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PRODUCTION OF SPECIAL COKE FROM LOW-CAKING COALS USED IN THE FERROALLOY INDUSTRY

This article draws attention to the importance of effective control of the composition and properties of the charge in the production of ferroalloys. The main focus is on carbon reducing agents, which play a key role in this process.

The problem of the shortage of special coke in Kazakhstan is considered and solutions are proposed – the using of substandard raw materials for the production of reducing agents. In particular, the possibility of using coal from the Zhalyn deposit in a mixture with coal from the Shubarkol deposit is being considered.

Researches of differential thermal analysis (DTA) of coals Shubarkol (100 %), Zhalyn (100 %), as well as in a mixture in a ratio of 50:50 % are presented. The detailed characteristic expressed by endothermic and exothermic peaks allows us to fully study the physico-chemical processes occurring as a result of thermal exposure.

The conducted studies show that the obtained special coke in a ratio of 50:50% has good performance for reducing agents used in the electrothermy of ferroalloy production.

In conclusion, it is emphasized that the use of coal fines helps to reduce the accumulation of coal «wastes», which has a positive effect on the environment. This shows the importance of further research in this area to optimize the ferroalloy production process.

Keywords: coals, reducing agent, special coke, coke, production of ferroalloys, low-caking coals, non-caking coals, Zhalyn.

Introduction

In the electrothermy of ferroalloy production, effective control of the composition and properties of the charge plays a key role in the production process, allowing to ensure stable product quality and optimize production costs [1–5].

In the production of ferroalloys, carbon reducing agents play a special role, which must have good reactivity, high electrical resistivity, the chemical composition of ash corresponding to each alloy, sufficient strength, optimal piece size, good gas permeability and thermal stability, low cost [6–8].

All known works devoted to research on the optimal selection of reducing agents show the prospects of using low-caking and non-caking coals for the production of special coke for the ferroalloy industry. To date, there is a shortage of special coke in Kazakhstan, the bulk of which is purchased abroad with high added value. This is due to insufficient production of special coke at local enterprises and high demand for it from the metallurgical industry [6–13].

At the moment, in the Republic of Kazakhstan, coals from the Shubarkol deposit, which have quite good quality indicators, low sulfur and phosphorus content, high reactivity and electrical resistivity, are widely used for the production of special coke, however, these coals are also used for municipal and energy needs, which carries the possibility of depletion of coal reserves of value to the ferroalloy industry.

The solution to this problem is possible by developing substandard raw materials for the production of reducing agents, with the required quality indicators in the metallurgical industry, allowing to reduce the consumption of coal from the Shubarkol deposit and increase its own coke production, which is also relevant. In addition, in the process of open-pit coal mining, a large amount of coal fines is formed (about up to 50 % of the total production), having characteristics similar in composition to whole, lump coals, which in turn shows the relevance of using coal fines for coke production, thereby reducing deposits of coal «waste» [14–16].

As an alternative to Shubarkol coals, the coals of the Zhalyn deposit of grade G were considered, the characteristics of which are presented in table 1.

Table 1 – Chemical composition of the coal deposits of Zhalyn and Shubarkol

№	Name of indicators	Shubarkol	Zhalyn
1	The mass fraction of total moisture in the working condition of the fuel, W^r, %	8,3	7,0
2	Mass fraction of analytical moisture, W^a, %	1,5	1,4
3	Ash content of the analytical sample, A^a, %	1,3	6,7
4	Ash content for dry condition, A^d, %	1.3	6.8
5	Ash content for the working condition, A^r, %	1.2	6.3
6	The lowest heat of combustion of fuel in working condition, Q_i^r, kcal/kg	6371	6432
7	Higher heat of combustion, kcal/kg	7115	7009
8	Volatile output, %	45,8	43,3

The studied coals of the Zhalyn deposit belong to low-caking coal grade G, which increases interest in obtaining a special coke with high reactivity, which is one of the main criteria in the selection of reducing agents for the ferroalloy industry. However, despite similar indicators with Shubarkol coal, Zhalyn coals have a slightly overestimated phosphorus content, which somewhat complicates its use in the ferroalloy industry.

To solve this problem, it is proposed to mix the coals of the Zhalyn deposit with other types of coals with a low phosphorus content, in this case with the coals of the Shubarkol field, which belongs to the non-caking coals of the D brand.

Methods and materials

As part of the research on the production of new types of reducing agents from substandard raw materials, work was carried out in the laboratory of the Department of Metallurgy to obtain a special coke of coal from the Zhalyn and Shubarkol deposits.

In the laboratory of the Department of Metallurgy of Toraighyrov University, researches were conducted on the study of physico-chemical processes as a result of thermal effects on coals on the Synchronous Thermal Analyzer derivatograph (Figure 1), Derivatography is based on a combination of differential thermal analysis (DTA) with thermogravimetric analysis (TGA). On the basis of DTA, thermal processes are considered, which are accompanied by endothermic and exothermic changes, in which it is possible to judge a change in the state of the sample under study and a phase change during heat treatment. The principle of TGA is based on a change in the mass of the sample with a change in temperature.

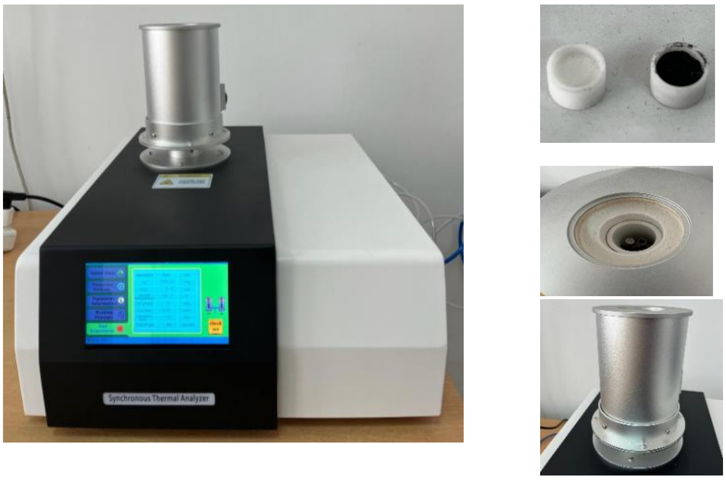

Figure 1 – Derivatograph Synchronous Thermal Analyzer

The work considered the coals of the Shubarkol and Zhalyn deposits at 100 %, as well as their ratios of 50:50 %. These coals were studied in an air atmosphere, the heating rate was 10 °C/min, alumina Al_2O_3 was adopted for the reference substance, the maximum temperature was set to 1150 °C.

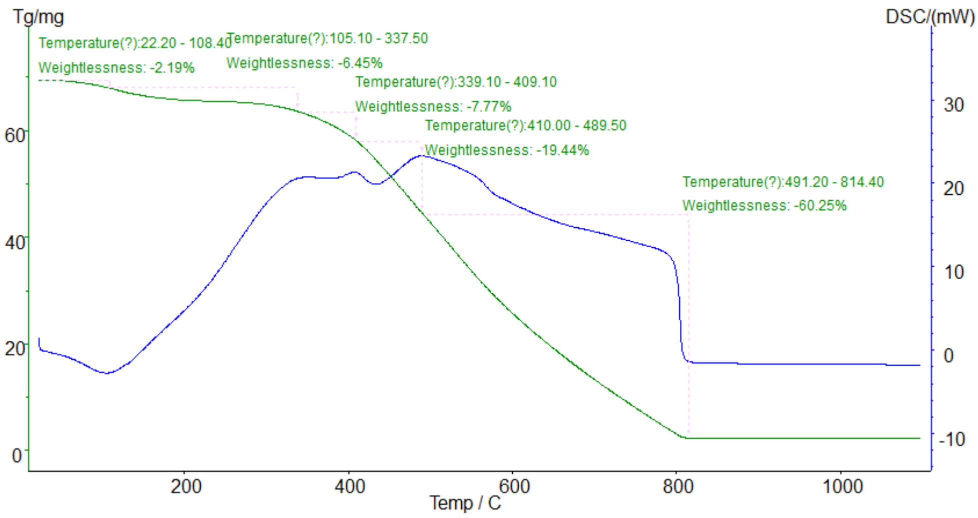

Figure 2 – Derivatogram of Shubarkol coal, 100%

A small endothermic peak, accompanied by heat absorption, occurs to a temperature of 104.9 °C with the removal of hygroscopic moisture, it turns into an exothermic effect to a temperature of 330 °C, when, presumably, the initial stage of coal destruction occurs, which in turn will affect the heat capacity (Figure 2). Further, in the temperature range of 350 and

490 °C, thermal effects associated with the destruction of the coal mass and the cost of heat for the release of volatile substances are traced. The endothermic failure at a temperature of 490 °C characterizes the period of coal degradation and the beginning of the process of semi-coke formation up to 790 °C.

The initial weight was 69.47 mg, the total weight loss as a result of the entire experiment was 95.7 % (Table 2).

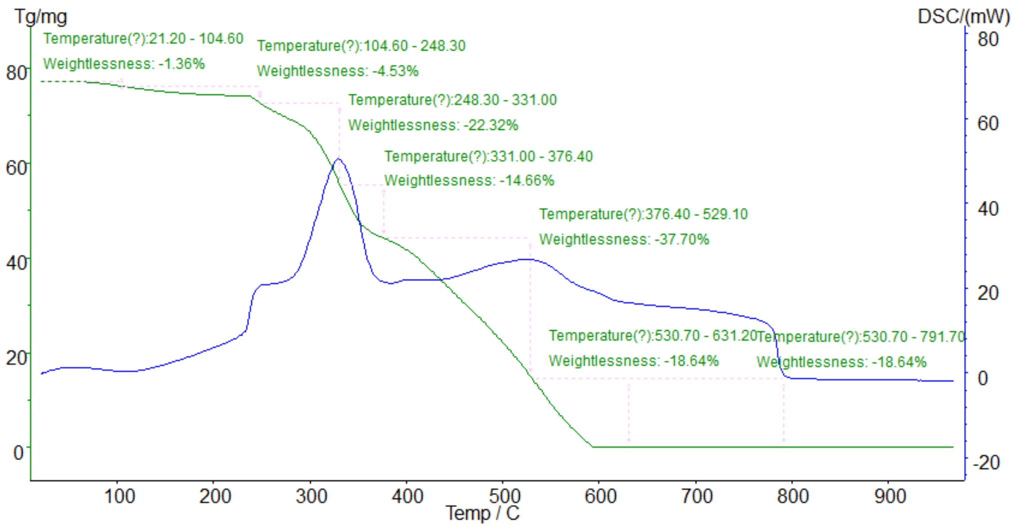

Figure 3 – Derivatogram of coal Zhalyn, 100 %

The derivatogram of the coals of the Zhalyn deposit, shown in Figure 3, is also characterized by a small peak of the endothermic reaction effect, accompanied by heat absorption and removal of hygroscopic moisture in the temperature range 97–130 °C. Further, two peaks of the exothermic reaction are observed at 250 and 330 °C, at which volatile substances are released and solid fuels are destroyed, associated with a change in the structure of coal. The subsequent endothermic peak at a temperature of 377 °C, followed by heat absorption to a temperature of 437 °C, is characterized by the absorption of latent heat of vaporization by boiling resins. The endothermic peak, where CO carbon monoxide is also reduced from CO_2 carbon dioxide and hydrogen (H_2) is reduced from water vapor, then passes into the phase of exothermic heat release and the continuation of coal destruction and the formation of the coke structure. In the range of 530 to 792 °C, an endothermic decline is observed, accompanied by the final stage of restructuring the structure of the semi-coke.

The initial weight was 77.25 mg, the total weight loss as a result of the entire experiment was 99.21 % (Table 2).

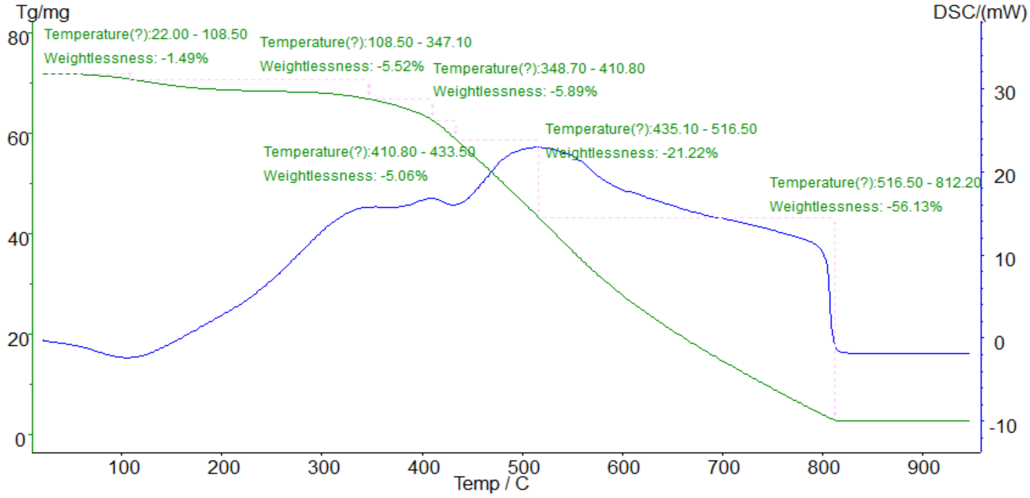

Figure 4 – Derivatogram of Zhalyn and Shubarkol coals, 50:50 %

In comparison with the thermal analysis of Zhalyn coals, thermal bursts of mixed Zhalyn and Shubarkol coals pass without sharp peaks (Figure 4). The initial stage of heating is accompanied by the removal of hygroscopic moisture, which is noticeable at the endothermic peak at a temperature of 108 °C. Further, exothermic growth is observed, explained by the release of volatile components and the primary destruction of the coal mass at temperatures of 347 and 410 °C. At 433 °C, a small endothermic peak is characterized by the absorption of latent heat of vaporization by boiling resins. The exothermic peak at 516 °C indicates further destruction of coal and the beginning of the formation of a semi-coke structure, the release of volatiles and the final stage of formation at a temperature of 812 °C.

The initial weight was 68.94 mg, the total weight loss as a result of the entire experiment was 95.31 % (Table 2).

Table 2 – Distribution of mass losses of gaseous products in specified temperature ranges according to derivatograms

Temperature, °C	Shubarkol		Temperature, °C	Zhalyn		Temperature, °C	Zhalyn + Shubarkol, 50x50	
	mg	%		mg	%		mg	%
22-104	1,36	1,96	22-104	1,05	1,36	22-108	1,12	1,49
104-330	5,54	6,01	104-248	3,5	4,53	108-347	3,97	5,52
330-407	5,62	8,09	248-331	17,24	22,32	349-411	4,51	5,89
407-434	4,04	5,82	331-376	11,33	14,66	411-433	3,64	5,06
434-488	9,62	13,85	376-529	29,12	37,70	435-516	15,57	21,22
488-800	41,66	60,07	530-791	14,4	18,64	516-812	40,39	56,13
Losses	67,84	95,8		76,64	99,21		69,2	95,31

The conducted studies in the oxidizing atmosphere of the air in the case of Shubarkol coal show the expediency of using thermo-oxidative coking. On the contrary, Zhalyn coals differ, which, as a result of pyrolysis, quickly lose mass, accompanied by endothermic effects, which indicate the expediency of using «standard» coking without oxygen access. Differential thermal analysis of a mixture of coals as a result of averaging physico-chemical properties shows the permissibility of pyrolysis in conventional coke batteries without air access.

Results and discussion

In a previously published work [17], the results of studies on the production of special coke by mixing coals from the Shubarkol and Zhalyn deposits in a ratio of 25 % to 75 % have already been presented. The samples obtained had good indicators for reducing agents used in the electrothermy of ferrous alloys, however, due to the excessive phosphorus content, their use is limited.

To reduce the concentration of harmful substances, tests were carried out on mixing coals in a ratio of 50/50 %. The method of conducting the experiments was as follows. Coal samples with a fraction of 0-3 mm were weighed on TechProm electronic scales. Next, the mixed coal was poured into a coking tank with a retracted tube having a rubber nipple valve for removing gases (Figure 5).

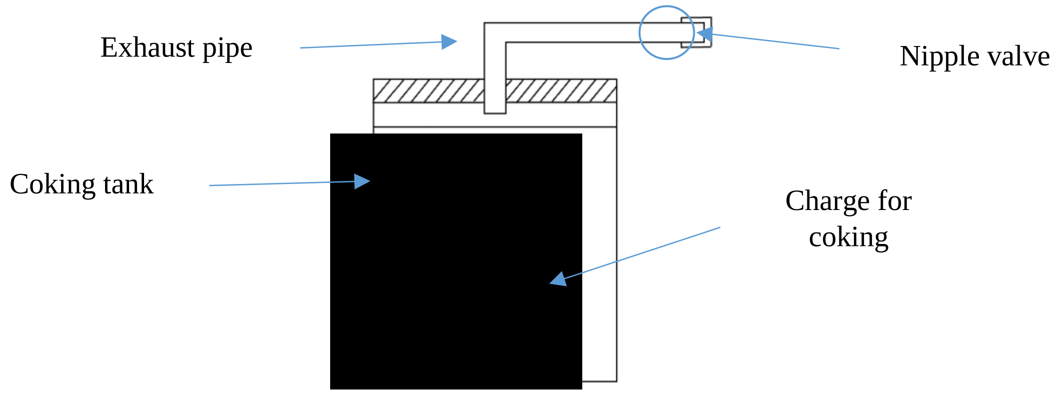

Figure 5 – Coking tank

The coking tank was placed in an electric muffle furnace manufactured by SNOL, with a programmed heating program up to 1150 °C. After reaching the required temperature and cooling, the container was removed from the furnace (Figure 6, a).

a)

b)

Figure 6 – The coking tank (a) and the samples obtained (b)

The obtained samples are shown in Figure 6 (b), they have small traces of salinity on the surface, the structure is porous, they have sufficient strength: when dumped, they break up into separate parts with dimensions of 20-30 mm, then when re-dumped, these fractions retain their integrity. The technical and chemical composition of the obtained special coke is shown below (Table 3), which also shows the conformity of their application.

Table 3 – The technical composition of the samples obtained

№	Name of indicators	Zhalyn and Shubarkol in a 50/50 % ratio
1	W^r	2,24
2	A^d	9,90
3	V^{daf}	4,03

Table 4 – Chemical composition of the ash of the obtained samples, %

Sample	Content, %							
	C	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	S	P
Zhalyn+ Shubarkol, 50/50 %	51,90	44,28	1,90	21,08	17,87	2,43	0,47	0.024

The presented data on the technical and chemical composition of the obtained samples indicate the possibility of their use in the ferroalloy industry, which, accordingly, will be reflected in further studies.

Conclusions

The results of the conducted research show the expediency of further study of the obtained samples, in particular, comparative indicators of electrical resistivity and reactivity, as well as strength characteristics.

The obtained results of differential thermal analysis of the physico-chemical properties of the studied coals Zhalyn and Shubarkol in a ratio of 50:50 indicate the possibility of averaging their properties, also, averaging the composition allows reducing the phosphorus content, which is not unimportant for the ferroalloy industry.

The samples obtained as a result of mixing two types of coals meet the requirements for reducing agents used in the ferroalloy industry.

In addition, the use of coal fines for coke production makes it possible to reduce the formation of coal waste, thereby reducing the environmental harm caused by the coal industry.

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ФЕРРОҚОРЫТПА ӨНЕРКӘСІБІНДЕ ҚОЛДАНЫЛАТЫН АЗ КҮЙЕЖЕНТЕКТЕЛЕТІН КӨМІРДЕН АРНАЙЫ КОКС АЛУ

Бұл мақала ферроқорытпаларды өндіру процесінде шихтаның құрамы мен қасиеттерін тиімді басқарудың маңыздылығына назар аударады. Бұл процесте шешуші рөл атқаратын көміртекті тотықсыздандырғыштарға баса назар аударылады.

Қазақстанда арнайы кокс тапшылығы мәселесі қаралуда және шешу жолдары – қалпына келтіргіштерді өндіру үшін кондициялық емес шикізатты пайдалану ұсынылады. Атап айтқанда, Жалын кен орнының көмірін Шұбаркөл кен орнының көмірімен қоспада пайдалану мүмкіндігі қарастырылуда.

Шұбаркөл (100 %), Жалын (100 %) көмірінің дифференциалды-термиялық талдауы (ДТА), сондай-ақ қоспада 50:50 % қатынасында зерттеулер келтіріледі. Эндотермиялық және экзотермиялық шыңдармен көрсетілген егжей-тегжейлі сипаттама термиялық әсер нәтижесінде пайда болатын физика-химиялық процестерді толық зерттеуге мүмкіндік береді.

Зерттеулер көрсеткендей, алынған 50:50 % арнайы кокс Ферроқорытпа өндірісінің электротермиясында қолданылатын тотықсыздандырғыштар үшін жақсы көрсеткіштерге ие.

Қорытындылай келе, көмір қалдықтарын пайдалану қоршаған ортаға жағымды әсер ететін көмір "қалдықтарының" жиналуын азайтуға көмектеседі. Бұл ферроқорытпаларды өндіру процесін оңтайландыру үшін осы саладағы қосымша зерттеулердің маңыздылығын көрсетеді.

Кілтті сөздер: көмір, тотықсыздандырғыш, арнайы Кокс, кокс, ферроқорытпа өндірісі, күйежентектелетін көмір, күйежентектелмейтін көмір, Жалын.

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ПОЛУЧЕНИЕ СПЕЦКОКСА ИЗ СЛАБОСПЕКАЮЩИХСЯ УГЛЕЙ, ПРИМЕНЯЮЩИХСЯ В ФЕРРОСПЛАВНОЙ ПРОМЫШЛЕННОСТИ

Данная статья обращает внимание на важность эффективного управления составом и свойствами шихты в процессе производства ферросплавов. Основной акцент сделан на углеродистых восстановителях, которые играют ключевую роль в этом процессе.

Рассматривается проблема нехватки спецкокса в Казахстане и предлагаются пути решения – использование некондиционного сырья для производства восстановителей. В частности, рассматривается возможность использования углей Жалынского месторождения в смеси с углями Шубаркольского месторождения.

Приводятся исследования дифференциально-термического анализа (ДТА) углей Шубарколь (100 %), Жалын (100 %), а также в смеси в соотношении 50:50 %. Детальная характеристика, выраженная эндотермическими и экзотермическими пиками позволяет в полной мере изучить физико-химические процессы протекающие в результате термического воздействия.

Проведенные исследования показывают, что полученный спецкокс в соотношении 50:50 % обладает хорошими показателями для восстановителей, используемых в электротермии производства ферросплавов.

В заключении, подчеркивается, что использование угольной мелочи помогает снизить накопление угольных «отходов», что положительно сказывается на окружающей среде. Это показывает важность дальнейших исследований в данной области для оптимизации процесса производства ферросплавов.

Ключевые слова: угли, восстановитель, спецкокс, кокс, производство ферросплавов, слабоспекающиеся угли, неспекающиеся угли, Жалын.

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