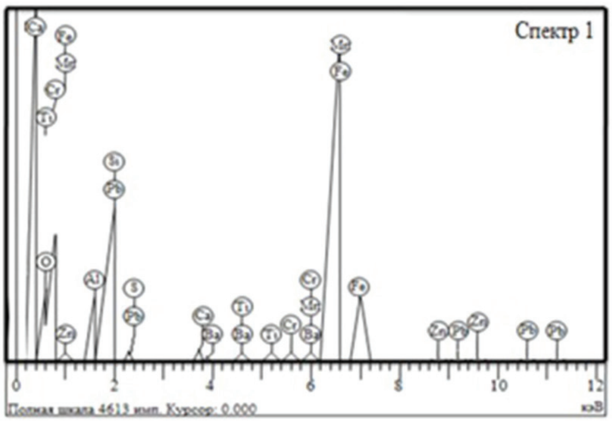


I – 3D picture
(-) - C_{Si+Al}, %



II – Horizontal sections of a response surface (-) - C_{Al}, %

Figure 7 – Temperature and iron amount effect on the total silicon and aluminum content in the alloy



I – Qualitative composition

Element	Content	Element	Content
Al	7.09	Fe	46.30
Si	41.83	S	0.07
Ca	0.13	Ba	0.06
Ti	0.69	Pb	0.03
Mn	0.42	Zn	0.04
Cr	0.01	O	2.90

II – Content of elements

Figure 8 – Electron microscopic analysis of the alloy

Conclusions. On the basis of the research results on obtaining an alloy contained silicon and aluminium from the silica clay it is possible to draw following conclusions:

- main products of the carbothermic reduction of silicon and aluminium from the silica clay are FeSi, Si, SiO(g), Fe_3Si, Fe_5Si_3, SiC, Al; the formation of iron silicides is observed at T ≥ 1300°C, and aluminium silicides – at T ≥ 1700°C;
- the increase in iron amount from 20 to 120 % from the silica clay mass allows to raise silicon transition degree from the silica clay in FeSi from 29.2 to 86.2 % and in the ferroalloy – from 79.6 to 94.9 %, reduces the undesirable silicon transition in gaseous SiO from 23.1 to 5.4 % and prevents practically completely the SiC formation;
- between the silicon and aluminum concentration in the alloy and silicon and aluminium transition degree in the alloy a inversely proportional dependence has been found: the increase in iron amount from 20 to 120 % from the silica clay weight at 2100°C reduces the aluminum concentration in the alloy from 10.4 to 3.4 %, the silicon concentration – from 50.3 to 20 %, and the silicon transition degree in the alloy increases from 79.6 to 94.9 %.
- from the thermodynamic point of view the Darbaza silica clay can be applied for obtaining a ferroalloy FS45A10 (40 % of Si, 7.5-10 % of Al) at 2048-2100°C in the presence of 20-45 % of iron and 36 % of carbon from the silica clay weight. At the experimental electrosmelting a charge contained 54 % of the silica clay, 22 % of coke and 24 % of steel shavings in an arc ore-thermal furnace a complex ferroalloy contained 46-52.8 % of ∑Si+Al has been obtained. In accordance with this parameter the ferroalloy obtained corresponds to ferrosilicoaluminum of a grade of FS45A10.

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ТҮЙІНДЕМЕ

Кремний құрамдас балқымалар өндірісінде технологиялық тиімділікті жақсарту үшін шикізаттағы SiO_2 реакциялық қабілеттілікті жоғарылату қажет. Осындай шикізатты материал ретінде айтарлықтай реакциялық қабілеті жоғары, аморфты түрде 90 % дейін SiO_2 кездесетін опока қолданылуы мүмкін. Мақалада Дарбаза кенорнының опокасын электрлібалқыту және термодинамикалық модельдеу зерттеулерінің қорытындысы келтірілген, термодинамикалық модельдеу Outokumpu кешенді бағдарламасы көмегімен, ал электрлі балқыту доғалы пеш көмегімен жүргізілді. Опока-Fe-C жүйесінде Si және Al бөліну дәрежесіне темір мөлшері (опоканың мөлшері 20 дан 120 % дейін) мен температураның (500 ден 2500 °C) әсер етуі анықталды. Балқымадағы кремнийдің бөлінуіне SiO(g)-ден кремнийдің жоғалуының төмендеуі және темірдің оң әсер етуі (FeSi, Fe_3Si, Fe_5Si_3, Si түрінде) анықталды. Термодинамикалық тұрғыдан қарастырсақ: опока массасынан 36 % көміртегі және 20-45 % темір қатысуында, 2048-2100 °C температурада ФС4А10 (40 % Si, 7.5 % – 10 % Al) ферробалқыма алуға болады. 54 % опока, 22 % кокс және 24 % болат жоңқасын құрайтын шихтаны (доғалы кендітермиялық пеште) эксперимент түрінде жүргізгенде, ФС45А10 маркалы ферросиликоалюминийге сәйкес кремний және алюминийді құрайтын 46-52,8 % ∑Si және Al кешенді ферроқорытпа түзілгендігі анықталды.

Түйінді сөздер: опока, кремний, алюминий, тотықсыздандыру, термодинамикалық модельдеу, электрлі балқыма, ферросиликоалюминий

РЕЗЮМЕ

Для улучшения технологической эффективности сырья в производстве кремний содержащих сплавов необходимо повысить в сырье реакционную способность SiO_2. В качестве такого сырьевого материала может быть использована опока, в которой SiO_2 до 90 % находится в аморфной, более реакционноспособной форме. В статье приводятся результаты исследований термодинамического моделирования и электроплавки опоки Дарбазинского месторождения, с получением комплексного ферросплава. Термодинамическое моделирования проводилось с помощью программного комплекса Outokumpu, а электроплавка - в дуговой печи. Определялось влияние температуры (от 500 до 2500 °C) и количество железа (от 20 до 120 % от массы опоки) на степень распределения Si и Al в системе опока-Fe-C. Установлено позитивное влияние железа на извлечение кремния в сплав (в виде FeSi, Fe_3Si, Fe_5Si_3, Si) и уменьшению потерь кремния с SiO(g). С термодинамической точки зрения из опоки можно получить ферросплав ФС4А10 (40% Si, 7.5 %-10% Al) при 2048-2100 °C, в присутствии 20-45 % железа и 36 % углерода от массы опоки: Экспериментально электроплавкой (в дуговой руднотермической печи) шихты, содержащей 54 % опоки, 22 % кокса и 24 % стальной стружкой установлено образование комплексного ферросплава с 46-52.8 % ∑Si и Al; который по содержанию кремния и алюминия соответствует ферросиликоалюминию марки ФС45А10.

Ключевые слова: опока, кремний, алюминий, восстановление, термодинамическое моделирование, электроплавка, ферросиликоалюминий

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