

# Thermodynamic Simulation of Iron Reduction

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Received October 22, 2021; revised October 29, 2021; accepted November 1, 2021

**Abstract**—Application of the iron-containing wastes, such as converter production sludge, iron-containing concentrates, mill scale, iron ore-dressing wastes, etc., is one of the promising areas in metallurgy. Development of new resource-saving technologies with application of those waste requires preliminary research and accumulation of the information on the iron reduction. The present work considers the processes of iron reduction under the various conditions. We engaged the thermodynamic simulation method based on search for the entropy maximum. The “Terra” software package (Bauman Moscow State Technical University) is the thermodynamic simulation tool. The “Terra” complex is designed to calculate thermodynamic properties and composition of the phases in the arbitrary system with chemical and phase transformations in the equilibrium state. With this software package, we investigate the iron disoxidation processes by various reduction agents (carbon, manganese, and silicon) in the model thermodynamic systems, and determine the optimal conditions for the temperature and the reducing agent consumption. The paper presents the results on the processes in the equilibrium metal–slag system. We analyzed the equilibrium state of the metal–slag system within the temperature range of 1773–1973 K under the different slag amounts; determined the domains of the oxidation–reduction processes; and assessed the influence of the metal components on the iron oxide reduction from slag to metal. Temperature dependences of the equilibrium system composition are obtained for various metal-to-slag ratios and the optimal conditions for the iron reduction are determined.

**Keywords:** thermodynamic simulation, instrumental system, iron recovery, metal–slag system, thermodynamic equilibrium

**DOI:** 10.3103/S0967091221110103

## INTRODUCTION

Use of the iron-containing waste is one of the promising areas of the modern metallurgy development [1–3]. Here, the converter industry sludge, iron-containing concentrates, mill scale, iron ore-dressing wastes, etc., are applicable [4–7]. Due to market considerations, the foreign technical information available [8–10] on industrial exploitation of the new reduction technologies is of a general and often promotional type. The attempts to engage the foreign press published recommendations do not provide stable and satisfactory results and require verification in specified conditions. Development of the new technologies engaging the oxide materials from the steel production always requires preliminary research and accumulation of the information in the field of the theory of iron disoxidation by means of various reducing agents [11–14]. Since practical and experimental research, as a rule, is quite expensive and often unrealizable, then a computational experiment is of great importance: it makes it possible to analyze the state of systems, with its physicochemical processes taking place as well as to draw the conclusions (based on the model representations) on the studied object behavior.

The work presents the investigation results on the process of iron disoxidation under various conditions. We engaged the method of thermodynamic simulation based on the search for the thermodynamic potential extreme, namely, the entropy maximum [15–17].

## METHOD AND INSTRUMENT OF THERMODYNAMIC SIMULATION

The thermodynamic simulation method provides a unique opportunity for generalized descriptions of any high-temperature state by means of the fundamental thermodynamics laws, regardless of the conditions and methods of achieving the equilibrium, with minimal information about the system itself. In that case, the thermodynamic system is considered as a set of particular subsystems: phases and individual condensed substances. As a result, for a complex system (working fluid), the problem is formulated for finding the equilibrium composition of components for the preset thermodynamic conditions; there, the thermodynamic criterion, namely, the system entropy, represented by the state parameter function, takes the extreme value. Such formulation leads to a complex

optimization problem; for its solution, the appropriate methods and software are engaged [15, 16]. The maximal entropy method makes it possible to assess the system composition under the equilibrium conditions, regardless of its achievement methods as well as to clarify a fundamental possibility of obtaining the particular substances: their release is used for solving the problem of the limit final state assessment.

As a tool in our numerical experiments with use of the thermodynamic simulation, we selected the “Terra” software package (Bauman Moscow State Technical University). This software package is designed to calculate the thermodynamic characteristics and the phase composition of the equilibrium state of the arbitrary systems with the chemical and phase transformations [17].

Using the “Terra” system, we performed a number of investigations of the metal recovery in the model thermodynamic systems. The results show good convergence and consistency with the literature data [18–20]. In this regard, application of this program is legal and acceptable.

The program simulates the limit equilibrium states applying the ideal gas model. The condensed phases might be described in the approximation of immiscible one-component phases, ideal or regular solutions. An additional option is provided to set composition and properties of the solutions. Not appointed yet is the list of substances for the expected condensed solutions, neither are the partial excess enthalpies of their components determined; in the software system, all individual substances in the condensed state are assumed to be one-component immiscible phases. For more complicated models of condensed solutions (strictly regular, quasi-regular, subregular, and the others), the expressions depending on the molar fraction of the component in solution and the temperature might be assigned as the excessive enthalpy [17].

Thus, the equilibrium state of any closed and isolated thermodynamic system is uniquely defined by the two state parameter values. As such characteristics, we might consider any two of the six thermodynamic parameters: pressure, temperature, specific volume, entropy, total enthalpy, total internal energy.

The program provides two options for the non-equilibrium state simulation:

- direct concentration setting (fixation) of a number of substances;
- setting the content of the “inert” (non-reactive) part of the substances in the condensed state.

The program presents the option of multivariate calculations both within the range of the initial substance concentrations, and within the range of thermodynamic parameters defining the equilibrium, as well as the option to write the calculation results into the Excel file: this makes the subsequent special data processing easier and provides charting. The compo-

nent concentrations are calculated in any user-preferred b dimension.

Setting the number of moles of the constituent components forms the elemental system; if necessary, the condensed solution compositions are formed. Then, given two selected thermodynamic parameters, the multivariate calculations are performed of the equilibrium compositions depending on these parameters and consumption of the initial materials. We determined the set of substances to be formed for a given elemental system composition as the numerical simulation result for the selected temperature range and various thermodynamic states. From the complete list of possible substances, we selected only the substances with the concentrations exceeding the value of  $10^{-4}$  mol/kg of the mixture. The metal recovery studies performed in the model thermodynamic systems show good convergence and consistency with the literature data [18–20].

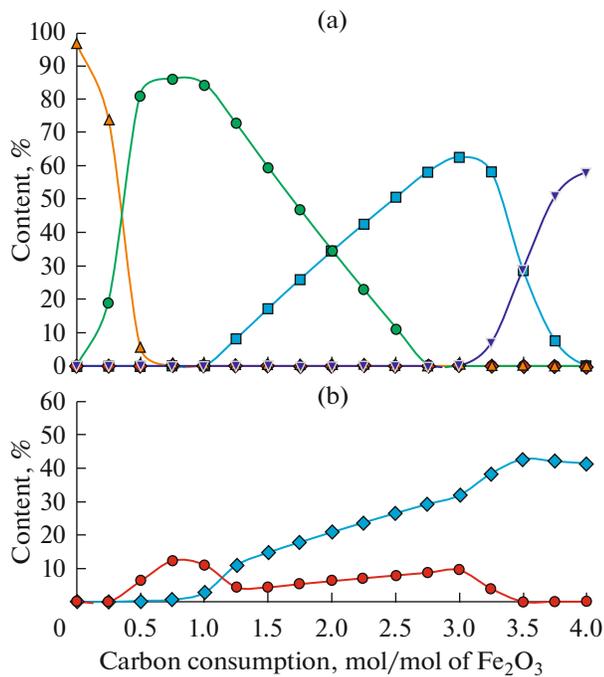
#### THERMODYNAMIC SIMULATION OF THE IRON REDUCTION PROCESSES ON THE MODEL SYSTEMS

We investigated the process of iron reduction by carbon on the  $\text{Fe}_2\text{O}_3\text{—C}$  model system. The preset iron oxide amount was 1 mol. We varied the carbon consumption from 0 to 4 mol: from a deficiency to an excess of the amount required in stoichiometry. Figure 1 shows the calculation results on the equilibrium system composition at the temperature of 1873 K; here, several domains are of interest. The first domain respects to the carbon consumption variation from 0 to 0.75 mol: the  $\text{Fe}_3\text{O}_4$  concentration decreases with a simultaneous increase in the FeO concentration in the system; the gas phase is fully represented by the  $\text{CO}_2$  oxide: its maximal concentration in the system respects to the carbon consumption of 0.75 mol and equals to 10%. Further, with the carbon consumption increase, FeO is reduced and the amount of disoxidated iron begins to increase in the system; its maximal concentration respects to the carbon consumption of 3 mol.

At the excessive carbon content in the mixture, the pure iron amount decreases and the system begins to accumulate the  $\text{Fe}_3\text{C}$  carbide. In the gas phase, the CO and the  $\text{CO}_2$  concentrations increase simultaneously. At the carbon consumption of 3 mol, the  $\text{CO}_2$  content begins to decrease until it completely disappears at the carbon consumption of 3.5 mol.

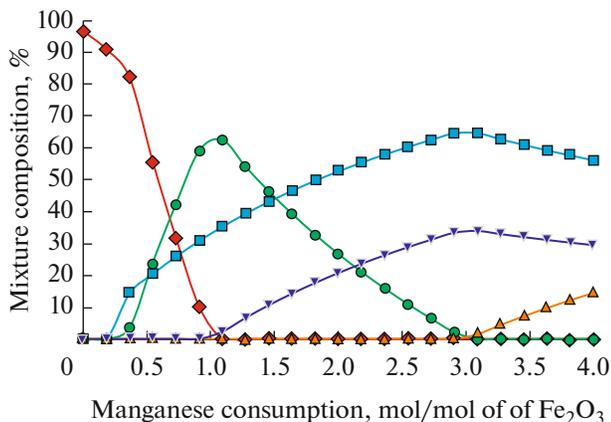
Results of the iron oxide interaction with manganese show that manganese completely reduces iron within the entire temperature range typical of the metallurgical processes.

Figure 2 shows the results of calculating the equilibrium compositions in the  $\text{Fe}_2\text{O}_3\text{—Mn}$  system within the manganese consumption range from 0 to 4 mol at a temperature of 1873 K.



**Fig. 1.** Dependences of the Fe<sub>2</sub>O<sub>3</sub>-C system equilibrium composition on the carbon consumption at 1873 K: (a)  $\blacklozenge$ -C;  $\blacksquare$ -Fe;  $\bullet$ -FeO;  $\blacktriangle$ -Fe<sub>3</sub>O<sub>4</sub>;  $\blacktriangledown$ -Fe<sub>3</sub>C; (b)  $\blacklozenge$ -CO;  $\bullet$ -CO<sub>2</sub>.

The manganese amount of 1 mol respects to the maximal FeO concentration in the system; then, it decreases with the manganese consumption increase. At the manganese amount of 3 mol, the FeO oxide completely disappears. This consumption respects to the maximal iron content of 65% and that of the manganese oxide—35%. Further manganese amount increase leads to its accumulation in the mixture and dilution of the other components.



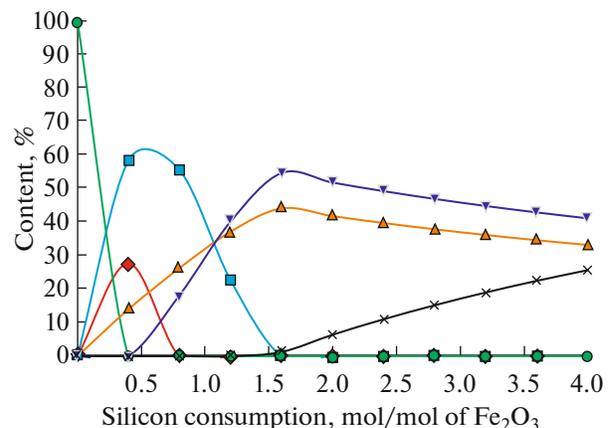
**Fig. 2.** Dependences of the Fe<sub>2</sub>O<sub>3</sub>-Mn system equilibrium composition on the manganese consumption at 1873 K:  $\blacklozenge$ -Fe<sub>3</sub>O<sub>4</sub>;  $\blacksquare$ -MnO;  $\bullet$ -FeO;  $\blacktriangle$ -Mn;  $\blacktriangledown$ -Fe.

The results on the iron oxide interaction with silicon show that iron recovers completely at the silicon consumption of 1.5 mol within the entire temperature range (Fig. 3).

### THERMODYNAMIC SIMULATION OF OXIDATION-DISOXIDATION PROCESSES IN THE METAL-SLAG SYSTEM

In the present work, we investigate the oxidation-disoxidation processes taking place in the metal-slag system being in equilibrium. The metal contains (%) C—4.0; Mn—0.7; Si—0.7; P—0.3%. The slag chemical composition is (%): MnO—10.0; P<sub>2</sub>O<sub>5</sub>—0.3; SiO<sub>2</sub>—20.0; CaO—50.0; FeO—17.0.

We performed calculations for 100 kg of metal within the temperature range of 1773–1973 K at the slag consumption of 8, 10, 12, 14, and 16 kg. Figures 4 and 5 show the temperature dependences of the equilibrium constituent contents in the metal at the different slag consumptions. With the temperature increase, the carbon concentration in the metal decreases (Fig. 4a), and at higher slag consumptions, the carbon concentration decrease begins at lower temperatures. Here, the carbon content decrease under the slag consumption of 8, 10, 12, 14, and 16 kg per 100 kg of metal begins at the temperatures of 1853, 1842, 1836, 1824, and 1803 K, respectively. In general, under the same temperature, at higher slag consumptions, the carbon concentration is less. For example, at the temperature of 1873 K, the carbon concentrations of 3.84, 3.73, 3.62, 3.50, and 3.39% respects to the slag consumption of 8, 10, 12, 14, and 16 kg/100 kg of metal. The manganese concentration in the metal changes insignificantly with the temperature change; yet, it depends significantly on the slag amount fed into the system (Fig. 4b). The maximal (1.82–1.86%) manganese content respects to the slag consumption of 16 kg/100 kg of



**Fig. 3.** Dependences of the Fe<sub>2</sub>O<sub>3</sub>-Si system equilibrium composition on the silicon consumption at 1873 K:  $\blacklozenge$ -Fe<sub>3</sub>O<sub>4</sub>;  $\blacksquare$ -FeO;  $\bullet$ -Fe<sub>2</sub>O<sub>3</sub>;  $\blacktriangle$ -SiO<sub>2</sub>;  $\blacktriangledown$ -Fe;  $\times$ -Si.

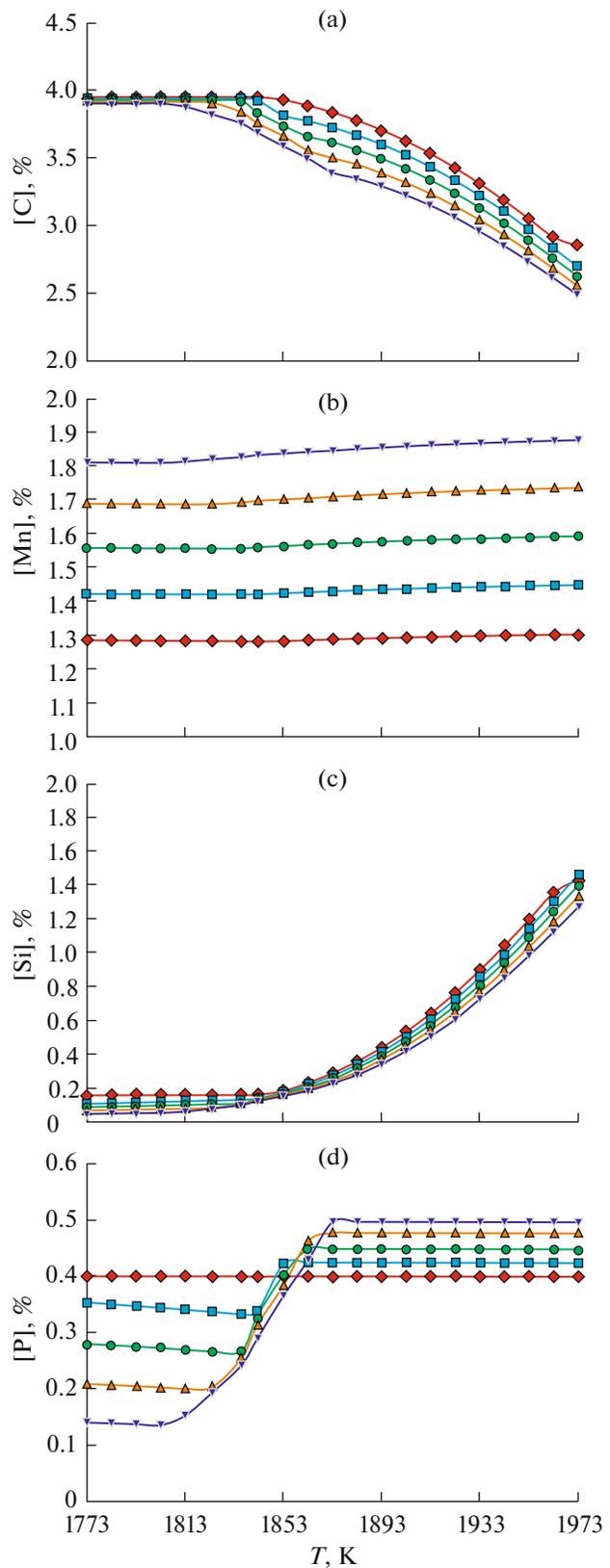
metal, the minimal (1.28–1.30%) – to the consumption of 8 kg/100 kg of metal.

On the contrary, the silicon concentration in the metal depends strongly on the temperature and slightly on the slag amount (Fig. 4c). At the temperatures below 1853 K, the silicon content in the metal does not change and equals to 0.05–0.11%. With the temperature increase, a sharp increase in the silicon concentration begins; it reaches, at 1973 K, the values of 1.30–1.45% depending on the slag consumption. The minimal silicon concentrations respect to the maximal slag consumptions.

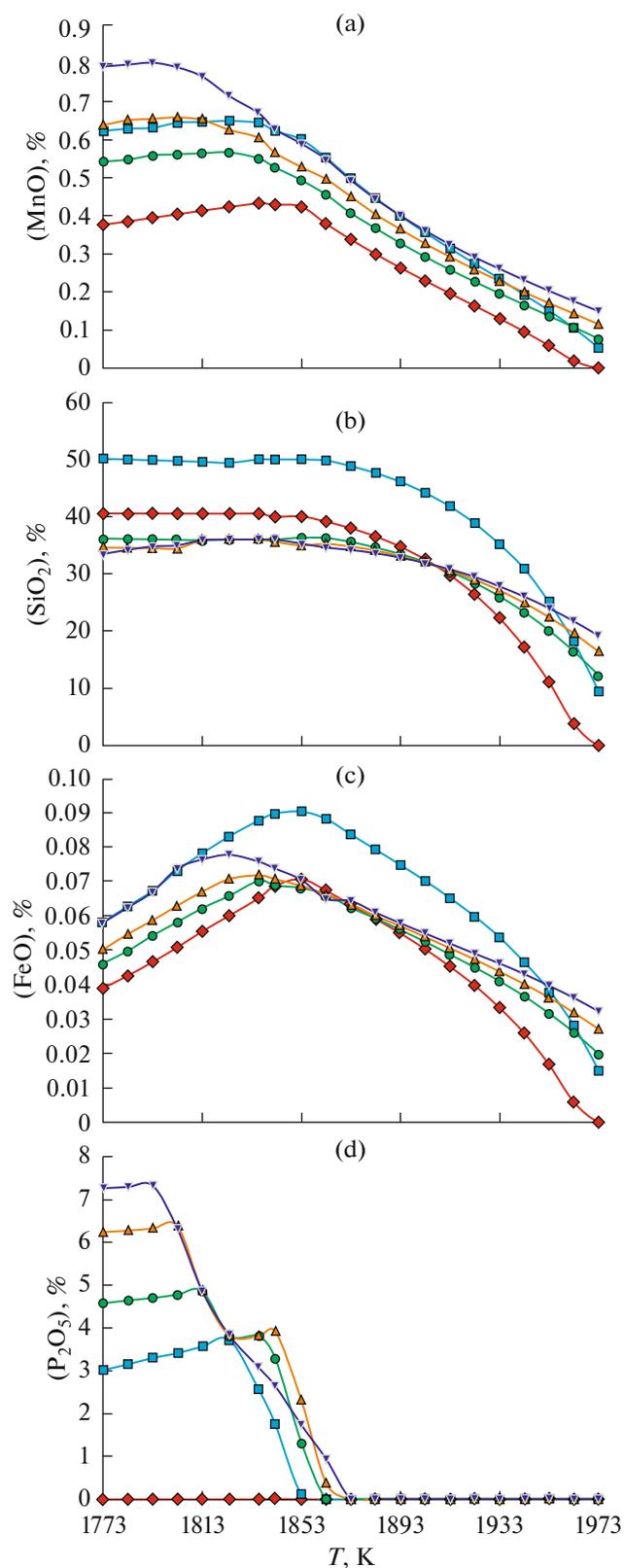
Figure 4d shows the temperature dependences of the phosphorus content in the metal at the different slag amount in the system. At the low temperatures, the phosphorus concentration is constant and only depends on the slag consumption. The maximal phosphorus concentration of 0.4% respects to the slag amount of 8 kg, the minimal, of 0.14%—to 16 kg. With the temperature increase, sharp phosphorus content increase begins; moreover, the temperature range of the phosphorus concentration changes depends significantly on the slag consumption: 1803–1873, 1823–1868, 1835–1863, 1843–1853 K and 0 at the slag consumptions of 16, 14, 12, 10, and 8 kg per 100 kg of metal. After the transition period, the phosphorus content stabilizes and depends on the slag amount in the system in the direct proportion: the phosphorus concentrations of 0.40, 0.42, 0.45, 0.48, and 0.50% respect to the slag consumptions of 8, 10, 12, 14, and 16 kg/100 kg of metal.

Figure 5a shows the temperature dependences of the equilibrium MnO content at the different slag consumptions. At low temperatures, the MnO concentration is constant and depends only on the slag consumption. At the temperature increase, the manganese oxide content begins to decrease, and the temperature of that MnO concentration decrease is the lower, the higher is the initial slag consumption: for the slag consumption of 16 kg/100 kg of metal, the temperature of the MnO concentration decrease beginning is 1793 K, and for 8 kg/100 kg metal—1853 K. The low manganese oxide concentrations respect to the minimal slag consumption in the initial system. We obtained similar dependences for the silicon oxide content in the slag (Fig. 5b); yet, the temperatures of the SiO<sub>2</sub> concentration decrease beginning are shifted to the right and respect to about 1853 K.

Temperature dependence of the equilibrium iron oxide content (Fig. 5c) has extrema. Here, the maximal FeO concentration of 0.09% respects to the temperature of 1853 K and the slag consumption of 10 kg/100 kg of metal. The FeO concentration of 0.078% respects to the temperature of 1873 K and the slag consumption of 16 kg/100 kg of metal, 0.072%—to 1835 K and 14 kg/100 kg, 0.070%—to 1835 K and 12 kg/100 kg, 0.071%—to 1853 K and 8 kg/100 kg. In general, the iron oxide concentrations in the slag are



**Fig. 4.** Temperature dependences of equilibrium content of C (a), Mn (b), Si (c), and P (d) in the metal at the different slag consumptions:  $\blacklozenge$ —8%;  $\blacksquare$ —10%;  $\bullet$ —12%;  $\blacktriangle$ —14%;  $\blacktriangledown$ —16%.



**Fig. 5.** Temperature dependences of equilibrium content of MnO (a), SiO<sub>2</sub> (b), FeO (c), and P<sub>2</sub>O<sub>5</sub> (d) in slag at the different slag consumptions:  $\blacklozenge$ —8%;  $\blacksquare$ —10%;  $\bullet$ —12%;  $\blacktriangle$ —14%;  $\blacktriangledown$ —16%.

low, iron is almost completely reduced by carbon, manganese, and silicon dissolved in the metal. Phosphorus is also reduced to a metal with the temperature increase (Fig. 5d). Analysis of the gas phase equilibrium composition depending on the temperature and the slag consumption shows that at low temperatures, 40% of CO and 60% of CO<sub>2</sub> are present in the system, whereas at high temperatures, the gas phase consists of 100% CO.

## CONCLUSIONS

In the model thermodynamic systems, we investigate the iron reduction processes by various reducing agents and determined the optimal conditions for the temperature and the reducing agent consumptions. In the Fe<sub>2</sub>O<sub>3</sub>–Mn system, the manganese consumption of 3 mol respects to the maximal iron content of 65%; in the Fe<sub>2</sub>O<sub>3</sub>–Si system, iron is completely reduced at the silicon consumption of 1.5 mol within the entire temperature range. We also analyze the metal–slag system equilibrium state within the temperature range of 1773–1973 K at the different slag amounts. The boundaries are determined of the oxidation–reduction process domains and an assessment is made of the metal component influence on the conditions of the iron oxide recovery from slag to metal. The FeO concentration of 0.09% respects to the temperature of 1853 K and to the slag consumption of 10 kg/100 kg metal, 0.078%—to 1873 K and 16 kg/100 kg, 0.072%—to 1835 K and 14 kg/100 kg, 0.070%—to 1835 K and 12 kg/100 kg, 0.071%—to 1853 K and 8 kg/100 kg.

## CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

## REFERENCES

- Lyungen, Kh.B., Knop, K., and Steffen, R., Current state of the processes of direct and liquid-phase iron recovery, *Chern. Met.*, 2007, no. 2, pp. 13–25.
- Yusfin, Yu.S., Gimmel'farb, A.A., and Pashkov, N.F., *Novye protsessy polucheniya metalla* (New Processes of Metal Production), Moscow: Metallurgiya, 1994.
- Tsybal, V.P. and Mochalov, S.P., Synergetics in the development of new metallurgical processes and control principles, *Steel Transl.*, 2012, vol. 42, no. 2, pp. 126–130.
- Nokhrina, O.I., Rozhikhina, I.D., Dmitrienko, V.I., Proshunin, I.E., and Golodova, M.A., Peculiarities of application of natural and man-caused materials for steel alloying and modifying, *Chern. Metall., Byull. Nauchno-Tekh. Ekon. Inf.*, 2019, vol. 75, no. 8, pp. 944–954. <https://doi.org/10.32339/0135-5910-2019-8-944-954>
- Romenets, V.A., *Protsess Romelt* (The Romelt Process), Moscow: Ruda i Metally, 2005.
- Kozhukhov, A.A., *Energosberegayushchie tekhnologii vyplavki stali na osnove vspenivaniya staleplavil'nykh*

- shlakov* (Energy-Saving Technologies of Steel Smelting based on Steelmaking Slags Foaming), Saarbrücken: LAP LAMBERT Academic, 2011.
7. Tsymbal, V.P., Protopopov, E.V., Rybenko, I.A., Olenikov, A.A., Kozhemyachenko, V.I., and Sechenov, P.A., Ecologically closed energy metallurgical technology of powdered iron ore and coal-cleaning wastes processing, *Chern. Metall., Byull. Nauchno-Tekh. Ekon. Inf.*, 2019, vol. 75, no. 4, pp. 507–513.  
<https://doi.org/10.32339/0135-5910-2019-4-507-513>
  8. Sakthivel, R., Vasumathi, N., Sahu, D., and Mishra, B.K., Synthesis of magnetite powder from iron ore tailings, *Powder Technol.*, 2010, vol. 201, no. 2, pp. 187–190.  
<https://doi.org/10.1016/j.powtec.2010.03.005>
  9. Jiabin, C., Wenlong, J., and Lianghui, Y., Survey and evaluation of the iron tailings resources in China, *Miner. Resour. Dev.*, 2010, vol. 3, pp. 60–62.
  10. Bates, P. and Muir, A., HIsmelt—low cost iron making, *Proc. Int. Conf. “Commercializing New Hot Metal Processes beyond the Blast Furnace,” June 5–7, 2000*, Atlanta, GA, 2000, pp. 1–12.
  11. Nokhrina, O.I., Rozhikhina, I.D., and Khodosov, I.E., Manufacturing and application of metalized ore-coal pellets in synthetic pig iron smelting, *IOP Conf. Ser.: Mater. Sci. Eng.*, 2016, vol. 142, art. ID 12068.  
<https://doi.org/10.1088/1757-899X/142/1/012068>
  12. Inada, Y., Improvements in the MIDREX(r) direct reduction process, *R&D Kobe Steel Eng. Rep.*, 2000, vol. 50, no. 3, pp. 86–89.
  13. Mouer, A., et al., *Direct from MIDREX, 2nd Quarter, 2009*, Charlotte, NC: Midrex Technologies, 2009, pp. 3–9.
  14. Kempken, J., Kleinschmidt, G., Schmale, K., Thiedemann, U., Gaines, H.P., and Kopfle, J.T., Short route—long-term success, integrated mini-mill solutions by Midrex and SMS Demag, *Arch. Metall. Mater.*, 2008, vol. 53, no. 2, pp. 331–336.
  15. 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.
  16. Belov G.V. and Trusov, B.G., *Termodinamicheskoe modelirovanie khimicheskii reagiruyushchikh sistem* (Thermodynamic Modeling of Chemically Reacting Systems), Moscow: Mosk. Gos. Tekh. Univ. im. N.E. Bauman, 2013.
  17. Trusov, B.G., TERRA software system for modeling phase and chemical equilibria at high temperatures, *Materialy III Mezhdunarodnogo simpoziuma “Gorenie i plazmokhimiya,” 24–26 avgusta 2005 g.* (Proc. III Int. Symp. “Combustion and Plasma Chemistry,” Almaty, Kazakhstan, August 24–26, 2005), Almaty: Kazak Univ., 2005, pp. 52–57.
  18. Golodova, M.A., Rozhikhina, I.D., Nakhrina, O.I., and Rybenko, I.A., Thermodynamic modeling of restoring items converter vanadium slag, *IOP Conf. Ser.: Mater. Sci. Eng.*, 2016, vol. 150, art. ID 012016.  
<https://doi.org/10.1088/1757-899X/150/1/012016>
  19. Rybenko, I.A., Nokhrina, O.I., Rozhikhina, I.D., Golodova, M.A., and Tsymbal, V.P., Resource-saving direct alloying of steel, *Steel Transl.*, 2017, vol. 47, no. 2, pp. 85–90.  
<https://doi.org/10.3103/S0967091217020097>
  20. 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.  
<https://doi.org/10.3103/S0967091216040082>

*Translated by I. Dikhter*