FEATURES OF THE PROCESS OF OBTAINING FERROVANADIUM UNDER CONDITIONS OF ELECTROSLAG MELTING

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Abstract

The process of obtaining ferrovanadium by the electro-aluminothermic process has been studied. This process involves reducing vanadium oxide with aluminum in a slag layer in an electric furnace, using iron additions to achieve a desired alloy composition and lime to flux alumina. The electro-aluminothermic process is more controllable than the aluminothermic process. The chemical composition and viscosity of the slag play a critical role in the smelting results, which can be optimized by adjusting the charge composition and temperature. Is also important to achieve as complete separation of metal and slag as possible. By changing the composition of the charge, the electro-aluminothermic process allows producing ferroalloys ranging from 40 % to 80 % vanadium. An essential advantage of this process is relatively low equipment investment, simple raw material preparation requirements, and high product quality. Waste-free production can be implemented based on this process.

Keywords: Ferrovanadium, vanadium, electroaluminothermic reduction, electroslag process

1. INTRODUCTION

More than 90 % of all extracted vanadium is used in the metallurgical industry to produce special steels and alloying of titanium alloys for the aerospace industry [1]. The addition of vanadium to the chemical composition of steel contributes to improved wear resistance, strength, and hardness of the metal. Vanadium binds nitrogen and reduces steel's sensitivity to aging while enhancing its heat resistance [2,3]. Microalloying with vanadium has found widespread use in structural steels, significantly enhancing their consumer qualities. Vanadium is also used for alloying cast irons. Titanium alloys containing up to 4 % vanadium are used in the manufacturing of glider parts and jet engines [4]. Global trends in metallurgy and related industries indicate a growing demand for vanadium-containing steels and alloys [5].

The addition of vanadium to metal is primarily done in the form of ferrovanadium [2,6]. Vanadium-containing alloys are less commonly used. Ferrovanadium with vanadium content ranging from 35 % to 85 % is available in the market [7]. However, most ferrovanadium produced and consumed is in the form of FeV80. A higher vanadium content in the alloy reduces production costs per unit and, consequently, makes the manufacturing process more profitable. On the other hand, metallurgical plants, as consumers, also prefer FeV80 to minimize the overall quantity of ferroalloy required for steel alloying.

The main raw materials to produce ferrovanadium are vanadium oxides [6,7,8]. Vanadium reduction from oxides can be achieved using carbon, silicon, and aluminum. The use of carbon as a reductant result in a metal with increased carbon content. Therefore, silicon and aluminum are used as reductants in industry. Aluminum reduces vanadium more efficiently than silicon due to the higher thermodynamic strength of aluminum oxide. Hence, alloys with a vanadium content of 70 % and above are obtained through aluminothermic reduction only, while alloys with lower vanadium content are produced using silicon as a reductant. All industrial processes involving the reduction of vanadium oxide by aluminum can be divided into aluminothermic (thermit) and electroaluminothermic processes [7,10].

The reaction of vanadium reduction by aluminum is highly exothermic:

$$3V_2O_5 + 10Al = 6V + 5Al_2O_3 \tag{1}$$

$$\Delta G^0 = -441707 + 24.7T \text{ J/mol } O_2 \tag{2}$$

Thermal energy released during the process is sufficient to melt the iron added to obtain an alloy and facilitate the separation of the alloy and slag with high aluminum content.

In the out-furnace aluminothermic process (thermit process) the charge consists of aluminum, vanadium pentoxide (other vanadium compounds may also be used), iron scrap (or iron oxide), and fluxes such as calcined lime and fluorspar [10]. All charge materials, except for iron scrap, with particle sizes of 0.3-1.0 mm, are thoroughly mixed in a mixing drum and loaded into the melting unit. Aluminum is added to the charge at a quantity of 100-102 % of the stoichiometric amount required for the reduction of vanadium pentoxide. The process is carried out in reactors lined with magnesite. The ferrovanadium obtained by this method contains 82-85 % V, up to 2 % Si, up to 1.5 % Mn, and up to 0.06 % C. Under industrial melting conditions, 90-95 % of the vanadium in the charge is transferred to the alloy. The final slag contains up to 4.5 % vanadium oxides. The main drawbacks of this process are its highly vigorous reaction, accompanied by significant dust and gas emissions, as well as substantial metal losses due to skulls remaining in the slag after the reaction.

To increase the vanadium transfer to the alloy, a technological scheme of ferrovanadium melting with additional electric heating during the production of ferrovanadium is employed [6,7,11]. Preheating the slag promotes more complete vanadium reduction and improves the conditions for the precipitation of the formed metal. This process is much less active and, thus, more controlled than the thermit process, and vanadium extraction increases to 95-97 %. The electroaluminothermic method also allows the use of lower vanadium oxides (V_2O_3, V_2O_4) as raw materials for ferrovanadium production.

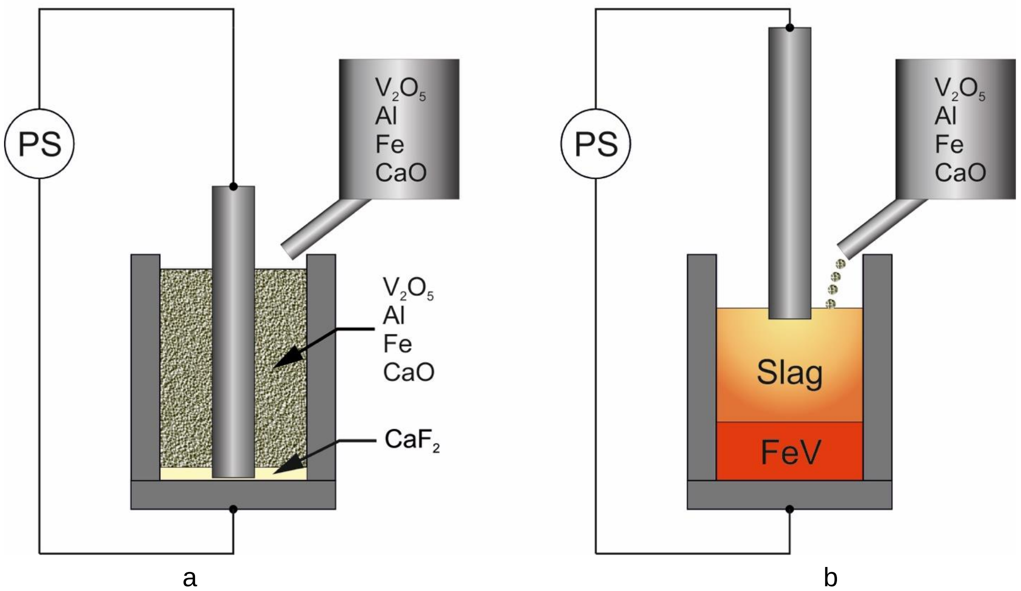
This study experimentally investigated the electroaluminothermic process of obtaining ferrovanadium by reducing vanadium pentoxide in an electric slag melting with the production of alloys with vanadium mass fractions ranging from 40 % to 85 %. In this process, vanadium is reduced by aluminum from the oxide in the slag layer, while simultaneously heating the slag bath with joule heat and adding a specific amount of iron necessary for the formation of the desired composition of the metallic alloy, as well as lime for fluxing the alumina, which is a byproduct of the reduction reaction. The electric slag process provides better conditions for vanadium reduction and the separation of melting products since the slag remains sufficiently liquid throughout the entire melting process, and the process proceeds with controlled intensity.

2. EXPERIMENTAL METHODOLOGY

The experiments were conducted using the laboratory electric slag resistance furnace of УШ-114 type and the semi-industrial furnace of A-550 type. The overall process organization scheme is shown on **Figure 1**.

The source of vanadium in the charge was granulated technical-grade vanadium pentoxide with a particle size of 3-5 mm with chemical composition, % wt., as follows: 82-86 V_2O_5; 3-8 Al_2O_3; 4-7 CaO; up to 2 Fe_2O_3; up to 1.5 TiO_2; up to 0.3 SiO_2; up to 0.5 other impurities. Aluminum waste with a 3-5 mm particle size was used as a reducer. Iron powder with a particle size fraction of up to 1mm was also included in the charge. Lime and calcium fluoride were used for adjusting the chemical composition of the slag bath.

The stoichiometric calculation served as the starting point for determining the composition of the charge. According to reaction (1) for the reduction of 3 moles of vanadium oxide, 10 moles of aluminum are required. Considering the molar masses of vanadium pentoxide $M_{V_2O_5} = 182\ g/mol$ and aluminum $M_{Al} = 27\ g/mol$, the aluminum consumption for the reduction of 10 kg of V_2O_5 is:



a b

Figure 1 The scheme of performing the electroslag melting process
(a - process initiation; b - melting of the charge)

$$m_{Al} = 270/546 \cdot m_{V_2O_5} = 0.49 \cdot 10 = 4.9\ kg$$

As a result of the reduction reaction, vanadium and aluminum oxide will be formed in the following quantities $\left(M_{Al_2O_3} = 102\ g/mol;\ M_V = 51\ g/mol;\right)$:

$$m_V = 306/546 \cdot m_{V_2O_5} = 0.56 \cdot 10 = 5.6\ kg$$

$$m_{Al_2O_3} = 510/546 \cdot m_{V_2O_5} = 0.93 \cdot 10 = 9.3\ kg$$

To obtain a ferroalloy with a specified vanadium content (C_V, %), iron needs to be introduced into the charge. The amount of iron can be calculated using the formula:

$$m_{Fe} = (100 - C_V)/C_V \cdot m_V = (100 - C_V)/C_V \cdot 0.56 \cdot m_{V_2O_5}\ , kg$$

Therefore, to obtain a ferroalloy with a vanadium content of approximately 50 % in the charge, 5.6 kg of iron should be added, and for a ferroalloy with 80 % vanadium, 1.4 kg of iron should be added. The expected total amount of obtained alloy will be 11.2 kg and 7 kg, respectively. Consequently, the total amount of slag formed, containing Al_2O_3 and CaO, will be 12.3-13.3 kg.

Since technical vanadium oxide containing impurities was used in the charge, 0.36-0.95 kg of aluminum oxide, up to 0.24 kg of Fe_2O_3, and up to 0.18 kg of TiO_2 may also enter the slag. These impurities can be reduced by aluminum to their corresponding metals and contribute to the metal composition. For example, assuming complete reduction of titanium oxide, a metal with 80 % vanadium content can have a titanium content of up to 1.5 %. Considering possible aluminum consumption for the reduction of iron and titanium oxides, the amount of aluminum in the charge should be increased by 1-2 % compared to the amount necessary for reducing vanadium oxide.

To ensure the successful progress of the electroslag process and maintain a liquid slag, lime and calcium fluoride are added to the charge. According to the equilibrium diagram in the CaO-Al_2O_3 system [10], the amount of lime should comprise 48-53 % of the quantity of Al_2O_3. The quantity of calcium fluoride was determined experimentally, as it serves not only as a slag diluent but also as a regulator of its electrical resistance. Laboratory experiments on the УШ-114 furnace involved the formation of the slag mixture based on the ANF-28 type flux.

The reduction process was conducted in a graphite crucible. The melting commenced with a solid start by melting a portion of the slag-forming materials in the crucible. Once a liquid slag bath was formed, the charge mixture was loaded into the gap between the graphite electrode and the crucible wall. This charge mixture comprised vanadium pentoxide, a reducing agent, and iron powder in predetermined proportions. To adjust the chemical composition of the slag, slag-forming components were periodically added. The rate of charge loading was adjusted according to the rate of melting. After the complete melting of the charge, a holding period was introduced with a supplied power to complete the reduction reactions within the bath and achieve a more thorough separation of metal and slag. Following the holding period, the power supply was disconnected, and the molten products were poured from the crucible into a prepared metal mold. After solidification, the weight of the molten products was measured on laboratory scales, and samples were taken for chemical analysis. The adjustment of the electrical regime during melting was manually performed.

3. DISCUSSION OF RESULTS

Under laboratory conditions on a small-scale furnace, a series of melts were conducted to experimentally study the electroslag process. In addition to examining the peculiarities of the reduction process and the state of the slag bath, conditions were identified to achieve the best results. **Table 1** and **Table 2** present the composition of the charge and the chemical composition of the obtained metal for five final laboratory melts.

Table 1 The composition of the charge during laboratory melting, g

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

Table 2 The obtained chemical composition of the metal, % wt.

Experiment	Al	Si	Ti	V	Fe
10	14.7	2.51	1.63	41.38	38.48
11	7.21	1.43	–	24.45	62.35
12	4.17	2.66	0.64	65.15	25.45
13	7.38	4.0	0.44	61.29	23.03
14	11.0	3.5	–	67.00	15.00

Experimental melts in a small volume (up to 1 kg) on the УШ-114 setup allowed for adjusting the composition of the charge mixture to ensure the desired density and electrical resistance of the slag for proper implementation of the reduction process and subsequent separation of slag and metal.

Since the melt volume was small, and the duration of charge melting did not exceed 5 minutes, the crucible did not have enough time to reach the temperature at which all the obtained metal remained in a liquid state. As a result, in the first 10 experiments, it was not possible to pour out most of the metal from the crucible. The rapid cooling of the melt during the melts negatively affected the completeness of the reduction process.

Based on the analysis of data obtained during laboratory melts, a charge mixture was developed for melting ferrovanadium using the electroslag technology on a larger scale in a semi-industrial furnace of the A-550 type (**Table 3**).

Table 3 The composition of the charge for electroslag melting of ferrovanadium on the furnace A-550, kg

V_2O_5	Al	Fe	CaF_2	CaO	Total
13	5.2	1.2	0.5	3.7	23.6

The ratio of slag-forming components in the charge mixture was chosen in such a way that at the start of the melt, a liquid slag bath consisting of CaF_2 and CaO was obtained, and subsequently, as Al_2O_3 entered the slag, the CaO content in the slag was maintained at around 48-53 %.

During the melting process, the charge melted quite rapidly, but without a pronounced pyro effect. The entire charge melting process took approximately 16 minutes, plus an additional 4 minutes of slag holding under the current. The power consumption amounted to 1.958 kWh/kg or 14 kWh per experiment. After the completion of the melt, the products were poured out from the crucible into a steel mold (**Figure 2**). No remnants of metal or slag were left in the crucible.

Figure 2 The appearance of slag and ferroalloy in the mold

The output of the process consisted of 7.15 kg of ferrovanadium and 15.9 kg of slag (2.22 kg of slag per kilogram of metal). The total weight of the melt products was 23.05 kg. Losses due to evaporation and volatilization amounted to 0.55 kg. The amount of ferrovanadium obtained in the 7.15 kg corresponds to 50.35 % of the total amount of V_2O_5 and iron in the charge (14.2 kg). The vanadium extraction into the metal accounted for 86 %. The chemical composition of the obtained alloy is provided in **Table 4**.

Table 4 Chemical composition of the obtained alloy, % wt.

Al	Si	Ti	V	Mn	C	Fe
1.67-2.93	0.6-1.17	0.3	72.68-74.27	0.08-0.11	2.082	21.44-21.69

To improve the vanadium content, it is necessary to increase the proportion of aluminum in the charge and add lime at the end of the process in such an amount that the lime/aluminum oxide ratio in the slag is 50/50 %. The high carbon content in the metal is attributed to the process being conducted in a graphite crucible. Conducting the process in a refractory-lined crucible would significantly reduce the carbon content.

The slag has a gray color and a fibrous structure (**Figure 3**). On the surface of the slag corresponding to the "slag-metal" boundary, a yellowish-white layer is observed. Investigations have shown that this layer does not contain vanadium oxide. The slag itself contains 4-8 % vanadium oxide, 52-59 % Al_2O_3, and 32-36 % CaO. The thickness of the slag layer in the ladle was approximately 0.05 m.

Examination of the slag under a scanning electron microscope revealed the presence of metal droplets near the "slag-metal" boundary, with an average size of approximately 125 nm (**Figure 4**). The thickness of the layer of metal-rich slag is approximately 8 mm. These metal droplets are primarily composed of nearly pure vanadium, with a small amount of aluminum impurities (up to 1-2 %) (**Figure 5**). Analysis of the slag in this zone showed that it mainly consists of calcium and aluminum oxides, with a small quantity of vanadium oxides (**Figure 6**).

Figure 3 General appearance of slag along the thickness of the layer (from below, the "slag-metal" border)

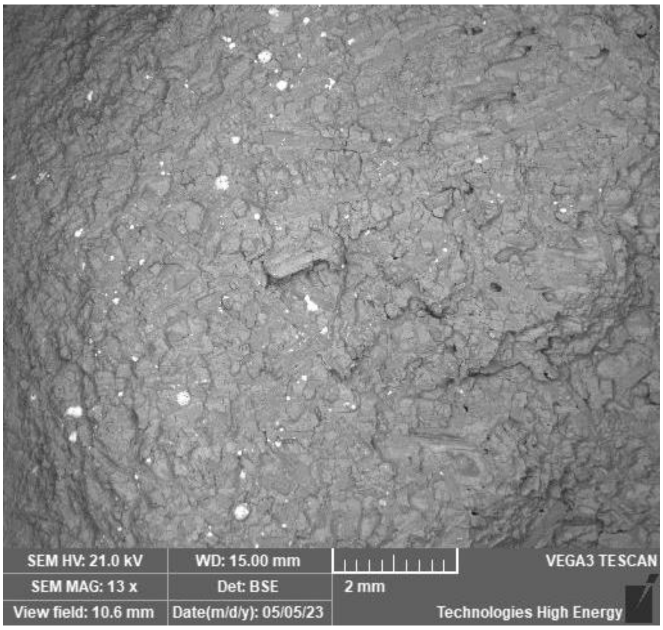
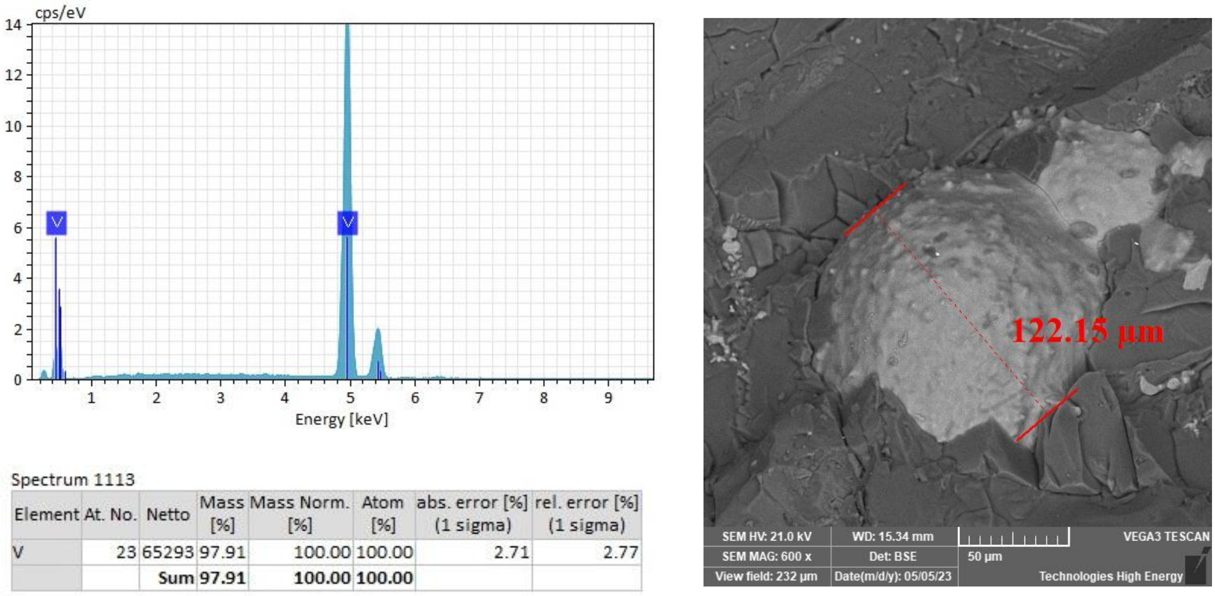


Figure 4 Metal balls in the slag layer near the slag-metal surface (right side)

In the middle section of the slag layer, towards its height, the quantity and size of inclusions decrease (approximately 70 nm) (**Figure 7a**). These inclusions also contain a lower amount of vanadium and a higher amount of aluminum. Near the slag-atmosphere boundary, the size of the metal inclusions further decreases to approximately 10 nm (**Figure 7b**), while the aluminum content in them increases to 4.31 %.

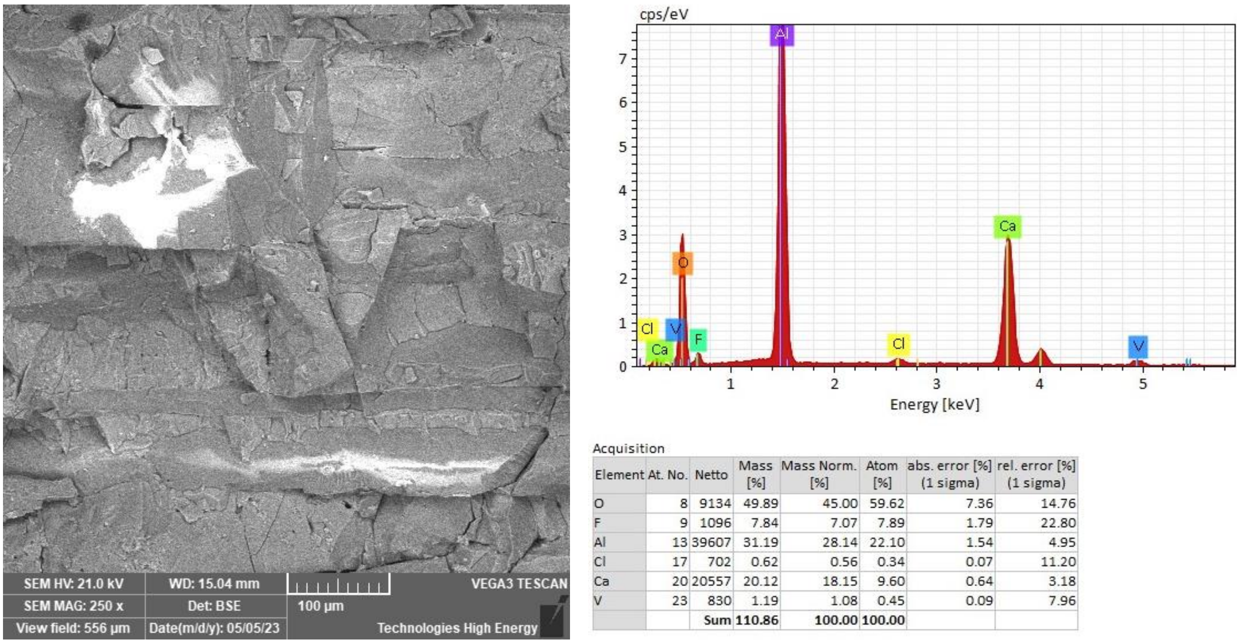
Regarding the vertical distribution within the slag layer, from the slag-metal boundary to the slag-atmosphere boundary, the vanadium content in the slag increases from 1.12-1.79-2.15 %. The vanadium content within the slag layer doubles from 1.12 % at the bottom to 1.79 % in the middle section and reaches 2.15 % close to the surface.



Spectrum 1113

Element	At. No.	Netto	Mass [%]	Mass Norm. [%]	Atom [%]	abs. error [%] (1 sigma)	rel. error [%] (1 sigma)
V	23	65293	97.91	100.00	100.00	2.71	2.77
		Sum	**97.91**	**100.00**	**100.00**		

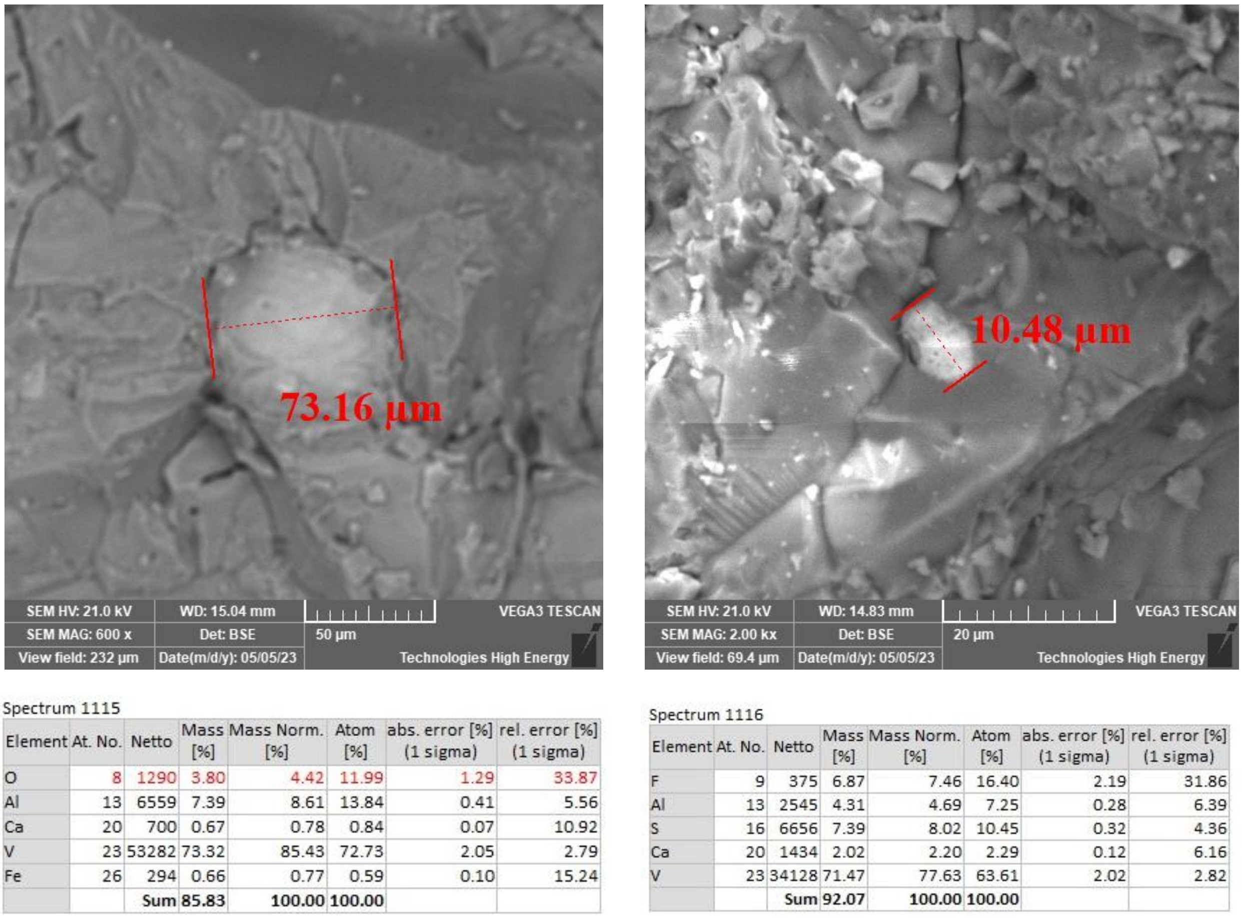
Figure 5 Size and chemical composition of a metal inclusion near the slag-metal interface in the slag



Acquisition

Element	At. No.	Netto	Mass [%]	Mass Norm. [%]	Atom [%]	abs. error [%] (1 sigma)	rel. error [%] (1 sigma)
O	8	9134	49.89	45.00	59.62	7.36	14.76
F	9	1096	7.84	7.07	7.89	1.79	22.80
Al	13	39607	31.19	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
		Sum	**110.86**	**100.00**	**100.00**		

Figure 6 Chemical composition of slag in the "belt" of metal inclusions near the slag-metal boundary



Spectrum 1115

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	85.43	72.73	2.05	2.79
Fe	26	294	0.66	0.77	0.59	0.10	15.24
		Sum	**85.83**	**100.00**	**100.00**		

a

Spectrum 1116

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	6.39
S	16	6656	7.39	8.02	10.45	0.32	4.36
Ca	20	1434	2.02	2.20	2.29	0.12	6.16
V	23	34128	71.47	77.63	63.61	2.02	2.82
		Sum	**92.07**	**100.00**	**100.00**		

b

Figure 7 The size and chemical composition of metal particles in the middle of the slag layer (a) and along the "slag-slag" atmosphere boundary (b)

It can be noted that almost all detected metal inclusions within the slag layer consist of vanadium with a small amount of aluminum impurities. They do not contain iron impurities, suggesting that the vanadium reduction process mainly occurs on aluminum droplets. On the other hand, other impurities (Si, Mn, Ti) are present in the alloy due to reduction and dissolution in iron. It appears that iron droplets, which have slightly higher density, are likely to separate from the slag more quickly. It is important to mention that in this study, iron powder with a fraction size of 1 mm was used as the source of iron in the charge. Thus, the movement and coalescence of metal droplets within the slag layer play a significant role in the separation of smelting products and the formation of the alloy.

4. CONCLUSION

The electroslag process for obtaining ferrovanadium by the electro-aluminothermic reduction of its oxide by aluminum in a slag layer in an electroslag furnace, with the simultaneous addition of a specified amount of iron and lime was experimentally studied. This process is less active and therefore more controllable than the aluminothermic process, allowing better control by the operator, to ensure product quality, vanadium yield, slag viscosity, separation of melt products, and control of refractory lining dissolution. By adjusting the composition of the charge, the process enables the production of ferroalloys with a wide range of vanadium concentrations, ranging from 40 % to 80 % as required. An important advantage of this process is its simple raw material preparation requirements, short melting time, and high product quality.

To verify and refine the concept of the developed process, an experimental smelting was conducted on the A-550 flux melting furnace under conditions approximating industrial conditions. During the experiment, 7.15 kg of ferrovanadium with a vanadium content of 73-74 % and 15.9 kg of slag with a residual vanadium oxide content of 4-8 % were obtained from a 23.6 kg charge. The vanadium extraction into the metal phase was 86 %. The smelting duration was 17 minutes, and the electrical energy consumption was 1.958 kWh/kg.

All detected metallic inclusions in the final slag consist of vanadium with a small amount of aluminum and have sizes from 10 nm to about 125 nm. They do not contain iron impurities, suggesting that the vanadium reduction process primarily occurs on aluminum droplets, while other impurities (Si, Mn, Ti) come to the alloy due to reduction with dissolution in iron. Metal droplet movement in the slag volume and their cohesion play an important role in the separation of melt products and alloy formation.

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