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RESEARCH OF THERMAL ANALYSIS OF NICKEL ORE AND MIXTURE WITH CARBON-CONTAINING REDUCING AGENTS BY NON-ISOTHERMAL METHOD

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The article presents the results of physicochemical studies of nickel ore and charges based on it for smelting nickel-containing ferroalloys. Using a derivatogram, the main phase transformations of nickel ore and mixtures with various carbon-containing reducing agents, such as coal and coke, are established. The activation energy of the processes occurring during the heat treatment of nickel ore and a mixture of nickel ore with various reducing agents by non-isothermal kinetics were determined.

Key words: nickel ore, coal, coke, differential thermal analysis, activation energy.

INTRODUCTION

Thermal analysis of charge materials is one of the main studies in the metallurgical process. Currently, one common method of thermal analysis is differential thermal analysis. This method makes it possible to identify and study phase transformations and chemical reactions in it, according to the thermal effect [1-3]. When studying charge materials, in our case nickel ore and mixtures with various reducing agents, it is necessary to establish what physical and chemical transformations will occur during heating at different temperatures. The non-isothermy method was used to fully study the properties of nickel ore and a mixture of ore with carbon-containing reducing agents.

The purpose of the work. Investigation of phase transformations occurring during gradual heating of nickel ore and mixtures with various reducing agents by non-isothermal method, determination of the activation energy of processes.

According to the results of the research, it is possible to determine the rate of the reactions of the reduction of the main elements, with regard to the smelting of nickel alloys.

RESEARCH METHODOLOGY

To determine the curves of differential thermal analysis (DTA) of charge materials, derivatograms of the F. Paulik, J. Paulik, L. Erdei Derivatograph Q = 1000 system were used in the temperature range of 20 - 1400 ° C with a heating step of 10 °C/min [4]. The temperature in the furnace was measured by a platinum-platinum-rhodium thermocouple. The studies were carried out in an oxidizing atmosphere.

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The charge for thermographic studies was prepared from the nickel ore of the "Batamasha" deposit and various reducing agents, which used the following materials in a fraction of 0 – 0,15 mm:

– coal;
– coke.

As the temperature in the furnace of the derivatograph increases, the writing device registers on the thermogram all the physico-chemical changes occurring in the sample in the form of curved lines T, TGA and DTA. The temperature (T), the change in weight (TGA) and the rate of change in the thermal content (DTA) of the test substance are simultaneously measured in the sample depending on time [5]. The composition of the charge materials is shown in Table 1.

Table 1 **Chemical composition of nickel ore and reducing agents / %**

Material	Ni_{total}	Fe_{total}	Cr_{total}	SiO_2	MgO
Nickel ore	1,23	14,38	1,69	51,57	3,52
Materials	Al_2O_3	Fe_{total}	P_{total}	SiO_2	MgO
Coke ash	14,61	10,25	0,14	40,59	6,08
Coal ash	21,30	5,03	0,20	56,97	1,77

Table 2 **Technical composition of reducing agents / %**

Materials	A^c	W	V_{daf}	C
Coke	19,38	2,44	6,19	73,86
Coal	9,85	4,8	35	49,99

A^c – ash; W – moisture; V_{daf} – volatile-matter yield; C – solid carbon.

For thermal analysis, the mass and ratio of the charge materials were as follows:

- nickel ore – 1 200 mg;
- nickel ore/coke – 1 115/55 mg.

The weight of the sample – 1 170 mg.

- nickel ore/coal – 1 005/75 mg.

The weight of the sample – 1 080 mg.

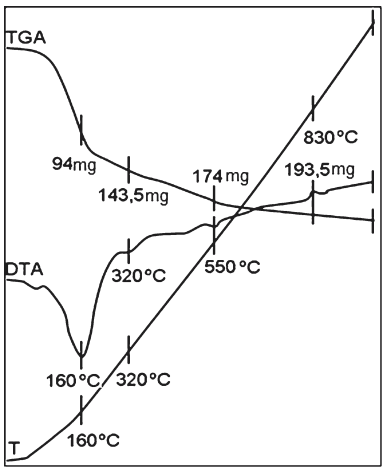

Figure 1 Derivatogram of nickel ore

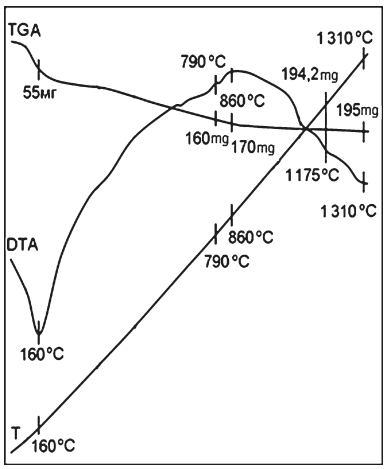

Figure 2 Derivatogram of a mixture of nickel ore and coke

Figure 1 shows the result of thermal analysis of nickel ore.

The processes occurring in nickel ore with gradual heating are accompanied by the following effects. The first sharp endothermic effect at a temperature of 160 °C indicates the removal of hygroscopic moisture with a decrease in sample weight by 94 mg. A further increase in temperature to 320 °C leads to a weak endothermic effect, which corresponds to the release of natural moisture and decomposition of hydrogetite with a decrease in mass in the amount of 143,5 mg. The third endothermic effect in the temperature range 350-550 °C can be associated with both magnetic transformations of small amounts of magnetite (Fe_3O_4) and decomposition of the mineral serpentine ($3MgO{\cdot}2SiO_2{\cdot}2H_2O$) with weight loss in the amount of 174,0 mg. At a temperature of 830 °C, the fourth exothermic effect is recorded with the decomposition of the mineral nontronite (Fe, Al)$_2[Si_4O_{10}(OH]_2{\cdot}nH_2O$) with a decrease in mass in the amount of up to 193,5 mg.

The process of removing hygroscopic and hydrated moisture (bound in nickel and iron hydroxides) is accompanied by pronounced endothermic effects in the temperature range 0-320 ° C with a weight loss of 237,5 mg.

The derivatogram of the charge mixture consisting of nickel ore and coke is shown in Figure 2.

There are two endothermic and two exothermic effects on the derivatogram of nickel ore with coke. The first, sharp (narrow) endothermic effect characterizing the release of hygroscopic moisture was recorded at a tempe-rature of 160 °C with a decrease in weight by 55 mg. A further increase in temperature to 790 °C leads to a weak second exothermic effect, showing complete removal of hydrated moisture and volatile components with a total weight loss of up to 99 mg.

In addition to these processes, some physico-chemical transformations occur in the temperature range 500 - 600 °C, such as: de-composition of serpentine minerals ($3MgO{\cdot}2SiO_2{\cdot}2H_2O$), siderite ($FeCO_3$) and the formation of magnetite (Fe_3O_4).

The third (widest) exothermic effect, recorded at a temperature of 860 °C, can be explained by the combustion of solid carbon and the beginning of decomposition of the mineral nontronite (Fe, Al)$_2[Si_4O_{10}(OH)]_2{\cdot}nH_2O$) with a total weight loss of 160 mg. The fourth endothermic effect at a temperature of 1 175 °C is accompanied by complete combustion of solid carbon, restructuring of the structure of the main components of natural minerals and with a total weight loss equal to 170 mg.

The results of the derivatogram of the composition - nickel ore and Shubarkol coal are shown in figure 3. The derivatogram represents four pronounced effects.

The first endothermic peak at a temperature of 200 °C is characterized by the removal of hygroscopic moisture, and the second one manifests itself at a temperature of 550 °C and corresponds to the decomposition of $FeCO_3$ siderite and serpentine mineral ($3MgO{\cdot}2SiO_2{\cdot}2H_2O$) with a decrease in mass in the amount of 70 mg and 139 mg, respectively. The third exothermic effect, corresponding to a temperature of 920 °C, indicates the comple-tion of the combustion process of solid carbon. The total weight loss at this temperature is 189 mg.

The last, fourth (with a sharp maximum) endothermic effect at a temperature of 1045 °C is accompanied by a partial transformation of the main phases (Fe_2O_3, Cr_2O_3, NiO) with a total weight loss of up to 194.5 mg. The total weight loss of the material is 200 mg.

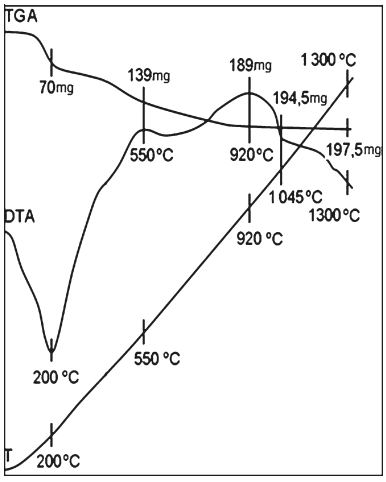

Figure 3 Derivatogram of a mixture of nickel ore and coal

RESULTS RESEARCH

Based on the determination of the temperature values and the magnitude of the deviation of the DTA curve from a given direction, according to Figure 4, dependences in coordinates lgΔt - 1/T for each thermal effect are constructed and the values of the E_{act} of processes corresponding to peaks on derivatograms are calculated according to the tangent of the angle of inclination of the direct dependence lgΔt - 1/T [6-10]. Based on the constructed graphs, the activation energy (E_{act}) values for thermal effects are calculated, where the reduction processes for nickel-containing materials begin (Table 1).

CONCLUSIONS

Analysis of temperature maxima and activation energy levels of processes accompanied by peaks on the curves of differential thermal analysis of nickel ore, nickel ore compositions with various reducing agents suggests that diffusion processes occurring during heat treatment occur under more favorable conditions. Therefore, it can be concluded that the processes occurring during the heat treatment of nickel ores with various reducing agents proceed at a sufficiently high speed and a high degree of completeness has been achieved at sintering temperatures of 600 – 1 000 °C.

The observed decrease in the activation energy of each peak individually is associated with the influence of a reducing agent, both coal and coke, on the processes taking place. And also the low value of the activation energy of each peak is associated with a decrease in the energy barrier, which accelerates pyrometallurgical processes.

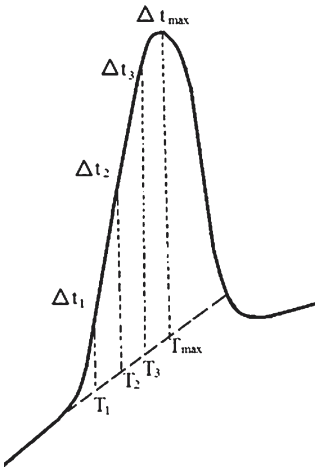

Figure 4 Diagram of determining the temperature values and the magnitude of the deviation of the DTA curve from a given direction

Table 1 **Values of the apparent activation energy determined by the tangent of the angle of inclination of the direct dependence lgΔt-1/T**

№	Material	Equation	Coefficient correl. R	E_{act}, kJ/mol	Temperature range, °C
1	Nickel ore	ln*Δt*=-254,03/T + 8,02	0,9752	4,864	80-160
		ln*Δt*=-789,73/ T+ 14,53	0,9893	15,121	280-320
		ln*Δt*=-2791,7/T + 35,05	0,9991	53,455	520-550
		ln*Δt*=-9231,9/ T+ 85,33	0,9813	176,772	800-830
2	Nickel ore+coke	ln*Δt*=-78,42/T + 3,95	0,9965	1,501	20-160
		ln*Δt*=-4 070,2/ T+ 39,40	0,9686	77,935	765-790
		ln*Δt*=-1138,4/T + 11,59	0,8963	21,798	740-860
		ln*Δt*=-12 536/ T+ 87,17	0,9999	240,044	1 160-1 175
3	Nickel ore+coal	ln*Δt*=-143,84/ T+ 5,17	0,9747	2,754	20-200
		ln*Δt*=-924,35/ T+ 12,87	0,9442	17,699	450-550
		ln*Δt*=-863,75/ T+ 9,00	0,9756	16,539	720-920
		ln*Δt*=-2 215,6/ T+ 18,37	0,8716	42,425	1 020-1 045

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REFERENCES

[1] Wendlandt U. Thermal methods of analysis / translated from English – M.: Mir, 1978. – 515 p.

[2] L. Cheng, W. Li, Y. Li, Y. Yang, Y. Li, Yi Cheng, D. Song. Thermal analysis and decomposition kinetics of the dehydration of copper sulfate pentahydrate Journal of Thermal Analysis and Calorimetry. 135 (2019), 2697 – 2703.

[3] D. Yessengaliyev, T. Kainenova, A. Angsapov, G. Zhexenbaeva, G. Zhaumitova, Z. Sultamuratova. Feasibility study of using with high basicity manganese ore for smelting refined ferromanganese. Metalurgija, 61 (2022) 2, 371-373.

[4] Paulik F, Paulik J., Erdey L. Der. Derivatograph II. Z. Anal. Chem., Vol. 160 (1958), 321.

[5] Shabanov, E., Izbembetov, D.D., Baisanov, S.O., Shadiev, M.F. Technology for the production of high-carbon ferrochromium using mono-briquettes. Izvestiya Ferrous Metallurgy, 61 (2018) 9, 702-707.

[6] Kelamanov, B., Sariev, O., Akuov, A.,Samuratov, Ye., Sultamuratova, Z., Orynbassar, R. Study of nickel briquettes by thermographic method. Metalurgija, 61 (2022) 1, 217-220.

[7] Piloyan G.O., Novikova O.S. Thermographic and thermogravimetric methods for determining the activation energy of dissociation processes // Journal of Inorganic Chemistry. 12 (1967) 3, 602 -604.

[8] Makhambetov, Y.N., Timirbayeva, N.R., Baisanov, S.O., Baisanov, A.S. Research of physical and chemical characteristics of the new complex calcium-containing ferroalloy//CIS Iron and Steel Review, 19 2020, 18-22.

[9] Kim, A. S., Akberdin, A. A., & Sultangaziev, R. B. Using Basalt Rocks for Agglomeration of Refractory Chromite Ores of Kazakhstan. Metallurgist, 63 (2020) 9-10, 1005-1012.

[10] Makhambetov, Y., Abdirashit, A., Myngzhassar, Y., Burumbayev, A., Zhakan, A., Onuralp, Y. Research on the possibility of obtaining medium-carbon ferromanganese from the Djezdinskoe deposit // Complex Use of Mineral Resources, 331 (2024) 4, 101-108. https://doi.org/10.31643/2024/6445.43

Note: The responsible for England language is Adilkhan Nurzhanov, Aktobe Kazakhstan