Managing the properties of cast products made from alloys of various structural classes using nitrided materials

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The article presents the research results aimed at studying the influence of the chemical composition and thermal conditions of crystallization on the level of the properties of cast iron and wear-resistant steels, which are used for manufacture of replaceable components of mining industry units as well as metallurgical production facilities.
The literature review states that the level of properties of cast products is significantly influenced by both the alloy chemical composition and the thermal conditions of casting formation in the mold. Managing the process of microstructure of cast products formation at the stages of primary and secondary crystallization, it is possible to obtain various parameters of the structures in the cast state of products. The resulting cast structure will determine further the parameters of microstructure after heat treatment, as well as the level of operation and mechanical properties. Experimental castings made of high-manganese steel, hypereutectoid steel and cast iron for rolls were obtained in laboratory conditions. In order to assess the complex influence of ther-mal conditions of formation of the cast products and the alloy chemical composition, experi-mental castings were obtained in casting moulds that are made from materials with different heat storage abilities. Further, the obtained cast products were tested in the conditions of abrasive and shock-abrasive wear. During the metallographic study of structures of experimental castings, quantitative characteristics of microstructures in the form of grain sizes, amount of carbide and graphite phases were determined, and the influence of thermal conditions of formation of the cast product in the mould on these parameters of microstructure was assessed. Moreover, the influence of alloying elements and nitrogen on the structure of the selected casting alloys was evaluated. At the final research stage, the operation and mechanical properties of the obtained castings were studied. The complex influence of chemical composition and thermal conditions of casting formation a casting mould on the level of operation and mechanical properties was established. The concentration intervals, in which the properties of experimental castings have maximal values, were determined.
Key words: wear resistance, cast iron for rolls, hypereutectoid steel, high-manganese steel, microstructure, nitrogen, grain, carbide phase.
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Introduction

Operating properties of cast products are forming at different stages of their manufacture and depend on various factors, such as quality of charge materials, alloy melting technology and methods of influence on liquid melt, operating conditions of crystallization processes, heat treatment etc. [1, 2].

Different technological operations, including most often such ways of influence on liquid melt as refining, alloying and modifying, are used for improvement of properties of finished products. Influence of introducing additives is manifested at different stages of cast product forming (primary and secondary crystallization, heat treatment), thereby it is necessary to determine experimentally regularities of influence on microstructure parameters of products in different periods of casting formation. It should be noted that structure forming process is influenced by the type of alloy (steel, cast iron) and conditions of heat removal from casting to mould, which are expressed numerically via melt cooling rate - in addition to chemical composition.

At present time, complex alloying and modifying by such elements as chromium, titanium, molybdenum, vanadium, niobium are used for increase of wear resistance of cast products. The authors [2-5] noted positive influence of the above-mentioned elements on qualitative and quantitative microstructure parameters, which leads to increase of wear resistance of steels and irons. This increase is caused by formation of carbide phase with definite morphology and quantitative parameters. To obtain this carbide phase, it is required to provide content of alloying elements within definite concentration ranges, their boundaries for several alloys are mentioned in the works [2-5]. Chromium concentration in wear-resistant steels is within the range 1.0-28.0 %, while such concentration ranges for titanium, molybdenum, vanadium and niobium are ip to 1.0 %, 0.5-5.0 %, 0.1-6.0 % and up to 0.5 % respectively.

Increase of wear resistance of cat products can be provided in several cases via optimization of chemical composition without additional alloying and modifying. It is mentioned [3] that optimization of chemical composition of cast iron for rolls leads to increase of operating resistance of rolling rolls by 10-15 %. Optimized chemical composition of high-manganese steel of austenite class Fe-1.1C-12.87Mn-0.6Si-0.4Cr is presented in the work [5]; it is possible in this case to achieve the maximal level of impact toughness without introduction of additional alloying elements.

To provide high level of wear resistance of steels for rolls manufacture, the relationships of concentrations of alloying elements are adjusted via equivalents [6]. Obtaining of molybdenum and tungsten equivalents within the ranges 1.0-1.5 and 12-13 respectively leads to formation of the required amount of carbide phase, as well as to formation of rational hardness, tensile strength and microhardness of metallic base of products. Heat treatment also plays an important role in forming the operating properties of steels for rolls, especially in determination of operating temperature and time parameters. The authors of the research [7] determined dependence of hardness and wear resistance on quenching temperature for the hypereutectoid steel 150KhNM.

Alloy microstructure determines a wear mechanism for products in the process of their operation. Presence of metastable residual austenite in the structure of steel 150KhNM from one side leads to decrease of hardness; from other side, its ability to martensite transformation provides increase of wear resistance [7].

Influence of microstructure on the surface wear mechanism for cast products from a high-manganese steel is observed in details in the research [8]. The authors of this work noted the role of carbide phase during abrasive and shock-abrasive wear with forming of “layered” worn structure under the effect of shock loads.

Thermal conditions of casting formation, i.e. melt crystallization rate in a casting mould, also make the effect on forming the properties of products which are manufactured from wear-resistant alloys [9]. As a result of non-equilibrium crystallization, redistribution of chemical properties between liquid and solid phases occurs at the moment of solidification, what has consequent effect on qualitative and quantitative parameters of carbide phase and sizes of grains. It is shown in the work [9], that increase of cooling rate for high-manganese steel melt in a casting moulds provides reducing of austenite grain size as well as decrease of carbide phase amount with variation of its chemical composition. The same relationship appears also for the hypereutectoid steel 150KhNM for rolls manufacture.

The researchers also pay a lot of attention to prospective materials and problems of their use for alloying the alloys with special properties. Nitrided ferroalloys and alloying compositions, allowing to improve operating properties of products via forming a carbonitride / nitride phase, as well as owing to influence on quantitative parameters of alloy microstructure (grain size of solid solution, quantitative parameters of the secondary phase), can be considered to such prospective materials [10-14].

The aim of this research is examination of the complex influence of nitrided materials and heat removal conditions from the melt on the structure and properties of ferrum-carbon wear-resistant steels of various structural classes.

Technique of the experiment conduction

Ferrum-carbon alloys, such as wear-resistance steel 110G13L, steel 150KhNM for rolls manufacture and indefinite cast iron LPKhNMd-71 for working layer of rolls were selected as objects for examination. Chemical composition of the base molten alloys before alloying and modifying is presented in the **Table 1**.

Melting of experimental alloys was carried out in the induction furnace IST-0,015 with basic lining from the following materials: carbon steel St3ps (GOST 380-94), steel-making iron PL1 (GOST 805-95), ferrosilicon FS 65 (GOST 1415-93) and ferromanganese FMn 90 (GOST 4755-91). The following additional alloying components were used: nitrided ferrochromium FKhN-10 (Cr – 66.2 %, N – 11.1 %) (TU 0840-024-21600649-2009); nitrided titanium-calcium alloying composition (Ti – 32.5 %; Ca – 10.0 %; N – 9.6 %) (TU 0821-016-21600649-2009); nitrided ferrovanadium (V – 40.4 %; N – 7.6 %) (TU 0857-042-21600649-2014). These materials were manufactured by the scientific and production company “Etalon” (Magnitogorsk).

Control of chemical composition was implemented via Spectrolab spectrometer.

Experimental alloys were poured in sand-loam (dry, wet) metallic moulds with various heat accumulating capacities. Dimension ranges of castings for different grades steel and cast iron were varied from 35x35x35 to 70x70x70 mm. Difference of thermal-physical properties and dimension ranges of castings allows to obtain finished cast products for different melt cooling rates in a casting mould: from 4.5 to 25.0 ^{o}C/s for high-manganese steel; from 5.77 to 28.35 ^{o}C/s for steel for rolls manufacture; from 5.1 to 15.2 ^{o}C/s for cast iron for rolls manufacture. Variation of the temperature in time was registered using tungsten-rhenium thermocouple and analogous-digital convertor LA-50USB.

Experimental castings were subjected to heat treatment before their testing. Castings from high-manganese steels

Table 1. **Chemical composition of cast alloys, %**

Alloy	C	Si	Mn	S	P	Cr	Ni	Mo	Al
110G13L	1.2	0.9	12.3	0.024	0.033	0.8	0.12	-	0.06
150KhNM	1.48	0.51	0.72	0.021	0.037	1.1	1.3	0.34	0.03
Cast iron for rolls*	3.05	0.93	0.87	0.021	0.049	1.80	3.56	0.34	-

* - niobium – 0.19 %.

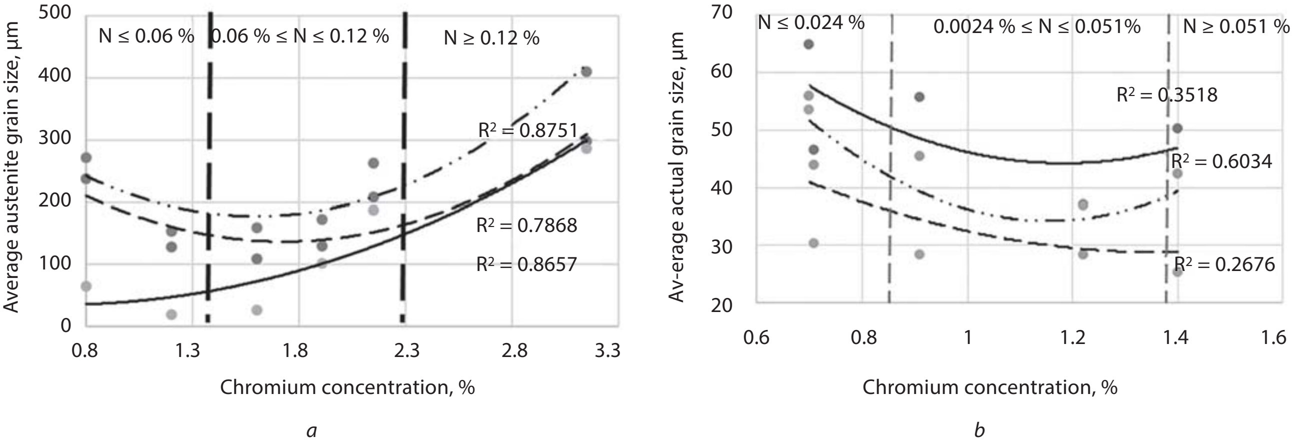


Fig. 1. Variation of average grain size in austenite steel 110G13L (*a*) and pearlite steel 150KhNM (*b*) with alloying by nitrided ferrochromium:
——— - dry mould; — — — — - wet mould; ——— - block mould

were quenched in water from the temperature 1100 ºC. Products from hypereutectoid steel for rolls manufacture were subjected at first to homogenization at the temperature 1050 ºC, then triple tempering at the temperature 540 ºC was carried out. Tempering at the temperature 650 ºC was selected as heat treatment procedure for cast iron for rolls manufacture.

Study of microstructure was conducted using optical microscope Meiji with built-in program Thixomet Standart Pro, as well as using scanning electron microscope JEOL JSM-6490 LV. Wear resistance of experimental castings was determined in accordance to GOST 23.208-79 (abrasive) and GOST 23.207 – 79 (shock-abrasive wear resistance). Steel strength was determined by bursting machine Shimadzu according to the GOST 1497-84.

Results and discussion

The complex influence of nitrided materials Cr-N, Ti-Ca-N, V-N and melt cooling rate on the processes of formation of casting structure during crystallization was examined at the first stage. The materials containing Cr-N и Ti-Ca-N were used for alloying of high-manganese steel and steel for rolls manufacture. Consumption of the above-mentioned materials varied from 1.0 to 4.0 % of melt mass. Influence of nitrided materials on microstructural parameters of selected steels is presented on the **Fig. 1** on the example of nitrided ferrochromium.

Depending on the type of mould (dry or wet sand-loam mould and block mould), the following cooling rates were obtained within the crystallization range for austenite / pearlite steels: 4.5 / 5.77 °C/s for dry sand-loam mould; 8.9 / 11.94 °C/s for wet sand-loam mould; 25.0 / 28.35 °C/s for block mould.

The same relationships were obtained during alloying of steels 110G13L and 150KhNM by Ti-Ca-N alloying composition. When concentration of alloying elements makes 0.981 % for Ti and 0.038 % for N, and consumption of alloying composition is 1-2 %, it is possible to achieve decrease of grain size to 250 μm in austenite steel and to 30-40 μm in pearlite steel, in comparison with non-alloy steels. Consequent elevation of additions of nitrided materials in amount of 3-4 % of melt mass leads to increase of average grain size in the examined steels by15-40 %, which is connected with rise of anisotropy coefficient – grain stretching in the direction of heat removal. It is caused by variation of physical and chemical properties of the melt, extraction speed of a solid phase, what finalizes in grain anisotropy along the heat removal direction into casting mould. Based on this, it can be concluded that concentration of the alloying elements (Cr, Ti) together with nitrogen should be restricted within definite ranges [15].

It should be noted that melt cooling rate has significant influence on structure forming processes in the selected steels; it is expressed in reducing of grain size in the case of cooling rate increase from 4.5/5.77 to 25.0/28.35 °C/s within the crystallization range. As soon as chromium and nitrogen concentrations rise to 3.0 and 0.3 % respectively, the anisotropy coefficient of austenite grain increases continuously, and it is an important feature of forming the structures of the selected alloys. At the same time, it was established via metallographic method, that anisotropy of actual grain, which is observed in austenite steels, is absent during 150KhNM steel alloying by nitrided ferrochromium, in the case when chromium concentration is close to steel grade composition (up to 1.5 %) and nitrogen content does not exceed 0.06 %.

Cast iron for rolls manufacture was alloyed by nitrided ferrovanadium instead of usual ferrovanadium. Consumption of nitrided materials was varied from 0.6 to 1.5 % of melt mass. The conducted metallographic investigations did not allow to reveal the complex influence of nitrogen and vanadium on microstructure of the examined cast iron within the temperature range of solid phase extraction.

It was found out via micro-X-ray spectral analysis, that nitrogen in cast iron melt forms Ti, Nb, Mo carbonitrides during solidification. Consequently, influence of nitrogen together with vanadium and other alloying elements in cast iron for rolls manufacture is manifested more strongly in the period of secondary crystallization, which is connected with variation of morphology and amount of extracting carbide / carbonitride phase as well as graphite during isothermal holding of the working layer of this cast iron after core pouring.

Influence of nitrided materials on the processes of secondary crystallization can be observed not only in cast iron, but also in steels. Alloying of the selected steels by chromium and titanium together with nitrogen has influence on parameters of carbide / carbonitride phase. Let us consider this influence on the example of 110G13L steel.

When alloying of high-manganese steel by nitrogen and chromium up to 3.0 and 0.03 % respectively, total amount of carbide / carbonitride phase increases from 2.5 to 3.5 %, while introduction of Ti-Ca-N alloying composition into melt in the amount up to 2-3 % of melt mass leads to reducing of its amount to 0.5-1.0 %. It was established via micro-X-ray spectral analysis that decrease of total amount of secondary phase during introduction of the above-mentioned titanium-base alloying composition is stipulated by reducing of cementite amount, which is alloyed by manganese. This observation is valid for the case when cementite is replaced unequally in quantitative relation by titanium carbonitrides.

Nitrided ferrovanadium in cast iron for rolls manufacture has influence on the processes of secondary crystallization via the most complicated mechanism. First of all, it effects on extraction of graphite phase (as a result of isothermal holding of a roll working layer during core pouring), as well as on qualitative and quantitative parameters of carbide / carbonitride phases. The obtained relationships are presented on the **Fig. 2**.

Use of nitrided ferrovanadium allowed to decrease residual vanadium concentration from 0.5 to 0.1 % (with additional nitrogen content within the range 0.01-0.025 %) without any damage to operating and mechanical properties of products. Additionally, lowering of vanadium concentration leads to decrease of residual austenite content from 15 to 5 % in cast state. It has positive influence during further realization of the measures aimed on reducing of the amount of residual austenite in the process of heat treatment and obtaining of its minimal content in finished products.

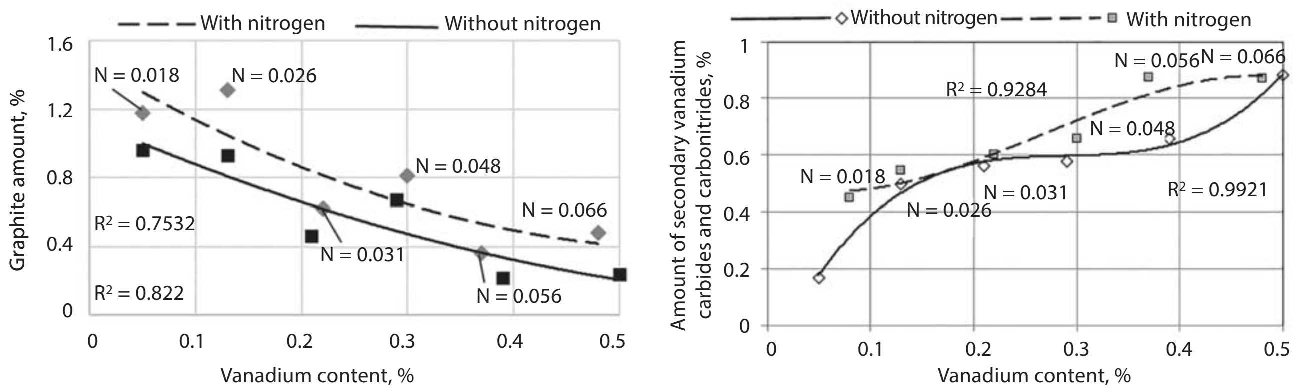
Formed cast microstructure is initial for obtaining qualitative structure in the process of heat treatment.

It was established during the conducted tests, that increase of austenite grain size in average by 5-8 % is observed in the process of heat treatment of high-manganese steel, which is additionally alloyed by the complex of Cr-N and Ti-Ca-N elements; it is less than increase of grain size by 8-13 % for the steels which are not alloyed by nitrogen. This increase of grain size is caused by dissolution of carbide network, which is located at grains boundaries. The positive effect during introduction of nitrided materials in a melt is initially manifested in decrease of grain size during primary crystallization, and then due to elevation of amount of hard-soluble carbonitrides, what leads to restriction of grain size increase in solid solution during quenching.

The amount of carbides / carbonitrides during heat treatment reduces by 2-3 % down to sufficient amount 0.5-0.7 %. The secondary phase, which remains after heat treatment, is presented mainly by complex nitrogen-containing titanium carbides / carbonitrides.

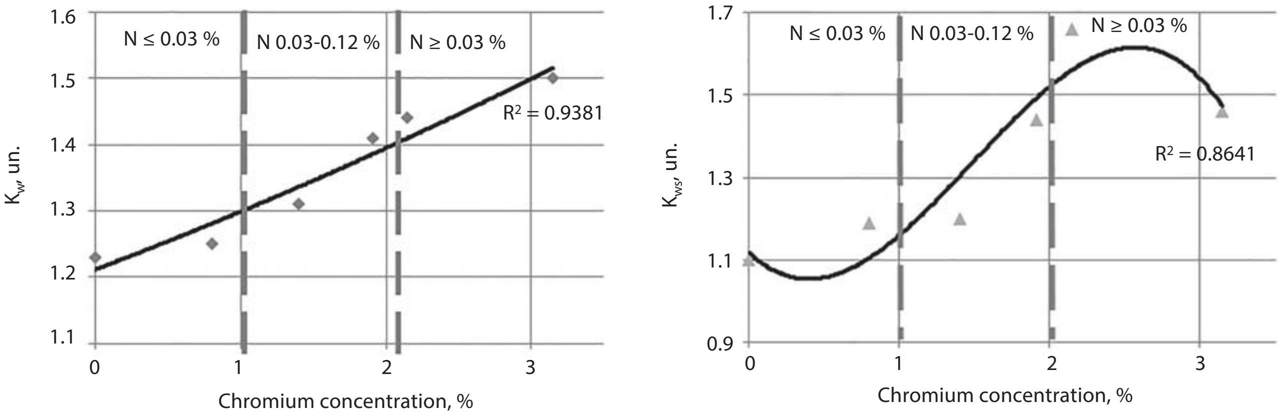
Heat treatment of the steel for rolls manufacture is accompanied by elimination of martensite structure, which is forming in cast state, and by final dissolution of cementite network, which is extracted along the boundaries of actual grains. At the same time, complex chromium and molybdenum carbonitrides were found out in the alloy microstructure. The amount of carbide / carbonitride phase achieves 14 % in several cases.

Extraction of graphite phase occurs in the process of heat treatment of cast iron for rolls manufacture, for the case when this cast iron is alloyed by vanadium and nitrogen. Amount of this phase rises from 1.2-1.5 % to 2.0-3.9 %; this rise is additionally contributed by lower vanadium concentration (0.1 % against 0.5 %), during alloying together with nitrogen. The amount of residual austenite reduces in this case to the level below 3.0 %. It is also important to mention that square of graphite inclusions decreases by



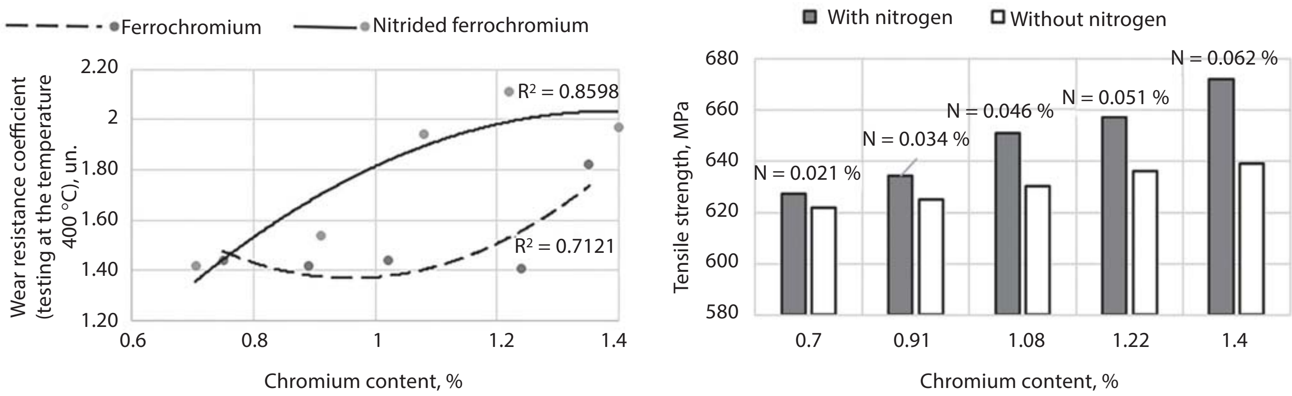
a *b*

Fig. 2. Influence of vanadium and nitrogen on the amount of graphite (*a*), carbide and car-bonitride (*b*) phases



a *b*

Fig. 3. Influence of chromium and nitrogen on abrasive (*a*) and shock-abrasive (*b*) wear resistance of the steel 110G13L



a *b*

Fig. 4. Influence of nitrogen and chromium on wear resistance (*a*) at the testing temperature 400 °C and tensile strength (*b*) of the steel 150KhNM

30-40 % after heat treatment, what testifies on extraction of more small graphite inclusions (3-10 μm); additional amount of carbide phase (about 3.0 %) is also extracted.

Alloying of the selected alloys by nitrogen in order to provide transformation of microstructure has influence on the properties of castings. The results of testing of the alloys for wear resistance as well as for bursting are presented on the **Fig. 3-5** [8, 9].

Rise of Cr and N concentration up to 2.0 and 0.12 % respectively led to increase of abrasive and shock-abrasive wear resistance coefficients by 20-45 % for the austenite steel 110G13L (Fig. 3).

Increase of abrasive wear resistance coefficient by 15-35 % also occurs owing to alloying of the pearlite steel for rolls manufacture by nitrogen (Fig. 4*a*). At the same time, tensile strength of the examined steel increases by 4-7 % (Fig. 4*b*).

Complex alloying of chromium-nickel cast iron for rolls manufacture by vanadium and nitrogen allows to achieve the required level of abrasive wear resistance with residual vanadium and nitrogen concentrations ~0.1 and 0.02 % respectively, i.e. to reduce ferrovanadium consumption by 4-5 times, comparing with the basic technology of alloy preparation (Fig. 5*a*).The positive effect is additionally manifested in increase of the shock-abrasive wear resistance coefficient, characterizing in this case cast iron ability to spalling (Fig. 5*b*).

It is possible to achieve residual vanadium concentration 0.5-1.0 % without lowering of operating properties in cast iron for rolls manufacture, due to use of nitrided ferrovanadium; it leads to cutting the consumption of a ferroalloy and reducing of product cost. Additionally. Decrease of vanadium residual concentration and formation of carbonitrides in microstructure of castings lead to saving of operating properties. It also provides favourable influence on morphology of graphite phase (amount, size and distribution in alloy structure).

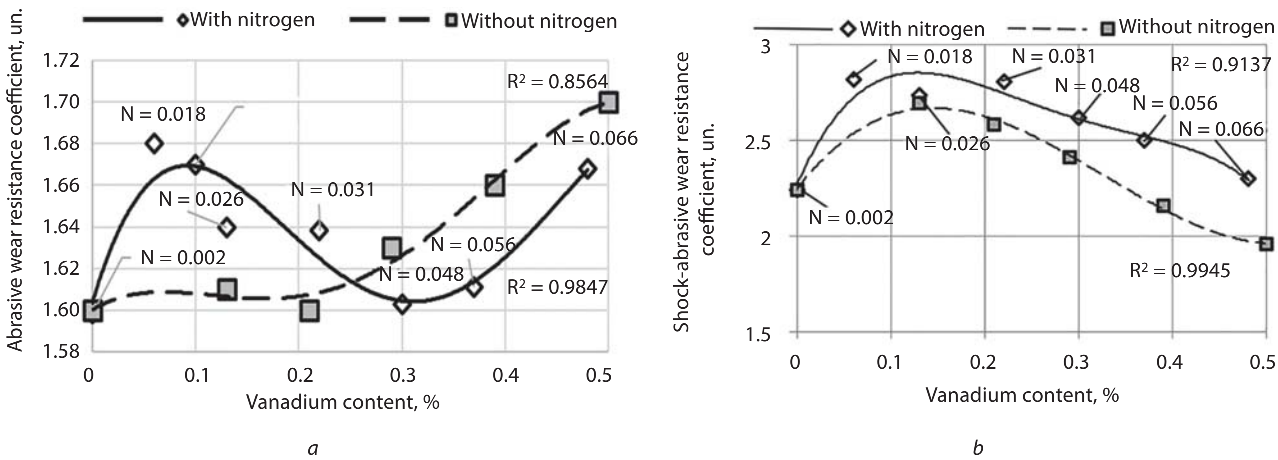


Fig. 5. Influence of vanadium and nitrogen on abrasive (*a*) and shock-abrasive (*b*) wear resistance of cast iron for rolls manufacture

Alloying of steel for rolls manufacture by ferrochromium promotes improvement of mechanical and operating properties by 2-5 % and wear resistance by 15 % in average.

Each used nitrided material should guarantee concentration of alloying elements within definite ranges in order to provide maximal level of mechanical and operating properties. In this case, influence of these materials on metal structure appears both during primary crystallization and within the range of extraction of secondary phases and heat treatment.

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