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Obtaining of ferrosilicon from technogenic magnetite concentrate

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Abstract. The article presents the results of studies on the production of ferrosilicon from iron ore (magnetite) concentrate and quartzite. The studies were carried out by thermodynamic simulation using the HSC-5.1 software package, based on the principle of Gibbs minimum energy and electric smelting of the concentrate together with coke and quartzite in a single-electrode arc furnace. Based on the studies, it was found that, under equilibrium conditions, the interaction of magnetite concentrate with silicon oxide (IV) and carbon is accompanied by the formation of FeSi (> 1200 °C), Fe₃Si (> 1100 °C), FeSi₂ (> 500 °C), Zn_g (> 800 °C) Pb_g (> 1200 °C); the degree of silicon extraction into the ferroalloy depends on the ratio in the SiO₂ / Fe₃O₄ mixture, decreasing from 85.6 to 66.1 (for example, at 1700°C) with an increase in the SiO₂ / Fe₃O₄ ratio from 0.42 to 1.25. When melting a mixture containing 70% concentrate, 11% quartzite, 19% coke, a ferroalloy containing 15-18% Si. The resulting ferroalloys are graded from FeSi15 to FeSi45.

Keywords: magnetite concentrate, quartzite, coke, thermodynamic modeling, electric melting, ferrosilicon.

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Introduction

Upon receipt of ferrosilicon, an obligatory component of the charge is iron shavings, the amount of which varies from 780 kg when smelting 1 ton of FS25 ferrosilicon to 250 kg when smelting FS75 ferrosilicon [1]. Now iron shavings are scarce material, the cost of which is 210-220 dollars per 1 ton [2]. It is possible to reduce the dependence of the production of silicon ferroalloys on scarce steel chips if another iron-containing material is used in

the technology. Research in this direction is carried out by several methods. Thus, proposals are known for replacing steel chips in the production of ferrosilicon with other types of iron-containing raw materials, such as ferruginous quartzite, scrap metal, iron ore, pellets of pyrite cinders, etc. [3-6, 15]. Processing plant wastes are important sources of various types of mineral raw materials [7]. For example, based on the fact that the tailings of the Balkhash ore dressing plant contain 17% Fe [8] at Iron Concentrate Company LLP [9] from the

flotation tailings of copper-containing Sayak and Shatyrkol ores of the Balkhash ore dressing plant, iron-containing concentrate is obtained - magnetite concentrate containing 58 - 64% Fe. This concentrate can be used as a substitute for steel chips [10].

From a thermodynamic point of view, the reaction

$$6SiO_2 + Fe_3O_4 + 16C = 3FeSi_2 + 16CO$$
 (1)

more preferred than reaction

$$2SiO_2 + Fe + 4C = FeSi_2 + 4CO \tag{2}$$

since it starts at 1392 0 C, and the second when 1617 0 C (table 1).

The aim of the work was to determine the possibility of obtaining a silicon alloy from magnetite concentrate, with the simultaneous extraction of lead and zinc from it.

Materials and methods

Table 1 Influence of temperature on $\Delta G (kJ / mol FeSi_2) *$

The studies were carried out by the method of thermodynamic modeling and electric melting of the charge in an arc laboratory electric furnace.

Thermodynamic modeling was carried out using the HSC-5.1 software package and using the Equilibrium Compositions option [11]. The calculation of the equilibrium state by the software package is based on the principle of minimum Gibbs energy. Determination of the equilibrium degree of distribution of elements between substances was carried out according to our algorithm [12]. The electric smelting of the charge was carried out in an electric arc furnace (Fig. 1)

Energy was supplied to the furnace from the TDZhF transformer through an upper graphite electrode 3 cm in diameter and a graphite bottom. Before melting, a graphite crucible with an inner diameter of 6 cm and a height of 12 cm was installed on a graphite hearth. Then, the crucible was heated by an arc for 15-20 minutes. During this period, the current strength was 300-350 A and voltage 30-40V.

Reaction number	Temperature, ⁰ C										
	1000	1100	1200	1300	1392	1400	1500	1600	1617	1700	1800
1	343,2	255,1	167,0	79,9	0,0	-7,1	-93,8	-180,3	-119,4	-263	-346,4
2	406,1	339,5	273,2	207,2	147,0	141,4	75,0	10,9	0,0	-53,4	-116,8

*- ΔG_0 calculation was performed using the software package HSC-5.1 [11]









furnace casing, 2 - chromomagnesite lining, 3-carbon graphite hearth,4-graphite crucible, 5-carbon graphite "pad",
 6-transformer TDZhF-1002, 7 - graphite electrode, 8 - lower current lead, 9-12 - controlling ammeters and voltmeters,
 13 - electrode movement mechanism, 14 - flexible part of the short network, 15 - furnace cover

I - general view; II - sketch of a furnace with knots

Figure 1 Single-electrode arc furnace

The constancy of the furnace power was supported by a terristor controller and the position of the electrodes in the crucible. The mass of the melted charge was 600-800g. The half-mass of the charge was initially loaded into the preheated crucible. Smelted it for 5-7 minutes. Then the remaining charge was loaded and melted in the furnace in three steps. When melting, the current strength was 400-450 A and voltage 20-30V. After melting, the crucible cooled in the furnace for 6-7 hours. Then it was removed from the furnace and cooled on a ceramic stand for another 4-5 hours. crashed. The content of the broken crucible was sorted into ferroalloy, slag. The concentration of silicon, aluminum, and iron in the alloy was determined by the atomic adsorption method on an AAS-1 device (Germany) using a JEOL JSM-6490LM scanning electron microscope (Japan). Using the pycnometric method, the density of the resulting alloy was determined. Then, by the density of the alloy, the silicon content in the alloy was determined [11]. The degree of extraction of metals in the ferroalloy was determined by the ratio of the mass of metal in the ferroalloy to the mass of metal in the charge. Iron ore (magnetite) concentrate of Concentrate Company LLP (Balkhash), Iron containing: - 85.9% Fe₃O₄, 9% SiO₂, 2% CaO, 1.4% Al₂O₃, MnO and K₂O at 0.3%, 0.2 % Na₂O, 0.4% MgO, 0.2% ZnO, 0.4% PbO; - coxic (86.5% C, 4.2% SiO₂, 1.5% CaO, 0.3% MgO, 1.9% Al₂O₃,

Research results

Thermodynamic modeling was carried out with two compositions of mixtures (table 2).

It follows from the figures that in the systems under consideration, the products of interaction are 2FeO * SiO₂ (from 500 to 1400 $^{\circ}$ C), CaSiO₃, Na₂SiO₃, K₂SiO₃ (from 500 to 1900 $^{\circ}$ C), FeSi (from 1200 to 1900 $^{\circ}$ C), Fe₃Si (from 1100 to 1900 $^{\circ}$ C), Fe₂Si (from 1500 to 1900 $^{\circ}$ C), SiO_g (from 1400 to 1900 $^{\circ}$ C), Fe (from 500 to 1900 $^{\circ}$ C), SiC (from 1500 to 1900 $^{\circ}$ C), Zn (from 800 to 1900 $^{\circ}$ C), Pb (from 1200 to 1900 $^{\circ}$ C).

Figures 2 and 3 show that at relatively low temperatures (500 - 760 $^{\circ}$ C), iron from Fe3O4 goes into 2FeO·SiO₂, and then (from 900 to 1300 $^{\circ}$ C) the iron completely goes into elemental. 2FeO·SiO2 - fayalite in the system exists up to 900 $^{\circ}$ C, i.e. to its melting point (1178 $^{\circ}$ C) [1]. At temperatures above 1300 $^{\circ}$ C, silicon begins to recover, which in the presence of reduced iron forms a ferroalloy containing FeSi, Fe3Si, Fe. A complete transition of silicon to the alloy from the first system does not occur due to the formation of more than 1600 $^{\circ}$ C gaseous SiO.

N⁰	The content in the mixture, kg								γ*		
Mixtures	Fe ₃ O ₄	SiO ₂	CaO	Al ₂ O ₃	MgO	Na ₂ O	K ₂ O	PbO	ZnO	С	
1	85,9	107,1	1,8	1,2	0,3	0,3	0,2	0,4	0,2	61	1,25
2	85,9	35,6	1,8	1,2	0,3	0,3	0,2	0,4	0,2	34	2,042
* γ- mass rat	io SiO ₂ /Fe ₃	O_4			•	•	•	•			

 Table 2 The composition of the mixtures



Figure 2 Effect of temperature on the quantitative distribution of silicon (I) and iron (II) in system № 1



Figure 3 Effect of temperature on the quantitative distribution of silicon (I) and iron (II) in system № 2



Figure 4 Effect of temperature on the equilibrium distribution of zinc and lead

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Figure 5 shows the effect of temperature on the equilibrium total degree of distribution of silicon in the alloy in the form FeSi₂, FeSi, Fe₃Si and SiC (α Si_{alloy}). It is seen that from the first mixture (at γ = 1.25) αSi_{alloy} is less than from the second (at $\gamma =$ 0.42). This is due to the fact that when the first mixture is heated, a significant transition of silicon to gaseous SiO_g is observed (at 1700 °C-16.2%, and at 1900 °C -31.8%), while from the second system the degree of transition of silicon to SiOg is, respectively 4.2% and 6.1%. From figure 6 it follows that the ferroalloy formed during heating of the first mixture contains more silicon than when heating the second. In accordance with [14], the conditions for the formation of vintage ferrosilicon can be determined from Figure 6. Vintage ferroalloy from magnetite concentrate can be obtained in the almfb region. So, in the acdb region (at 1400-1500 ⁰C) ferrosilicon of the FeSi10 brand is formed, and the cefd region (at 1470-1900 °C) - of the FeSi15 brand, and in the *ebmf* region (at 1510-1900 °C) the FeSi25 brand. The extraction of zinc and lead in the gas phase is shown in table 3.



Figure 5 Effect of temperature and mixture composition on the equilibrium degree of silicon distribution

It can be seen that regardless of the composition of the initial mixtures $\alpha Zn_g > \alpha Pb_g$. Moreover, the complete distillation of zinc occurs at a temperature of more 1500 °C. High (\geq 70%) distillation is observed at a temperature of more 1700 °C. Before electrofusion, the magnetite concentrate was poured together with bentonite clay and liquid glass, then granules (4-7 mm) were dried at 120 0 C coke and quartzite were used with a 3-5 mm fraction.



1-mixture № 1, 2-mixture № 2

Figure 6 Effect of temperature and composition of the mixture on the concentration of silicon in the alloy

Table 3 Effect of temperature on the degree of formation of gaseous zinc and lead (aZng, aPbg)

№ mixture	Metal	Temperature, ⁰ C								
		1100	1200	1300	1400	1500	1600	1700	1800	1900
1	Zn	75,6	86,2	92,5	96,2	98,8	99,4	99,9	99,9	99,9
	Pb	0,4	1,2	3,1	8,1	23,7	46,7	62,2	73,9	82,8
2	Zn	61,4	76,2	85,6	92,5	97,5	99,4	99,9	99,9	99,9
	Pb	0,2	0,6	1,6	4,1	14,2	38,4	70,8	82,5	88,9

Table 4 The composition of the charges for meltingmagnetite concentrate

	Co	The predicted		
<u>№</u> Charge	Concentrate	Quartzite	Coke	Si content in the alloy, %
1	37,5	37,5	25,0	45
2	59,0	22,0	21,0	25
3	70,0	11,0	19,00	15

We carried out electric melting of granular magnetite concentrate together with coke and quartzite. The mixture was compiled on the basis of obtaining 15%, 25%, 45% silicon in the alloy (the composition of the mixture is given in table 4).

Using the pycnometric method (according to the density of the ferroalloy), it was found that the silicon content in the ferroalloy obtained from the first charge was 29-41%, from the second 21-26%, for the third - 15-18%. In accordance with [13] obtained ferroalloys corresponds to ferrosilicon grades FeSi15 and FeSi45. Figure 7 shows a photograph of the alloy, and Figure 8 shows the results of electron microscopic analysis of the surface of ferroalloys.



Figure 7 Photograph of a sample of ferroalloy, obtained from the mixture of the first composition



Element	Weight,%	Element	Weight,%
Al	0,77	Cr	0,78
Si	32,87	Mn	0,18
Ca	0,12	Fe	64,44
Ti	0,29	Ni	0,55



Element	Weight,%	Element	Weight,%
Al	1,17	Cr	0,09
Si	16,26	Mn	0,11
Ca	0,20	Fe	81,68
Ti	0,26	Cu	0,21

I - ferroalloy from the charge of the first composition, II - ferroalloy from the charge of the second composition
 Figure 8 Electron microscopic analysis of the surface of ferroalloys

Conclusions

Based on the results of obtaining ferroalloy from magnetite concentrate, the following conclusions can be drawn:

- under equilibrium conditions, the interaction of a magnetite concentrate with silicon oxide (IV) and carbon is accompanied by the formation of FeSi (> 1200 $^{\circ}$ C), Fe₃Si (> 1100 $^{\circ}$ C), FeSi₂ (>500 $^{\circ}$ C), Zn_g (>800 $^{\circ}$ C), Pb_g (>1200 $^{\circ}$ C); the degree of extraction of silicon in the ferroalloy depends on the ratio in the mixture SiO₂/Fe₃O₄ decreasing from 85.6 to 66.1 at 1700 $^{\circ}$ C with increasing ratio SiO₂/Fe₃O₄ from 0,42 to 1,25;

- formation 2FeO·SiO₂ from Fe₃O₄ occurs in the temperature range 500 – 900 $^{\circ}$ C, that is, to the melting point of fayalite (1178 $^{\circ}$ C), therefore, the formation of ferrosilicon comes from the system SiO₂ – Fe – C

-during electrosmelting of a mixture consisting of 37.5% concentrate, 37.5% quartzite, 25% coke, a ferroalloy containing 29-41% silicon is formed, and when melting a mixture containing 70% concentrate, 11% quartzite, 19% coke, a ferroalloy containing 15- 18% Si; the resulting ferroalloys have a brands from FeSi15 дo FeSi45.

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Техногенді магнетитті концентраттан ферросилиций алу

Шевко В.М., Каскин П.В., Бадикова А.Д., Аманов Д.Д

Түйіндеме. Мақалада теміркенді (магнетитті) концентраттан және кварциттен ферросилиций алу бойынша зерттеу нәтижелері келтірілген. Зерттеу Гибсстің минимизация энергиясының приципіне негізделген, HSC-5.1 кешенді бағдарламасын қолданумен термодинамикалық модельдеу әдісін және доғалы бір электродты пеште кокс, кварцит, концентратты бірге электрлі балқытумен жүргізілді. Жүргізілген зерттеу нәтижелері бойынша: магнетитті концентрат, кремний оксиді (IV) және көміртегімен біркелкі жағдайда әрекеттесіп FeSi (> 1200 $^{\circ}$ C), Fe3Si (> 1100 $^{\circ}$ C), FeSi2 (>500 $^{\circ}$ C), Znr (>800 $^{\circ}$ C), Pbr (>1200 $^{\circ}$ C) түзіледі; кремнийдің ферроқорытпаға өту дәрежесі қоспадағы SiO₂/Fe₃O₄ қатынасына тәуелді 85,6-дан 66,1 –ге дейін (мысалы 1700 $^{\circ}$ C) төмендейді,

SiO₂/Fe₃O₄ қатынасы 0,42-ден 1,25-дейін болғанда көтеріледі. 37,5% концентраттан, 37,55% кварциттен, 25 % кокстан тұратын шихтаны электрлі балқытуда 29-41% кремний3 бар ферроқорытпа, ал 70% концентраттан, 11% кварциттен, 19% кокстан құралған шихтаны электрлі балқытуда 15-18% Si бар ферроқорытпа түзіледі. нәтижесінде FeSi15 тен FeSi45 дейінгі маркалы ферроқорытпа алынады.

Түйін сөздер: магнетитті концентрат, кварцит, кокс, термодинамикалық модельдеу, электрлі балқыту, ферросилиций.

Получение ферросилиция из техногенного магнетитового концентрата

Шевко В.М., Каскин П. В., Бадикова А.Д., Аманов Д.Д.

Аннотация. В статье приводятся результаты исследований по получению ферросилиция из железорудного (магнетитового) концентрата и кварцита. Исследования проводили методом термодинамического моделирования с использованием программного комплекса HSC-5.1, основанного на принципе минимума энергии Гиббса и электроплавкой концентрата совместно с коксом и кварцитом в дуговой одноэлектродной печи. На основании проведенных исследований установлено что, в равновесных условиях взаимодействие магнетитового концентрата с оксидом кремния (IV) и углеродом сопровождается образованием FeSi (> 1200 $^{\circ}$ C), Fe₃Si (> 1100 $^{\circ}$ C), FeSi₂ (>500 $^{\circ}$ C), Zn_r (>800 $^{\circ}$ C), Pb_r (>1200 $^{\circ}$ C); степень извлечения кремния в ферросплав зависит от отношения в смеси SiO₂/Fe₃O₄ уменьшаясь от 85,6 до 66,1 (например при 1700 $^{\circ}$ C) при увеличении отношения SiO₂/Fe₃O₄ от 0,42 до 1,25. При электроплавке шихты, состоящей из 37,5% концентрата, 37,5% концентрата, 11% кварцита, 19% кокса –ферросплав с содержанием 15-18% Si. Полученные ферросплавы обладают марочностью от FeSi15 до FeSi45.

Ключевые слова: магнетитовый концентрат, кварцит, кокс, термодинамическое моделирование, электроплавка, ферросилиций.

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