

Iron Reduction from Concentrates of Hydrometallurgical Dressing

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Abstract—The article presents results of theoretical and experimental studies of the processes of iron solid-phase reduction from an iron-containing concentrate obtained as a result of hydrometallurgical dressing of ferromanganese and polymetallic manganese-containing ores with coals of grades D (long-flame) and 2B (brown). The method of thermodynamic modeling using TERRA software complex was used to study the reducing properties of hydrocarbons by calculating equilibrium compositions in the temperature range of 373–1873 K. The authors obtained the dependences of compositions and volume of the gas phase formed as a result of the release of volatile components during heating on the temperature for the coals of the grades under consideration. As a result of thermodynamic modeling, the optimal temperatures and consumption are determined, which ensure the complete iron reduction from an iron-containing concentrate. The results of experimental studies were obtained by modern research methods using laboratory and analytical equipment, as well as methods of statistical processing. Results of the coals analysis carried out using the Setaram LabSys Evo thermal analyzer showed that the process of thermal decomposition of coals of the studied grades proceeds according to general laws. The process of thermal decomposition of long-flame coal proceeds less intensively than of brown coal. The results of an experimental study of the processes of thermal decomposition of reducing agents have shown that volumes of the gas phases, formed when coals are heated to a temperature of 1173 K in an argon atmosphere, practically coincide with the calculated values. As a result of thermodynamic modeling and experimental study, the optimal consumption of D and 2B grades of coal is determined at a temperature of 1473 K. The best reducing agent with a minimum specific consumption is long-flame coal of D grade. When determining the optimal amount of reducing agent in charge mixtures during the study of metallization processes, it was found that with an excess of reducing agent, it is possible to achieve almost complete extraction (98–99%) of iron from the concentrate.

Keywords: thermodynamic modeling, iron-containing concentrate, long-flame coal, brown coal, iron reduction

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INTRODUCTION

Presently, the modern state and development of metallurgy require introducing new power- and resource-saving technologies, which will partially allow solving the problem of reduction of power and raw material costs in metallurgical industry [1–10]^{1, 2}.

One of such promising branches in metallurgy is direct reduction of metals from oxide materials [11–13] of both natural and technogenic origin.

For ferromanganese ores of Kemerovo region – Kuzbass, on the basis of theoretical and experimental studies, a two-stage enrichment scheme was proposed, which allows obtaining high-quality concentrates of manganese (58–60 % Mn) and iron-containing concentrates (48–54% Fe) [14]. The pointed concentrates are applicable in metallurgical production.

Development of technologies of direct metal reduction requires preliminary studies in order to determine the optimal conditions of realization of reduction processes, which are accompanied by a complex of physical-chemical transformations occurring under conditions of solid, liquid and gaseous media.

¹ <http://docs.cntd.ru/document/420204426>).

² <http://ietd.iipnetwork.org/content/slrn-process>).

Table 1. Characteristics of reducing agents

Indicator	Indicator value	
	coal of grade D	coal of grade 2B
W^r	15.4	35.3
A^d	5.64	7.83
V^{daf}	43.53	46.76
S^d	0.26	0.68
Content of carbon (C_{sol}), %	55.6	49.1
Element content per organic mass, %:		
C^{daf}	72.02	70.41
H^{daf}	6.12	3.88
N^{daf}	1.74	0.98
O^{daf}	20.12	22.58
S^{daf}	0.34	1.15
Content of oxides in ash, %		
SiO_2	55.3	11.4
Al_2O_3	20.1	5.2
Fe_2O_3	8.5	10.3
CaO	9.7	42.7
MgO	3.7	4.8
P_2O_5	1.80	0.02

A^d —ash content; V^{daf} —output of volatile compounds; W^r —humidity; S^d —sulfur content.

RESEARCH METHODS AND MATERIALS

Thermodynamic modeling and laboratory researches of the processes of thermal decomposition and the reducers and metallization of the concentrate were carried out in order to determine the optimal conditions of the processes of reduction of iron from the concentrate obtained during hydrometallurgical enrichment of ferromanganese ores.

Determination of the range of admissible values of thermodynamic functions and parameters of complex multicomponent metallurgical systems, where state changes are accompanied by phase, polymorphous and chemical transformations, is a complicated problem as compared with formulations of classical thermodynamics for elementary systems or separate reactions. Such a problem can be solved only by complete thermodynamic analysis, which allows determining equilibrium composition of the system by the properties of its components at given thermodynamic parameters. For this purpose, it is proposed to use the method of thermodynamic modeling based on searching for an extremum of the thermodynamic potential, and namely the maximum of entropy.

As a tool for carrying out computational experiments using the methods of thermodynamic modeling, we selected software complex “Terra” developed in N.E. Bauman Moscow State Technical University and assigned for computing thermodynamic properties and the composition of equilibrium state phases of arbitrary systems with chemical and phase transformations [15, 16].

The considered software complex is currently widely used in thermodynamic researches due to high credibility of the obtained data [17, 18].

The process of reduction of iron from the concentrate, obtained as a result of hydrometallurgical enrichment of ferromanganese ores, was researched using coals of two grades (long-flaming (D) and brown (2B)). The chemical composition of iron-containing concentrate is as follows: 82.3% Fe_2O_3 ; 4.15% SiO_2 ; 4.9% $CaCl_2$; 2.35% Al_2O_3 ; 2.69% CaO ; 3.6% Mn_2O_3 ; 0.005% S; 0.005% P. Characteristics of the reducers are presented in Table 1.

The processes of thermal decomposition of coals were studied using thermal analyzer Setaram LabSysEvo. The methods of thermogravimetry allow determining the change of mass loss during heating of a sample in the given conditions with a high accuracy. Samples of the reducers were heated to temperature of 1373 K at speed of 10 K/min in conditions of free air access.

The volumes and compositions of gaseous phases, formed during heating of the reducers to temperature of 1173 K, were determined during experimental studying of the processes of thermal decomposition of the reducers. The researches were carried out using experimental assembly presented in Fig. 1.

The experimental methodology was concluded in the following. Samples for the experiments were prepared by refining of the reducer and screening fractions from -0.125 to $+0.050$. The obtained powder with mass of 4 g was placed into a ceramic boat and slightly compacted. The boat 3 with the hinge was placed into the center of quartz pipe 2, after which the system was sealed. Then, the system was blown by a neutral gas at open atmosphere valve 9 during 15 min. Pressure in the system was maintained within the range of 5–15 mm WC according to the indications of the U-shaped manometer 6. After stopping the supply of the neutral gas, the furnace was turned on and heated to a temperature of 1273 K at speed of 20 K/min. The resulting gases displaced the brine solution from the gas collector 5. When the set temperature was reached, the sample was held for 15 min until the water flow into flask 13 complexly stopped, after which the shut-off valves 8 and 12 were closed. Volume of the formed gas corresponded to that of water in flask 13. Temperature for the collected gas was registered by the thermometer 11 and displacement of gas through the dryer into working chamber of the

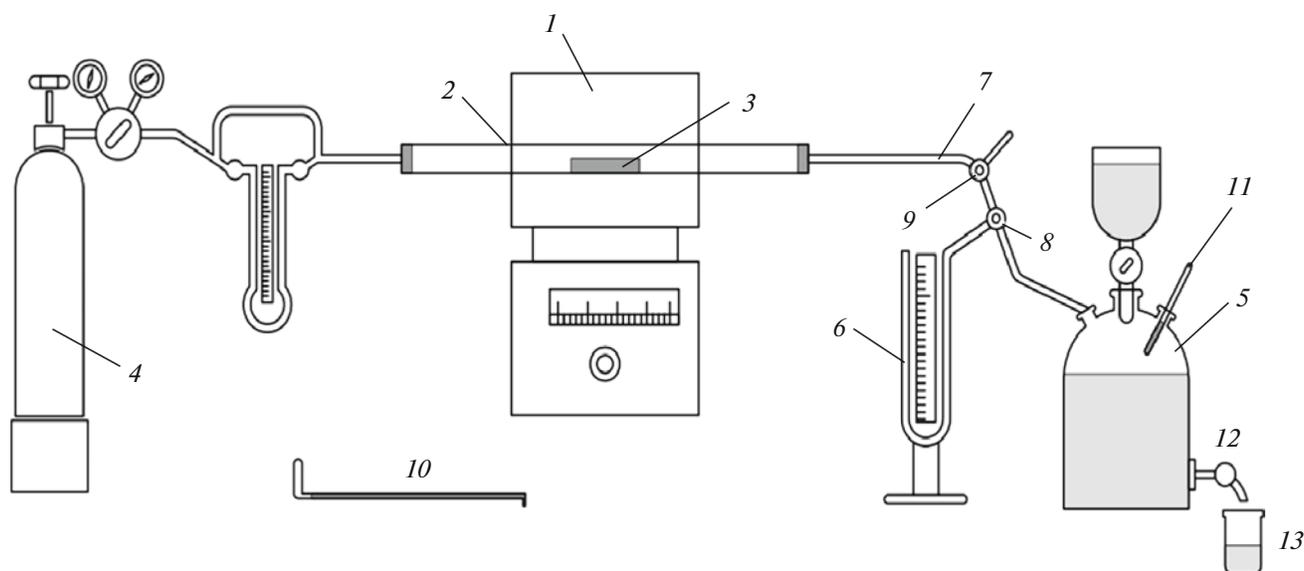
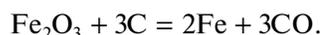


Fig. 1. Scheme of experimental installation for gas phase analysis: (1) heating furnace; (2) quartz tube; (3) ceramic tube with charge attachment; (4) inert gas cylinder (argon); (5) gas collector; (6) U-shaped pressure gauge; (7) glass tube; (8) shut-off valve; (9) atmospheric valve; (10) pusher; (11) thermometer; (12) tap; (13) flask for water collecting.

chromatograph was carried out. Analysis of the sampled gases was carried out on chromatograph LKhM-8D.

When studying the metallization process, reduction firing was carried out in Tamman furnace at temperatures of 1173, 1273, 1373, and 1473 K and isothermal holding time of 30–80 min.

To study the effect of temperature and duration of reduction firing on the processes of metallization, briquettes were made from iron-containing concentrate, brown, long-flaming coals and a binder. As a binder, we used liquid glass. The content of carbon in the briquette was calculated for the complete reduction of iron from the iron-containing concentrate:



The composition of the briquettes is presented in Table 2.

The resulting briquettes (one at a time) were placed in a graphite crucible, after which the crucible with the briquette was covered with a graphite lid. To release the excess amount of gas, a hole was preliminarily made in the cover.

The crucibles with briquettes were placed into the furnace preliminarily heated to the experimental tem-

perature. When the required holding time was reached, the crucibles with briquettes were removed from the furnace and cooled in the open air. The obtained materials were subjected to chemical analysis.

RESULTS AND DISCUSSION

At first stage, reductive properties of the coals were researched using software complex "Terra" by computing equilibrium compositions in temperature range 373–1873 K. Figure 2 presents dependences of the compositions and volume of gas phase, which is formed as a result of emission of volatile components during heating, from temperature for coals of grades D and 2B. Temperature range 373–1173 K is characterized by decreasing of the volume concentration of water vapor as well as increasing of the concentrations of hydrogen and carbon monoxide CO. At the same temperatures, carbon dioxide CO₂ is present in slight amount in the system, the maximal concentration of which constitutes 0.16 and 0.08 m³/kg at temperature of 873 K for coals of grades D and 2B. At temperature of 1173 K compounds H₂O, CH₄ and CO₂ completely disappear, the composition of the system is stabilized, and gas phase consists of only H₂ and CO. The content

Table 2. Composition of experimental briquettes

Briquette	Reducer	Content, g, in 100 of mixture		Content of element, %				
		concentrate	reducer	Fe _{tot}	SiO ₂	Al ₂ O ₃	CaO	MgO
B	Brown coal	62.32	34.68	33.40	15.23	3.11	0.92	0.63
D	Jet coal	67.35	29.65	35.38	15.45	3.05	0.86	0.62

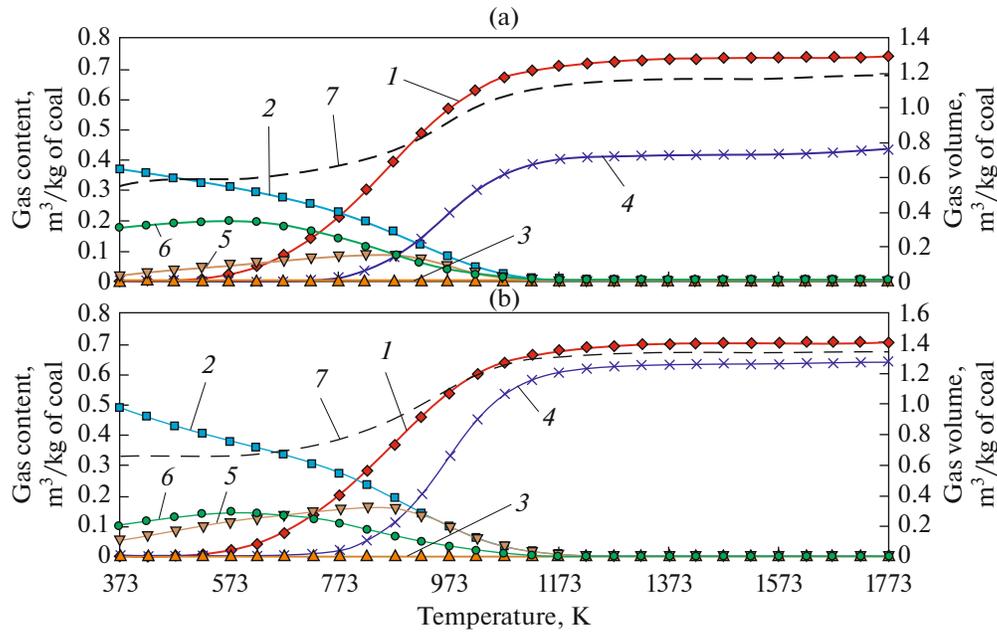


Fig. 2. Dependences of parameters of equilibrium composition and volume of the gas phase on temperature when heating coals of grades D (a) and 2B (b): (1) H₂; (2) H₂O; (3) N₂; (4) CO; (5) CO₂; (6) CH₄; (7) volume of the gas, m³.

of carbon monoxide CO at temperatures above 1173 K constitutes 0.42 m³/kg for coal of grade D and 0.62 m³/kg for coal of grade 2B. The content of hydrogen in gas phase for the considered grades of coal is almost identical and constitutes about 0.7 m³/kg. Sharp increase in the gas volume begins at temperature of 673 K.

At temperature of 1173 K, emission of volatile components is completely stopped. The volume of gas phase does not change with growth of temperature and constitutes 1.17 and 1.34 m³/kg of coal of grades D and 2B.

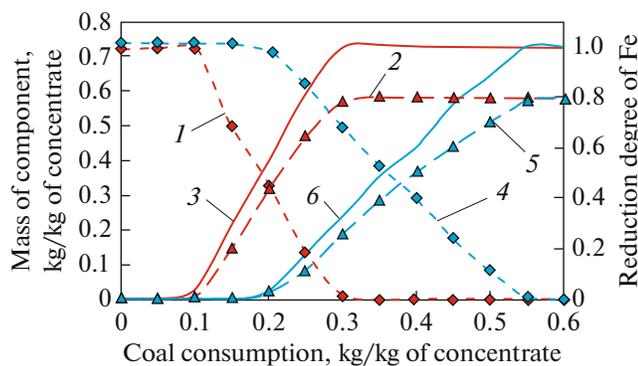


Fig. 3. Dependences of parameters of iron reduction from iron-containing concentrate on consumption of coal of different grades at a temperature of 1473 K: (1) weight of FeO (grade D); (2) weight of Fe (grade D); (3) reduction degree (grade D); (4) weight of FeO (grade 2B); (5) weight of Fe (grade 2B); (6) reduction degree (grade 2B).

Then, the process of solid-phase reduction of iron from the concentrate, obtained as a result of hydrometallurgical enrichment of ferromanganese ores by coals of grades D and 2B, was researched. The computations were carried out for 1 kg of concentrate, coal consumptions varied in the range 0.1–0.7 kg/kg of concentrate. Since the results of thermodynamic modeling of reduction processes obtained earlier showed that the reduction of iron from iron-containing materials occurs at temperatures above 1073 K [14–18], then the researches were carried out in the range from 1073 to 1773 K. The research results showed that the given temperature range does not influence the reduction process. Also, the amount of reduced iron depends only on consumption of the reducer. Dependences of the degree of iron reduction on the consumption of coal of different grades at temperature of 1473 K are presented in Fig. 3, which implies that the required amount of coal of grades D and 2B for complete reduction of iron from 1 kg of ore constitutes 0.30 and 0.55 kg. At these consumptions of reducers in the system, iron oxides disappear. During the increase of coal consumptions above the pointed values, the mass of reduced iron remains constant and constitutes 0.58 kg/kg of concentrate (Fig. 3).

The results of analysis of coals, carried out using thermal analyzer Setaram LabSys Evo, are shown in Fig. 4, and the graphs were plotted using the values of mass change (TG).

The research results showed that the process of thermal decomposition of the researched grades of coal occurs according to the general regularities and

includes two stages: *I*—removal of hygroscopic and colloid-bound moisture; *II*—sharp change of coal mass caused by emission of volatile products and gasification of coal.

For brown coal, stage *II* begins at temperature of 716 K, i.e., 60 K lower than thermal decomposition of long-flaming coal. The amount of gaseous products emitted during thermal decomposition of brown coal is significantly larger than during decomposition of long-flaming coal. Mass loss of brown and long-flaming coals constituted 90.6 and 84.5%, respectively. The process of thermal decomposition of long-flaming coal is less intensive than of brown coal.

The results of experimental studying of the thermal decomposition processes of the reducers showed that the gas phase volumes formed during heating of 1 g of reducers to 1173 K in the atmosphere of argon constitute 1.20 and 0.85 L for brown and long-flaming coals, which almost coincides with the computed data (Fig. 2). The compositions of gas phases are presented in Table 3.

Analysis of the gases showed that the coal phase mainly consists of hydrogen. The largest amount of hydrogen is contained in the gas phase of brown coal and the largest amount of carbon monoxide CO is contained in gas phase of coke breeze. Gases formed

Table 3. Content of gas phase when reducing agents are heated to a temperature of 1173 K in an argon atmosphere

Reducer	Gas content, %					
	CO ₂	CO	H ₂	CH ₄	O ₂	N ₂
Coal of grade D	10.73	16.03	66.01	4.86	2.36	—
Coal of grade 2B	11.47	6.09	75.59	6.63	0.22	—

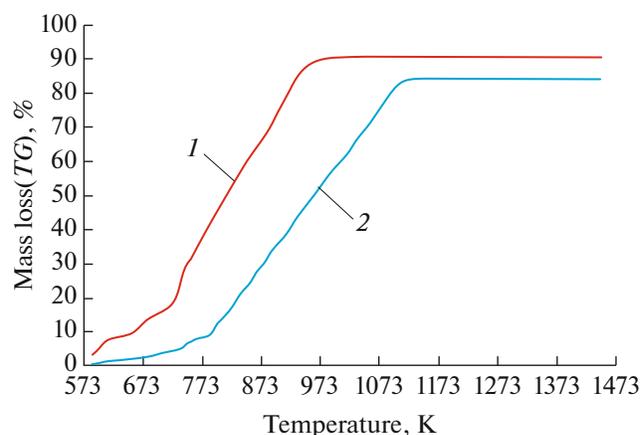


Fig. 4. Results of thermogravimetric analysis of coals: (1) coal of grade 2B; (2) coal of grade D.

during thermal decomposition of coals mainly consist of the mixture of H₂ and CO (over 80%), gas of such a composition has a high reduction potential. Gases of close composition (H₂ + CO = 90–92%) are obtained during catalytic conversion of natural gas by technologies Midrex and HyL III, which allows assuming that along with solid carbon, the formed gases will also participate in the processes of reduction of iron from oxides [19].

The research results on the determination of the optimal amount of the reducer in furnace-charge mixtures during studying the processes of metallization (Table 4) showed that in excess of the reducer almost complete (98–99%) extraction of iron from the concentrate can be reached.

The optimal correlations of the components iron-containing concentrate : coal : binder in furnace-charge mixture for briquetting using brown or long-

Table 4. Average results of experiments to determine the optimal amount of coal in charge mixture

Reducer	Amount of reducer (C/C _{stoich})	Content of the main components in metallization products, %			Degree of metallization, %
		Fe _{tot}	Fe _{met}	C	
Brown coal	1.1	76.80	76.10	2.7	99.1
	1.0	79.10	77.40	2.5	97.9
	0.9	80.90	78.20	2.1	96.7
	0.8	83.50	79.10	2.1	94.7
Long-flame coal	1.1	81.10	80.90	2.1	99.8
	1.0	82.51	81.24	2.1	98.6
	0.9	84.81	82.30	1.9	97.0
	0.8	85.10	80.30	1.8	94.4

flaming coals constitute 68 : 35 : 3 and 74 : 22 : 3. Such correlations correspond to the consumption of brown and long-flaming coals of 51.4 and 29.7 kg/kg of concentrate. The obtained experimental results are close in their values to the data of thermodynamic modeling.

CONCLUSIONS

Reduction properties of coals (long-flaming of grade D and brown of grade 2B) were researched using software complex “Terra” by computing equilibrium compositions in temperature range 373–1873 K, dependences of the parameters of equilibrium composition of gas phase on temperature during heating of coals of grades D and 2B were determined. The process of thermal decomposition of coals during heating was studied. It was established that the process of thermal decomposition of coals of the considered grades occurs according to the general regularities. At the same time, the process of thermal decomposition of long-flaming coal is less intensive as compared with brown coal. The optimal consumptions of coals of grades D and 2B at temperature of 1473 K were determined as a result of thermodynamic modeling and experimental studying of the process of reduction of iron from iron concentrate. The best reducer with minimal specific consumption is long-flaming coal of grade D. When determining the optimal amount of a reducer in furnace-charge mixtures when studying metallization processes, it was found that with an excess of a reducer, it is possible to achieve almost complete (98–99%) extraction of iron from the concentrate.

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SUPPLEMENTARY INFORMATION

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REFERENCES

- Rudyka, V.V., Prospects of the technology of iron direct reduction in metallurgical production, *Chern. Metall., Byull. Nauchno-Tekh. Ekon. Inf.*, 2017, no. 10, pp. 14–23.
- Rutherford, S.D. and Kopfle, J.T., Mesabi nugget: World’s first commercial ITmk3(r) plant, *Proc. AISTech 2009 Iron and Steel Technology Conf.*, Warrendale, PA: Assoc. Iron Steel Technol., 2009, vol. 1, pp. 177–185.
- Seki, K. and Tanaka, H., *Changes in Paradigm—Development of Iron & Steel Industry by Applying Coal Based DR Processes: Fastmelt(r) & ITmk3(r)*, Tokyo: Kobe Steel, 2008.
- Nagano, K.I., The current status and future of iron ore and coal resources for Japanese steel mills, *Tetsu-to-Hagane*, 2004, vol. 90, no. 2, pp. 51–60. https://doi.org/10.2355/tetsutohagane1955.90.2_51
- Zhang, Y.Y., Qi, Y.H., Zou, Z.S., and Li, Y.G., Development prospect of rotary hearth furnace process in China, *Adv. Mater. Res.*, 2013, vol. 746, pp. 533–538. <https://doi.org/10.4028/www.scientific.net/AMR.746.533>
- Wiesinger, H., Eberle, A., Siuka, D., Freydorfer, H., and Bohm, C., Status, realized improvements and future potentials of the Corex technology, *Stahl Eisen*, 2002, vol. 122, no. 6, pp. 23–28.
- Nobuhiko, T., Development of iron-making technology, *Nippon Steel Tech. Rep.*, 2012, no. 101, pp. 79–88.
- Kirschen, M., Badr, K., and Pfeifer, H., Influence of direct reduced iron on the energy balance of the electric arc furnace in steel industry, *Energy*, 2011, vol. 36, no. 10, pp. 6146–6155. <https://doi.org/10.1016/j.energy.2011.07.050>
- Tanaka, H., Miyagawa, K., and Harada, T., *Fastmet, Fastmelt, and ITmk3: Development of new coal-based iron-making processes, Direct Midrex*, 2007/2008, pp. 8–13.
- Nikitchenko, T.V. and Timofeeva, A.S., Production of direct reduction iron, *Chern. Metall., Byull. Nauchno-Tekh. Ekon. Inf.*, 2014, no. 3, pp. 46–50.
- Hryha, E. and Dudrova, E., The sintering behavior of Fe–Mn–C powder system, correlation between thermodynamics and sintering process, Mn distribution and microstructure, *Mater. Sci. Forum*, 2007, vols. 534–536, pp. 761–764. <https://doi.org/10.4028/0-87849-419-7.761>
- Sheshukov, O., Mikheenkov, M., Vedmid, L., Nekrasov, I., and Egiazaryan, D., Mechanism of ion-diffusion solid-phase reduction of iron oxides of technogenic origin in the presence of the liquid phase and without it, *Metals*, 2020, vol. 10, no. 12, pp. 1–12. <https://doi.org/10.3390/met10121564>
- Nokhrina, O.I., Rozhikhina, I.D., Rybenko, I.A., and Khodosov, I.E., Energy-efficient reduction of iron from its ores, *Steel Transl.*, 2016, vol. 46, no. 4, pp. 245–250.
- Nokhrina, O.I., Rozhikhina, I.D., Golodova, M.A., and Izrail’skii, A.O. Possibility of dressing of Kuzbass ferromanganese ores, *Chern. Metall., Byull. Nauchno-Tekh. Ekon. Inf.*, 2020, vol. 76, no. 9, pp. 904–909.
- Vatolin, N.A., Trusov, B.G., and Moiseev, G.K., *Termodinamicheskoe modelirovanie v vysokotemperaturnykh neorganicheskikh sistemakh* (Thermodynamic Modeling in High-Temperature Inorganic Systems), Moscow: Metallurgiya, 1994.
- Trusov, B.G., TERRA software system for modeling phase and chemical equilibria at high temperatures,

- Materialy III Mezhdunarodnogo simpoziuma "Gorenie i plazmokhimiya," Almaty, Kazakhstan, 24–26 avgusta 2005* (Proc. III Int. Symp. "Combustion and Plasmochemistry," Almaty, Kazakhstan, August 24–26, 2005), Almaty: Kazak Univ., 2005, pp. 52–57.17
17. Rybenko, I.A., Nokhrina, O.I., Rozhikhina, I.D., and Golodova, M.A., *Modelirovanie i optimizatsiya uslovii i rezhimov protsessov pryamogo vosstanovleniya metallov* (Modeling and Optimization of Conditions and Modes of Direct Metal Reduction), Novokuznetsk: Sib. Gos. Ind. Univ., 2019.
18. Khodosov, I.E., Nokhrina, O.I., Rozhikhina, I.D., and Rybenko, I.A., Modeling of solid-phase reduction of iron by black coals, *Materialy XVI Mezhdunarodnoi konferentsii Sovremennye problemy elektrometallurgii stali* (Proc. XVI Int. Conf. "Modern Problems of Steel Electrometallurgy"), in 2 parts, Magnitogorsk: Yuzh.-Ural. Gos. Univ., 2015, pp. 210–214.
19. Yusfin, Yu.S. and Pashkov, N.F., *Metallurgiya zheleza* (Iron Metallurgy), Moscow: Metallurgiya, 2007.

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