

Process Improvement for Liquid-Phase Metal Reduction from Steelmaking Dump Slags

Andrey N. Dildin*, Evgeny A. Trofimov and Ilya V. Chumanov

South Ural State University, Russia; dildinan@susu.ru, trofimovea@susu.ru, chumanoviv@susu.ru

Abstract

Background/Objectives: This work was aimed at experimental studying the laboratory process and the results of liquid-phase carbon (coke) reduction of the steelmaking slag conducted to obtain the metal and oxide phases which can be used in the metallurgical industry and building materials industry. **Methods:** The slag from the slag dumps of Zlatoust Metallurgical Plant (the Russian Federation) was an object of the study. The composition of the experimental samples of metal and slag was determined by electron probe microanalysis. **Findings:** The conducted experiments give grounds to assert that the process allows recovering almost completely iron, chromium and nickel contained in the slag. Major part of manganese, as well as some other components, including valuable elements – tungsten, molybdenum, titanium and vanadium, also passes into the molten metal. It has been shown that liquid-phase recovery of slag is acceptable to be carried out at temperatures of about 1500-1550°C. In this case, the slag reduction time (after heating the mixture up to the operating temperature) should not exceed 30 minutes. For a more complete recovery of valuable metals it is recommended to use the moment of the ‘boiling’ (intensive separation of gaseous carbon oxides) period completion as an indicator of the isothermal time end. **Improvements/Application:** Useful products of the recovery process are liquid metal and heavy metal-depleted oxide melt consisting mainly of calcia, silica, magnesia and alumina which may be used in cement manufacturing.

Keywords: Experimental Study, High-Temperature Processes, Liquid-Phase Reduction, Steelmaking Slags

1. Introduction

Studies aimed at improving the technique for processing and recycling of smelter slags (including steelmaking slag) do not lose their relevance¹⁻⁵. Traditionally, steelmaking and blast-furnace slags are used in the production of building materials and products⁶⁻¹¹. Along with the traditional approaches new lines of slag processing are actively being developed^{12,13}. However, the methods currently used, enable only partially to solve the problem of slag dumps disposal. Complete processing of steelmaking slags is a particularly difficult problem¹⁴⁻¹⁶. It was shown in recent years that the slag disposal can be arranged so that it allows obtaining not only building materials, but also metal suitable for further processing and use¹⁷⁻²⁰.

Processing of steelmaking dump slags for the purpose

of extracting metal component should include a step of high-temperature reduction of matter. Efficiency of the reduction step depends on temperature conditions and reactivity of the components determined by the composition of slag and introduced additives^{21,22}.

The key challenges facing developers of slag processing technologies are to determine the composition and sequence of slag material preparation procedures for high-temperature reduction, as well as the determination of the optimal temperature of the liquid-phase reduction process.

With a view to creating the most effective scheme of slag metal component reduction while analyzing the results of previously conducted studies²³⁻²⁵ the authors developed a flow chart for steelmaking slag processing which is shown in Figure 1.

* Author for correspondence

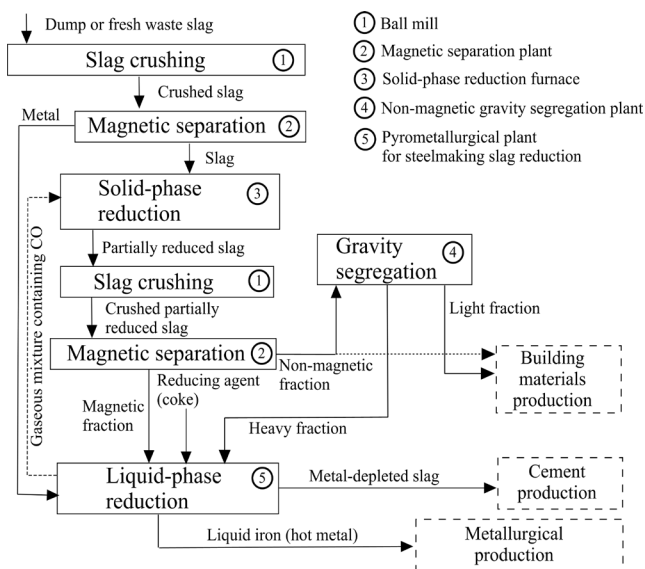


Figure 1. Flow chart for steelmaking slag processing.

In accordance with the presented flowchart the pyrometallurgical reduction of steelmaking slag includes the following stages:

1. Slag matter crushing is carried out to facilitate further matter segregation procedures, and to increase the contact surface of the slag matter with the reducing atmosphere during solid-phase reduction. As a rule, slag is crushed in ball mills (or other suitable grinding equipment complying with the main requirement– average particle size of the obtained matter oxide part should not exceed 2 mm). Grinding time is determined experimentally (for the given definite type of the processed slags) so that the procedure duration would provide proper grinding extent.

2. Magnetic separation of the crushed slag is carried out to segregate metal lumps and particles from the non-metallic component matter of slag dumps. Magnetic separation plants of any design may be used to implement the process which ensure slag matter separation into metallic and non-metallic fractions and possess the required capacity. The process time is determined by the plant capacity.

3. Solid-phase reduction of non-metallic component of slag is carried out to recover partially non-metallic matter of slag dumps in view of increasing susceptibility of fractions containing valuable metals for subsequent magnetic separation. It is performed in the pyrotube furnace of special design or any other furnace providing

the possibility to implement the required process parameters.

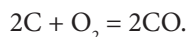
These parameters include:

Process temperature – 1100–1200°C;

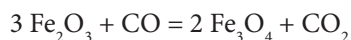
Furnace body dimensions should ensure the volume not filled with slag exceeding by approximately 5-10 times the volume taken by the processed slag;

The extent of the furnace body tightness enabling to create stable atmosphere therein with considerable (up to 20 vol. %) content of carbon monoxide.

To create the reducing atmosphere coke lumps (sized 5-10 cm) are placed into the furnace space together with the processed slag so that coke would not contact directly with the slag. Glowing coke reacts with oxygen inside the furnace body according to the following reaction:



Then, while the generated carbon monoxide is contacting with slag, reduction processes occur and the following process can be considered the key one of them:



Average residence time of the processed matter at a processing temperature in the contact with the reducing atmosphere makes 30-50 minutes.

4. Partially reduced slag crushing is carried out to break slag particles partially sintered during solid-phase reduction before the subsequent magnetic separation to prevent capture of non-magnetic particles sintered with the magnetic ones by the latter. Slag is crushed in a mill of any type (a ball mill is preferable in terms of cost efficiency) to particle size not more than 2 mm.

5. Magnetic separation of partially reduced slag is carried out to segregate magnetic part of slag (this part primarily contains iron and other valuable metals) from non-magnetic (with low content of valuable metals). Magnetic separation plants of any design may be used to implement the process which ensure slag matter separation into metallic and non-metallic fractions and possess the required capacity. The process time is determined by the plant capacity.

6. Gravity segregation of non-magnetic part of the reduced slag is carried out to separate non-magnetic

heavy components (not more than 10% of the total weight of the fraction) that are characterized by increased concentrations of chromium, tungsten and molybdenum from non-magnetic fraction obtained at the previous stage.

This procedure is not compulsory, but it makes sense to perform it in case of processing slag that is known to contain high concentrations of these elements.

In the course of implementation of this stage the device specifically designed for this purpose and other types of devices, enabling to achieve the desired effect, can be used.

The obtained heavy part of non-magnetic fraction is fed to liquid-phase reduction. Light part (90 % or more of the total weight of non-magnetic fraction) is sand that can be used to manufacture concrete, slag stones, roadway construction and so on. If this procedure is not carried out, the entire mass of non-magnetic fraction is considered to be a product for building materials.

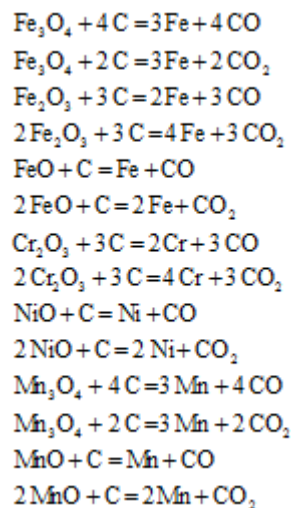
7. Reducing agent crushing and preparation of a mixture for reduction is carried out to break the reducing agent (coke) down to particles sized approximately 2 mm and less and to mix the reducing agent with a magnetic fraction of slag that had undergone solid-phase reduction and (if necessary) with the heavy part of a non-magnetic fraction. The procedure is required to intensify the liquid-phase reduction process. A mill of any type can be used to conduct this stage (a ball mill is preferable in terms of cost efficiency). When charging the mixed components it is required to control the weight ratio of reducing agent and all mixture components.

8. Liquid-phase reduction is a key stage of the technological process. It is performed to obtain a metallic product and raw material for cement clinker manufacturing. A pyrometallurgical plant for steelmaking slag reduction is designed specially to carry out this stage (however, if necessary, the procedure can be conducted with less convenience in other furnaces providing the required process conditions).

The following materials are used as initial ones:

- metallic fraction of slag dump matter;
- a mixture of magnetic fraction of the slag that had undergone solid-phase reduction with coal coke crushed to the particle size of 2 mm and less (at the amount of approximately 10–12 wt % of furnace burden having lump size less than 10 mm);
- heavy part of non-magnetic fraction which is possible but not obligatory mixture component.

The following reactions occur mainly during the liquid-phase reduction:



Along with the above reducing reactions of tungsten, vanadium, molybdenum, phosphorus, titanium and a number of other minor additives are implemented.

Molten metal (cast iron) and heavy metal-depleted non-metallic material obtained as a result of liquid-phase reduction of steelmaking slags are the process products. A large amount of carbon monoxide is a harmful side-product of the process. While carrying out the process it is required to create conditions for afterburning of the resulting CO or its use and disposal in the solid-phase reduction.

Characteristics of the liquid-phase reduction stage mainly determine the quality of products obtained during processing of slags, and thus have a decisive impact on the economic feasibility of such processing. However, to date such key issues remain unclear as a sufficient time for the recovery process, the depth of possible metal recovery from the slag, the optimum process temperature, etc. With a view to improving the process of liquid-phase reduction of metal from steelmaking dump slag, experiments were conducted with dump slags of Zlatoust Metallurgical Plant (the Russian Federation), the results of which are shown.

2. Research Method

The following technique was used to specify liquid-phase reduction parameters.

A slag material sample from the dumps of Zlatoust steel mill (magnetic fraction crushed to particle sized not exceeding 3 mm) was mixed with coke at the ratio 5:1.

In the course of each experiment 55 g of the obtained mixture were placed into the graphite crucible and heated in the UPI-60-2 laboratory induction furnace up to the temperature 1500-1550 °C. Temperature was controlled by means of DT-8869H laser pyrometer.

Four experiments were conducted. In the first case the isothermal holding time after achieving the desired temperature was 30 minutes, in the second – 20 min, and in the third – 10 min. Visual observation of the surface of the molten slag mass made it possible to monitor the process of its 'boiling', whose intensity was gradually decreased toward the end of high-temperature processing. During the fourth experiment it was decided to terminate the isothermal exposure at the time corresponding to the practical completion of the 'boiling' process. This happened in 18 minutes after the mixture temperature achieved the required values. Parameters of the conducted experiments are given in table 1.

Upon completion of isothermal exposure, the crucible content was poured onto the iron plate, where it was solidified in the air, and then the resulting fractions (metal and slag phases) were weighed and examined for determination of the total composition and the composition of the phases formed during the crystallization of recovery products. It should be noted that the examination of the inner surface of the used graphite crucibles did not allow revealing its noticeable thinning or corrosion. This indicates that the amount of coke used in the experiment was sufficient for reduction.

The results of measuring formed fraction weights enabled to calculate the proportion of the metallic product obtained in the reduction process.

The chemical composition of the studied materials (obtained metal and separate phases, included in its composition, initial and depleted slag after the liquid-phase reduction) was examined with JOEL JSM-6460 LV scanning electron microscope using microslices of the obtained samples. To study the composition of the initial slag and metal-depleted slag samples obtained in the course of high-temperature reduction, the test material was ground to 50-micron particle size and less, then multiple visual fields were scanned with subsequent averaging of the results (the range of the obtained concentration values of various slag components did not exceed ± 1.2 %, see Table 1).

3. Results and Discussion

The test findings are given in tables 1–9. Slice micrographs shown in Figures 2–8 also provide insight into the microstructure of the obtained samples of the metallic material.

The composition of dump slag contains a certain amount of carbonates which are largely decomposed after high-temperature processing. On the other hand, significant amounts of carbon are introduced in the slag during the treatment. For ease of comparing the compositions of the initial and depleted slag samples, they are given in Table 2 without taking into account carbon contained in them (total carbon content in the samples varied in the range of 3.5-8 wt %).

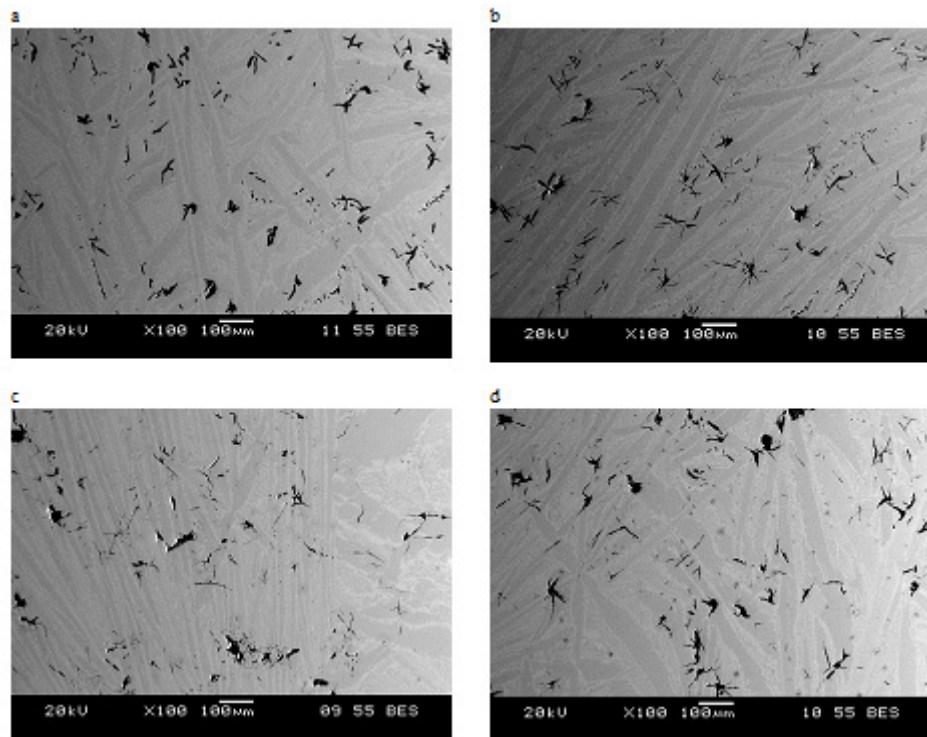
Table 1. Basic parameters characterizing the obtained experimental results

Heat No.	Holding time, min	Initial mixture, g		Obtained, g			Metal yield, % (by weight of initial slag)
		slag	coke	metal	slag	gas*	
1	30	50	5	22.38	17.33	15.29	44.76
2	20	50	5	22.56	17.78	14.66	45.12
3	10	50	5	21.81	18.11	15.08	43.62
4	18	50	5	22.00	17.64	15.36	44.00

* – calculation data

Table 2. Compositions of initial slag and slag phases obtained after the reduction according to EPMA (without carbon), wt %

	Fe	Cr	Mn	O	Ca	Mg	Al	Si	S	Other elements
Initial slag	28.49	1.19	1.73	37.76	16.13	4.40	2.38	7.61	0.12	0.19
Slag after 1 st heat	0.35	–	0.77	44.67	28.10	8.83	4.14	12.31	0.22	0.61
Slag after 2 nd heat	0.24	–	1.19	45.82	25.92	9.26	4.29	12.68	0.16	0.44
Slag after 3 ^d heat	0.38	–	2.45	43.71	27.17	9.22	4.08	12.26	0.15	0.58
Slag after 4 th heat	–	–	1.15	43.20	27.93	9.54	4.75	12.67	0.15	0.61


Figure 2. Surface microstructures of metal sample slices of heats No 1–4 (a–d, respectively).

The results of sample area electron probe microanalysis scanning are given in table 3.

Table 3. Compositions of metal according to the EPMA data. The results of scanning the entire display area (wt %)

Figure	Fe	C	Mn	Cr	Ni
2a	84.79	8.84	3.19	2.79	0.38
2b	85.07	8.52	2.89	3.09	0.43
2c	87.06	7.20	2.26	2.95	0.54
2d	84.85	8.73	3.12	2.86	0.43

The results of electron probe microanalysis (EPMA) of compositions in the intersections of white lines are given in table 4

The main thing that should be noted while analyzing the results presented is a great similarity between the chemical and phase composition of the obtained metal samples, as well as the chemical composition of the slag.

The analysis of the obtained metal samples demonstrates that they consist mainly of two types of metal phases – with high and low content of chromium. Also the metal composition has graphite inclusions in a

Table 4. Compositions of carbide inclusions according to the EPMA data (wt %)

Figure	C	Ti	Nb	Mo	W	V	Fe	Cr	Mn
3a	8.84	29.32	12.01	10.90	20.76	3.11	8.60	2.37	4.07
3b	6.49	11.05	4.64	3.98	10.17	1.06	58.21	1.46	2.95

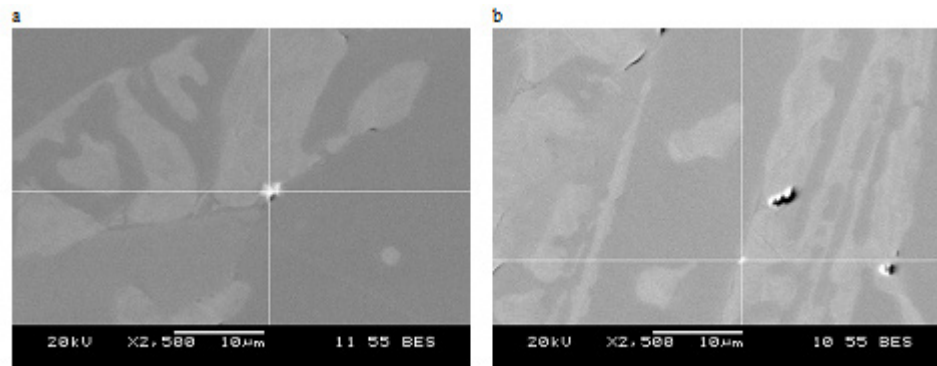


Figure 3. Carbide inclusions in the metal sample slices of heats No 1 and 4 (a and b, respectively).

large amount and inclusions of carbides, phosphides and manganese sulfide-based inclusions in relatively small amounts. The composition of the metal phases indicates that during the liquid-phase recovery process cast iron was obtained that can be used as foundry iron or for steelmaking.

The analysis of the slag samples (Table 2) shows a high degree of iron and chromium reduction (these elements are almost fully recovered). According to the findings, the nickel and (considering the weight ratio of the obtained

phases) more than half of manganese completely pass to the metal composition.

In all experimental heats isothermal exposure for 10 minutes or more made it possible to achieve a satisfactory degree of the metal component recovery. At the same time there is observed certain dependence of the obtained metal weight on the exposure time. Certain dependence of the increased degree of manganese recovery on the isothermal exposure time can also be noticed.

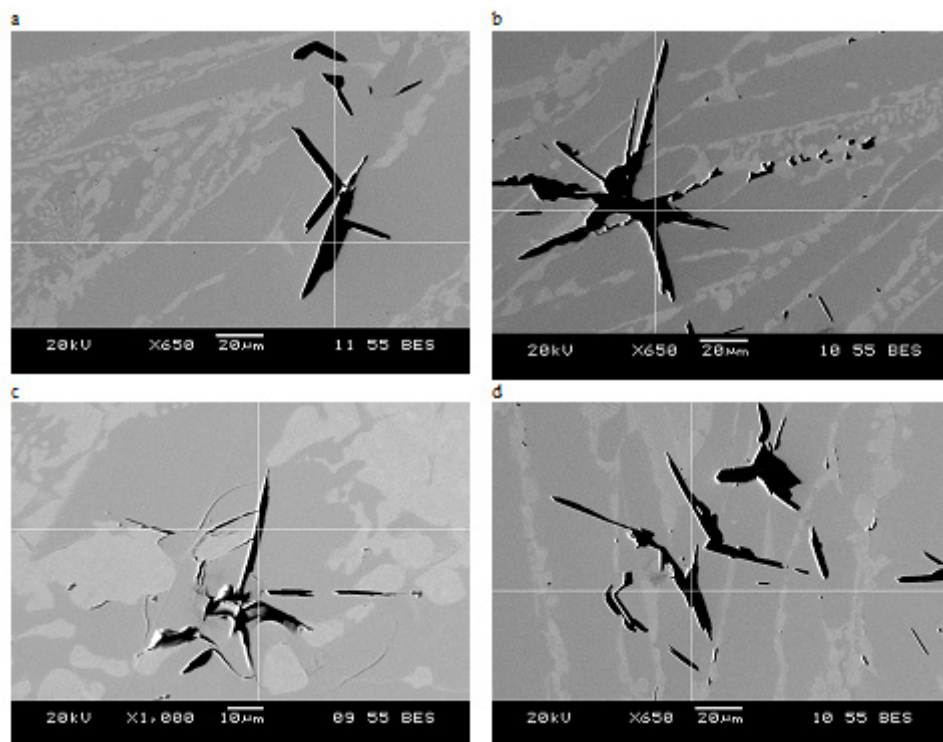


Figure 4. Graphite inclusions in the metal sample slices of heats No 1-4 (a-d, respectively).

The results of electron probe microanalysis of compositions in the intersections of white lines are given in table 5.

Table 5. Compositions of graphite inclusions according to the EPMA data (wt %)

Figure	C	Si	Cr	Mn	Fe
4a	92.27	–	0.50	–	7.23
4b	96.34	0.34	–	–	3.32
4c	74.00	–	0.74	–	25.27
4d	91.75	–	0.58	0.42	7.26

The results of electron probe microanalysis of compositions in the intersections of white lines are given in table 6.

Table 6. Compositions of metal phase with decreased content of chromium according to the EPMA data (wt %)

Figure	Cr	Fe	Mn	Ni
5a	0.95	95.84	2.46	0.74
5b	0.84	94.55	2.66	1.94
5c	1.46	96.20	1.69	0.64
5d	0.92	95.38	2.67	1.03

The results of electron probe microanalysis of compositions in the intersections of white lines are given in table 7

Table 7. Compositions of metal phase with increased content of chromium according to the EPMA data (wt %)

Figure	Cr	Fe	Mn
6a	5.40	91.05	3.54
6b	5.62	90.96	3.42
6c	4.98	92.67	2.35
6d	5.84	90.19	3.96

The results of electron probe microanalysis of compositions in the selected sections are given in table 8.

Table 8. Compositions of phosphide phases according to the EPMA data (wt %)

Figure	P	Cr	Mn	Fe	Ni
7a	9.74	0.56	3.24	84.91	1.56
7b	7.73	0.55	3.50	86.00	2.22
7c	8.68	0.61	2.61	86.26	1.84
7d	12.94	0.53	3.36	81.28	1.90

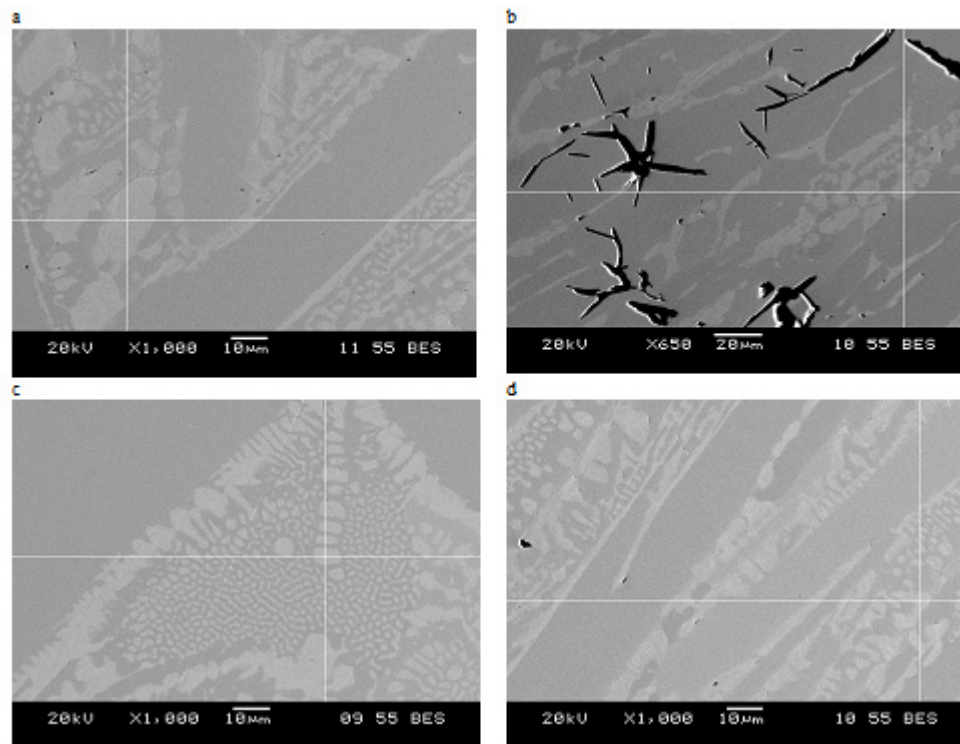


Figure 5. Phases with low content of chromium in the metal sample slices of heats No 1-4 (a-d, respectively).

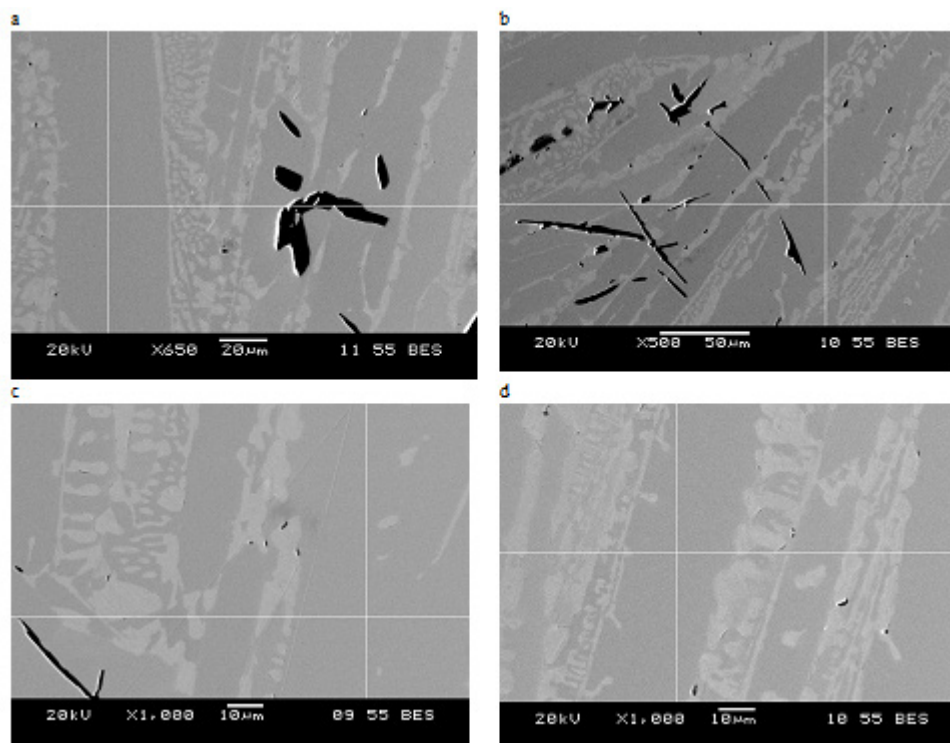


Figure 6. Phases with increased content of chromium in the metal sample slices of heats No 1-4 (a-d, respectively).

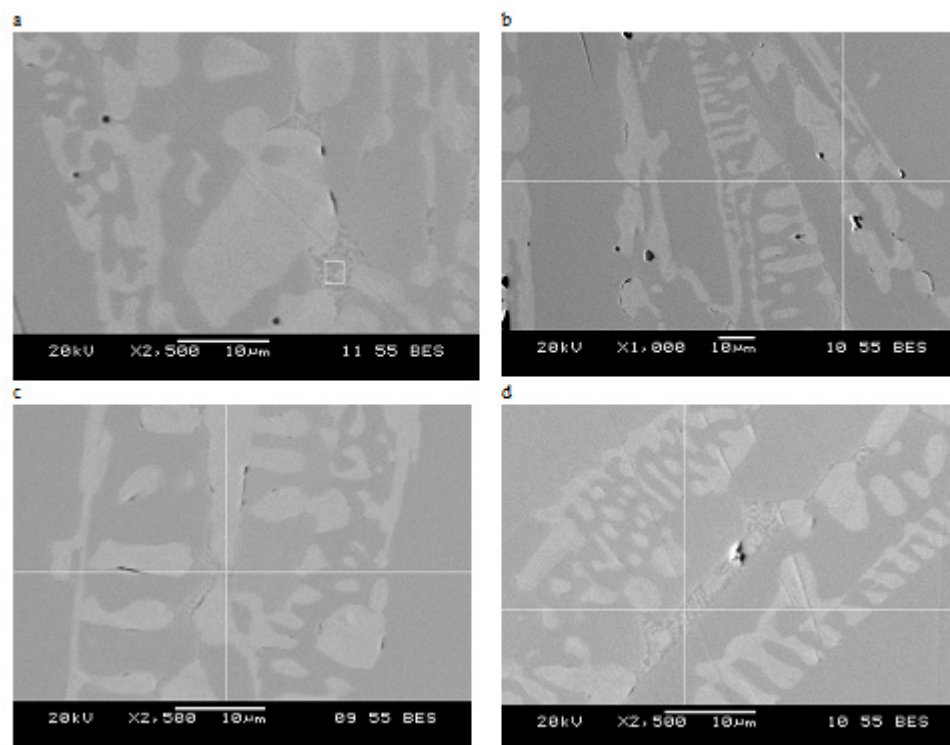


Figure 7. Phosphide phase inclusions in the metal sample slices of heats No 1-4 (a-d, respectively).

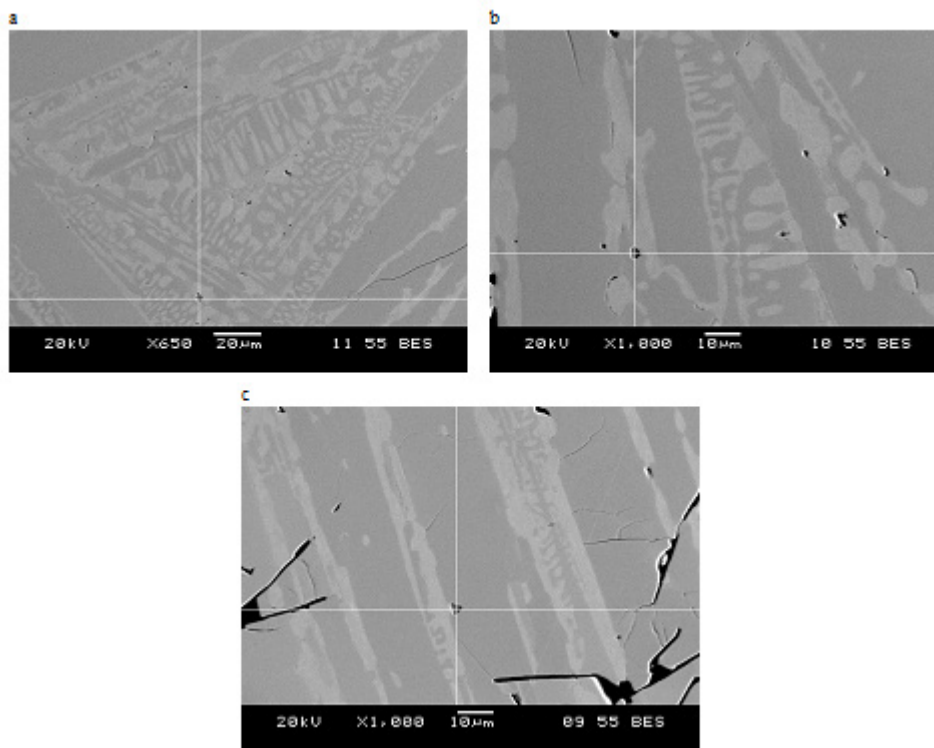


Figure 8. Sulfide inclusions in the metal sample slices of heats No 1-3 (a-c, respectively).

The results of electron probe microanalysis of compositions in the intersections of white lines are given in table 9.

Table 9. Compositions of sulfide phase inclusions according to the EPMA data (wt %)

Figure	S	Mn	Fe	Cr	P
8a	24.78	47.98	26.50	-	0.73
8b	26.48	55.84	17.05	0.63	-
8c	23.81	44.62	30.42	1.15	-

4. Conclusion

The conducted experiments have shown that the weight of metal phase obtained as a result of liquid-phase reduction of the magnetic part of slag material may amount to 40 % and higher of the initial slag weight. It is possible to achieve almost complete reduction of iron, chromium and nickel contained in slag. Major part of manganese, as well as some other components, including valuable elements – tungsten, molybdenum, titanium and vanadium, also passes into the molten metal.

Liquid-phase slag reduction may be conducted at temperatures ranging from 1500 to 1550 C. Slag reduction time (after mixture is heated up to the operating

temperature) should not exceed 30 minutes. For a more complete recovery of valuable metals it is recommended to use the moment of the ‘boiling’ (intensive separation of gaseous carbon oxides) period completion as an indicator of the isothermal time end. Useful products of the reduction process are liquid metal and heavy metal-depleted oxide melt consisting mainly of calcia, silica, magnesia and alumina which may be used in cement manufacturing.

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