Smelting of vanadium-containing alloys with using non-standard reducing agents

E. N. Makhambetov, *Dr. Eng., Head of the Laboratory of Ferroalloys and Recovery Processes* [1];
N. R. Vorobkalo, *Master Eng., Researcher, Laboratory of Pyrometallurgical Processes* [1]*; Doctoral student* [2],
e-mail: nina.timirbaeva23@gmail.com;
A. S. Baisanov, *Cand. Eng., Prof., Head of Laboratory of Pyrometallurgical Processes* [1];
E. A. Mynzhasar, *Master Eng., Doctoral student* [3]

[1] *Zh. Abishev Chemical and Metallurgical Institute (Karaganda, Kazakhstan)*
[2] *Abylkas Saginov Karaganda Technical University (Karaganda, Kazakhstan)*
[3] *Karaganda Industrial University (Karaganda, Kazakhstan)*

The object of the study in this work is the process of smelting of vanadium alloying composition and vanadium ferroalloy using non-standard reducing agents, such as silicon-aluminum ferroalloy (ferrosilicoaluminum) and high-ash coal. Within the framework of this work, it is proposed to use silicon-aluminum reducing agents and high-ash coal as a replacement for expensive aluminum powder, ferrosilicon, and metallurgical coke which are used in conventional technologies for smelting of vanadium alloys and alloying compositions. To develop the technology for smelting of vanadium alloying composition using a silicon-aluminum reducing agent, a series of large-scale laboratory tests was carried out in the smelting furnace with provided installation for temperature recording, which was specially assembled by employees of the Zh. Abishev Chemical and Metallurgical Institute (ChMI). Tests on the smelting of a vanadium-containing ferroalloy using vanadium slag obtained by smelting of vanadium alloying composition by ladle treatment method, as well as converter vanadium slag, quartzite and high-ash coal (ash content 45-50 %) as a reducing agent, were also carried out in large-scale laboratory conditions in the ore smelting furnaces with 200 kVA transformer power. Experimental tests have shown positive results on the use of these non-conventional reducing agents in the composition of charge materials for smelting of vanadium-containing alloys and alloying compositions. Vanadium alloying composition was obtained by ladle treatment method using ferrosilicoaluminum, the average chemical composition of this alloying composition was, %: V 55; Si 10-24; Al 4-9 and Fe 10-30. Extraction of vanadium in the alloy was 70-80 %. Vanadium alloy was obtained by carbothermal method using high-ash coal and is characterized by the following average composition, %: V 4-10; Si 40-55; Al 15-20 and Fe 13-25. The degree of vanadium extraction makes 70 %.

Key words: vanadium pentoxide, silicon-aluminum alloy, vanadium alloying composition, ferrovanadium, ferrosilicovanadium, high-ash coal, ferrosilicoaluminium.
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Introduction

Vanadium in the form of alloying compositions and ferroalloys is one of the most widely used alloying elements, owing to its favourable effect on several mechanical and physico-chemical properties of processing metal [1-6]. Approximately 70-80 % of manufactured vanadium is used as an alloying element for the following steels: high-strength construction steels for welded metal structures; heat-treatable steels for machine-building; spring steels; high-temperature steels and alloys; high-strength non-magnetic steels; tool and bearing steels; low-alloy steels for cast essential components; steels for railroad transport.

Microalloying by vanadium is one of the prospective directions for rise of operating and mechanical properties, saving of critical alloying elements. Based on the generalized data [7-11], it is suggested that vanadium is more string deoxidizer in comparison with silicon, but more weak one than aluminium. Vanadium is widely used in production of low-alloy steels, due to its high hardenability, high strength and ductility both in rolled and normalized state, as well as good weldability. Ferrovanadium introduction in steel (in the amount up to 0.15-0.25 %) rises its strength, toughness, fatigue resistance and wear resistance [12].

Global ferrovanadium production and consumption makes 86,000 tons per year (data of 2013-2016). Global vanadium consumption increases permanently and reached 102,000 tons in 2019. In this connection, permanent increase of production volume of this alloy was noted and it was predicted that in 2020 it will reach 140,000 tons [13-15]. Average annual speed of increase of vanadium consumption in the most developed industrial countries makes 5-7 %. It is connected with vanadium application [6] in production of low-alloy steels for oil and gas pipelines, bridge construction, skyscrapers, large-span constructions, production of railroad rails etc. It should be mentioned, that vanadium and its compounds are widely used in nuclear and hydrogen power engineering and in manufacture of vanadium accumulators, in addition to metallurgical and chemical industries [16-20].

The following countries are the main producers of vanadium-containing alloys and alloying compositions: China 49.7 %; South Africa 13.9 %; Russia 7.8 %; Europe 6.7 %, North America 4.5 %. So, about 46 % of global vanadium production is consumed by China, the rest part leaves for Europe, North America, Japan and CIS countries [13, 15, 19, 21].

In Kazakhstan Republic, vanadium is manufactured as vanadium pentoxide (at Ust-Kamenogorsk titanium-magnesium integrated works) and as ammonium metavanadate (by “Balausa” company) and is exported in non-processed form. At the same time, the industry of Kazakhstan and other CIS countries consumes and imports large amount of metal products which contain vanadium – as railroad rails and pipe products for gas and oil pipelines. Thereby it is required to develop the technologies for primary processing of Kazakh vanadium raw materials in order to obtain products with higher added value.

The conventional process of manufacture of vanadium alloying compositions via aluminothermal method is based on reduction of metal oxides by aluminium, while for silicothermal melting ferrosilicon is used. Taking into account high cost of ferrosilicon and aluminium powder, and aiming on lowering the cost of melting of vanadium alloying compositions, the authors suggested to develop the technology of alumosilicothermal melting of vanadium alloying composition, using silicoaliminium alloy, which is molten via single-stage carbothermal method from high-ash coals, as a reducing agent. As concerns ferrosilicovanadium, the conventional technology of its manufacture includes use of vanadium-containing slag, ferrosilicon and expensive metallurgical coke.

The suggested technology differs from the conventional one: it is based on use of ferrosilicoaluminium – a cheap complex silicoaluminium ferroalloy with high silicon and aluminium content – as a reducing agent, instead of conventional aluminium powder and ferrosilicon. This complex silicoaluminium alloy, which was obtained via single-stage carbothermal method from high-ash coals, has the following chemical composition, %: Si – 55-65; Al – 15-25; P – 0.024; Fe – res. It is suggested to replace metallurgical coke by high-ash coal (ash content 45-50 %), which can’t be used as energetic material due to high ash content.

Based on the above-mentioned conclusions, it is evident that there is high necessity in development of such technology together with all required components for organization of production of vanadium ferroalloys and alloying compositions using silicoaluminium reducing agents and high-ash coals. Demand on products, vanadium raw materials and silicoaluminium reducing agents, such as ferrosilicoaluminium, which is molten at domestic works, is noted.

In this connection, the aim of this work is conducting of large-scale laboratorial tests on melting of vanadium alloying composition by ladle treatment method, using silicoaluminium reducing agents.

Methods and materials

The tests on manufacture of vanadium-containing alloying composition using vanadium pentoxide and silicoaluminium ferroalloy (ferrosilicoaluminium) as a reducing agent were conducted in specially assembled melting unit. The complex silicoaluminium ferroalloy, which was obtained via single-stage carbothermal method from high-ash coals of Kazakhstan Republic, was used for these tests; its chemical composition is presented in the previous section of the article.

The charge material mixture, which was used in large-scale laboratorial melting tests, was calculated for definite amount of substance. In this research, charge material was calculated for 1 t of vanadium pentoxide, so that the final alloy includes 60-70 % of vanadium as a result of alumosilicothermal reaction. The following exothermal reducing reactions will take place during the process of alumosilicothermal manufacture of vanadium alloy:

$$3V_2O_5 + 10Al = 6V + 5Al_2O_3 \quad (1)$$

$$2V_2O_5 + 5Si = 4V + 5SiO_2 \quad (2)$$

Used vanadium pentoxide has grain size 1 mm. It is known that optimal size of particles of the reducing agent should correspond to oxidizing fraction, thereby silicoaluminium reducing agent (ferrosilicoaluminium), which corresponds to the fraction not more than 1 mm, was used for by ladle treatment. According to the Zhemchuzhnyi rule, spontaneous alumosilicothermal process is possible, when the heat amount, which is emitted during the reaction, exceeds 550 kcal per kg of charge material. It was already mentioned that chemical property of vanadium alloys manufacture via ladle treatment is described generally by the reactions (1) and (2). The conducted calculations of charge material mixture, i.e. relation between oxides and reducing agent, are completely governed by the Zhemchuzhnyi rule.

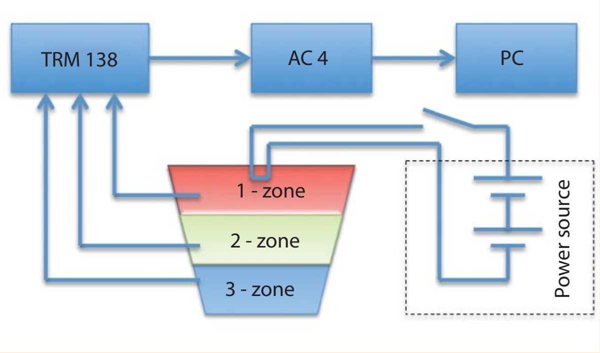

Fig. 1. The functional scheme of switching on thermocouples to the furnace (melting hearth)

The special melting hearth from fireclay bricks was assembled in the conditions of the Zh. Abishev Chemical and Metallurgical Institute for conducting of large-scale laboratorial tests on melting of vanadium alloying composition via ladle treatment. The gaps between hearth bricks were filled by fine fireclay powder, the internal side of melting hearth was sealed by the mixture of refractory magnesite powder and water.

The experimental unit for temperature recording with using the basic digital equipment (**Fig. 1**) was also assembled for examination of the temperature procedure of melting process for vanadium alloying composition. The essence of the temperature measuring technique includes the following operations. The melting hearth is virtually separated by three temperature zones, and the signals are transmitted from these zones to the regulating measuring device TPM 138 using tungsten-rhenium thermocouples. Automatic converter of interfaces AC-4 is switched on between personal computer (PC) and TPM 138, while the program Owen Process Manager is installed on this PC. Automatic converter of interfaces AC-4 transformed interface for exchange of information between TPM 138 and personal computer. The ignition system located at the safe distance using nichrome wire and laboratorial power transformer is used in the melting hearth instead of ignition charge. Wire heating provides the minimal energy required for activation of exothermal reactions. Thus, the functional scheme for temperature recording in different zones of the melting hearth was assembled.

Charge material for melting of vanadium-containing ferroalloy via carbothermal method contains from vanadium slag (which was obtained during melting of vanadium alloy composition via ladle treatment), converter vanadium slag, quartzite and high-ash coal (ash content 45-50 %).

The experiments were conducted in the conditions of the Zh. Abishev Chemical and Metallurgical Institute, in the ore smelting furnace with power transformer capacity 200 kVA (**Fig. 2**).

Power supply of the electric furnace was provided from power transformer OMU-200. The temperature of arc discharge was 2500-4500 °C, it was provided by graphite electrode with diameter 150 mm. The furnace had fireclay brick lining. The voltage step 36.6 V on the lower part of power transformer was used during the experiment. Melting process was conducted in continuous mode, with charge feed by small batch load, depending on top throat shrinkage and with periodical metal tapping in iron moulds each 2 hours (Fig. 2*b*). After each tapping, metal was weighed and samples for chemical analysis were taken.

Obtained results and their analysis

Melting of vanadium alloying composition in a hearth was conducted with top ignition. The process was characterized by active run of the furnace; visual observation of the melting process allowed to reveal smoke emission, sparking and burning, together with active oxidation of aluminium and silicon. Essential amount of sublimates were noted during melting, these sublimates contain mainly small amount of vanadium [22, 23]. Vanadium losses as a result of evaporation make 1.5 – 2.0 %.

The temperature procedure of the process was recorded using tungsten-rhenium thermocouples, the results are presented on the **Fig. 3**. It displays relationship between temperature and time; it can be seen that the temperature 2085 °C was achieved (it was measured by the thermocouple which was mounted in the medium furnace area – thermocouple No. 2). The first thermocouple was mounted above charge material mixture, and after start of burning


a *b*

Fig. 2. General view of the electric furnace (*a*) and ingot (*b*)

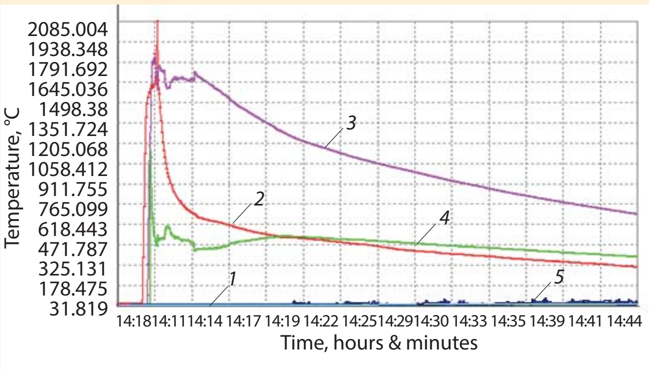

Fig. 3. Temperature variation during melting of vanadium alloy via ladle treatment method

1 – Temperature in the top hearth area; *2* – Temperature in the medium hearth area; *3* – Temperature in the lower (central) hearth area; *4* – Temperature in the lower hearth area near the wall; *5* – Temperature on the external wall part

Chemical composition of obtained metal and slag

Metal, mass.%.					Slag, mass.%.			
V	Al	Fe	Si	P	V_2O_5	CaO	SiO_2	Al_2O_3
55.49	9.37	10.85	24.30	0.06	18.54	18.81	41.26	19.37
50.72	6.63	10.47	21.36	0.07	20.39	18.45	40.12	22.40
47.72	7.06	9.79	21.74	0.09	13.94	18.63	41.40	22.30
50.86	7.26	10.44	21.10	0.09	17.08	22.95	32.54	20.80
60.96	7.26	10.88	19.69	0.07	17.08	25.59	33.11	19.28
43.03	4.22	37.57	10.21	0.08	18.38	35.23	31.69	14.42
40.08	4.26	37.57	10.96	0.09	18.21	34.43	31.84	14.33
53.27	5.00	14.69	12.96	0.07	21.95	28.20	32.12	3.78

it measured the temperature 70-100 °C. Thermocouples No. 4 (inside the wall) and No. 5 (outside the wall) were mounted for monitoring of heat loss. The temperature of internal wall in the melting hearth achieved 500 °C, while outside temperature near the wall was up to 70°C. The processes of metal forming and slag separation occurred in the lower part of melting hearth, and thermocouple No. 3 recorded parameters in this conditionally separated temperature area.

It can be seen from the Fig. 3 that relatively stable "isothermy" with duration 3 min was established in the temperature range 1645-1791 °C. After metal forming and slag forming, the process of their solidification (crystallization) starts. Low productivity can be mentioned as one of deficiencies of ladle treatment, because it is necessary to wait complete cooling of metal and slag in a hearth to start their separation after melting. For example, the process of melt cooling to the environment temperature (for assembled hearth) required 1.5 hours, though the melting process itself is rather quick. After metal and slag cooling, the hearth was disassembled for extraction and separation of metal and slag. Slag scull (1-2 mm) was formed near the furnace wall, it allowed to extract completely metal and slag during consequent melting processes.

The results of conducted series of tests for melting of vanadium alloying composition via ladle treatment with use of silicoaluminium alloy are presented in the **Table**.

Above-mentioned investigations for melting of ferrosilicovanadium from vanadium slag and high-ash coals in large-scale laboratorial conditions via carbothermal method in an ore smelting furnace with power transformer capacity 220 kVA were conducted consequently.

The melting process was started on hot run of the ore smelting furnace after melting of ferrosilicoaluminium. The tests showed stable furnace operation without forming of sculls and vanadium carbides. When notch was opened, metal was actively tapped out of the furnace, the process was completely slag-free. The chemical composition of obtained metal was characterized by the following average composition, %: V 4-10, Si 40-55, Al 15-20 and Fe 13-25. Vanadium extraction degree makes 70-80 %.

Conclusions

Thus, large-scale laboratorial works for melting of vanadium alloys with use of non-standard reducing agents – silicoaluminium alloys and high-ash coals – were conducted. Vanadium alloying composition with average chemical composition (%):V 55, Si 10-24, Al 4-9 and Fe 10-30 was obtained via ladle treatment with use of ferrosilicoaluminium. Slag basicity was 1.5-2.0. The obtained alloy is characterized by high vanadium content (up to 60 %), while vanadium extraction degree achieves 70-80 %. The obtained slag is characterized by small vanadium content in the form of vanadium oxide, what makes it applicable for consequent melting of ferrosilicovanadium.

Vanadium alloy, obtained via carbothermal method from vanadium slag, converter vanadium slag, quartzite and high-ash coal, is characterized by the following average composition (%):V 4-10, Si 40-55, Al 15-20 and Fe 13-25. Vanadium extraction degree makes 70-80 %.

As a result of conducted theoretical and experimental researches, the optimal temperature procedure and the melting conditions for melting of vanadium alloys were established. The samples of ferrosilicovanadium and vanadium alloying composition were obtained in large-scale laboratorial conditions. The obtained results have significant importance for practice of production of vanadium alloys and can be used for development of the new processing methods of vanadium-containing materials and improvement of the existing techniques.

Based on the obtained data, it can be concluded preliminarily about possible economical and technological expedience of manufacture of vanadium-containing ferroalloys from non-conventional reducing agents (such as high-ash coals instead of expensive coke and silicoaluminium ferroalloys instead of ferrosilicon and aluminium powder).

To establish more exact economical and technological efficiency of this technology, it is necessary to conduct further technical and economical investigations and putting it into practice in the conditions of real production for melting of high-quality steel grades, or as a reducing agent for melting of high-percentage ferrovanadium.

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