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INFLUENCE OF COMPLEX V, CU, TI AND B ALLOYING ON STRUCTURAL AND PHASE STATE, MECHANICAL PROPERTIES AND WEAR RESISTANCE OF WHITE CAST IRON

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ABSTRACT

The paper presents the results of complex investigations of influence of chemical composition and metal cooling rate in a mould on phase composition, structure, wear resistance and mechanical properties of white vanadium cast iron. The technique has been developed for examination of amount and structure of excessive phases and eutectics; it includes determination of parameters of special carbides VC, (Ti,V)C on metallographic samples before pickling and examination of structure of binary and ternary eutectics — on metallographic samples after pickling. The fractional factorial experiment of DFE 25-2 kind has been planned and undertaken for determination of rational carbon, vanadium, copper, titanium and boron content providing maximal wear resistance. Optimal composition providing maximal wear resistance of complex-alloyed vanadium cast iron in different conditions of abrasive wear are defined. Regularities of influence of chemical composition, temperature conditions of metal cooling in a mould and processing on structure, morphology, phase chemical composition, mechanical properties, wear resistance of complex-alloyed vanadium white cast iron have been established. Influence of cooling rate in a mould and additional alloying on vanadium critical concentration has been defined, as well as influence of cooling conditions on C, V, Cu, Ti and B concentration intervals, providing equal level of mechanical properties and wear resistance. The kinds of eutectics and basic structural types, forming in white vanadium cast iron, have been determined on the base of the results of investigation.

1. Introduction

Thite alloyed cast iron is often used as a material for tools and components of machines and equipment, operating in the conditions of intensive wear and oxidation. Modern white cast iron is a multi-component alloys with complicated alloying, its grades are characterized by different structure and special properties. Different grades of white cast iron compose the separate group of industrial cast iron, with forming of composite structure during their solidification [1].

Investigations devoted to influence of alloying elements and cooling conditions on crystal growth and structure forming processes, on mechanical and special properties of this cast iron, are still actual, nevertheless on a lot of previous researches [1–13]. It is especially true regarding the conditions of forming of different eutectics and carbide phase, metallic matrix in the case when several alloying elements and modifiers are presented in cast iron composition.

The works [1, 3–7, 14, 15] have displayed that manufacture of cast iron with the corresponding scope of mechanical and special properties is concluded in the correct choice of its chemical composition. To choose the content of carbon and alloying complex, it is necessary to know about influence of each element, as well as joint influence (with other elements) on forming of structure and properties of castings for different cooling conditions of solidification process.

It is possible to improve the properties of vanadium white cast iron via variation of density (varying the amount of carbide phase) and features of eutectic compositions. Another option to adjust amount, type and morphology of cast iron carbide phase, as well as structure of metallic base, is to vary cooling rate (pouring in different kinds of moulds) and additional cast iron micro-alloying and modification using small additives of high-active elements.

This research work is devoted to examination of influence of chemical composition, micro-alloying and modification, temperature procedure of metal cooling in a mould on structure, phase chemical composition, mechanical properties and wear resistance of vanadium white cast iron. The aim of the work was also to determine optimal content of carbon, vanadium, copper, boron and titanium, providing high wear resistance and mechanical properties.

2. Materials and methods of the research

The researches have been conducted on complex-alloyed white cast iron. Experimental alloys have been melted in UCT-006 induction furnace with basic lining and cast in dry and wet sand-clay moulds (SCM) and metal mould. Colling rate in crystal growth interval for a dry SCM made 2–10 grad/min, for a wet SCM — 8–12 grad/min, for cast iron mould — up to 30 grad/min. Chemical composition of samples has been determined by Baird emission spectrometer and OBLF QSG 750 spectrometer, according to the requirements of GOST 18895-97.

Structure and phase composition of cast iron have been examined using metallographic method (MEIL 2700 light microscope) and X-ray diffraction method. X-ray photography has been conducted at DRON-UM1 (\square POH-YM1) diffractometer (in cobalt K α radiation).

Quantitative metallographic analysis, automatized processing of the results of microhardness measurement have been conducted using Thixomet PRO image analyzers. X-ray spectral micro- examinations of phase components in the alloys and on oxidizing surface have been conducted using scanning electronic microscopes "JEOL" JSM-6460 LV, "TESCAN VEGA II XMU", "Camscan" with X-ray spectral micro-analyzers.

Tensile strength has been determined in accordance to GOST 1497-75 at "Instron-1195" tensile testing machine. Measuring of micro-hardness has been realized at PMT-3 device (TU 3-3.1377-83) according to GOST 9450-76.

Comparative testings for wear resistance of the alloys and cast iron grades during friction with loosely fixed (semi-fixed) abrasive particles have been conducted using the technique defined by GOST 23208-79. Wear has been realized by abrasive particles of different hardness (electrocorundum and periclase), to determine different wear mechanisms.

Building of mathematical models has been done according to the standard techniques and using the standard packages of electronic tables in Excel 2000 program. Optimization of composition of the new wear-resistant cast iron has been executed via the steepest ascent method (Box-Wilson method). Ratios of friction effect of alloying elements on cast iron properties have been determined using neural network program "Model" developed by the Institute of Biophysics of the Siberian branch of the Russian Academy of Sciences (RAS) in Krasnoyarsk.

3. Results of the research and discussion

Structure and wear resistance of ternary Fe–V–C alloys, with the following composition (mass%): C 2.0–3.5

and V 3.0–9.0, have been examined in order to choose cast iron basic composition. At least three melts have been conducted for each composition. Chemical composition and properties of the examined alloys are presented in the **tab. 1**.

Phase composition of cast vanadium cast iron can be considered as α (BCC)-phase, vanadium carbide (VC) and ferrous carbide (Fe₃C). Two carbide phases determine forming of two eutectics: binary austenite — vanadium carbide (γ +VC) and ternary ledeburite-like (γ + Fe₃C + VC) [16,17].

Analysis of the data presented in the table 1 allowed to determine the concentration intervals for carbon and vanadium (C 2.0-3.5% and V 3.0-9.0%) for conduction of qualitative and quantitative metallographic analysis of cast iron carbide phase.

The distance between vanadium carbide particles is determined during image analysis on non-pickled polished section both in the special eutectic and between carbides of neighbor eutectics separated by ledeburite fields (**fig. 1**, *a*). Thereby it was decided to determine the distance between particles on pickled polished sections, because it is possible to exclude visually ledeburite net from the analysis on such sections.

Finally the technique has been developed; it includes determination of volumetric part and measurement of shape parameters of special carbides on non-pickled polished sections, volumetric part of ledeburite and distance between vanadium carbide particles (maximal, minimal and average) on the pickled polished sections (**fig. 1**, *b*) [18].

X-ray spectral micro-investigations have displayed that vanadium is partly dissolving in cementite and pearlite (former austenite), and eutectic carbide component of the structure is mainly enriched by vanadium. Small Fe amount (up to 3%) is dissolving in vanadium carbide.

Influence of carbon and vanadium content on features of carbide phases and eutectic components has been revealed by metallographic analysis of cast iron. Different

Content of elements,%		Hardness HRC, units			Wear resistance K_{κ} and K_{n} , units			Strength $\sigma_{_{\! R}}$, MPa		
		Mould type								
С	V	Dry	Wet	Mould	Dry	Wet	Mould	Dry	Wet	Mould
2	3	35	39	43	2.3/5.0	3.1/6.8	4.9/9.7	556	560	575
2	5	37	42	47	2.6/5.7	4.3/9.0	6.3/13.2	530	540	545
2	7	45	47	48	3.5/7.7	7.0/13.2	7.4/16.2	518	525	530
2	9.0	37	40	44	1.57/3.5	3.6/7.8	4.35/9.1	500	520	530
2.5	3	44	48	51	3.2/7.0	4.6/10.1	5.8/12.2	570	574	580
2.5	5	46	50	53	3.4/7.5	5.9/12.9	6.4/13.6	570	574	586
2.5	7	48	52	53	4.7/10.3	7.1/15.1	7.6/16.3	614	620	630
2.5	9	40	44	48	2.4/5.2	5.8/12.5	5.1/11.2	518	520	530
3	3	48	51	55	3.5/7.5	5.0/10.9	6.2/13.4	570	575	586
3	5	52	55	58	7.9/17.4	11.7/25.1	13.6/29.2	599	600	610
3	7	53	56	60	8.5/18.7	14.8/4	15.1/	610	615	630
3	9	50	54	58	7.4/15.9	10.2/22.3	11.0/23.1	599	600	610
3.5	3	50	53	53	4.6/10.1	4.8/10.5	6.97/15.2	610	610	620
3.5	5	52	56	59	6.1/13.4	10.7/23.4	10.8/23.7	622	620	625
3.5	7	54	58	61	7.7/16.9	11.6/25.3	12.2/25.6	599	600	610
3.5	9	48	50	53	5.7/12.6	9.5/20.7	6.2/13.6	556	560	565

cast iron grades with insufficient vanadium content have only partly inversed structure. So, cast iron grades with low carbon and vanadium content (2% and 5% respectively) are characterized by forming of eutectic vanadium carbide in the form of net on the boundaries of austenite (pearlite) grains and its dissemination in the grain volume as thin plates, and the most long of them — as spreads (see **fig. 2**, *a* and *e*). As for cast iron grades with carbon content 3.0—3.5%, it is reported that eutectic cementite is pre-

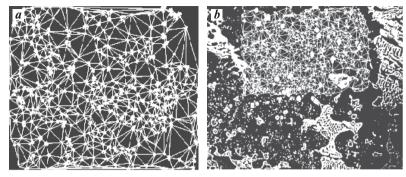
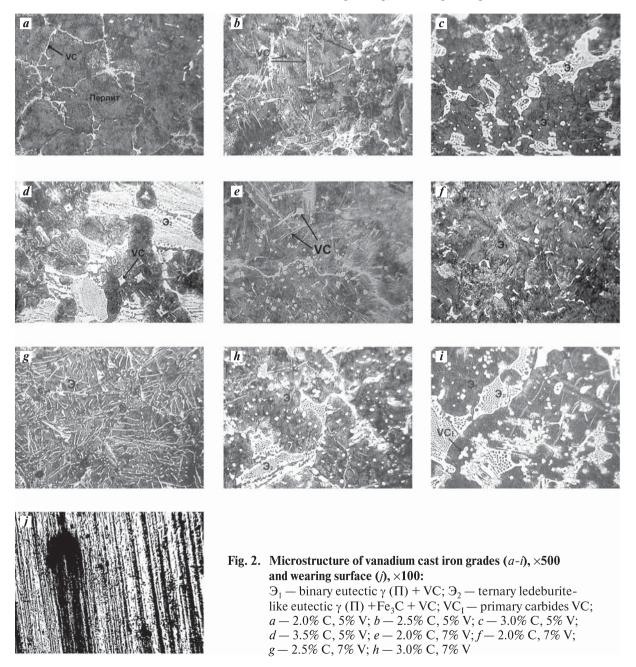


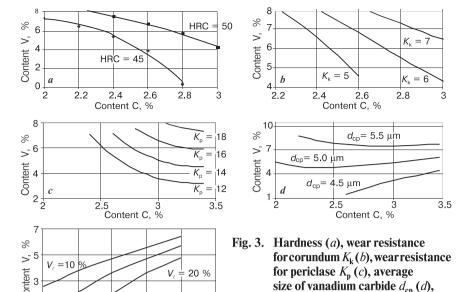
Fig. 1. Determination of the distance between particles on polished sections: a — before pickling; b — after pickling



cipitating along the boundaries of binary austenite / vanadium carbide eutectic (see fig. 2, c, d, g and i).

Crystal growth in the alloys containing 2.0–2.5% C and 7.0% V is occurred practically without forming of

eutectic cementite. cast iron structure mainly consists of thin-dendrite fibrous (fig. 2, g) or compact eutectic (fig. 2, e) vanadium carbide and pearlite matrix. Such correlation between vanadium and carbon leads to a sharp



volumetric part of ledeburite $V_{e}(e)$

in the structure of vanadium cast iron

decrease of carbide phase volume in the structure to 10%. As a result, relative wear resistance decreases substantially down to 3-4 units (for corundum) and 7-8 units (for periclase). Dispersity of vanadium carbide and binary eutectic increase with carbon content rise up to 2.5-3.0%; vanadium carbide content in this eutectic also elevates up to 12%, cast iron inversion becomes incomplete, amount and dimensions of the colonies of ledeburite-like component increases up to 25-27%, and this component locates as solid or partially torn net along the boundaries of binary eutectic colonies (see fig. 2, b, c and b).

3,4

3,6

3,2

Content C. %

15 %

2,8

2,6

It is mentioned that cast iron with carbon content more than 3.0% becomes more hyper-eutectic. Volumetric part of VC vanadium carbides decreases. Massive primary vanadium carbides having compact or dendrite form (fig. 2, c and i) appear in the structure. The main part of structure consists of ledeburite colonies. Such cast iron grades are characterized by increased brittleness for periclase and corundum due to carbide dislodging.

Rise of the part of VC carbides in cast iron structure in the case of vanadium concentration increase is more intensive for alloys poured in a metal mould. If content of carbon and vanadium makes 2.5% and 5.0% respectively, ledebirite disappears completely in the cast iron structure. Thereby, rise of cooling rate for the same alloy composition leads to decrease of ledeburite amount, as well as to lowering of critical vanadium concentration (from 7.0 to 5.0%) with saving the inversed eutectic structure.

Maximal wear resistance is achieved at carbon content in cast iron as much as 2.6-3.0%. If content is less than 2.6% or exceeds 3.0%, cast iron wear resistance drops sharply. In the first case lowering of wear resistance is connected with decrease of general amount of carbide phase, in the second case inversion of cast iron structure becomes incomplete and compact carbide inclusions are also forming, with their consequent dislodging and rise of wear (fig. 2, j).

Rise of vanadium content up to 7% leads to increase of number of vanadium carbides, while number of ledeburite colonies decreases respectively. Compact carbides with regular geometric form, with "butterfly" form etc. appear in cast iron structure in the case of excessive carbon and vanadium (fig. 2, d and i).

Influence of composition and cooling conditions on volumetric part of vanadium carbides and ledeburite, on dimensions of vanadium carbide, on inter-carbide distance in vanadium eutectic, on relationship between eutectics in the structure, on microhardness of structural components, on hardness and wear resistance for corundum and periclase is determined. The adequate mathematical relationships describing the effect of

carbon and vanadium content on wear resistance for corundum (K_k) and periclase (K_p) , on hardness HRC, on volumetric part of ledeburite (V_ℓ) and vanadium carbides (V_k) , on dimension of vanadium carbide (d_k) and intercarbide distance (L_k) are received.

Graphic interpretations of these mathematic relationships are presented on the **fig. 3**.

The highest values of strength ($\sigma_{\rm B}$), hardness (HRC), wear resistance for corundum ($K_{\rm k}$) and for periclase ($K_{\rm p}$) are observed for the alloys poured in a metal mould. If poured in a sand-clay mould (SCM), these parameters make 500–550 MPa, 40–45 HRC, 4–5 and 10–12 units respectively, while during pouring in a metal mould they are equal to 550–600 MPa, 45–55 HRC, 5–7 and 15–18 units. Taking that fact into account and being informed about parameters of castings (such as mass, wall thickness, overall dimensions) and mould type, it is possible to adjust vanadium and carbon content in the alloy and to receive the required properties. It allows to use white vanadium cast iron more widely for production of special castings.

Concentration intervals on carbon and vanadium (basic composition, 2.6–3.0% C and 5.0–8.0% V) have been determined on the base of the investigation results. These intervals provide maximal wear resistance of vanadium cast iron in different conditions of abrasive wear. It is shown that it's impossible to achieve simultaneously rather high wear resistance and completely inversed structure of white cast iron for the case of only vanadium alloying. It is caused by incomplete inversion of eutectic and forming of pearlite structure of metallic base.

It is possible to improve the properties of white vanadium cast iron by varying the conditions of crystal growth (pouring in different mould types) and their additional microalloying and modifying with small additives of high-active elements. Copper, titanium and boron have been chosen as such elements. Fractional factorial experiment of DFE 2^{5-2} kind has been planned and undertaken. Content of the ele-

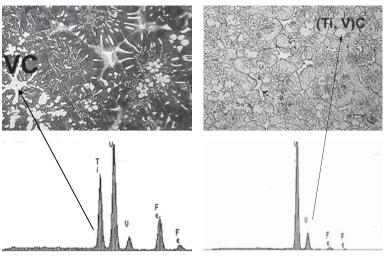


Fig. 4. Micro-pictures of the structure of complex-alloyed vanadium white cast iron, poured in a dry SCM (a) and metal mould (b), $\times 1000$

Table 2. The factors of influence of microstructural parameters on the properties of experimental cast iron grades												
Param-	Properties											
eters	Wear	esistar	nce, K_k ,	Hardness, HRC			Tensile strength, $\sigma_{_{\!\scriptscriptstyle B}}$					
of micro-	Mould type											
structure	Dry	Wet	Mould	Dry	Wet	Mould	Dry	Wet	Mould			
$V_{\rm k}$	0.46	0.05	0.67	0.24	0.14	0.71	0.01	0.15	0.21			
V_ℓ	0.05	0.38	0.15	0.63	0.28	0.11	0.47	0.33	0.23			
d _K	0.26	0.25	0.07	0.11	0.24	0.1	0.36	0.32	0.28			
НМ	0.23	0.32	0.11	0.02	0.34	0.08	0.16	0.2	0.28			

ments in complex-alloyed cast iron was as follows (mass.%): C 2.6–3.0; V 5.0–8.0; Cu 0.8–1.2; Ti 0.3–0.6; B 0.01–0.05; Si 0.4–0.6; Mn 0.4–0.6.

Microhardness, amount of carbides, their size and amount of ledeburite have been examined as parameters of microstructure. Quantitative analysis of inclusions of vanadium carbides has been conducted on polished sections without pickling. Microstructure of metallic base, amount of ledeburite and microhardness of structural components have been examined on pickled polished sections.

Alloying by copper decreases critical vanadium content in cast iron that provides inversion of microstructure. Amount of ledeburite in the structure of complexalloyed cast iron decreases to 3–15%, while in vanadium cast iron ledeburite part makes 25–47%. If copper content in the solid solution is excessive, copper precipitates partly in the form of dispersed inclusions strengthening metallic base of cast iron.

Microalloying by titanium leads to forming of binary carbides of TiC–VC type with high hardness, excessing hardness of vanadium carbide particles. It was established that additional alloying bu Ti, Cu, B and increase of cooling rate during solidification (pouring in a metal mould) has essential effect on type, morphology and chemical composition of carbide phase, eutectic component and metallic base of vanadium cast iron: ledeburite amounts is essentially decreased (down to its complete disappearing) and volumetric part of VC and (Ti,V)C carbides is

increased. The structure of metallic base can be varied by alloying and cooling rate during solidification from pearlite (SCM) (fig. 4, a) to martensite-austenite (metal mould) (fig. 4, b) with different quantitative phase relation. Increase of cooling rate during solidification varies form and size of carbides: vanadium carbides become less dendrite, wile their dispersity increases (fig. 4, b).

X-ray spectral micro-investigations have displayed that dendrite-form inclusions presents vanadium carbides, and compact-form inclusions are complex vanadium and titanium carbides (Ti,V)C. Modification by titanium leads to dispersion of a carbide phase. Increase of titanium content in composition of complex carbides rises their compactness and dispersity (see fig. 4, *b*). Forming of complex carbides (Ti,V C with compact form in iron structure results in increase of wear resistance in the conditions of friction with half-fixed abrasive. Microhardness of vanadium carbides makes 20,000–22,000 MPa, and even higher (up to 27,500 MPa) for complex carbides.

Boron in cast iron shifts equilibrium between eutectics in the area of large vanadium concentrations. Therefore rise of boron content up to 0.05% and increase of cooling rate results in growth of ledeburite part.

Microcutting has been considered as the main wear mechanism during testing for corundum, where its hardness is comparable with vanadium carbide hardness (20–22 GPa) and exceeds cementite hardness (10 GPa) and cast iron metallic base hardness (6-10 GPa). Periclase hardness (10-11 GPa) is lower than hardness of vanadium carbides and is almost equal to hardness of cementite and metallic base. Thereby base destruction during interaction of cast iron and periclase occurs via the mechanism of plastic edging. It is shown that cast iron with mainly martensite structure is characterized by the most high wear resistance in the case of wear due to microcutting, while cast iron with austenite-martensite structure has the best wear resistance after wear owing to plastic edging.

Adequate mathematical relationships between microhardness $H\mu$ and microstructural parameters of experimental cast iron grades (from one side) and chemical composition (from other side) have been obtained after processing of the results of microstructure investigation. The weight factors of influence of alloying elements on microstructural parameters, as well as the weight factors of influence of microstructural parameters on the properties of experimental cast iron grades have been determined using obtained mathematical relationships and neural "Model" program. The weight factors of influence of microstructural parameters on the properties of examined cast iron grades are presented in the **table 2**.

Influence of alloying elements on cast iron properties depends on cooling conditions that are determined by heat

removal rate during metal pouring in different kinds of moulds. Influence of vanadium, copper, boron and titanium increases with rise of a cooling rate, mainly due to dispersity elevation and forming of martensite-austenite base structures and forming of complex carbides (Ti, V)C with high dispersity and hardness. If cooling rate and carbon content rise (for mould pouring), feature of crystal growth varies substantially — hypoeutectic and eutectic cast cast iron transform into hypereutectic cast iron. Volumetric part of vanadium carbide decreases, while ledeburite part increases. These structural variations of complex alloyed cast iron result in decrease of their properties. Therefore, carbon effect on hardness and wear resistance for corundum and periclase diminish with rise of cooling rate.

When pouring in dry and wet SCM, influence of alloying elements on hardness and wear resistance does not vary principally, while their effect on strength increased sharply due to copper positive effect as a result of its precipitation in the form of dispersed particles during slow cooling, with cast iron metallic base strengthening by these particles. That's why it is necessary to take into account cooling conditions in a mould in the process of fabrication of such cast iron grades. It is noted that the most strong effect on the properties of cast alloys is made by carbon and vanadium, due to the fact that they are the main regulators of variations of matrix structure and amount of strengthening phase.

If we shall take into account the force of the effect on strength (a), hardness (b) and wear resistance (c), alloying elements can be written in the following rows (directed to decrease of the effect):

a)
$$Cu \rightarrow C \rightarrow V \rightarrow Ti \rightarrow B$$
;

b)
$$C \rightarrow V \rightarrow Ti \rightarrow B \rightarrow Cu$$
;

c)
$$C \rightarrow V \rightarrow Ti \rightarrow B \rightarrow Cu$$
.

Optimization of cast iron compositions has been conducted with aid of the steepest ascent method. Mathematical relationships between properties of the alloys and chemical composition have been used for calculations of alloys poured in different moulds; these relationships have been obtained during the fractional factorial experiment. Optimization of chemical compositions has been conducted for the maximal wear resistance for corundum and periclase. The following optimized compositions have been obtained (%):

for corundum -2.6-3.0 carbon; 7.0-8.0 vanadium; 0.8 copper; 0.03-0.05 boron; 0.1-0.3 titanium;

for periclase: 2.8–3.0 carbon; 5.0–6.5 vanadium; 1.0–1.2 copper; 0.01–0.03 boron; 0.30–0.45 titanium.

4. Conclusions

1. The kinds of eutectics and the main types of structures forming in the alloys of Fe–V–C system have been determined.

The following structures of the alloys are mentioned:

hypoeutectic structure containing austenite dendrites (or products of austenite decomposition) and $\gamma + Fe_3C+VC$ ternary eutectic;

- completely inverted structure of γ + VC eutectic;
- structure containing two eutectics: γ + VC and γ + + Fe₂C +VC;
- structure containing excessive carbides VC and two eutectics: γ + VC and γ + Fe₃C+ VC.

The following kinds of eutectics in vanadium cast iron (analyzing for amount and morphology of eutectic-forming phases) are mentioned:

- binary γ + VC eutectic (with fibrous or compact vanadium carbides);
 - ternary ledeburite-like γ + Fe₃C + VC eutectic.

It is shown that just structure and amount of eutectics has the decisive effect on all cast iron properties via forming the cast composite structure in these cast iron grades.

- 2. Compositions of the alloys (7% of V and 2.0–2.5% of C) have been established; they provide forming of the composite and completely inversed structure of vanadium cast iron during cooling in a dry SCM. Increase of a cooling rate during pouring in a metal mould leads to decrease of ledeburite amount for the same alloy composition; lowering of critical vanadium concentration (from 7 to 5%) occurs as well with saving of inversed eutectic structure.
- 3. Mathematical relationships describing the effect of carbon and vanadium content on wear resistance and hardness of vanadium cast iron, on volumetric part of ledeburite and vanadium carbides, on average size and distance between carbides are obtained. Based on these relationships, the concentration intervals (basic alloy composition) for carbon (2.6–3.0%) and vanadium (5.0–8.0%) have been determined; theu provide maximal wear resistance of vanadium cast iron in different conditions of abrasive wear. It is shown that it's impossible to achieve simultaneously rather high wear resistance and completely inversed structure of white cast iron via alloying only by vanadium, owing to incomplete eutectic inversion and forming of pearlite structure in metal base.
- 4. Additional alloying of vanadium cast iron by Ti, Cu and B as well as increase of cooling rate during solidification (pouring in a metal mould) reduces substantially ledeburite amount (down to its complete elimination) and rises volumetric part of VC and (Ti,V)C carbides (by 2–3 times). Metal base structure varies from pearlite one (SCM) to martensite-austenite structure (metal mould). Thereby wear resistance of complex-alloyed cast iron elevated by 1.5–2.0 times for periclase and by 2–4 times for corundum. Concentration intervals of C, V, Ti, Cu and B, providing the same level of mechanical properties and wear resistance, vary depending on cooling conditions in a mould.
- 5. Mathematical relationships of interactions between chemical composition, structure, mechanical properties and wear resistance of complex-alloyed vanadium cast iron poured in dry and wet SCM and metal mould are obtained. In the base of these relationships, the weight

factors describing the effect of the elements on structure and properties of complex-alloyed vanadium cast iron have been determined. The weight factors describing the effect of microstructural parameters on the properties of experimental cast iron grades are defined as well.

6. The following optimized compositions have been obtained (%): for microcutting — 2.8–3.0 carbon; 6.7–7.4 vanadium; 1.0–1.2 copper; 0.03–0.02 boron; 0.3–0.4 titanium; for the mechanism of plastic edging — 2.8–3.0 carbon; 5.0–6.5 vanadium; 1.0–1.2 copper; 0.01–0.03 boron; 0.30–0.45 titanium.

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