Study of phase transformations during heating of briquetted mono-charge from chromium-containing materials and carbon reducing agents

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The article presents the results of a study of phase transformations occurring during gradual heating of briquetted mono-charge. A complex of physical and chemical studies aimed at establishing the possibility of mono-charge use for smelting of standard carbon ferrochromium was carried out in the laboratorial conditions on the basis of the Chemical and Metallurgical Institute named after Zh. Abishev. In order to study the phase transformations occurring in a mono-charge for smelting of high-carbon ferrochromium, thermograms of chromium briquettes of different variants were obtained in air oxidizing atmosphere and nitrogen inert atmosphere. Among them the following variants are mentioned: chromium fines mixed with a reducing agent, option I - Shubarkol coal; option II - Borlinsky coal; option III - China coke; as well as option IV - pure dust from Aktobe ferroalloy plant gas cleaning; option V - dust from pellet production site at Donskoy GOK with China coke and option VI - flash from production of briquettes with China coke. As a result of processing of thermograms, the peak temperatures and temperature intervals of behaviour of the thermal effects of chromium oxide interaction with used reducing agents were established. The method of differential thermal analysis (DTA) is based on the most important properties of a substance which are related to its chemical composition and structure and are reflected in the thermal changes of a substance when heated. The reason for the widespread use of this method of non-isothermal kinetics is that one experiment can determine all the kinetic constants, including the activation energy. Analyzing the calculated data on the activation energy, it is possible to assume the diffusion nature of inhibition of the reduction reaction for all studied chromium ore materials. Based on the values of the activation energy of the process, briquettes with Borlinsky coal and complex reducing agent have the highest reducibility.
Key words: ferroalloys, differential thermal analysis, mono-charge, reducing agents, briquette, chromium ores, coal.
DOI: 10.17580/cisisr.2023.01.05

Introduction

Large-scale laboratorial tests, aimed on establishment of possibility of briquetted mono-charge for smelting of standard carbon ferrochromium were conducted in the Chemical and Metallurgical Institute named after Zh. Abishev, in the ore smelting furnace with power transformer capacity 250 kVA. The results of these tests on smelting of high-carbon ferrochromium using briquettes containing from ordinary chromium ore (0-10 mm) and different chromium-bearing products, as well as carbon reducing agents, are presented in the research [1].

The aim of this work is examination of phase transformations occurring during permanent heating of briquetted mono-charge.

To optimize the technological processes of production of high-carbon ferrochromium using briquetted mono-charge, it is required to know kinetic parameters of the interaction process between charge materials during melting, in particular activation energy.

Technique of the experiment

At present time, the differential thermal analysis (DTA) is the most widely used and distributed method of thermal analysis; it allows to reveal and examine phase transformations and chemical reactions in the investigating alloy during its gradual heating based on the thermal effects accompanying occurred variations. The obtained results provide determination of speed of conducting of interaction reactions during smelting of carbon ferrochromium in industrial furnaces and selection of the most optimal composition of charge materials.

DTA method is based on the most important properties of a substance, which are connected with its chemical composition and structure and are reflected in thermal variations of a substance during heating. The new methods of research of solid phase reactions during heating of interacting substances with permanent speed are developing using DTA, thermogravimetry (TG) and differential thermogravimetry (DTG). Wide use of the methods of non-isothermal kinetics provides possibility of determination of all kinetic constants (E_{act}, A and n) during one experiment. It should be mentioned that reliability of the kinetic analysis, which is conducted in this research, requires first of all increased accuracy of measurements and correct statistical processing of the obtained results. Different techniques for energy determination of the processes after processing of TG or DTG curves are described in technical literature [2-7].

Thermographic researches were conducted for Derivatograph Q-1000 of MOM company (F. Paulik, J. Paulik, L. Erdey systems). Ceramic crucible was used as a container for the sample.

The researches were conducted in oxidizing atmosphere, in the temperature range 20-1000 °C with heating speed 10 °C/min. The temperature was varied using platinum – platinum-rhodium thermocouple. As soon as the temperature in derivatograph furnace increases, the recording device registers on

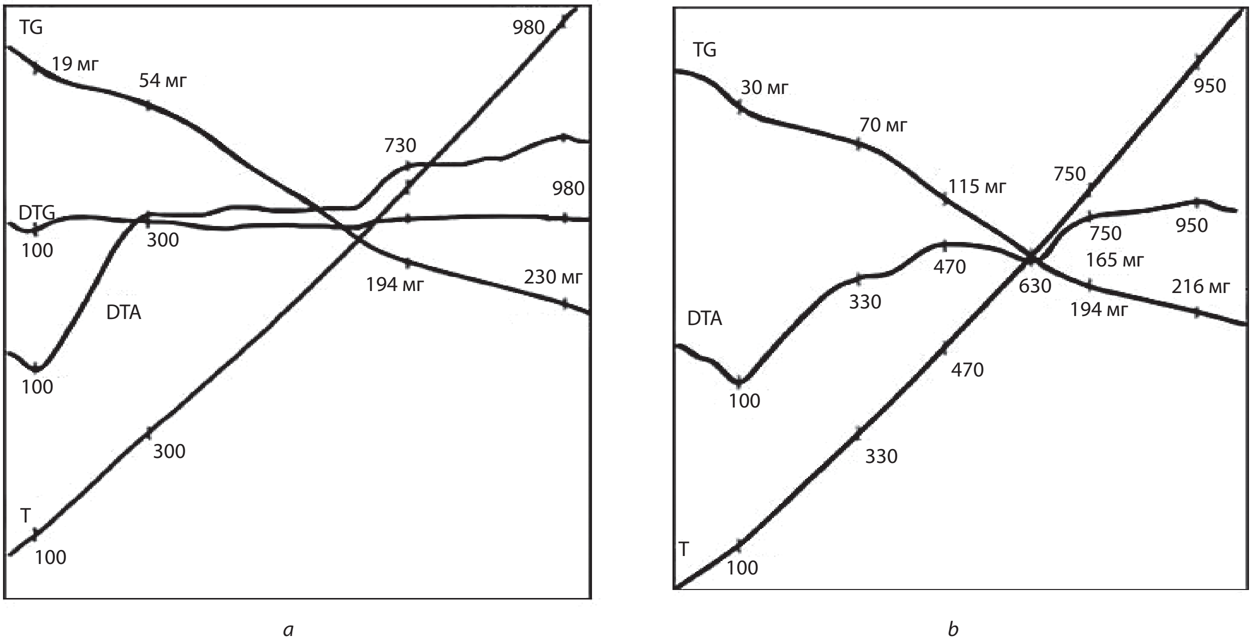

Fig. 1. Thermograms of chromium briquettes with Shubarkol coal (portions 1670 mg and 1980 mg), which were obtained in air oxidizing atmosphere (*a*) and inert nitrogen atmosphere (*b*) [8]

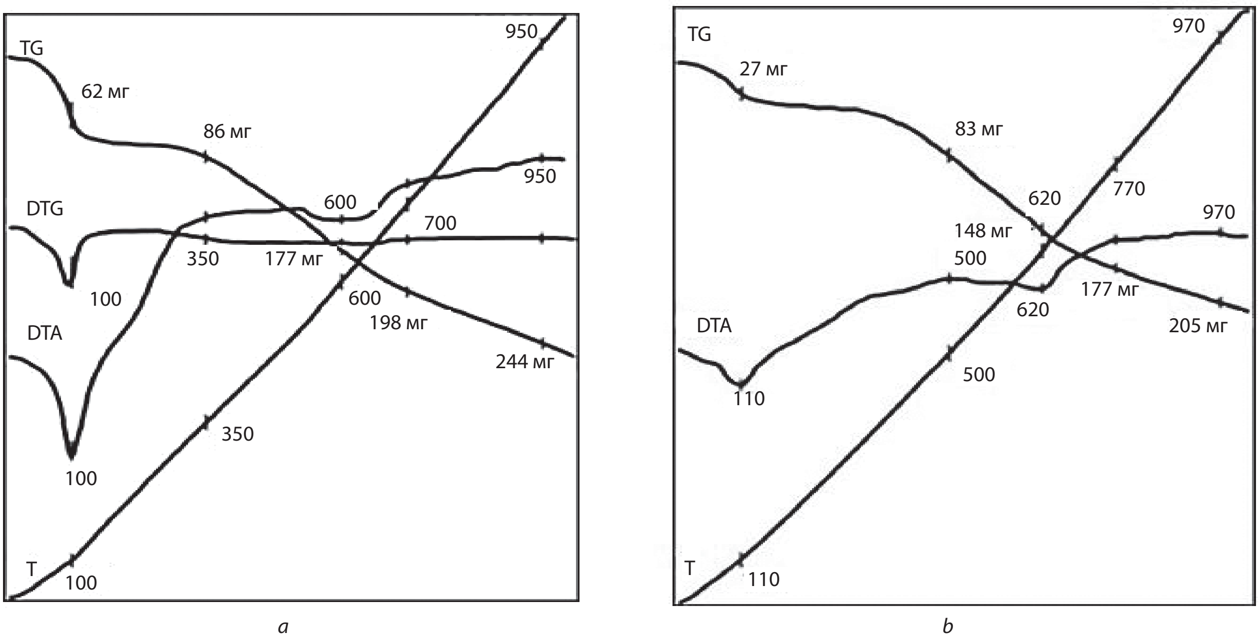

Fig. 2. Thermograms of chromium briquettes with Borlinsky coal (portions 14000 mg and 1750 mg), which were obtained in air oxidizing atmosphere (*a*) and inert medium (*b*) [8]

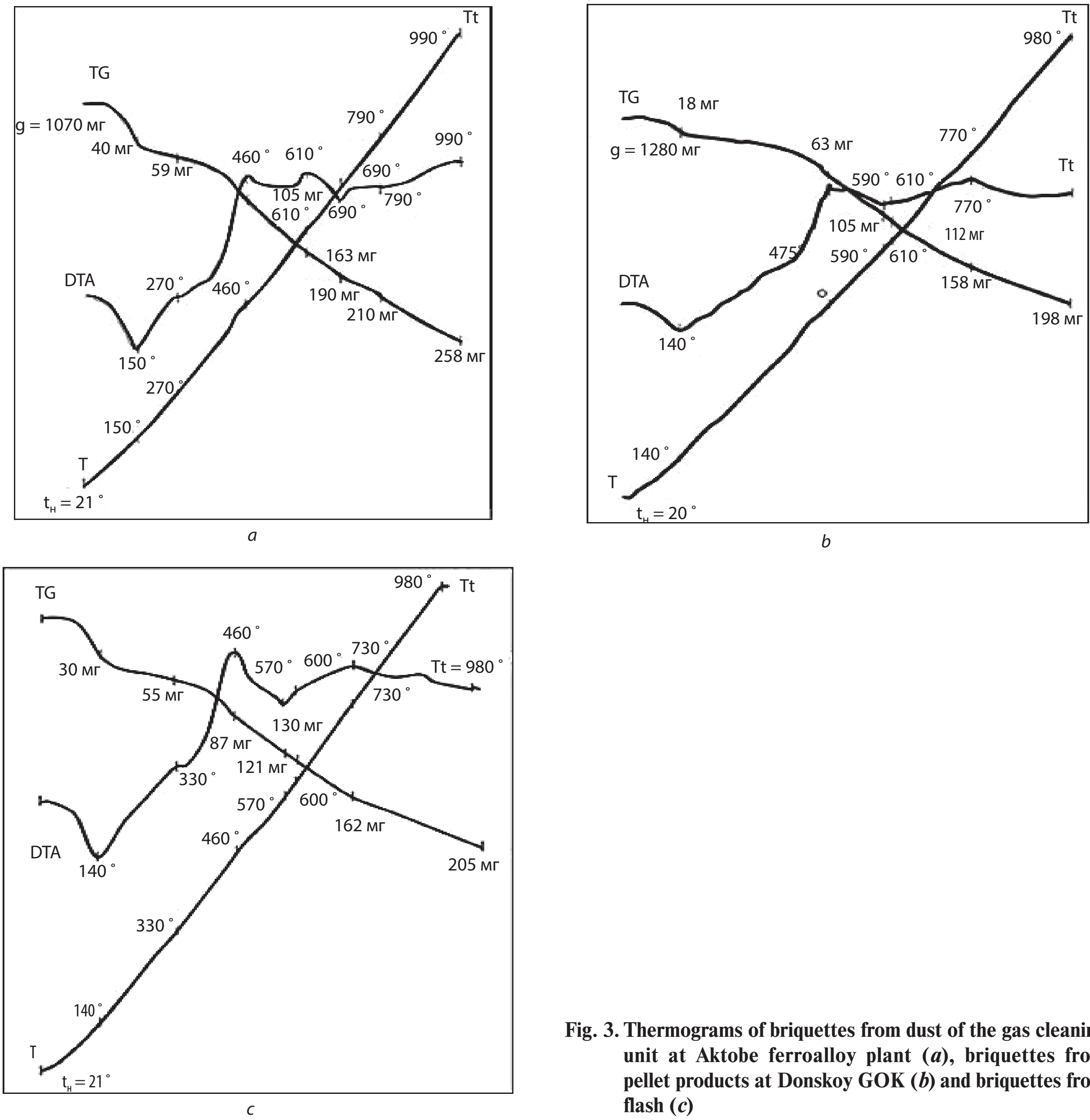

Fig. 3. Thermograms of briquettes from dust of the gas cleaning unit at Aktobe ferroalloy plant (*a*), briquettes from pellet products at Donskoy GOK (*b*) and briquettes from flash (*c*)

a thermogram all physical and chemical variations occurring in a sample in the form of T, TG and DTA curves. The temperature (T), weight variation (TG) and speed of heat content variation (DTA) of the investigating substance depending on time are measured simultaneously in the sample.

It should be noted that thermograms from the previous researches (**Fig. 1***a*, 1*b*, **2***a* and 2*b*), which had been obtained by the scientists of the Chemical and Metallurgical Institute named after Zh. Abishev, were used in this work for comparison of the results [8].

Experimental results and their discussion

Thermograms of three kinds of chromium briquettes were obtained in the conditions of air oxidizing atmosphere (**Fig. 3***a*, 3*b* and 3*c*):

- dust from the gas cleaning unit at Aktobe ferroalloy plant;
- dust from pellet production site at Donskoy GOK with China coke;
- flash from production of briquettes with China coke.

As a result of processing of thermograms, the peak temperatures and temperature intervals pf thermal effect during interaction between chromium oxide and used reducing agents were established. The strong exothermic effects are noted in thermograms on DTA curve in the oxidizing atmosphere; they are explained by oxidation of a reducing agent. In the inert atmosphere, DTA curves have weak exothermic features, changing by strong endothermic peaks. Endothermic effect is noted for all thermograms in the inert atmosphere within the temperature range 530-630 °C.

Table 1. **Distribution of mass loss in briquettes within preset temperature ranges according to thermograms (Fig. 3*a*, 3*b*, 3*c*)**

Temperature range, °C	Mass losses					
	Briquette from flash		Briquettes from dust from pellet production site at Donskoy GOK		Briquettes from gas cleaning dust	
	mg	%	mg	%	mg	%
0-330	55	26.44	43.84	21.88	75.19	28.68
330-570	66	31.73	54.78	27.33	74.03	28.24
570-660	24.1	11.59	25.1	12.52	32.38	12.35
660-850	37.1	17.84	45.04	22.47	44.54	16.99
850-1000	25.8	12.4	31.65	15.79	36.0	13.73
0-1000	208	100	200.41	100	262.14	100
Portion mass	1290	100	1280	100	1070	100

As a result of processing of the TG curve on the thermogram (Fig. 2*a*, 2*b*, 2*c*, 3*a*, 3*b*, 3*c*) it was revealed that briquettes with Borlinsky coal are characterized by maximal summarized mass loss which achieves 12.11 % at 1000 °C. At the temperature below 750 °C, mass losses in briquettes with Shubarkol coal are higher compared with briquettes with Borlinsky coal; it is connected with high content of volatile components in Shubarkol coal and their active removal at low temperatures. Minimal mass losses were noted in briquettes with China coke (9.81 %), what probably can be explained by their low reaction ability.

The first endothermic effect at the temperature 90-150 °C means loss of adsorbed water.

The second endothermic effect in thermograms at 640-695 °C corresponds to extraction of "structural" water from serpentines (antigorit and chrysotile) during decomposition with forming of forsterite, quartzite and water via the following reaction:

$$2Mg_3Si_2O_5(OH) = 3Mg_2SiO_4 + SiO_2 + 4H_2O$$

SiO_2 presents in serpentine decomposition product as amorphous silica.

The following exothermic effect on thermograms within the temperature range 770-820 °C was stipulated by forming of enstatite $MgSiO_3$ from serpentine decomposition products. This exothermic peak is very various in its value. Perhaps dehydration process is followed by enstatite forming so quickly, that exothermic peak is overlapped by endothermic one and decreases owing to endo-effect.

It was established as a result of processing of thermogram TG curve (Fig. 3*a*, 3*b*, 3*c*), that briquettes from gas cleaning dust have maximal summarized mass loss achieving 24.5 % at the temperature 1000 °C. Briquettes from dust from pellet production site at Donskoy GOK and from flash have minimal mass losses – 15.6 % and 16.1 % respectively, what probably can be explained by their low reaction ability. The results of mass loss determination in the different temperature ranges are presented in the **Table 1**.

Based on determination of the temperature values and deviation value of DTA curve from preset direction, relationships for each thermal effect in the coordinates lg Δt - $1/T$ were built, and the values Eact for the processes, which correspond to peaks on thermograms, were calculated by slope ratio of direct relation lg Δt - $1/T$ (**Fig. 4**).

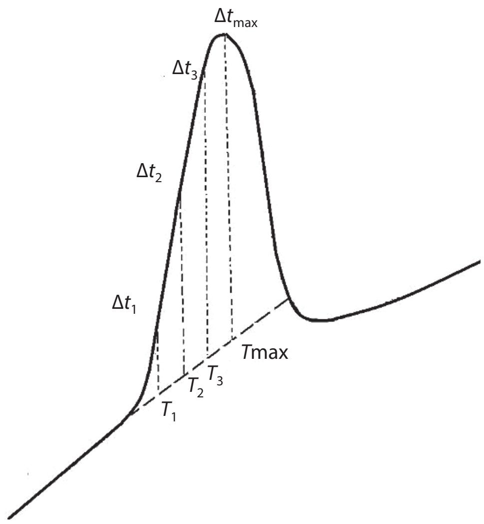

Fig. 4. Scheme for determination of temperature values and deviation value of DTA curve from preset direction

The values of activation energy for thermal effects, where reduction processes for chromium-containing materials start, were calculated on the base of the above-mentioned graphs (**Table 2)**.

Conclusions

When analyzing the calculated data of energy activation (Table 2), we can suggest diffusion features of braking the reduction reaction for all studying chromium ore materials. Based on activation energy values for this process, briquettes with Borlinsky coal and complex reducing agent are characterized by maximal reducibility. It can be explained in such way.

The coal which was introduced in composition of briquettes, contains silica and alumina in its ash part.

Table 2. **Kinetic parameters of reduction of agglomerated chromium ore materials by carbon**

Material	Equation	Correlation ratio, R	E_{act}, kJ/mol
Briquettes with China coke [8]	lnk= −25854.2/T + 8.492	0.982	214.96
Briquettes with Borlinsky coal [8]	lnk= −28359.8/T+9.746	0.994	235.79
Briquettes with Shobarkol coal [8]	lnk= −23408.4/T+7.257	0.975	194.63
Briquettes from gas cleaning dust at Aktobe ferroalloy plant and China	lnk= −29465.6/T+2.906	0.995	56.4
Briquettes from dust from pellet production site at Donskoy GOK	lnk= −27052.9/T+2.929	0.957	51.8
Briquettes from flash	lnk= −14175.9/T+1.828	0.960	27.14

It is mentioned in [9-11], that silica accelerates reduction of iron oxides and chromium in chromium ores, while in [12, 13] it is noted that silica retards the process of solid phase reduction by closing the ways of reducing agent feed to reaction surface between grains of chromium spinelides and reducing agent.

Frontal reduction of iron and chromium oxides by carbon leads to forming of metal-slag shell around the grains of chromium spinelides in chromium ores. Its thickness depends on structure of ores, temperature, time and reduction degree. The shell looks like a metal-slag barrier for reduction development through depth of grains in chromium ores. Silica and aluminium contain in coal ash in increased amount; they are dissolved during reduction process in high-melting and tough slag-forming oxides – products which appear during reduction of chromium spinelides. As a result, low-melting and fluid slags are forming on the contact surface. These slags destruct easily slag diffusion barrier and strip off the surface of nucleus in chromium spinelides for new contact between iron and chromium oxides and carbon.

The conducted researches confirm the principal possibility of use of briquetted mono-charge, but at the same time it is required to provide more deep and comprehensive examination of melting of carbon ferrochromium in an ore smelting furnace with conduction of pilot batches in large-scale laboratorial conditions, aimed on reveal of the features of reduction processes.

This research was funded by the Committee of science of the Ministry of education and science of Kazakhstan Republic (Grant No. AP14871610).

REFERENCES

1. Shabanov E. Zh., Izbembetov D. D., Baisanov S. O., Shadiev M. F. Technology of high-carbon ferrochromium production using mono-charge briquettes. *Izvestiya vysshikh uchebnykh zavedeniy. Chernaya metallurgiya*. 2018. Vol. 61. No. 9. pp. 702-707.
2. Tiunova T. G., Yakushev R. M. et al. Determination of activation energy for solidification of epoxyacrylate lacquer compositions based on DTA data. *Plasticheskie massy*. 1998. No. 8. pp. 28-30
3. Wagner M. Thermal analysis in practice. Fundamental Aspects. Carl Hanser Verlag GmbH & Co. KG. 2018. p. 349.
4. Tanzi M. C., Farè S., Candiani G. Techniques of Analysis Foundations of Biomaterials Engineering. 2019. p. 393-469.
5. Gabelchenko N. I., Khantimirova S. B., Mishustin O. A., Savchenko A. I. Investigation of local interval of steels and cast irons primary crystallization using differential thermal analysis. *Science, Education and Culture in Eurasia and Africa: The 7 International Academic Congress (France, Paris, 23-25 April 2017. Proceedings. Vol. VII. Paris: University Press, 2017*. pp. 489-494.
6. Gabelchenko N. I., Khantimirova S. B., Shtepina E. V. Study of local intervals of crystallization process for steel and cast iron via the method of differential thermal analysis. *Izvestiya VolgGTU. Seriya "Problemy materialovedeniya"*. 2016. No. 9 (188). pp. 113-116.
7. Differential thermal analysis. Methodical recommendations for laboratorial workshop and self-guided work of students within the course "Physical chemistry of high-melting nonmetallic and silicate materials". Collected by Prof. Lotov V.A. et al. Tomsk. Izdatelstvo TPU. 2020. 30 p.
8. Tolymbekov M. Zh., Baisanov S. O., Abdulabekov E. E., Baicanov A. S. Investigations on development of the smelting technology for high-carbon ferrochromium using complex briquetted charge. Report of the scientific and research study. Chemical and metallurgical institute named after Zh. Abishev. 2007. 63 p.
9. Kaliakparov A. G., Suslov A. V., Nurmaganbetova B. N., Zhdanov A. V., Nurmaganbetov Z. O. Smelting of high-carbon ferrochrome from chromium agglomerate produced with alumina-silica flux. *Steel in Translation*. 2017. Vol. 47. No. 1.pp. 65-69.
10. Salina V. A., Zhuchkov V .I., Sychev A. V. Thermodynamic Simulation of the Carbothermic Reduction of Chromium from the Cr_2O_3–FeO–CaO–SiO_2–MgO–Al_2O_3 Oxide System. *Russian Metallurgy (Metally)*. 2021. No. 2. pp. 229-233.
11. Kelamanov B., Samuratov Y., Zhumagaliyev Y., Akuov A., Sariev O. Titanium and chrome oxides system thermodynamic diagram analysis. *Metalurgija*. 2020. Vol. 59. No. 1. pp. 101-104.
12. Sariev O., Kelamanov B., Zhumagaliyev Y., Kim S., Abdirashit A., Almagambetov M. Remelting the high-carbon ferrochrome dust in a direct current arc furnace (DCF). *Metalurgija*. 2020. Vol. 59. No. 4. pp. 533-536.
13. Akuov A., Samuratov Y., Kelamanov B., Zhumagaliyev Y., Taizhigitova M. Development of an alternative technology for the production of refined ferrochrome. *Metalurgija*. 2020. Vol. 59. No. 4. pp. 529-532.