

Study of the Processes of Metal Recovery from Steel Slags

Andrey Nikolaevich Dildin* and Iliya Valerievich Chumanov

South Ural State University (National Research University), Zlatoust Branch, Zlatoust, Russia

Abstract

The methods of waste processing and salvaging are considered for steelmaking slags. The dump slags of the Zlatoust metallurgical works are analyzed. A scheme of two-stage metal reduction from the dump slags using the reduction-melting scheme is developed and tested under laboratory conditions. The reduction parameters that correspond to the maximum recovery of a metallic component from the slags are found. Experimental researches included experiments on solid-phase and liquid-phase recovery of slag samples at temperatures of 1000-1500°C. The results of thermodynamic modeling and experimental high-temperature slag processing allow speaking about the advisability of preliminary solid-phase recovery slag in the atmosphere of carbon monoxide with subsequent high-temperature (liquid phase) recovery to obtain the separate metal fractions.

Keywords: Experimental Research, High-Temperature Processes, Steel Smelting Slag, Thermodynamic Modeling

1. Introduction

The issues of processing and salvaging of steel-making slags, mainly dump slags, are challenging. The significance of these issues was highlighted in many works in this field and is determined by technological and ecological aspects. V. N. Kovalev showed the necessity of deep recycling of steelmaking solid waste and identified the main problems of such recycling in his work¹. There is experience in salvaging steel and blast furnace slag exemplified by the Magnitogorsk Metallurgical Combine². A technological complex for separation of the metal component from slags is rather interesting, however, the proposed technology does not allow fully extracting the valuable metals³. The liquid-phase reduction of iron, including from man-made waste, was considered by⁴, who highlighted the need for further research in this area, because existing technologies are not high performance ones.

These issues are also 0 important for semi-integrated steel works, such as the Zlatoust Metallurgical Works (ZMW), because of the complex compositions of forming compounds and the absence of sufficiently simple and

effective technologies for their processing. According to estimation, slag dumps in ZMW amount to more than 5 mln t, including 61% of steelmaking slags, 19% of a metallic material, 12% of refractory scrap, and 8% of refuse of various origins.⁵

All this necessitates the development of efficient technologies to recover the metallic part of the slags and to use it again in metallurgy as metal-containing raw materials for making low-alloy steel.

The selection of the optimum scheme of slag processing is determined by the following two types of flow charts: Solid-phase reduction – melting (liquid-phase reduction) – two-stage process and melting – liquid-phase reduction – one-stage process⁶. Based on the raw materials (slags) composition and experimental results, it was determined that the two - stage process is the most rational option for the dump slags of ZMW.

This work is aimed at developing the stages of two-stage reduction and the recovery of the metallic component from the dump slags of ZMW under laboratory conditions.

* Author for correspondence

Table 1. Average chemical composition of the magnetic and nonmagnetic parts of the slag

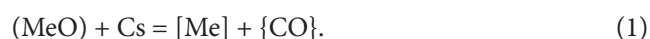
Slag	Components, wt. %										
	SiO ₂	CaO	P	S	MgO	Al ₂ O ₃	MnO	Cr ₂ O ₃	TiO ₂	V ₂ O ₅	FeO
Magnetic part	25.6	31.60	0.20	0.34	11.90	10.6	3.20	2.00	0.80	0.10	14.5
Nonmagnetic part	26.20	33.20	0.20	0.21	11.90	10.00	3.30	2.10	0.84	0.10	9.80

2. Concept Headings

To refine the chemical and phase compositions, we performed physicochemical studies of slag samples taken from various horizontal dumps. Using local infrared and Raman Spectroscopy (RS), we found that the slags have the following complex heterogeneous composition: Enstatite MgSiO₃, ilmenite FeTiO₃, augite Ca(Fe, Mg)^xSi₂O₆, plagioclase (Na, Ca)^x(Si, Al)₄O₈, magnetite Fe(Fe₂O₄), fayalite (Fe, Mg)₂SiO₄, and hematite Fe₂O₃. The chemical composition of the slags determined with an Oxford INCA X-max 80 X-ray energy dispersive spectrometer in a JEOL JSM-7001F electron microscope is also heterogeneous. Its average values in horizontal dumps calculated for simple oxides vary in the following ranges (wt %): 17.7–40.0 SiO₂, 21.9–47.4 CaO, 6.2–16.5 MgO, 7.2–10.1 Al₂O₃, 1.2–5.3 MnO, 1.7–11.3 Cr₂O₃, 0.3–1.5 TiO₂, 0.1–0.3 V₂O₅, 3.7–25.0 FeO, and 0.1–0.4 NiO.

As is known, the completeness with which the alloying components in a metal–slag system are reduced depends on the temperature at which the process is carried out, the activities of the components of the slag melt, and the amount of reducing agent that is used. Principles from the theory of regular ionic solutions were used to evaluate the activity of several components of slag melts: It was determined for the oxide systems which were

analyzed that at 1300–1600°C the activity of manganese oxide MnO changes within the range 0.015–0.074 and the activity of ferrous oxide FeO changes within the range 0.22–0.66. Calculations performed for the system Fe–C–O showed that the actual concentrations of FeO in slags of the above-indicated composition exceed the equilibrium values. Thus, it is best to use carbon as the reducing agent and to attempt to recycle the slag using a reaction of the type:



We constructed diagrams of the solubility surfaces of the metal components (MCSSD) in order to perform a thermodynamic analysis of multi-component oxide systems that simulate the composition of the above-described steelmaking slags. The analysis was performed to determine the conditions under which these systems are stable and are in equilibrium with one another and the metallic melt. It was found that a metallic melt can be obtained from the given slags at temperatures above 1300°C by using carbon, silicon, and aluminum as reducing agents. However, it is best if carbon is used to reduce the slags at the ZMZ, since silicon and aluminum that are already present in the above-indicated complex compounds would impede the reduction of the target

Table 2. Chemical composition of the magnetic part of slag after reduction at 1100°C, wt %

Region	O	Mg	Al	Si	Ca	Cr	Mn	Fe	Total
1	38.82	0.38	0.24	0.88	0.34	0.34	0.35	58.65	100.00
2	2.70	0.26	0.30	0.45	0.27	1.09	0.30	94.64	100.00
3	45.59	9.30	5.85	18.05	2.77	5.60	1.96	10.88	100.00
4	3.76	1.27	0.13	0.37	0.23	1.57	0.54	92.14	100.00
5	33.94	21.96	0.55	0.11	0.05	2.25	5.19	35.95	100.00

Table 3. Chemical composition of the nonmagnetic part of slag at 1100°C, wt %

Region	O	Mg	Al	Si	Ca	Ti	Cr	Mn	Fe	Total
1	1.76	0.12	0.09	0.10	0.07	0.03	79.63	0.40	17.76	100.00
2	49.51	25.52	0.14	17.20	6.18	0.15	0.32	0.72	0.13	100.00
3	47.23	21.81	0.63	14.14	12.76	0.54	1.53	0.91	0.33	100.00
4	48.95	27.11	1.93	18.42	1.19	0.05	1.17	0.24	0.46	100.00
5	48.06	10.09	2.87	14.56	6.09	0.33	4.63	6.90	6.12	100.00

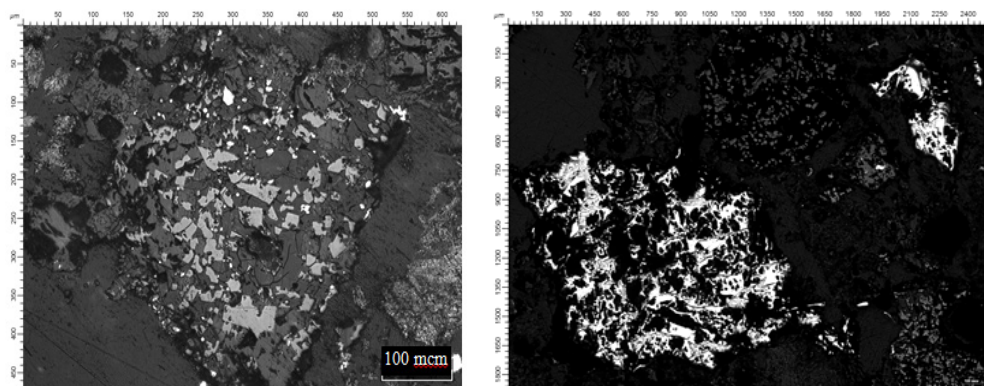


Figure 1. Structure of a sample of the magnetic component of slag after heat treatment at 1100°C ($\times 100$). Optical microscopy (Carl Zeiss D1m Observer).

metals. Here, silicon and aluminum would slow the reduction reactions even though they have a greater affinity for oxygen than does carbon. Average chemical composition of the magnetic and nonmagnetic parts of the slag is given in Table 1.

The application of solid-phase reduction of the dump slags in ZMW, which was considered and studied⁷ for the two-stage technology, required refining of the temperature regime of this stage in terms of the two-stage process. The initial slag, which was preliminarily separated into magnetic and nonmagnetic components, was mixed with coke in the ratio 10:2 (100 g slag, 20 g slag), and 5–15 mL liquid glass was added as a binder. The mixture was then subjected to mixing to reach homogeneity and complete wetting of slag and coke particles with liquid glass. The obtained mass was then pressed in a mold: 40 pellets were formed with a magnetic part and 40 pellets were formed with a nonmagnetic part.

The samples were heated in a PVK-1.4–1.7 furnace to a temperature in the range of 1000–1300°C with increments of 100°C in an air atmosphere and held at the given temperature for 15, 20, and 25 min. After annealing, the samples were removed from the working space and cooled in air. Tables 2 and 3 give the chemical compositions of some regions in the samples obtained from the magnetic and nonmagnetic parts and reduced at 1100°C.

3. Results and Discussion

Figures 1 and 2 show the results of metallographic analysis of the magnetic components of the slag after reduction at 1100°C. White particles of the reduced

metallic component and bright gray and dark gray grains of the conglomerate formed by changed slag, liquid glass, and coke are clearly visible. In addition, edge zones, along which metals are mainly reduced, are also clearly visible.

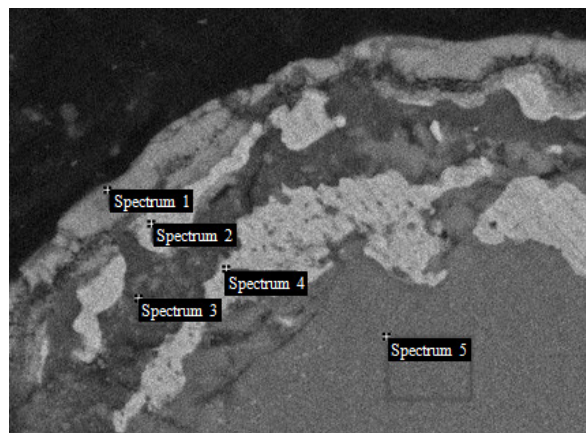


Figure 2. Sample of slag and metal after heat treatment at 1100°C, magnetic part. Scanning electron microscopy (JEOL JSM-7001F). Spectrum numbers correspond to Table 1.

Sample regions with a high content of reduced iron (more than 80%) are formed in the sample volume. This fact is supported by the results of repeated magnetic separation of the reduced samples and results of intense solid-phase reduction. It was also assumed earlier that intense metal reduction begins at a temperature above 1100°C. The magnetic component separated upon repeated separation contains both a reduced metal and metal-containing oxide components. An increase in the fraction of the magnetic component indicates that, at 1100°C, the separation of the unreduced iron-containing part of the slags is improved due to the increase in their

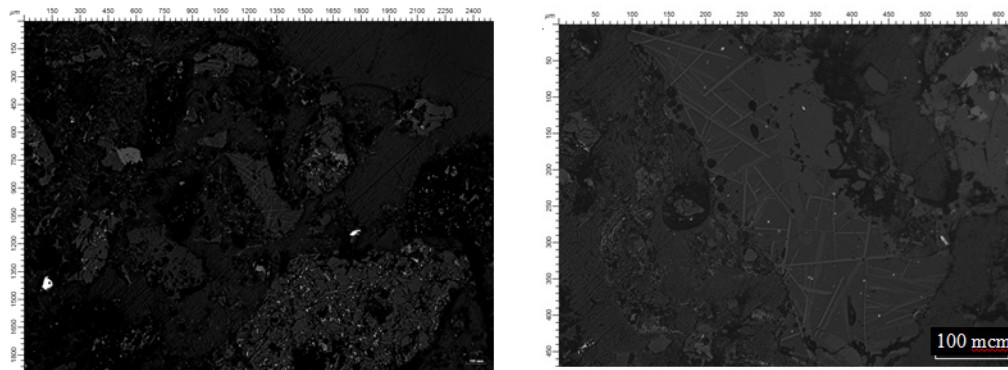


Figure 3. Structure of the nonmagnetic component of slag after heat treatment at 1100°C (×100). Optical microscopy (Carl Zeiss D1m Observer).

magnetic susceptibility, the increase in the grain size, and the separation of crystals of these phases. The presence of metal-containing oxide components indicates the necessity of further metal reduction from the separated metallic part. When comparing the samples reduced at 1000, 1100, and 1200°C, we were able to find similarity between the changes and an increase in the precipitation of a metallic component when the heat-treatment temperature increases.

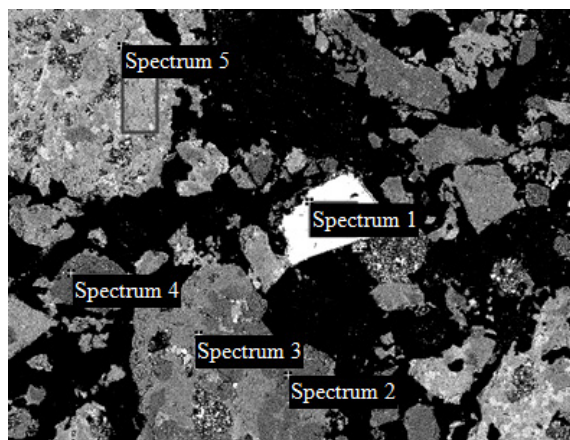


Figure 4. Sample of slag and metal after heat treatment at 1100°C, nonmagnetic part. Scanning electron microscopy (JEOL JSM-7001F). Spectrum numbers correspond to Table 3.

Figures 3 and 4 show the results of metallographic analysis of nonmagnetic component samples of the slag reduced at 1100°C. The absence of changes in these samples after similar heat treatment allows us to state a low efficiency of solid-phase reduction for this part of slag.

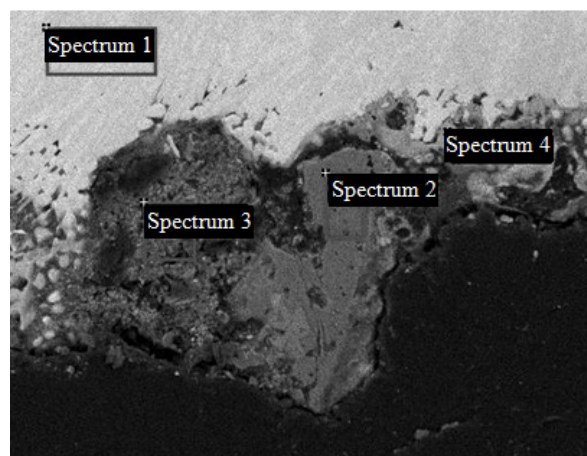


Figure 5. Sample reduced at 1500°C, magnetic part. Scanning electron microscopy (JEOL JSM-7001F). Spectrum numbers correspond to Table 4.

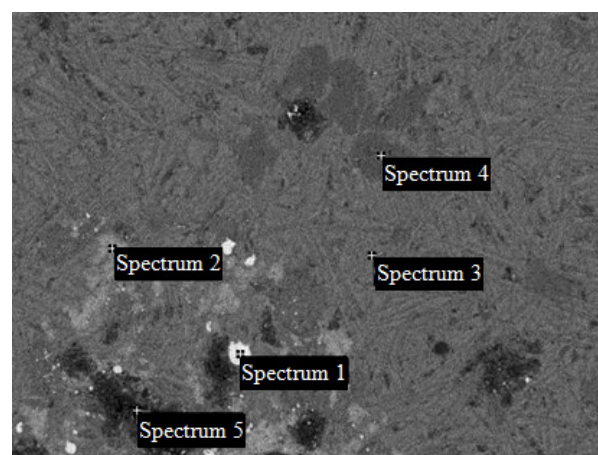


Figure 6. Sample reduced at 1500°C, nonmagnetic part. Scanning electron microscopy (JEOL JSM-7001F). Spectrum numbers correspond to Table 5.

Table 4. Chemical composition of the magnetic part of the sample reduced at 1500°C, wt %

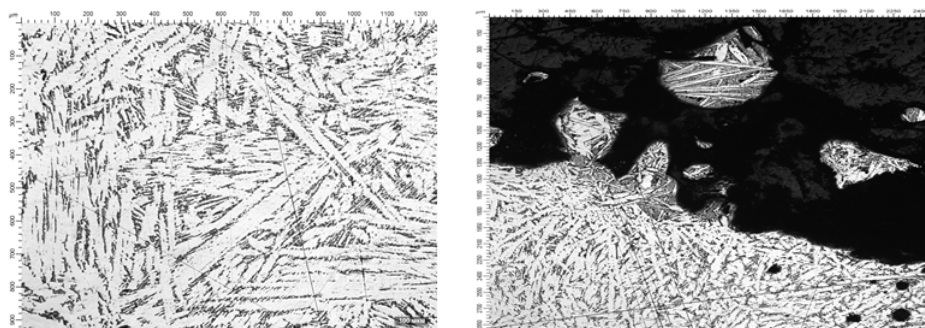
Region	O	Mg	Al	Si	Ca	Ti	Cr	Mn	Fe	Ni	Cu	Total
1	0.38	0.00	0.01	0.13	0.06	0.00	10.99	1.85	85.88	0.75	0.18	100.00
2	35.87	10.39	2.32	16.62	21.99	0.68	1.95	8.99	1.29	0.00	0.00	100.00
3	22.10	0.74	0.72	6.18	1.32	0.66	37.41	0.27	28.69	0.00	2.05	100.00
4	11.81	0.10	0.11	0.25	0.37	0.00	0.67	1.30	85.75	0.13	0.12	100.00
5	0.27	0.00	0.02	0.09	0.12	0.00	12.68	2.02	84.41	0.45	0.01	100.00
6	0.20	0.04	0.00	0.00	0.04	0.00	12.89	2.06	83.90	0.45	0.29	100.00
7	0.30	0.10	0.02	0.07	0.01	0.00	12.43	1.91	84.01	0.70	0.26	100.00

Table 5. Chemical composition of the nonmagnetic part of the sample reduced at 1500°C, wt %

Region	O	Mg	Al	Si	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Total
1	2.72	1.21	0.28	0.70	0.17	0.00	0.10	3.39	0.43	91.12	0.08	0.12	100.00
2	39.83	8.16	4.88	0.40	0.20	0.35	0.39	33.01	6.73	6.33	0.05	0.02	100.00
3	47.79	15.37	5.68	17.29	7.67	0.34	0.01	1.12	3.58	0.39	0.06	0.00	100.00
4	40.56	27.06	0.45	17.10	0.51	0.10	0.00	12.55	0.16	1.98	0.00	0.00	100.00
5	21.03	3.31	0.75	1.67	1.33	0.03	0.06	61.98	3.49	5.12	0.26	0.84	100.00

Table 6. Balance of the metal yield

Component in initial slag	Mass				Masses of slag components after liquid-phase reduction, g		
	Specified		Real		metal	slag	losses
	g	%	g	%			
Magnetic	80	100	76	95	13.75	81.25	5
	80	100	75	93.75	10.00	83.75	6.25
	80	100	73	91.25	12.50	78.75	8.75
Nonmagnetic	80	100	77	96.25	3.75	92.5	3.75
	80	100	74	92.5	6.25	86.25	7.5
	80	100	75	93.75	5.00	88.75	6.25

**Figure 7.** Structure of reduced metal particles after liquid-phase reduction (magnetic part).

All samples after solid-phase reduction were subjected to crushing. The formed powder 80 g in mass was charged in a graphite crucible and placed in the working space of a UPI-60-2 induction furnace to perform liquid-phase reduction of metal. The samples were held in the furnace at 1500°C for 20 min. Tables 4 and 5 present the

chemical compositions of some regions in the samples of the magnetic and nonmagnetic components of slag at annealing temperature of 1500°C. Figures 5 and 6 show polished sections of these samples.

Figures 7 and 8 depict the structure of reduced metal particles after liquid-phase reduction. As follows from

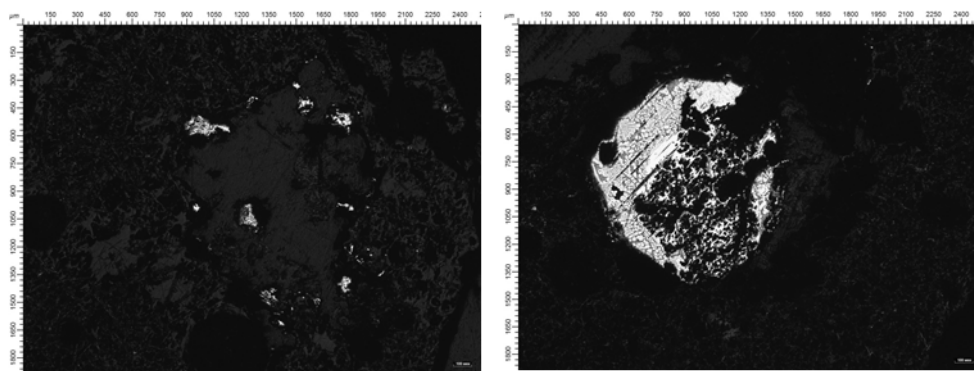


Figure 8. Structure of reduced metal particles after liquid-phase reduction (nonmagnetic part).

the left-hand side of Figure 7, an almost the entire sample surface is represented by white cast iron, and the right-hand side shows transition from a ledeburitic structure at the edge of the sample to the structure of white cast iron in the direction toward the center of the sample. Figure 8 shows reduced metal particles in slag and a ledeburitic structure.

The quantity of formed metallic phase totaled to 35% of the initial slag mass. The relatively high carbon content of the resulting metal can be attributed to the fact that a certain amount of carbon in the graphite crucible was transferred to the metallic melt. The data obtained from the trial heats were used to calculate coefficients describing the distribution of several of the elements between the metal and the slag. For example, $LCr = 5.83$, $LMn = 1.17$, $LNi = 12.37$, $LFe = 14.31$.

Table 6 gives the full balance of the metal yield to estimate the efficiency of each stage and the entire process of two-stage reduction.

4. Conclusion

When performing a physicochemical analysis of the ZMW dump slags, we detected a significantly nonuniform distribution of chemical components and the presence of complex phases of iron-free and iron-containing compounds.

The results obtained from repeated magnetic separation of the specimens after heat treatment also point to an improvement in the efficiency with which metals are reduced when the reduction temperature is increased (Table 4). The magnetic component obtained in the separation process contains not only reduced metal, but also metal-bearing oxides. The high concentration of magnetic material indicates that the separation of

the unreduced iron-bearing material from the slags improves at 1200 and 1300°C due to the increase in the slag magnetic susceptibility and isolation of the crystals of these phases. The presence of metal-bearing oxides shows that it is necessary to develop a technology for further reducing metals from the separated magnetic part of slag.

The processes of solid-phase reduction and enrichment of slags at a temperature of 1000–1200°C were studied. The quantity of metallic component was found to increase as a result of the reduction processes, which was supported by the results of chemical analysis. The liquid-phase reduction of the slags reduced earlier by a solid-phase method allowed us to form an iron–carbon melt containing Cr, Ni, Mn, V, Ti, and other elements, which corresponded to alloyed cast iron.

Preliminary solid-phase reduction of slags that have a complex phase composition and are preliminarily enriched (separation into magnetic and nonreduction at a temperature of 1000 and °C was shown to be a necessary stage of slag enrichment (metallization), which precedes liquid-phase reduction of the metallic component. The metal yield for the two-stage process of the dump slags in ZMW is 13–14% of the initial slag.

The scheme of two-stage reduction of metal from steelmaking slags according to the reduction–melting scheme, which was developed and tested under laboratory conditions, is recommended for testing under industrial conditions.

5. Acknowledgments

The research was financially supported by Ministry of Education and Science of the Russian Federation. Unique Identification Number RFMEFI57414X0090.

6. References

1. Kovalev VN. Metallurgical plant for the manufacture of products from technical and natural materials. *Stal'*. 2013; 4:78–83.
2. Panishev NV, Bigeev VA, Chernyaev AA. Processing of the small-grain wastes of metallurgical production with the formation of granulated cast iron and the recovery of zinc. *Bulletin of MGTU*. 2013; 4:26–9.
3. Seregin AN, Ermolov VM, Stepanyan AS, Arsent'ev A. Technology and equipment complexes for the processing of metal-containing wastes with the separation of marketable products. *Problemy Chernoi Metallurgii Materialovedeniya*. 2010; 1:35–40.
4. Keplinger W. State of the art of iron liquid-phase reduction processes. *Chernye Metally*. 2010; 1:19–29.
5. Dildin AN, Chumanov VI, Chumanov IV. Combined use of the wastes of steelmaking. *Metallurg*. 2010; 10:42–4.
6. Yu YS, Pashkov NF. *Metallurgy of iron: A tutorial*. Moscow: Akademkniga; 2007.
7. Dildin AN, Chumanov VI, Chumanov IV, Eremyashev VE. Solid-phase reduction of the wastes of steelmaking. *Metallurgist*. 2012; 2:36–40.