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STUDYING THE SHUBARKOL DEPOSIT COAL AS THE CARBONACEOUS REDUCING AGENT IN FERROALLOY PRODUCTION

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ABSTRACT

One of the promising trends in the development of ferroalloy production is the use of coals as carbonaceous reducing agents. There are presented the results of comprehensive studies of the physical-and-chemical and technological properties of coals from the Shubarkol deposit (Central Kazakhstan) for the coke-free production of various ferroalloys (ferrosilicon silicomanganese, high-carbon ferrochrome). Semi-coke was obtained as an active reducing agent based on high-speed thermal-oxidative pyrolysis of Shubarkol coals with specified quality characteristics: ash content 4.36%; the yield of volatile substances 47.24%; low sulfur content 0.35% and phosphorus 0.01%. The optimal temperature parameters and heat treatment modes were determined to ensure the production of carbonaceous reducing agents with sufficient structural strength and high reactivity. One can expect increasing the efficiency of coke-free production of ferroalloys when selecting the optimal proportion of coal in the charge composition, making appropriate changes to the operating modes of ferroalloy furnaces to improve technical and economic indicators, and introducing instrumental methods of express analysis of the ash content of the coal used, the yield of volatile substances, combustion heat and chemical composition.

Keywords: low-ash coal, semi-coke, carbonaceous reducing agent, porosity, volatile substance yield, thermal-oxidative process, chemical composition.

INTRODUCTION

Recently, the problem of replacing expensive coke with other carbonaceous materials has become urgent in the ferroalloy industry. In the production of various ferroalloys, there are mainly used coke nuts: waste from sorting gross and blast-furnace coke classes. In the assessment of carbonaceous reducing agents for ferroalloys, it is noted [1] that coke nuts (KO-1 and KO-2 grades) regulate the indicators for ash content (11-14%) and the composition of fines (10-16% with a particle size of smaller than 10 mm). According to the content of sulfur, phosphorus and the yield of volatile substances, it must comply with the requirements provided for these indicators by the standards for blast-furnace coke. Alongside with this, low reactivity of the coke nut, relatively low electrical resistivity leading to increased power consumption, somewhat limit its use in ferroalloys smelting [2, 3]. All this makes it important to search for alternative types of carbonaceous reducing agents for ferroalloy production. In this context, the technological idea of replacing costly coke with fossil coals is of particular interest. The attractiveness of this technological approach is explained by the favorable physical-and-chemical and technological properties of coals, lower cost characteristic and significant cheapness of natural coals. Unlike coke, they have specific features due to the diversity of the chemical and material composition of the organic and mineral parts, a wide range of physical-and-chemical and thermodynamic properties of porous structure.

In Russia, selecting coals for the production of ferroalloys is recommended to be carried out in accordance with GOST R 51588-2000 that regulates the grade of coal (lean, anthracite, weakly caking), quality indicators: ash content (10-14%), fineness (13-50; 25-50 mm), humidity (5-10%), fines content (20% less than the lower limit). It is noted [4] that these requirements do not allow complete assessing the suitability of coals as a carbonaceous reducing agent in ferroalloy production. Natural coals claiming to be a carbonaceous reducing agent must have sufficient thermo-mechanical strength and reactivity, high electrical resistivity, and favorable chemical composition.

The studies of VUHIN and its Kuznetsk Center have shown that reactivity and electrical resistivity of a carbonaceous reducing agent largely depends on the degree of metamorphism of the coals used [5]. The highest values of these physical-and-chemical parameters are characteristic of cokes obtained with the use of low metamorphosed long-flame coals with a high yield of volatile substances.

The experience of using charcoal is known, which is a classic example of a carbonaceous reducing agent for electro-thermal production. It satisfies (with the exception of increased abrasion) most of the requirements of smelting technology. A promising substitute for charcoal can be coke of lignin (hydrolysis production waste), which is similar in basic physical and chemical properties to charcoal. Direxil made of charcoal is of practical interest as a carbonaceous reducing agent for smelting grade silicon [6]. There is known an attempt to use anthracite mixed with charcoal in smelting ferrosilicon. A.I. Pluzhnikov and others presented the data of the quality indicators of special coke made of the

Shubarkol coal at different values of the volatile substances yield [7]. There is an analysis of using the coal from the Shubarkol deposit in the smelting of commercial silicon [8]. V.M. Strakhov and others presented the results of coke-free production of silicon ferroalloys [4]. The works by E.L.J. Kleynhans, J.P. Beukes J.P. *et al*. showed the effect of a carbon-containing reducing agent on the ferrochromium production process with an estimate of specific energy consumption [9, 10].

Strict requirements for almost all the types of ferroalloys are put forward for the concentration of phosphorus (GOST 1932) and sulfur (GOST 8606). Phosphorus is contained in the ash of the reducing agent in the form of P_2O_5 which is a harmful and hard-to-remove impurity. For the production of high-silicon ferroalloys, the amount of phosphorus in coke should not exceed 0.04%. When smelting ferroalloys, the main source of sulfur (74%) is coke, so carbon reducing agents should contain no more than 0.4-0.5% S.

An important qualitative characteristic of carbonaceous reducing agents for smelting ferroalloys is their physical and mechanical properties, which include structural strength and particle-size distribution. Selecting the optimal particle-size distribution of the reducing agent depending on the technological features of the process and the physical and chemical properties of the carbonaceous material itself, is a significant factor in improving technical and economic indicators of production. There is a growing need to use instrumental methods of the ash content express analysis, combustion heat, volatile substance yield, and chemical composition of coal [11].

Thus, the analysis of the current state of the problem of using coal as a carbonaceous reducing agent indicates the need to study physical-and-chemical and technological properties of coals from the Shubarkol deposit in the context of producing various ferroalloys.

FEEDSTOCK AND RESULTS OF THE STUDIES

Coal from the Shubarkol deposit, Kazakhstan with the fraction of 25-50 mm was used as a feedstock for the production of a carbonaceous reducing agent, semi-coke. The use of natural coal of such a fractional composition provides relatively high gas permeability, stable electrical and technological modes of operation of ferroalloy furnaces [12]. The Shubarkol coal deposit is located in the Tengiz district of the Karaganda region and has three coal levels. The most powerful is the upper level. Here more than 80% of the reserves are concentrated. The balance reserves of coal are about 1.8 billion tons. Shubarkol coals belong to long-flame gas coals; they are petrographically homogeneous, vitrinized coals.

In the ongoing studies, a sample of Shubarkol coal in the amount of 2.0 tons was used to study the physical-and-chemical and technical characteristics, as well as to develop coking modes and to obtain prototype semi-coke samples.

Determining the technical analysis and chemical composition of the ash of the provided coal sample was carried out in an accredited testing laboratory of the R&D Center UGOL LLP according to standard methods. The test results are shown in Table-1.

Table-1. Technical analysis of Shubarkol coal and the ash chemical composition.

Fraction, mm	Technical analysis, %						Ash chemical composition, %			
	W^r (humidity)	W^a (humidity)	A^d (ash)	V^d (volatile substance yield)	S	P	Fe_2O_3	SiO_2	Al_2O_3	CaO
25-50	10.7	8.10	4.36	47.24	0.35	0.01	9.0	51.71	26.8	2.21

According to the results of technical analysis, the yield of volatile substances exceeds 47%, which makes it possible to carry out coal coking in the mode of thermal-oxidative pyrolysis.

The chemical composition of the mineral (ash) part of Shubarkol coal is mainly Si, Fe, Al, Ca. Their content is shown in Table-1. At this, a low ash content in coal contributes to the production of a carbonized product with the ash content regulated by ferroalloy production: no higher than 11-12%. A low content of sulfur and phosphorus makes it possible to obtain semi-coke with an acceptable level of harmful impurities.

To obtain a strong lumpy material using fractionated coal, the method of high-speed thermal-oxidative coking was used that was based on high-speed heating of coal particles with heat released during the combustion of volatile products of thermal destruction. The formation of the coke substance structure passes through the reactions of the coal substance destruction and synthesizing new compounds with the formation of semi-coke substances, the further transformations of which lead to the formation of the carburized material [4].

Shubarkol coal with specified characteristics was subjected to thermal-oxidative coking: ash content 4.36%; the content of volatile substances 47.24%; humidity 8.1-10.7%; solid carbon content 50.1%; sulfur content 0.35%; phosphorus content- 0.01%; bulk density 0.77g/cm^3.

The experiments were carried out in a shaft furnace (retort), which is a shaft-type apparatus of periodic operation made in the form of a steel cylinder with the diameter of 230 mm and the height of 1200 mm. The coking process was carried out in the oxidative roasting mode with the formation of a combustion zone in the material layer. The temperature and speed of the process were controlled by changing the flow rate of air supplied to the combustion zone. The carbonization process was

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provided by heat obtained directly in the layer of coal loading from the combustion of volatile substances of coal. Coking was carried out within 4 hours at the temperature of 870°C. After completion of pyrolysis (coking), semi-coke was cooled in the furnace to 100-150°C within 1 hour. The yield of finished semi-coke was about 48%.

There was studied the effect of the main technological parameters of coal heat treatment (the heating rate and the temperature in the coking layer) on the structure and properties of semi-coke. In the temperature range of 320-820^{0}C, the heating rate of the coal load depended on the given temperature gradient and was 29.4-90.9 deg/min (Figure-1). It was a sufficient value for the formation of a strong structure of the coke residue.

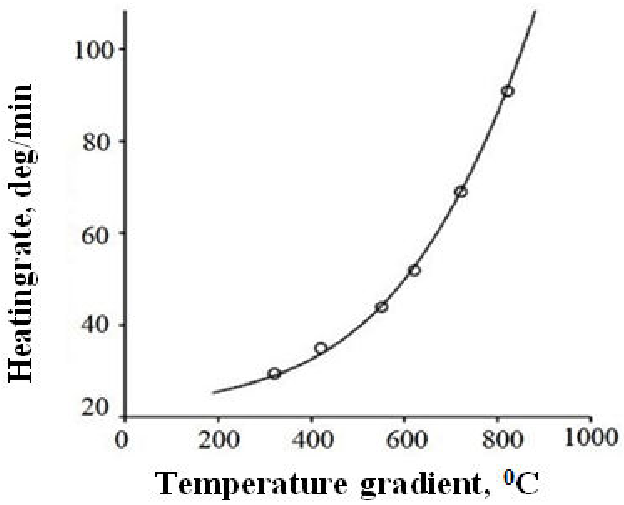

Figure-1. The temperature gradient effect on the coal charge heating rate.

Figure-2 shows the results of technical analyzing semi-coke samples obtained in the given temperature range of 600-1100ºC and heating rates of 29.4-90.9 deg/min.

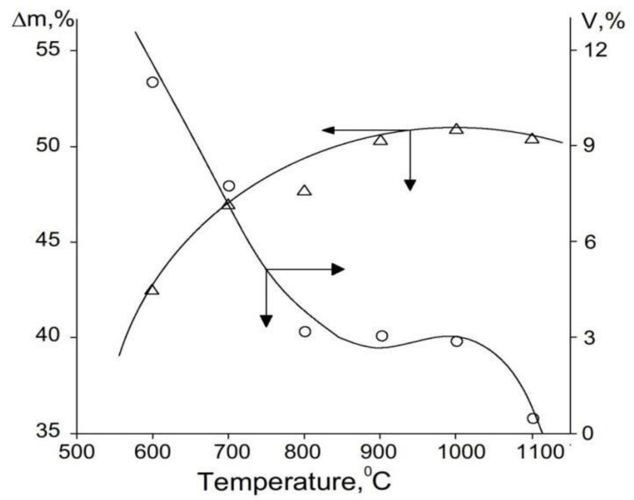

Figure-2. The mass loss (Δm) and residual content of volatiles (V) dependence on the coking temperature.

In the process of thermal-oxidative coking, the temperature mode is closely related to the share of combustion of volatile components of coal. The residual amount of volatile substances in semi-coke is in full accordance with the value of the mass loss of coal. The most intense loss of the coal mass is observed in the temperature range of 600-800°C. Moreover, with increasing the temperature in the coking layer from 600 to 900°C, the residual content of volatile substances decreases from 11.7 to 3.0%. In the temperature range of 800-1000^{0}C, a saturation region sets in, in which the yield of volatile substances stabilizes at the level of 3%. At the temperatures above 1000^{0}C, the yield of volatiles sharply decreases, which is caused by the processes of destruction of the semi-coke structure. It was experimentally established that porosity of semi-coke increases almost linearly depending on the heating rate. With increasing the heating rate from 29 to 67 degrees per minute, porosity of semi-coke increases from 48.9 to 54.8% according to GOST 10220-82. Such dynamics of changing porosity is associated with gas permeability and swelling coal in the area of destruction, at which the formation of the semi-coke structure occurs. This increases the rate of volatile substances yield and the total specific surface area of semi-coke. Due to the development of the pore structure, semi-coke obtained from long-flame coal has increased reactivity needed to ensure a high rate of carbon dissolution and the most complete reduction of ferroalloys. The results of measuring reactivity of semi-coke according to GOST 10089-89 showed that in the studied temperature range, reactivity of semi-coke fluctuated within 3.5-9.7 ml/g·s. Moreover, with increasing the final coking temperature, reactivity changes according to a complex pattern (Figure-3).

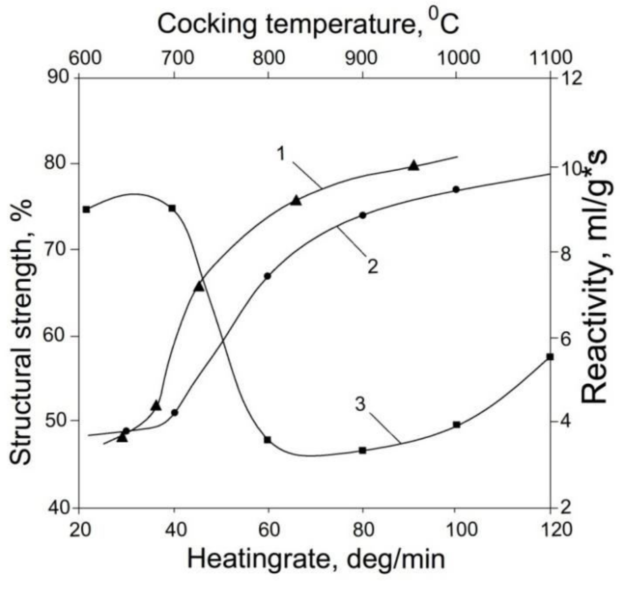

Figure-3. The heating rate (1) and temperature (2) effect on structural strength and the temperature (3) effect on the semi-coke reactivity.

In the temperature range of 600-700ºC, semi-coke obtained is characterized by high reactivity that reaches 9.7 ml/g·s. In the range of 700-800ºC, reactivity sharply decreases to 3.5 ml/g·s and remains practically unchanged up to the temperature of 900ºC. With a further increase in the final coking temperature, its rate increases.

The quality of semi-coke obtained as a carbonaceous reducing agent depends on its structural strength (mechanical and thermal stability). The effect of coking temperature and heating rate on the structural strength of semi-coke was experimentally studied (Figure-3). In the temperature range of 700-800ºC and the heating rate range of 40-60 deg/min, there is a noticeable increase in the semi-coke strength. With a further increase in temperature and heating rate, structural strength increases monotonically and reaches 80%. The results obtained indicate that there are prerequisites for the successful use of Shubarkol coal as a carbonaceous reducing agent for the production of ferroalloys.

Table-2 shows the chemical analysis of charge materials used to obtain silicomanganese. The composition of the charge is as follows: manganese ore 53%; semi-coke 20.4%; lime 9.6%; quartzite 17%.

Table-2. Chemical composition of the charge materials.

Material	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	P_2O_5	Mn_{tot}
Manganese ore	27.86	3.00	6.70	1.85	1.45	0.21	30.73
Shubarkol semi-coke	51.28	23.52	15.63	1.89	0.62	0.03	0
Lime	0	0	0	90	0	0	
Quartzite	96.52	1.69	0.5	0.4	0.34	0.02	0

The accepted component-material composition of the charge provides the elemental composition of the finished alloy, silicomanganese (Table-3).

Table-3. Metal amount and composition.

Element	Source of supply			Total
	Manganese ore	Quartzite	Shubarkol semi-coke	kg
Si	4.551	0.158	0.172	4.880
Fe	6.457	0.000	0.213	6.671
Mn	26.118	0.000	0.000	26.118
S	0.001	0.000	0.003	0.005
P	0.087	0.000	0.000	0.087
C	0.500	0.000	0.000	0.500
Всего	37.714	0.158	0.389	38.261

The specific power consumption in the smelting of silicomanganese in standard electric arc furnaces was 4200 kWh/t. With the total charge load of 145 kg, a finished alloy was obtained: silicomanganese in the amount of 38.3 kg. The chemical composition of the obtained silicomanganese was as follows: manganese 68%, silicon 12.8%, iron 17.4%, carbon 1.4%, sulfur 0.01%; phosphorus 0.23%. It meets the technical requirements of the interstate standard GOST 4756-91 (ISO 5447-80) "Ferrosilicomanganese".

Table-4 shows the chemical analysis of charge materials used to produce high-carbon ferrochromium.

Table-4. Chemical analysis of charge materials.

Material	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	P_2O_5	Cr_2O_3
Chrome ore	10.2	8.49	14.21	0.1	13.02	0.005	44.43
Semi-coke	51.28	23.52	15.63	1.89	0.62	0.03	0
Quartzite	96	2.17	1.04	0.33	0.4	0.004	0

The three-component charge contains chromium ore 81%, semi-coke 15%, quartzite 4%. Such a component-material composition of the charge provides the elemental composition of the finished alloy, ferrochrome (Table-5).

Table-5. Metal amount and composition.

Element	Source of supply		Total
	Chrome ore	Semi-coke	kg
Si	0.714	0.075	0.789
Fe	8.500	0.218	8.717
Cr	25.840	0.000	25.840
S	0.003	0.007	0.010
P	0.002	0.000	0.002
C	0.500	2.671	3.171
Total	35.558	2.971	38.529

The specific power consumption in the smelting of high-carbon ferrochromium in standard furnaces was 3500 kWh/t. With the total charge in the amount of 124 kg, there were obtained 38.5 kg of ferrochromium. The chemical composition of the resulting ferrochrome was as follows: chromium 67%, iron 22.6%, carbon 8.2%, silicon 2%, sulfur 0.02%, phosphorus <0.01%. It fully complies with the technical requirements of GOST 4757- 91 (ISO 5448-81) "Ferrochrome".

Thus, the obtained research results show the technological possibility of producing various ferroalloys using Shubarkol coal as a carbonaceous reducing agent.

CONCLUSIONS

a) The carried out studies of coals from the Shubarkol deposit showed the practical possibility of their use as a carbonaceous reducing agent for the production of various ferroalloys.
b) A low ash content and its balanced chemical composition, a low content of sulfur and phosphorus, and a sufficient yield of volatile substances make it possible to obtain semi-coke by the thermal-oxidative coking of Shubarkol coal, which is not inferior in quality to coke nuts used in ferroalloy production.
c) The temperature intervals and heat treatment modes that ensure the production of an active carbonaceous reducing agent with sufficient structural strength and high reactivity have been studied.
d) Favorable physical and chemical properties of Shubarkol coal as a carbonaceous reducing agent and their relative cheapness make it possible to improve technical and economic indicators of ferroalloy production with the optimal selecting of the quantitative proportion of coal in the composition of charge materials individually for each type of ferroalloys.
e) For a mass transition to coke-free production of various ferroalloys using a carbonaceous reducing agent, additional studies are needed to optimize the particle size distribution of the coal used, its ash content, combustion heat and volatile substance yield. One can expect increasing the efficiency of coke-free production of ferroalloys in the presence of instrumental methods of the ash content express analysis for the coal used its heat of combustion, volatile substance yield and chemical composition.

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