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FERROSILICON PRODUCTION METHOD USING SINTERED IRON SILICATE - FAYALITE

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The study aims experimentally investigate how to obtain a ferrosilicon alloy using iron silicate - fayalite generated after flotation enrichment of slag in pyrometallurgical production of copper. This material contains about 46 % iron and about 27 % silicon dioxide. Due to its dispersed structure, fayalite is first sintered. The article describes mathematical and physical modeling of the agglomeration and ore thermal process for the production of ferrosilicon. The main fraction of the obtained agglomerate (57,60 %) is over 15 mm. In the electric arc furnace, the time for refining the agglomerate tap to tap is 40 - 60 minutes. The obtained alloy yield is 46 %. In the three melts, the silicon content in the alloy averaged 44 %, meeting the ferrosilicon standard.

Keywords: ferrosilicon, electric arc furnace (EAF), sintering, Gibbs free energy, iron-silicate - fayalite

INTRODUCTION

Ferrosilicon is an alloy of iron and silicon. It is usually produced in submerged arc furnaces by reduction of silicon dioxide or quartz sand (SiO_2) with coke in the presence of iron. Its application for the deoxidation of steel makes it the so-called basic alloy in steel production [1 - 3]. In terms of end-use, ferrosilicon is mainly used for the production of carbon and other alloy steels, stainless steel, cast iron, and electrical steel. In addition, there is a growing demand for alloys in the semiconductor and automotive industries. In 2020, the global ferrosilicon market was estimated at $ 10,6 billion, with an expected annual growth rate of 0,4 % over the period 2020 - 2027 [4].

Pyrometallurgical production of copper from copper concentrates results in copper slag, which contains mainly iron, silicon, and some valuable metals such as copper, zinc, lead, cobalt, and nickel. After flotation enrichment, iron silicate - fayalite is obtained, and the main part of it is deposited. Globally, the deposit of fayalite in annual terms is about 50 million tons, of which in Bulgaria alone there are about 1 million tons. These waste resources have a potential impact on the environment and in particular, they pollute water. This is the main reason to look for opportunities for their utilization.

The main element in the composition of iron silicate is iron, which is about 46 %; Fe_2O_3 is over 60 %. The content of silicon dioxide is about 27 %. The main phases are fayalite, magnetite and in some cases in smaller quantities - quartz and mica. Given the high iron content, this material could be a raw material in the production of iron-based alloys. Iron silicate has a finely dispersed structure with a predominant content (about 95 %) of a fraction below 100 μm. [5]. Given the atypical composition and grain size [6], for extractive ferrous metallurgy, this material could not be used directly for pyrometallurgical processing. The present work aims to study how to sinter and process this iron silicate - fayalite, which falls out after the flotation of copper slags, to ferrosilicon.

Molten fayalite is reduced with the help of hard carbon easier. In the presence of CaO, its reduction is significantly facilitated [6, 7]. Based on the theoretical thermodynamic data from the literature [7 -9], it can be concluded that the following reactions will take place under reduction heating of iron silicate:

$$CO_2 + C = 2CO,$$
$$\Delta G^0 = -1\ 606\ 550 - 171\ T\ /\ J\cdot mol^{-1} \qquad (1)$$

$$Fe_3O_4 + C = 3FeO + CO,$$
$$\Delta G^0 = 196\ 720 - 199{,}38\ T\ /\ J\cdot mol^{-1} \qquad (2)$$

$$FeO + C = Fe + CO,$$
$$\Delta G^0 = 149\ 600 - 150{,}36\ T\ /\ J\cdot mol^{-1} \qquad (3)$$

$$Fe_2SiO_4 + 2C = 2Fe + SiO_2 + 2CO,$$
$$\Delta G^0 = 353\ 924 - 338{,}91\ T\ /\ J\cdot mol^{-1} \qquad (4)$$

$$Fe_3O_4 + CO = 3FeO + CO_{2,}$$
$$\Delta G^0 = 30\ 170 - 29{,}38\ T,\ /\ J\cdot mol^{-1} \qquad (5)$$

$$FeO + CO = Fe + CO_2,$$
$$\Delta G^0 = -16\ 950 + 20{,}64\ T\ /\ J\cdot mol^{-1} \qquad (6)$$

$$Fe_2SiO_4 + 2CO = 2Fe + SiO_2 + 2CO_2,$$
$$\Delta G^0 = 12\ 510 + 10{,}54\ T\ /\ J\cdot mol^{-1} \qquad (7)$$

$$Fe_2SiO_4 + CaO = 2FeO + CaSiO_3,$$
$$\Delta G^0 = -82\ 600 - 32{,}39\ T\ /\ J\cdot mol^{-1} \qquad (8)$$

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From equations (1) - (8), it can be established that under experimental temperature conditions (1 050–1 300 °C), Fe_3O_4 and FeO can be reduced by carbon and carbon monoxide. Equation (7) shows that Fe_2SiO_4 cannot be reduced directly by carbon monoxide, but in the presence of CaO, Fe_2SiO_4 can be easily decomposed to produce FeO, which can be reduced by both carbon and carbon monoxide. Equation (4) shows that Fe_2SiO_4 can be reduced directly by carbon. However, this reaction is very slow on the kinetic level. Therefore, it can be concluded that carbon monoxide is still the main reducer of copper slag reduction. Based on the theoretical data for establishing equilibrium in isobaric-isothermal systems - Gibbs free energy, it can be said that the iron compounds in copper slag can be reduced to metallic iron by carbon and carbon monoxide.

In the reaction process itself, whether a reaction can occur also depends on the pressure in the system, the concentration of the reagent, the rate of the reaction, and so on. Therefore, the kinetic model of the reaction is an important tool for studying the reaction process. According to Zhang et al. [10], the best conditions for fayalite reduction are those in which the reduction temperature is 1 573 K, the reduction time is 30 minutes, the amount of coal added is 35 % by weight and the CaO addition dose is 20 % by weight (at 0,75 basicity). Warczok and T.A. Utigard [11] have reduced synthetic fayalite under laboratory conditions in the temperature range 1 523 K – 1 723 K.

EXPERIMENTAL

The mass ratios of the components in the charge mixture for each production are based on preliminary mathematical modeling of the process. Balance calculations predict the initial parameters and the products obtained based on the composition and specificity of the raw materials used. The methodology of McLean and Bazanov was used in compiling the material balance of the sintering production [6]. The chemical composition of the materials used is presented in Table 1. Slag fayalite, fuel, and hydrated lime (containing 75,70 % by weight CaO) were used.

Table 1 **Chemical composition of charge materials / wt. %**

Material	Fe-total	MnO	SiO_2	Al_2O_3	CaO	C
Fayalite	48,78	1,40	15,26	3,65	6,99	-
Fuel	3,71	0,26	6,08	2,31	1,18	78,62

In the balance calculations of the sintering process, the following technical indicators were used: basicity – 1 %, moisture – 9 %, powder and mechanical losses – 2 %, and return fines – 5 %. The material balance for obtaining the sinter is presented in Table 2.

The input part included iron silicate-fayalite, flux (lime), and fuel. The output part included sinter, return fines, and fume gases. The balance was calculated to obtain 100 kg. sinter. The theoretically calculated consumption of coke was lower than when using an ore and concentrate. In iron silicate, iron was bound in the form of magnetite (Fe_3O_4) and fayalite ($2FeO.SiO_2$). The estimated chemical composition of the obtained sinter is presented in Table 3.

Table 2 **Material balance / kg per 100 kg sinter**

Input charge materials		Output products	
Fayalite	94,71	Sinter	100,00
Lime	10,44	Return fines	5,00
Fuel	1,38	Fume gases	34,25
Return fines	5,00	Total production / kg	139,25
Air	18,14		
Moisture	9,59		
Total / kg	139,25		

Table 3 **Chemical composition of the obtained sinter / %**

Fe_2O_3	FeO	MnO	SiO_2	Al_2O_3	CaO
4,88	55,00	1,33	14,53	3,50	14,53
MgO	AsS_2	ZnO	PbO	CuO	S
0,65	0,03	1,65	0,09	1,65	0,11

As can be seen from Table 3, the content of Fe- total in the obtained sinter is 46,21 %, the difference of 2,57 % Fe- total relative to the initial fayalite is due to the percentage of charge materials and agglomeration losses. Due to the excess of FeO in the charge, some of it oxidized to Fe_2O_3. At temperatures above 1 370 ^{0}C part of the hematite (Fe_2O_3) dissociated to magnetite (Fe_3O_4), which increased the concentration of oxygen in the exhaust gases. The amount of total sulfur in the resulting agglomerate was 0,36 %, which showed that 2,04 % of fayalite oxidized and passed into the gas phase. This was in correlation with the specifics of the sintering process in which about 95 % of sulfide sulfur was released, and the degree of sulfur sulfate release was 40 - 70 %. The content of non-ferrous metals in the obtaining sinter slightly decreased.

Based on the calculations in Table 2, the charge materials were mixed and subjected to agglomeration in a laboratory sinter installation. The mixing, wetting, and granulation of the charge were carried out in a disk laboratory granulator. Three sintering processes were made with the calculated charge materials (Table 2). The time in the laboratory sintering pot varied from 19 to 24 minutes at a working height of the laboratory sintering pot - 280 mm. The vacuum under the grate was in the range of 460 - 520 mm. water column. The vertical sintering rate varied in a narrow range of 11,67 mm / min. up to 14,74 mm / min.

As a result of the heat released during the quenching of lime, the charge was preheated to a temperature of 40 - 45 ^{0}C. With the use of $Ca(OH)_2$ the strength of the raw and dried granules increased. Due to the formation of a solid phase of easily soluble ferrates, the temperature-heat regime of the sintering process decreased. The formation of these ferrites lowered the surface tension of the melt, which reduced its viscosity and improved its wetting ability.

After cooling, the resulting agglomerate was sieved. The main quantitative distribution of the agglomerates was in fractions over 20 mm about 36 % and on average about 21,60 % in fractions 20 - 15 mm. The fractional composition below 5 mm was the most insignificant – 8,10 %. This part transformed into hot return fines. The type of physical (macro-) structure of the obtained sinter, according to B. Miller's classification, has a coarse-pore structure with unevenly distributed pores (15 mm).

OBTAINING FERROSILICON IN AN ELECTRIC ARC FURNACE (EAF)

The next step in this study was to convert the obtained sinter to ferrosilicon FeSi45. Calculations of the ongoing processes during the processing of the sinter in a low-shaft electric arc furnace were made. The well-accepted in practice distributions of the reduced elements and oxides between the metal, slag, and gas phases were used in the balance calculations. The material balance of the production process of FeSi45 is presented in Table 4.

Table 4 **Material balance of ferrosilicon production process**

Input charge materials			Output products		
	Mass / kg	/ %		Mass / kg	/ %
Quartzite	75	30,6	FeSi45	95,7	39,1
Coke	65,6	26,8	Slag	7,05	2,88
Sinter	100	40,8	Gas	135,9	55,5
Electrode mass	2,7	1,1	Reduced elements	5,3	2,2
Fe furnace shell	1,4	0,6	unbound	0,8	0,3
Total	244,7	100,0	Total	244,7	100

Based on the calculations in Table 4, experiments were performed for real laboratory preparation of the alloy. A monophase electric arc furnace with a transformer power of 75 kVA was used (Figure 1). The premixed charge components, in the respective quantitative ratios (Table 4), were added in small portions to the furnace. The duration of the process (tap to tap) was 40 - 60 minutes.

The chemical composition of the obtained metal and slag, respectively, is shown in Table 6.

Working with the monophase electric arc furnace there is a high concentration of electrical and thermal energy in the reaction space of the bath [1]. When operating with a permissible secondary current of 1 500 – 2 000 A, its volumetric current density is 1,20 - 2,04 A/ cm^3. The load on the floor is 2,35 - 4,1 cm^2. The specific electricity consumption using sinter in the charge is 9,84 kWh / kg.

After melting, the alloy was casted into cast iron ingots (crucibles), which were painted with lime milk. After cooling to room temperature, the hardened alloy from each crucible was smashed with a hammer and the pieces from each sample were exposed to the outside atmosphere. The quantities of the obtained metal, slag, and the calculated yield are presented in Table 5.

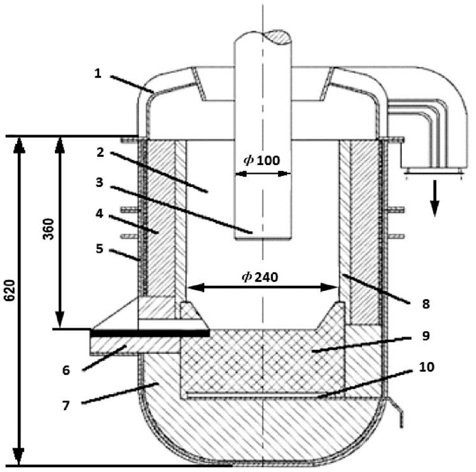

Figure 1 Schema (cross section) of monophase electric arc furnace:
1- furnace roof; 2- furnace bath; 3- graphite electrode; 4- fire clay bricks; 5- furnace shell; 6- tap hole (runner); 7- foam thermal insulator; 8- graphite refractory ramming; 9-graphite electrode; 10- water cooled copper plate

The composition of the resulting alloy meets the standard of the ferrosilicon 45 (Si–41 - 47 %, Mn – 2,0 %, Cr – 0,5 %, P – 0,05 %, S – 0,02 %, Al - 2,0 %.) – Table 6.

Using sintered iron silicate - fayalite and adding quartzite, FeSi with a chemical composition corresponding to the existing standard can be obtained. Slag fayalite replaces steel scrap and partly quartzite in the production of ferrosilicon. The production cost of ferrosilicon is expected to be lower, and the utilization of slag fayalite will prevent environmental pollution.

Table 5 **Experimental data and obtained metal, slag, and yield**

№	Experimented charge			Metal / kg	Slag / kg	Yield / %
	Sinter / kg	Coke / kg	Quartzite / kg			
1	10	8,5	10	12,8	1,6	44,9
2	10	8,5	10	14,3	1,3	50,2
3	10	8,5	10	12,4	1,1	43,5

Table 6 **Chemical composition of metal and slag / wt. %**

№	Elements	Fe	Si	Cu	S	Mn	Al	Ca
1	Metal 1	49,80	38,80	0,09	0,03	1,64	1,73	2,14
2	Metal 2	44,83	47,53	0,06	0,06	1,82	1,84	3,18
3	Metal 3	45,78	46,61	0,09	0,04	1,73	1,59	4,48
		FeO	SiO_2	Cu	S	MnO	Al_2O_3	CaO
1	Slag 1	0,43	49,19	0,07	0,05	0,92	25,44	23,10
2	Slag 2	0,36	55,61	0,08	0,06	0,48	27,06	14,35
3	Slag 3	1,07	54,31	0,04	0,05	1,17	24,47	18,19

CONCLUSION

The use of secondary raw materials stimulates the circular economy by reducing the impact on the environment and the use of natural raw materials.

The iron silicate (slag fayalite) sinters very well. The use of lime improves the degree of granulation of the charge due to the binding properties of $Ca(OH)_2$ and increases the gas permeability of the sinter. The resulting agglomerate has a coarse-pore structure.

All the conducted laboratory and semi-industrial experiments confirmed the theoretical calculations and proved the successful possibility for the refinement processing of iron silicate-fayalite to obtain ferrosilicon FeSi45. The composition of the obtained alloy is close to existing standards. The results provide a perspective for further industrial experiments with a steady energy and economic efficiency.

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Note: The responsible for English language is PhD Maria Todorova, Sofia, Bulgaria