PRODUCTION OF FERROVANADIUM UNDER THE CONDITIONS OF ELECTROSLAG MELTING

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ABSTRACT

The electroaluminothermic process is considered for ferrovanadium production from a vanadium-containing charge mixture by reducing vanadium oxide with aluminium in a slag layer with simultaneous electrical heating of the slag bath. The key factors influencing the fundamental parameters of the process have been identified. Samples of final slag were examined, and chemical composition and metal particle distribution in the slag layer were determined.

KEYWORDS: electroslag process, ferrovanadium, electroaluminothermic reduction, slag, chemical composition, metal, inclusions
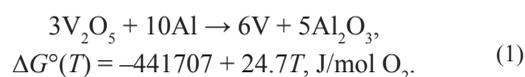
INTRODUCTION

More than 90 % of all the vanadium mined in the world is used in the metallurgical industry for production of special steels and doping titanium alloys [1–4]. Vanadium addition to chemical composition of steel promotes an increase in wear resistance, strength and hardness of the metal [2, 5]. Vanadium binds nitrogen and reduces the steel sensitivity to aging, while simultaneously increasing its heat resistance. Vanadium microalloying became widely applied in structural steels, greatly improving their consumer qualities [6, 7]. Vanadium is also used for cast iron alloying [8]. Titanium alloys containing up to 4 % vanadium are widely applied in the aerospace industry to manufacture parts of jet engines and flying vehicle airframes [3].

World tendencies in metallurgy and related sectors are indicative of a stable growth in demand for vanadium-containing steels and alloys [4]. During steel smelting vanadium is added to the metal predominantly in the form of ferrovanadium [2, 9]. Other vanadium-containing alloys, so-caller master alloys, are used more seldom. Ferrovanadium grades with vanadium content from 35 to 85 % are available in the market [9, 10]. The majority of ferrovanadium, however, is produced and consumed in the form of FeV80 ferroalloy. On the one hand, during its manufacture the higher vanadium content in the alloy reduces the specific production costs per a product unit, making production more cost-effective. On the other hand, metallurgical enterprises, as consumers, also give preference to FeV80, so as to minimize the total quantity of the ferroalloy that needs to be spent during steel alloying.

Vanadium oxides are the main raw material for ferrovanadium production [9–11]. Vanadium reduction from its oxides may be performed with carbon, silicon and aluminium. Carbon application as a reducing agent, leads to production of an alloy with higher carbon content. Therefore, silicon and aluminium are used in industry for vanadium reduction from its oxides. However, silicathermic method does not allow producing ferrovanadium with high vanadium content and low carbon content [9, 10]. On the other hand, aluminium reduces vanadium more completely than silicon does, owing to a higher thermodynamic strength of the aluminium oxide. Therefore, low-carbon ferroalloys with more than 70 % vanadium content are produced only by aluminothermic reduction. Alloys with lower vanadium content are often produced by silicathermic method [9, 10].

The reaction of vanadium reduction with aluminium from pentoxide is highly exothermic:

$$3V_2O_5 + 10Al \rightarrow 6V + 5Al_2O_3,$$
$$\Delta G°(T) = -441707 + 24.7T, \text{ J/mol O}_2. \quad (1)$$

The heat released during this reaction, is sufficient not only for melting the iron added to produce the alloy, but also for ensuring an effective separation of the produced metal and slag, enriched in aluminium oxide [12].

All the production processes with vanadium oxide reduction with aluminium can be divided into aluminothermic (thermite) and electroaluminothermic [7, 10].

In out-of furnace aluminothermic process (thermite) the charge consists of iron scrap (or iron oxide), granules of vanadium pentoxide, aluminium and such fluxes as soda ash or fluorspar [9, 12]. Aluminium is added to the charge in the amount of 100–102 % of that required for reduction of vanadium pentoxide by the stoichiometry. Before loading into the reactor, the charge materials are thoroughly mixed in the mixing drum. The reduction process is performed in reactors lined with magnesite. The thus produced ferro-

vanadium usually contains 82–85 % V, up to 2 % Si, 1.5 % Mn and 0.06 % C. Under production conditions, 90–95 % of vanadium passes into the alloy from the charge. Final slag contains up to 4.5 % vanadium oxides. The main disadvantages of this process are the high reaction intensity accompanied by considerable dust and gas emissions, and significant metal consumption with remains in the slag after the reaction.

To increase vanadium extraction into the alloy, the melting scheme with additional electric heating of the slag during ferrovanadium production is used [6, 9, 10]. Additional heating of the slag promotes a more complete reduction of vanadium and improves the conditions for melting product separation, as the slag remains sufficiently liquid during the entire melting operation. The electroslag process is less active and more controlled, accordingly, than the thermite one, while vanadium extraction under certain conditions increases up to 95–97 %. The electroaluminothermic method also allows using lower vanadium oxides (V_2O_3, V_2O_4) for ferrovanadium production, where the reduction reactions are accompanied by smaller thermal effect [10].

This work is an experimental study of the electroaluminothermic process of ferrovanadium production for vanadium-containing raw materials by reducing vanadium oxide with aluminium in a slag layer, with simultaneous electric heating of the slag bath.

Experiments were conducted in a laboratory electroslag furnace of USh-114 type and in semi-industrial flux-melting furnace of A-550 type. The vanadium source in the charge was granulated commercial vanadium pentoxide of 3–5 mm fraction with the following chemical composition, wt.% 82–86 V_2O_5, 3–8 Al_2O_3, 4–7 CaO, up to 2 Fe_2O_3, 1.5 TiO_2, 0.3 SiO_2, 0.5 of other impurities. Crushed aluminium wastes with particle size of 3–5 mm were used as a reducing agent. The charge composition also included powder of 1 mm fraction. Lime and calcium fluoride were used to adjust the slag pool chemical composition. A starting point for determination of the charge composition was stoichiometric calculation in keeping with reaction (1). In order to obtain a ferroalloy with the specified vanadium content (C_V, %), it is necessary to add iron to the charge composition in the amount which can be calculated by the following formula:

$$m_{Fe} = \frac{100 - C_V}{C_V} m_V = \frac{100 - C_V}{C_V} 0.56 m_{V_2O_5}, \text{ kg}.$$

Thus, in order to produce a ferroalloy with 50 % vanadium content from 10 kg of vanadium pentoxide, it is necessary to add 4.9 kg of aluminium and 5.6 kg of iron to the charge, and to produce a ferroalloy with 80 % vanadium, 1.4 kg of iron should be added. Here, the total calculated quantity of the produced alloy will be equal to 11.2 and 7.0 kg, respectively. The total amount of slag which will form from Al_2O_3 and CaO will be equal to 12.3–13.3 kg. Since commercial vanadium oxide containing impurities, is used in the charge, 0.36–0.95 kg of aluminium oxide and 0.48–0.83 kg of calcium oxide will enter the slag together with it. In addition, up to 0.24 kg Fe_2O_3 and 0.18 kg TiO_2 will enter the slag with vanadium pentoxide, which can be reduced with aluminium to the respective metals and can go into the ferroalloy. For instance, under the condition of total reduction of titanium oxide, ferrovanadium with 80 % vanadium can have up to 1.5 % titanium in its chemical composition. In view of the possible aluminium consumption for reduction of iron and titanium oxides, the amount of aluminium in the charge should be increased by 1–2 % of that required for reduction of all the vanadium oxide in the charge.

Lime and calcium fluoride are added to the charge to produce slag of the desired composition. To have liquid slag, in keeping with the equilibrium diagram of CaO–Al_2O_3 system [13], lime content in it should be equal to 48–53 % of Al_2O_3 content. A rational quantity of calcium fluoride in the charge was determined experimentally, as it is not only the slag diluent, but also a regulator of its electric resistance. During the laboratory experiments in USh-114 furnace, the slag mixture was formed on the base of flux of ANF-28 type [14], which contains 41–49 % CaF_2, 26–32 % CaO, 20–21 % SiO_2 and up to 5 % Al_2O_3. The reduction process was performed in a graphite crucible. The general scheme of organizing the melting is shown in Figure 1.

Melting was begun with a solid start with melting of part of the slag-forming materials in the crucible. After the liquid slag bath formation, the charge mixture was loaded in portions into the space between the
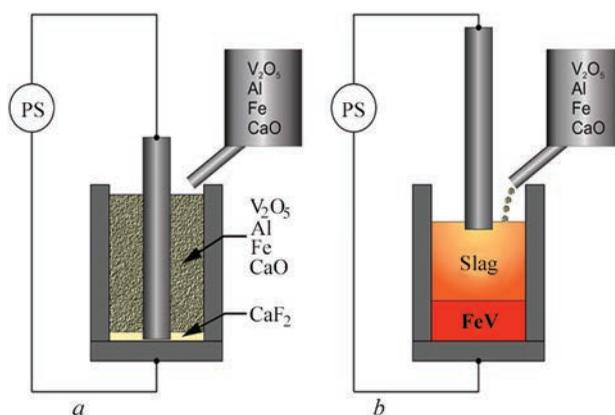

Figure 1. Schematic of realization of the process of reduction electroslag melting of ferrovanadium: *a* — process initiation; *b* — charge melting

Table 1. Composition of laboratory melt charge, g

Experiment	V_2O_5	CaF_2	ANF-28	Fe	Al	Total
10	400	20	100	50	200	770
11	200	—»—	—»—	—»—	100	470
12	500	—»—	—»—	—»—	170	840
13	—»—	70	—»—	—»—	140	860
14	510	150	–	—»—	—»—	850

Table 2. Chemical composition of the produced metal, wt.%

Experiment	V	Al	Si	Ti	Fe
10	41.38	14.7	2.51	1.63	38.48
11	24.45	7.21	1.43	N/D	62.35
12	65.15	4.17	2.66	0.64	25.45
13	61.29	7.38	4.0	0.44	23.03
14	67.0	11.0	N/D	N/D	15.0

graphite electrode and the crucible wall. Slag-forming components were added periodically, to adjust the chemical composition of the slag. The speed of the charge loading was regulated in keeping with its melting rate. After melting of the entire charge, the slag bath was kept for some time with power supply on, for completion of the reduction reactions and achievement of a more complete separation of the metal and the slag. After completion of the soaking, the power source was disconnected, and the molten products of melting were poured out of the crucible into the prepared metal mould. After their solidification and cooling, the weight of the produced metal and slag was measured on the laboratory scales and samples were taken for chemical analysis. During melting the electric mode was adjusted manually.

A series of melts were conducted under the laboratory conditions in electroslag furnace of USh-114 type, during which the features of running of the main reduction electroslag process and state of the slag bath were experimentally studied, and the conditions were determined for achievement of the best results. Tables 1, 2 give the composition of the charge and the chemical composition of the produced metal for the five final laboratory melts.

Experimental melts in a small volume allowed adjustment of the charge composition to obtain a slag bath of the required density and electric resistance, so as to ensure an appropriate running of the process of reduction and separation of the slag and the metal. However, because of the small volume of the melt

and short melting duration, which was not longer than 5 min, the melting crucible did not have time to heat enough for all the produced metal to stay in the liquid state up to process completion in the entire volume of the melting zone. As a result, a certain part of the metal could not be poured out of the crucible after melting was over. Considerable specific losses of heat from the melting space, as a manifestation of the scale factor, also negatively influenced the completeness of the reduction process, which is illustrated by increased aluminium content in the produced metal (Table 2), even under the condition of its actual lack in the charge compared to the calculated value by the stoichiometry. Increase of the slag bath temperature promoted an increase of vanadium extraction into the metal (melts 12-14, Table 2).

Analysis of the laboratory melt data was the basis to develop a charge mixture for smelting ferrovanadium by the electroslag technology without application of ANF-28 flux. Charge composition shown in Table 3 was selected for experimental melting on a larger scale, performed in a furnace of A-550 type.

The ratio of the slag-forming components in the charge was selected so as to obtain at the start of melting a liquid slag bath, consisting of CaF_2 and CaO, and, later on, maintain CaO percentage content in the slag at the level of 48–53 %, with aluminium oxide entering the slag as a result of running of reaction (1).

During melting, the charge melted rather quickly, but without a pronounced pyroeffect. The total amount of the charge was 23.6 kg per melt. The duration of the process of charge melting was close to 16 min, and the bath was kept under current for another 4 min. After completion of the process, the melting products were poured into a steel mould (Figure 2). Here, no remains of the metal or the slag were left in the melting

Table 3. Composition of the charge for an experiment on electroslag melting of ferrovanadium, %

V_2O_5	Al	Fe	CaF_2	CaO	Total
55	22	5	2	16	100

Figure 2. Appearance of slag and ferroalloy in the mould

crucible. The overall weight of the melting products was 23.05 kg, of which 7.15 kg were ferrovanadium and 15.9 kg were slag (2.22 kg of slag per kilogram of metal). Evaporation losses were 0.55 kg. The quantity of the produced ferrovanadium is equal to 84.3 % of the total calculated quantity of vanadium and iron in the charge. Here, the specific power loss is equal to 1.958 kW·h/kg or 14 kW·h per one experiment.

Chemical composition of the produced alloy is given in Table 4. A too high carbon content in the metal is due to conducting the reduction process in a graphite crucible. However, application of a crucible with lining from a refractory material, not containing any carbon, will ensure production of an alloy with carbon content meeting the requirements. Extraction of the charge vanadium into the metal was equal to 72 %. Here, reduction was performed with actual lack of aluminium in the charge compared to the theoretically required one, in order to determine the degree of its utilization and absorption by the metal. Analysis of the obtained data showed that 89 % of aluminium from the charge was consumed directly for reduction of vanadium passing into ferrovanadium, and 3.9 % of aluminium from the charge entered the alloy. The rest of the aluminium was consumed in iron and titanium oxide reduction, and was lost to evaporation and oxidation. The process of metallic aluminium interaction with the slag bath obviously requires additional study. However, in any case, to increase vanadium extraction into the alloy, it is necessary to increase the aluminium fraction in the charge, taking into account the respective stoichiometric relationships.

Slag from experimental melt, entering the mould together with the metal, was studied. The thickness of the slag layer in the mould was approximately 0.05 mm (Figure 2). The slag was of gray colour

Figure 3. General view of a layer of slag in section (below is the slag-metal interface)

and had a dense fibrous structure (Figure 3). A thin yellowish-white layer was observed on the slag surface, corresponding to slag-metal interface. Studies showed that it does not contain any vanadium oxide at all. On the other hand, the slag proper contains up to 4 % of vanadium oxide, 52–59 % aluminium oxide and 32–36 % calcium oxide. These data show that in order to improve this result, it is necessary to not only increase the aluminium fraction in the charge, but also add lime to the slag bath before soaking in such an amount, that the lime/aluminium oxide ratio was equal to 1:1 in the slag.

Electron microscopy studies of the slag samples revealed clusters of fine metallic inclusions along the slag-metal interface in a layer approximately 8 mm thick (Figure 4). Average size of the detected metal particles was 120–125 nm (Figure 5). By their chemical composition they are vanadium (97–98 %) with aluminium admixture (Figures 5, 6). Analysis of the slag chemical composition in this layer showed that it consists predominantly of aluminium oxide, calcium oxide and a small amount of vanadium oxide (Figure 6).

Average size of metal particles detected in the slag layer, gradually decreases from 125 nm near the metal-slag interface to 70 nm (Figure 7, *a*) in the middle of the layer and to 10 nm near the slag-atmosphere boundary (Figure 7, *b*). Here, aluminium content in its chemical composition becomes higher (Figures 6, 7). Residual vanadium content in the slag layer in the direction away from the slag-metal interface (lower layers) towards the slag-atmosphere surface (upper layers) is doubled from 1.08 to 2.15 % near the surface. In the middle layers the residual vanadium content is

Table 4. Chemical composition of the produced ferrovanadium, wt.%

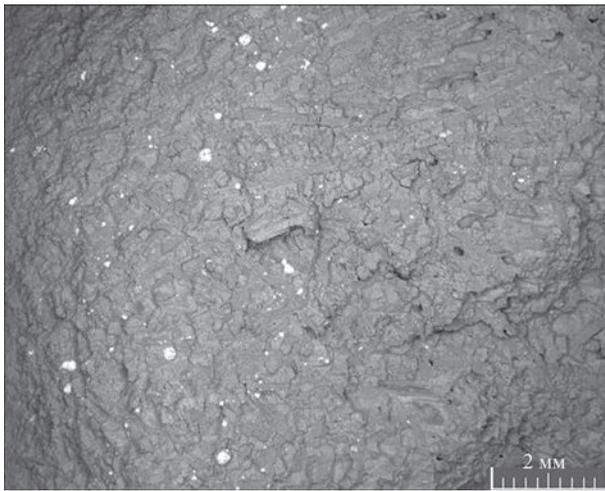| V	Si	Al	C	Mn	Ti
72.68–74.27	0.6–1.17	1.67–2.93	2.08	0.08–0.11	0.3

Figure 4. Clusters of metal particles in the slag layer near the slag-metal interface (surface on the right)

equal to 1.79 %. Such a picture is the result of continuation of the reduction process running in the slag layer after its penetration into the mould with simultaneous precipitation of metal drops in the liquid slag under the impact of the force of gravity. Reaction (1)

is strongly exothermic, so that with temperature lowering the equilibrium in it is shifted further towards vanadium reduction. In view of that it may be rational to take measures aimed at slowing down the slag cooling in the mould during production.

It should be noted that coarse metal inclusions were not detected in the studied slag samples which is an indication of rather good separation of the melting products. All the metal particles detected in the slag layer consist of vanadium and aluminium and do not contain any iron. It can be assumed that during melting of the charge iron (in the experiment this was powder of 1 mm fraction), the forming coarse drops of molten iron are not fragmented in the slag pool and rather quickly separate from it, passing into the liquid metal pool. At the same time, vanadium reduction occurs predominantly on aluminium drops. They have smaller specific weight than the iron ones and lower precipitation rate, accordingly, and they can be entrapped by liquid slag flows. Moreover, running of a highly exothermic reaction of vanadium reduction significantly heats the reaction zone that leads to
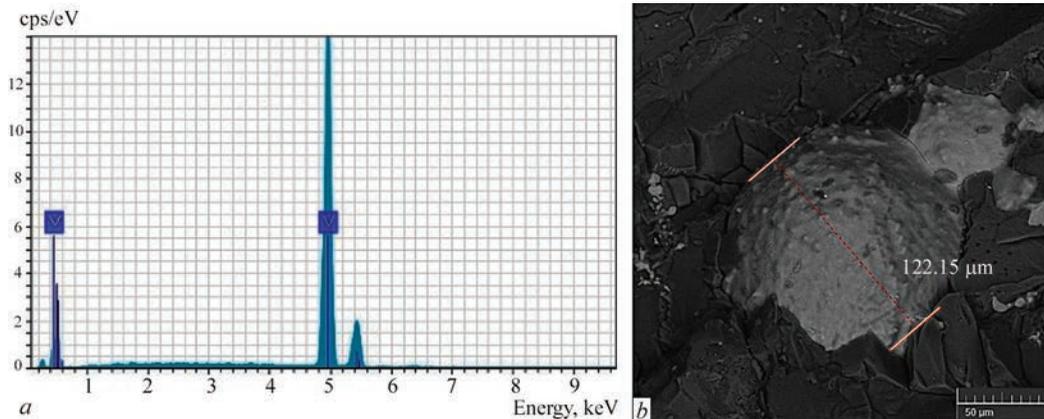

Figure 5. Size (*a*) and chemical composition (*b*) of the metallic inclusion in the slag near the slag-metal interface
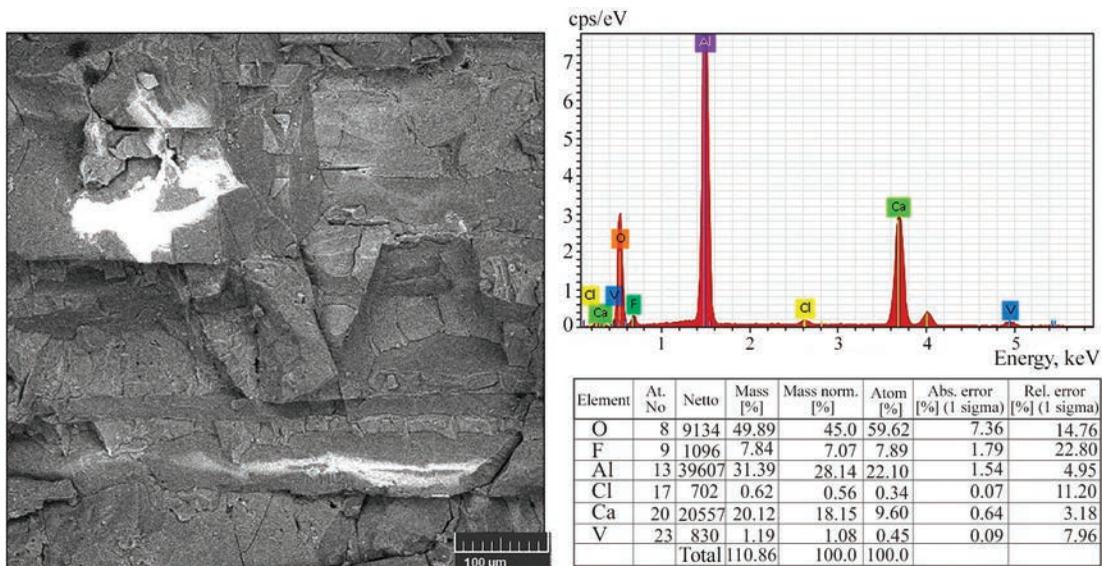

Element	At. No	Netto	Mass [%]	Mass norm. [%]	Atom [%]	Abs. error [%] (1 sigma)	Rel. error [%] (1 sigma)
O	8	9134	49.89	45.0	59.62	7.36	14.76
F	9	1096	7.84	7.07	7.89	1.79	22.80
Al	13	39607	31.39	28.14	22.10	1.54	4.95
Cl	17	702	0.62	0.56	0.34	0.07	11.20
Ca	20	20557	20.12	18.15	9.60	0.64	3.18
V	23	830	1.19	1.08	0.45	0.09	7.96
		Total	110.86	100.0	100.0		

Figure 6. Composition of slag in the layer saturated with metal inclusions near the slag-metal interface

Element	At. No	Netto	Mass [%]	Mass norm. [%]	Atom [%]	Abs. error [%] (1 sigma)	Rel. error [%] (1 sigma)
O	8	1290	3.80	4.42	11.99	1.29	33.87
Al	13	6559	7.39	8.61	13.84	0.41	5.56
Ca	20	700	0.67	0.78	0.84	0.07	10.92
V	23	53282	73.32	85.83	72.73	2.05	2.79
Fe	26	294	0.66	0.77	0.59	0.10	15.24
		Total	85.83	100.0	100.0		

Element	At. No	Netto	Mass [%]	Mass norm. [%]	Atom [%]	Abs. error [%] (1 sigma)	Rel. error [%] (1 sigma)
F	9	375	6.87	7.46	16.40	2.19	31.86
Al	13	2545	4.31	4.69	7.25	0.28	5.39
S	16	6656	7.39	8.02	10.45	0.32	4.36
Ca	20	1434	2.02	2.20	2.29	0.12	5.16
V	23	34128	71.47	77.53	63.61	2.02	2.82
		Total	92.07	100.0	100.0		

a   *b*

Figure 7. Size and chemical composition of metal particles in the middle of the slag layer (*a*) and near the slag-atmosphere boundary (*b*)

reduction of the surface tension value of the present substances, dilution of the liquid phases and this way it promotes dispersion of the metal phase in the slag as a result of drop deformation under the impact of dynamic pressures of the environment, which are greater than the interphase tension forces [15]. Thus, the movement, coalescence and dispersion of the metal drops of different composition in the slag layer have a significant role in separation of the melting products and alloy formation.

CONCLUSIONS

1. The process of producing ferrovanadium by electroaluminothermic method, during which vanadium is reduced from its oxide with aluminium in a slag layer in the electroslag furnace, is less active and, therefore, more controlled than the aluminothemic (thermite) process. At such organization of the reduction process it is easier to control the slag viscosity, separation of the melting products, dissolution of the refractory lining and achievement of high product quality. Owing to the possibility of flexible adjustment of the charge composition, it is possible to produce ferroalloys with vanadium content from 40 up to 80 %, depending on the demand. Another important advantage of the electroaluminothermic process is simplified requirements to raw material preparation.

2. During the experiment on testing the developed procedure of producing ferrovanadium performed in electroslag melting furnace of A-550 type under the conditions close to the industrial ones, 7.15 kg of ferrovanadium with vanadium content of 73–74 % and 15.9 kg of slag with up to 4 % residual vanadium oxide content were produced from the charge of 23.6 kg weight. Here, vanadium extraction into the metal phase was equal to 72 %, and power consumption was 1.958 kW·h/kg.

3. Metal inclusions detected in the final slag, are of the size of 10–125 nm and by their chemical composition they consist of vanadium with a small aluminium addition. Their distribution by size and chemical composition in the slag layer shows that vanadium reduction and melting product segregation go on also in the mould during slag cooling.

4. Work on further improvement of the tested technology and its adaptation to the conditions of the specific production require solving the tasks on increasing the degree of vanadium extraction into the alloy and optimization of the specific power losses.

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CONFLICT OF INTEREST
The Authors declare no conflict of interest

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