COMPLEX VANADIUM-CONTAINING FERROALLOYS

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The possibility of preparing complex vanadium-containing ferroalloys directly from vanadium slag and their application in steelmaking are considered in a review. Complex alloys make it possible to expand the ore base for ferroalloy production since it may involve poorer and more complex charge materials.

Due to this it is possible to regulate parameters of the production process of their preparation more flexibly. Dependences of the physicochemical and thermophysical properties of complex ferroalloys (melting temperature, density, heat capacity, thermal conductivity, melting time in liquid steel, changes in steel temperature during ferroalloy introduction) on the concentration of vanadium, silicon, titanium and manganese in the ferroalloy are studied. The most favorable effect on properties of the ferroalloys studied appears to be an increase in silicon concentration, in view of which with complex vanadium ferroalloy it is useful to include an element such as silicon, and the vanadium-containing oxide component of the charge may be leaner with respect to the basic element content than commercial vanadium pentoxide. Use of vanadium converter slag makes it possible to exclude the vanadium pentoxide preparation stage from the production chain for processing vanadium. It is beneficial for production because vanadium pentoxide processing is characterized by a high level of environmental pollution and loss of vanadium (about 25%).

Use of complex vanadium ferroalloys during steel treatment demonstrates the expediency of their use. Combined introduction of vanadium with silicon, calcium, and manganese into a steel melt makes it possible to create a favorable composition and shape for non-metallic inclusions. The main advantages of preparing and using complex vanadium ferroalloys are demonstrated.

Keywords: ferrous metallurgy, ferroalloy, vanadium, silicon, manganese, physical and chemical properties, steel.

Vanadium is one of the most extensively used alloying elements due to its favorable effect on various mechanical and physiochemical properties of treated metal over a wide range of properties with a low element concentration in steel [1–5]. The average annual rate of increase in requirement for vanadium in the most developed industrial countries is 5–7%. This is connected with its use [6] in production of low-alloy steels used for preparing pipes for oil and gas pipelines, bridge structures, high buildings, large-span structures, railway rail production, etc.

Presence of vanadium leads to steel grain refinement, increased strength, hardenability, durability with alternating loads, and wear resistance for objects. Addition of vanadium makes it possible to use a lower carbon content in steel due to an improvement in weldability. Combined alloying of steel with vanadium and nitrogen

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Table 1
Conversion Stage Vanadium Extraction, %

Conversion stage	Achieved	Prospective
Ore enrichment	73–74	75.0
Concentrate lumping	98–99	99.5
Blast furnace smelting	78–80	84.0
Converter smelting	82.5–83.0	86.0
Vanadium pentoxide preparation	73–75	80.0
Ferroalloy melting	95–96	97.0
Steel alloying with vanadium	90	92.0

as a result of forming carbonitride improves cold resistance [7]. The vanadium content is several hundredths (economically alloyed structural and rail steels with 0.04–0.015% V) up to several percent (high-speed steels 2–5% V, precision steels and alloys 2–14% V). Castings of white cast iron contain 1.5–6.0% vanadium and gray cast iron contains 0.15–0.30% [5, 7].

A significant amount of vanadium is used in nonferrous metallurgy, for example in the production of titanium alloys for aircraft construction and space technology, which contain from 2 to 5% vanadium. The main sources of this element in world industry are titanium-magnetite and ilmenite-titanium-magnetite ores [7–10] relatively lean with respect to vanadium (0.1–1.5% V_2O_5).

Pyrometallurgical processing of vanadium-containing titanium-magnetite raw material by coke-blast furnace and coke-free production schemes is most widespread within the world. Vanadium is extracted incidentally transferring it first into vanadium cast iron containing 0.4–1.4% V, then into low-lime vanadium slag containing less than 4% CaO and 15–22% V_2O_5. Then treatment provides vanadium pentoxide with 85–99% V_2O_5, ferrovanadium with 50–80% V, vanadium metal, and various alloys [11–15].

In each of the stages listed there is unavoidably some loss of vanadium that leads finally to a reduction in thorough extraction, starting from the ore to final product.

Extraction indices are provided in Table 1 for vanadium from ore to alloy steel [1].

The authors in [10] consider that thorough vanadium extraction in conversion from raw material to steel may be increased from 25–30 to 36–38% by improving production processes and achieving prospective indices for its extraction in the individual conversion stages. It is seen from data provided that in each metallurgical conversion there are reserves for an increase in the degree of vanadium extraction into semiproduct and finished product.

The process of ferroalloy preparation, based on vanadium-containing ferroalloy, is complex and multi-stage [1, 16]. During melting of ferrovanadium containing 35–45% V, 1–3% Si, a silicothermal method is used: commercial vanadium pentoxide (72–80% V_2O_5, lime, ferrosilicon (75% Si), iron scrap, aluminum and vanadium slag (16–18% V_2O_5). The silicothermal melting process consists of three periods. Two reducing periods and one refining period with intermediate skimming of slag into arc electric furnaces of the DS-3 and DSP-3A types. Transformer capacity: DS-3 1800 kW, DSP-3A 2800 kW.

Metal chemical composition is adjusted to limits determined by engineering conditions. In refined metal from silicon (oxidation of excess silicon) vanadium pentoxide is added in excess in an amount of 2–30% with

respect to the stoichiometrically required amount. Slag from the refining period in view of higher (9–18% V_2O_5) is returned to the furnace in the first period of the next melt.

In order to prepare ferrovanadium enriched with respect to vanadium (> 80% V) and commercially pure vanadium (95–97% V) a furnace or extra-furnace aluminothermal melting method is used. The charge consists of rich (> 85% V_2O_5) and pure vanadium pentoxide, aluminum, and lime. The melting process may be both single- and two-stage [1, 11].

Therefore, the complexity and high cost of producing standard ferrovanadium from commercial vanadium pentoxide leads to a requirement for finding alternative preparation methods and composition of vanadium ferroalloys, including complex alloys [17].

The Aim of the Work is revelation of the main advantages of obtaining and using complex vanadium-containing ferroalloys with determination of their rational composition.

Preparation of vanadium ferroalloys makes it possible to expand the ore base for their production since its does not concern lean and complex ores [18, 19]. The possibility appears of more flexible control of production parameters for their preparation (selection of optimum indices of slag viscosity, slag and alloy melting temperatures, charge electrical resistance, etc.) [20].

Complex (multicomponent) ferroalloys fulfil a function of a deoxidant, modifier, alloying addition, or a collection of deoxidation and alloying, modifier, and deoxidant, etc. [21]. The base of complex ferroalloys is iron, silicon, vanadium, nickel, aluminum, etc. With an increase in the number of elements in ferroalloys they lose universality, but an increase in number of components makes it easier to obtain the service properties required and to reduce the number of forms of added ferroalloys. It is apparent that the advantages of complex master alloys are more marked than their weak points, which is indicated by their prolonged preparation practice and application [22, 23].

During determination of a rational composition of complex ferroalloys it should be considered that the optimum melting temperature (start of crystallization) for ferroalloy intended for steel treatment should be within the limits of 1350–1400 °C; the optimum density should be within the limits of 5000–7000 kg/m^3 [24]; the chief elements for total assimilation by metal should not be oxidized by air oxygen for which to a complex ferroalloy it is necessary add inexpensive elements with greater chemical activity than for the main ferroalloy components; for a ferroalloy intended for micro-alloying the content of the leading element should be 10–25%, and individual cases 2–5%; it is useful to add silicon to complex vanadium ferroalloy, and the vanadium-containing component of a charge may be leaner with respect to the main component than for commercial vanadium pentoxide. Use of vanadium converter slag makes it possible to exclude from the production chain for adding steel to steel (see Table 1) chemical conversion of the vanadium pentoxide obtained distinguished by a greater degree of contamination of the surroundings into which about 25% of vanadium is lost.

A comprehensive approach to determining the composition required for ferroalloy will make it possible to consider its properties and reaction with alloys being treated, and to select more substantially elements and their ratio within the alloy.

Research Materials and Procedures

In order to select the optimum master alloy composition providing good efficiency for their production and use during steel smelting a study was made of the effect of vanadium-containing master alloy chemical composition (V, Si, Ti, Mn) on the main physicochemical and thermophysical properties, i.e., melting temperature T_m (°C), density ρ (kg/m^3), heat content in solid and liquid conditions C_{so} (J/kg·K) and C_l (J/kg·K),

Table 2
Vanadium Ferroalloy Chemical Composition and Physicochemical Properties

Alloy num- ber	Grade	Content,* %				T_m, °C	C_{so}, J/kg·K	C_1, J/kg·K	L, kJ/kg	ρ, kg/m³	λ, W/m·cal	$\Sigma_\tau T$, sec	$\Sigma_\Sigma T$, deg
		V	Si	Ti	Mn								
1	FS40Vd5	5.0	40.0	–	–	1325	518	790	1149	5800	26.7	89.7	–14.6
2	FS38Vd10	10.0	38.0	–	–	1330	516	792	1116	5850	27.4	89.6	–8.1
3	FS34Vd20	20.0	34.0	–	–	1325	518	803	1050	5900	28.8	88.4	–4.3
4	FS29Vd30	30.0	29.0	–	–	1350	512	804	965	6000	30.2	88.3	–11.4
5	FS30Vd5	5.0	30.0	–	–	1355	498	777	981	6250	26.7	90.7	–19.2
6	FS28Vd10	10.0	28.0	–	–	1320	498	779	944	6300	27.4	87.6	–10.9
7	FS26Vd20	20.0	26.0	–	–	1340	497	788	907	6400	28.8	89.1	–8.3
8	FS22Vd30	30.0	22.0	–	–	1300	494	788	831	6700	30.2	88.1	–12.7
9	FS20Vd5	5.0	20.0	–	–	1215	480	766	785	6750	26.7	82.1	–21.6
10	FS19Vd10	10.0	19.0	–	–	1220	480	768	765	6750	27.4	81.7	–17.0
11	FS17Vd20	20.0	17.0	–	–	1270	481	774	724	6700	28.8	81.2	–16.3
12	FS15Vd30	30.0	15.0	–	–	1340	482	780	683	6800	30.2	84.1	–10.8
13	FS26Vd8Mn5	9.5	26.5	–	5.0	1295	495	782	914	6650	29.7	90.3	–19.3
14	FS25Vd9Mn10	9.0	25.0	–	10.0	1270	495	787	891	6700	31.9	90.1	–13.9
15	FS26Vd9MnTi3	9.2	26.0	3.0	4.8	1275	497	781	904	6450	29.0	86.6	–17.4
16	Fs29Vd9MnTi6	8.9	25.2	6.0	4.7	1260	523	780	889	6350	28.5	87.0	–12.0
17	FVd365	35.0	2.0	–	–	1450	468	771	359	7200	31.0	82.8	–22.0
18	FSVd10	10.0	14.0	3.0	10.0	1350	488	793	657	6500	31.6	80.0	–
19	FMn50Vd10	10.0	3.0	–	50.0	1300	490	937	369	6800	50.1	70.6	–

* Balance iron.

thermal conductivity in a liquid condition λ (W/m·cal), heat of melting L (kJ/kg), melting time in molten steel τ (sec), and change in temperature $(\Sigma_\Sigma T)$ for steel with addition to it of 1% vanadium alloy at 1600 °C. Ferroalloy properties were determined by known experimental and calculation methods [1, 25].

The chemical composition and properties of the test alloys are provided in Table 2.

Alloy 1–12 are synthetic containing vanadium from 5 to 30% and the ratio Si/Fe = 0.27–0.73. Alloys 13 and 14 were prepared from alloy 6 with addition of 5 and 10% Mn respectively. Alloys 15 and 16 were prepared from alloy 13 with addition of 3 and 6% titanium respectively. Alloys 17–19 are standard.

Determination of test alloy melting temperature was conducted in a high-temperature laboratory unit according to the cooling and crystallization curve of an alloy specimen melted previously in a vacuum furnace. Analysis of experimental data for the Fe–Si–V system shows that T_m is determined primarily by the silicon content in an alloy, similar to the melting temperature for the binary alloy system Fe–Si. Addition of manganese (up to 10%) to alloy based on the Fe–Si–V system reduces the melting temperature by 30–50 °C, and additional introduction of titanium (up to 6%) reduces the melting temperature even more by 20–35 °C. Therefore, the melting temperature of the complex vanadium-containing alloys is within the limits of 1215–1260 °C, which is 90–230 °C below the T_m for standard ferrovanadium.

The density of solid vanadium-containing ferroalloys was determined in a specialized laboratory unit by a pycnometric method at room temperature. The density of Fe–Si–V alloys with an increase in silicon content falls, but with an increase in vanadium content it increases. Addition of manganese to alloy FS28Vd10 increases the density. All of the alloys apart from standard FVd35 have an optimum density of 5600–6800 g/m^3.

Thermophysical properties of vanadium-containing alloys were calculated by additive superimposition of the corresponding reference values (see Table 2). In order to calculate $\Sigma\tau$ the following conditions were used: vanadium-containing alloys were dissolved in steel at 1600 °C; the steel melting temperature is 1500 °C; density in a liquid condition 700 kg/m^3; heat of melting $1.79 \cdot 10^6$ J/kg; heat flow from steel towards a lump of ferroalloy $1.6 \cdot 10^6$ W/m^2; mass transfer coefficient $1.3 \cdot 10^4$ K^{-1}.

In order to study the melting time for vanadium-containing ferroalloys in molten steel a mathematical model was used developed by scientists of IMET UrO RAN and UGGU-UPI. The model includes hydrodynamic and thermal parts. The hydrodynamic apart of the model determines the movement rate of ferroalloys with respect to a metal bath taking account of forces operating in each instant of time. The thermal part of the model is based on classification of ferroalloys in relation to the ratio of their temperature for the start of crystallization, bath temperature, and crystallization of iron-containing melt [26]. The duration of melting alloys of the ternary Fe–Si–V system varies insignificantly. With an increase alloy content of vanadium $\Sigma\tau$ decreases, with the exception of alloy FS30Vd5. With a reduction in silicon content in alloys below 20% the melting duration decreases by 6–7 seconds that apparently is connected with a reduction in the third melting period, which in turn depends on L, decreasing significantly with an increase in alloy silicon content. Addition of manganese to alloy FS2Vd10 somewhat increases the melting duration as a result of an increase in alloy density. Standard alloys FVd35 and FSVd10 melt at the same rate as low-silicon vanadium alloys.

Standard ferroalloy FVd35 has a melting temperature and density higher than recommended (1450 °C and 7200 kg/m^3 respectively), and also a very fast steel cooling rate with addition of the alloy $\Sigma_\Delta T = -22$ deg).

Results and Discussion

A study of the service properties of complex vanadium-containing ferroalloys of the Fe–Si–V and Fe–Si–Mn–Ti–V systems has shown their complete conformity with specifications laid down for them by steel smelters [1, 25].

Complex vanadium-containing alloys after development by industrial technology for their preparation have been produced within ferroalloy enterprises (Chelyabinsk Electrometallurgical Combine, Klyuchev Ferroalloy Plant) and used by metallurgical plants (Nizhnetagil' Metallurgical Combine, Chelyabinsk Metallurgical Combine), during smelting rail, pipe, and other forms of steels [1, 7, 22, 27–29].

Technology for preparing complex ferroalloys with vanadium included silico-alumino- and carbothermal melting in refining electric furnaces, and also by mixing melts.

Ferro-silico-vanadium, containing 8–16% V and 10–20% Si was prepared by silicothermal and combined carbo-silicothermal methods; ferrosilicocalcium-vanadium containing 7–14% Ca, 40–50% Si, 8–12% V was

prepared by silicothermal reduction melting and by mixing silico-vanadium and ferrosilicocalcium. The production processes developed make it possible to prepare more complex vanadium alloys, i.e., ferrosilicon-chromium-vanadium, ferro-silico-manganese-vanadium, etc.

CONCLUSIONS

Use of complex vanadium ferroalloys during steel treatment has demonstrated the expediency of their use. Combined introduction into a steel melt of vanadium with silicon, calcium, and manganese makes it possible to create a favorable composition and shape for nonmetallic inclusions, to perform simultaneously alloying and deoxidation, modification, to provide the required level of steel mechanical properties, and to improve ductility properties.

Complex ferroalloys with vanadium have been tested successfully and introduced in a number of Russian metallurgical enterprises during smelting rail, wheel, and cast steels.

The main advantages have been demonstrated for preparation and use of comprehensive vanadium ferroalloys:

- the possibility of using vanadium converter slag instead of expensive vanadium pentoxide excluding chemical conversion and an increase in complete extraction of vanadium in the production scheme;

- improvement of production parameters for melting complex ferroalloys by optimizing the production process, and furnace bath temperature regimes;

- more effective microalloying of steel with vanadium and a high degree of vanadium assimilation as a result of reducing oxidation due to presence in complex alloy o chemically active and modifying elements (Si, Ca, Al).

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