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STUDY OF THE EFFECT OF COMPLEX ALLOYING OF HIGH-MANGANESE STEEL BY Ti−Ca−N ALLOYING COMPOSITION ON ITS MICROSTRUCTURE, MECHANICAL AND OPERATING PROPERTIES

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Key words:

high-manganese steel, complex alloying composition titanium-calcium-nitrogen, quenching, cooling rate, crystallization

ABSTRACT

The paper presents examination of the effect of complex alloying of high-manganese austenite steel by Ti−Ca−N alloying composition (1−3%) in cast state and after quenching. The regularities of variation of grain size and austenite micro-hardness, amount of carbide phase, hardness, abrasive and impact-abrasive wear resistance are determined depending on amount of introducing alloying composition and alloy cooling rate in the crystallization temperature range. It is shown that introduction of 1−2% of alloying composition in the alloy is the most rational option; at the same time abrasive and impact-abrasive wear resistance of the alloy increases. Based on this study, it is recommended to use this alloying complex for the components made of high-manganese steel that are working in complicated conditions including combination of high contact and impact loads.

Introduction

High-manganese steel is used for manufacture of details operating in the conditions of abrasive and impact-abrasive wear resistance. Some products made of this steel are subjected to effect of only contact loads, while other are operated only under impact loads. To reach high level of abrasive resistance, the alloy microstructure should include hard wear-resistant phase (e.g. martensite). However, such structure is not suitable for impact load resistance owing to its excessive brittleness. In this connection, those products that are operated in complicated conditions characterized both by abrasive and impact wear, require the unique complex of properties. In its turn, it can be obtained in complex micro-alloying of high-manganese austenite steel.

A row of works [1−12] are devoted to the problems of rise of abrasive wear resistance of austenite steel. They elucidate the experience of melting, alloying and modifying of high-manganese steel. It is noted that definite concentrations of titanium, calcium and nitrogen increases resistance of austenite steels in different kinds of wear.

Cooling rate of castings during crystallization and influence of heat treatment are other important factors in manufacture of details made of high-manganese steel [13, 14].
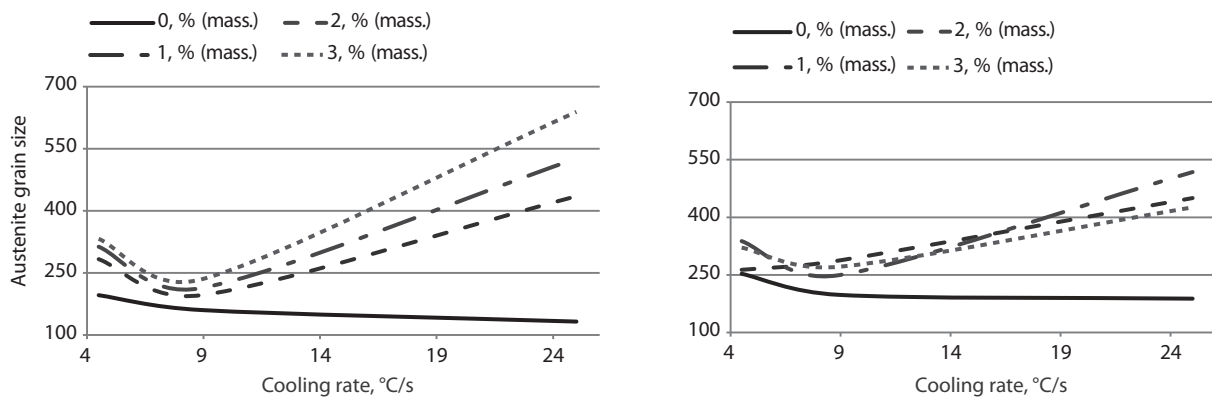
Fig. 1.   Dependence of austenite grain size on cooling rate of the alloy during crystallization and alloying degree:
a — in cast state; *b* — after quenching

In view of this, it seems to be interesting to study the effect of complex micro-alloying by Ti–Ca–N alloying composition on microstructure, mechanical and operating properties of castings made of high-manganese steel that has been cooled with different rates in cast and heat treated states.

Technique of the experiment

Experimental alloys for study of structure and properties have been molten in the induction furnace IST-006 with basic lining. Heating of the samples for heat treatment (water quenching from the temperature 1100 °C) has been conducted in the electric furnace with oxidizing atmosphere.

Micro-alloying of Hadfield steel has been undertaken by Ti–Ca–N complex with chemical composition presented in the **tab. 1**.

Investigations have been conducted on standard samples with size 35×35×10 mm. To realize different cooling rates, the alloy has been cast in the moulds with different heat accumulating capacity: dry sand-clay mould, wet sand-clay mould, chill mould. Variations of metal temperature have been measured using formed tungsten-rhenium thermocouple and the results have been recorded on analog-digital converter with frequency 50 Hz.

Chemical composition of the samples has been determined on SPECTRO optical-emission spectrometer (MAXx model).

Qualitative and quantitative analysis of microstructure have been conducted on optical microscope Meiji (Ticsomet Standard Pro program) and on scanning electronic microscope JEOL JSM-6490 LV. X-ray microanalysis has been executed using attachment to scanning microscope INCA Energy. To analyze microstructure, microslices have been prepared via the standard technique by pressing-in the samples in Transoptic resin at automatic press Simplimet 1000 in the sample preparing line of Buechler company. To reveal microstructure, surface of microslices has been subjected to pickling in the mixture of concentrated nitric and hydrochloric acids (HNO_3 — 65%, HCl — 35%) via dipping of polished surface in the bath with chemical reagent (these researches have been conducted the Center of collective usage of Scientific-research institute of nanosteels at Nosov Magnitogorsk State Technical University).

Microhardness has been determined by the hardness meter Buchler Micromet in correspondence with GOST 9450-60 by indentation of a diamond pyramid with angle between the opposite planes 136° at load 50 g and loading duration 10 s. Hardness has been detected using the hardness meter EmcoTest M4C 075 G3 in correspondence with GOST 9013-59.

Wear resistance of the alloys has been investigated in correspondence with GOST 22.207-79 and GOST 23.208-79. The wear resistance coefficient has been calculated as the average value of the coefficients obtained after testing of at least three experimental samples poured in a mould from one melt.

Results of investigation

4 types of pilot melts in cast and heat treated states have been obtained after the series of experiments; their chemical composition is presented in the **tab. 2**.

The alloy No. 1 is basic one, without complex microalloying, while the alloys No. 2—4 contain alloying composition in the amount 1% (mass.), 2% (mass.) and 3% (mass.) respectively. Usage of three types of moulds allowed to obtain different cooling rates for castings: 4.5 °C/s, 8.9 °C/s and 25 °C/s.

Microstructure of all samples is presented by austenite, its grain size depends on cooling rate and on microalloying degree of the alloy (**fig. 1, a**). At the same time the features of variation of austenite grain size in quenched state has direct heredity and corresponds to cast state (**fig. 1, b**).
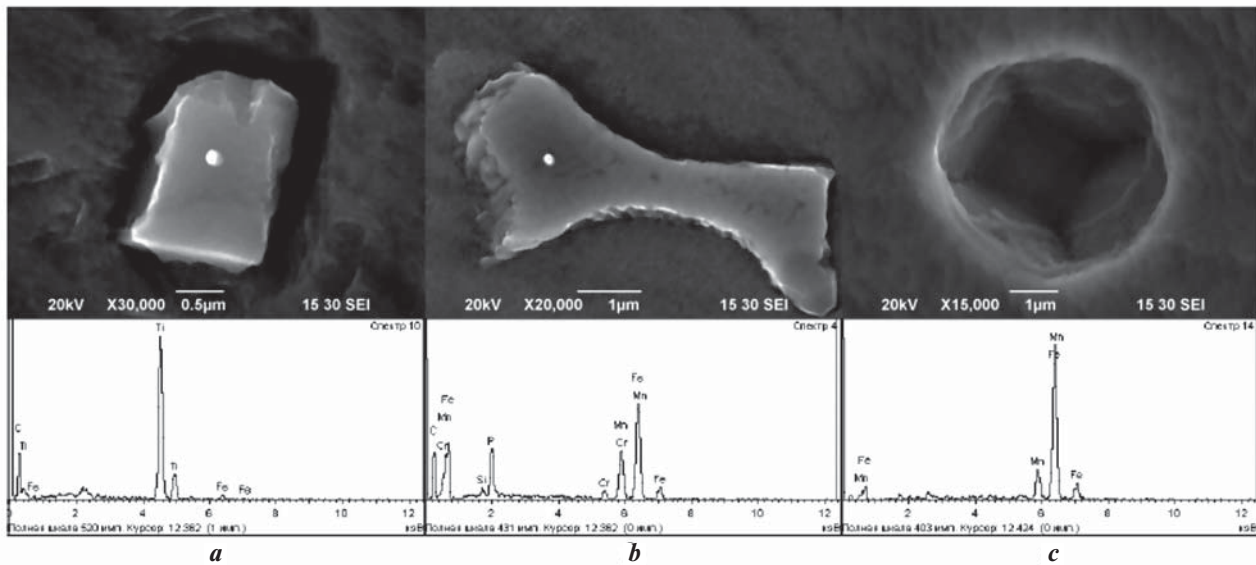
Table 1. Chemical composition of Ti–Ca–N complex

Element	Ca	Ti	C	Si	P	S	Al	N
Mass part, %	10.0	32.5	0.34	18.7	0.02	0.02	1.9	9.6

Table 2. Chemical composition of experimental samples

№№	Amount of alloying composition, % (mass)	Content of chemical elements, %					
		C	Si	Mn	S	P	Ti
1	0	1.15	1.05	11.6	0.03	0.04	0.0
2	1	0.91	1.00	11.5	0.017	0.057	0.48
3	2	0.98	0.95	11.8	0.03	0.05	0.081
4	3	0.97	1.01	11.9	0.017	0.05	0.085

Fig. 2. **Microstructure and results of X-ray microanalysis of three kinds of the carbide phase:**
a — titanium carbide; *b* — phosphide eutectics; *c* — alloyed cementite
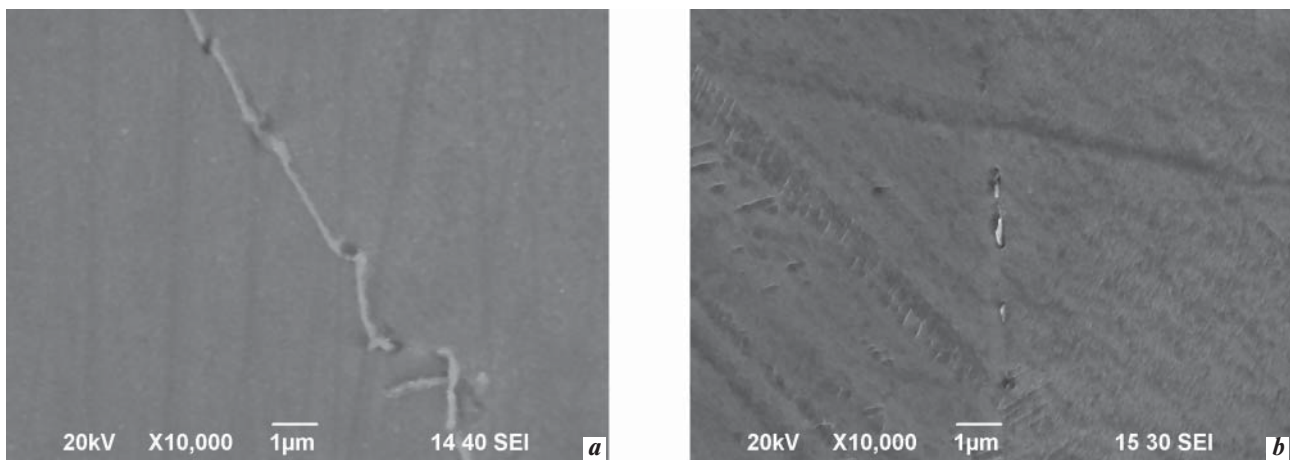

Fig. 3. **Microstructure of the carbide phase in the alloys cooled during crystallization with the rate 4.5 °C/s:**
a — the basic alloy; *b* — the alloy alloyed by Ti−Ca−N alloying composition in the amount 2 %

The presented graphs display that complex alloying leads to increase of austenite grain size in comparison with the basic alloy, where increase of cooling rate (from 4.5 to 25 °C/s) leads to monotonous decrease of grain size (from 200 to 130 μm).

In alloying alloys this decrease of grain size occurs at cooling rates during recrystallization in the range from 4.5 to 9 °C/s. In this case austenite grain size for all alloyed samples decreases by 100 μm. Additional increase of cooling rate up to 25 °C/s leads to harsh increase of austenite grains in cast structure of complex-alloyed high-manganese steel: from 196, 213 and 234 μm to 435, 526 and 639 μm respectively for the alloys alloyed by Ti−Ca−N alloying composition in the amount 1% (mass.), 2% (mass.) and 3% (mass.). After quenching the authors observed increase of austenite grain size in the structure of basic alloy by 30−50 μm and absence of this appearance in alloyed high-manganese alloys.

In addition to austenite, the carbide phase of three types is presented in the structure of all alloys along the boundaries and inside grains. The first type is titanium carbide (**fig. 2, a**), the second — phosphide eutectics (**fig. 2, b**) and the third — cementite alloyed by manganese (**fig. 2, c**). Its amount and morphology depend on alloy cooling rate during crystallization and alloy alloying degree both in cast and quenched states. Complex alloying changes cardinally the morphology of carbide phase. In alloyed alloys the carbide phase is extracted as separate inclusions trying to reach round forms (**fig. 3, b**) in comparison with the basic alloy (**fig. 3, a**) where the carbide phase is extracted as solid carbide net along the boundaries of austenite grains.

Taking into account the chemical composition and different resistance to pickling agent, the carbide phase has been conditionally separated by two kinds. The first kind is presented by titanium carbides, the second — by carbides alloyed by manganese (phosphide eutectics and cementite alloyed by manganese). It also allowed to determine quantitative parameters of total carbide phase as well as its separate kinds in cast and quenched states (**fig. 4**).
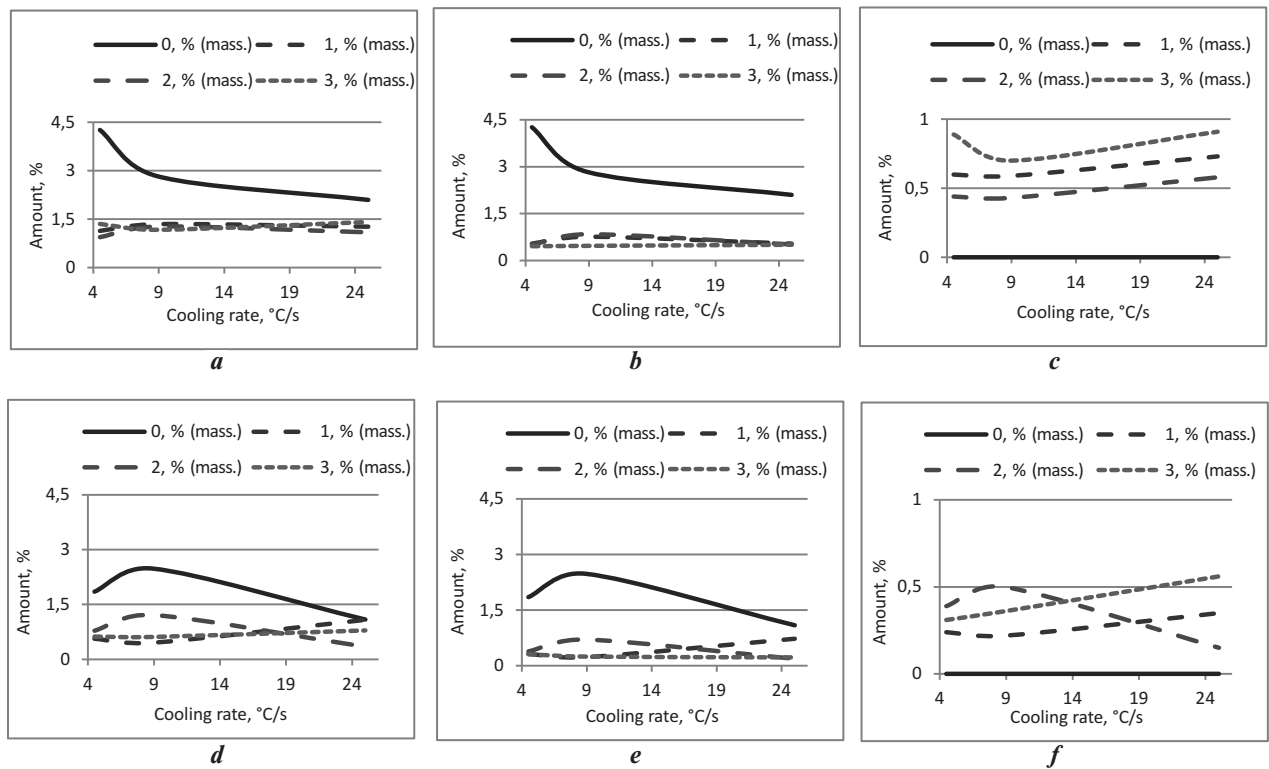
Fig. 4. **Dependence of total amount of the carbide phase (*a*, *d*), amount of carbides alloyed by manganese (*b*, *e*) and amount of titanium carbides (*c*, *f*) on cooling rate during crystallization and alloy alloying degree:**
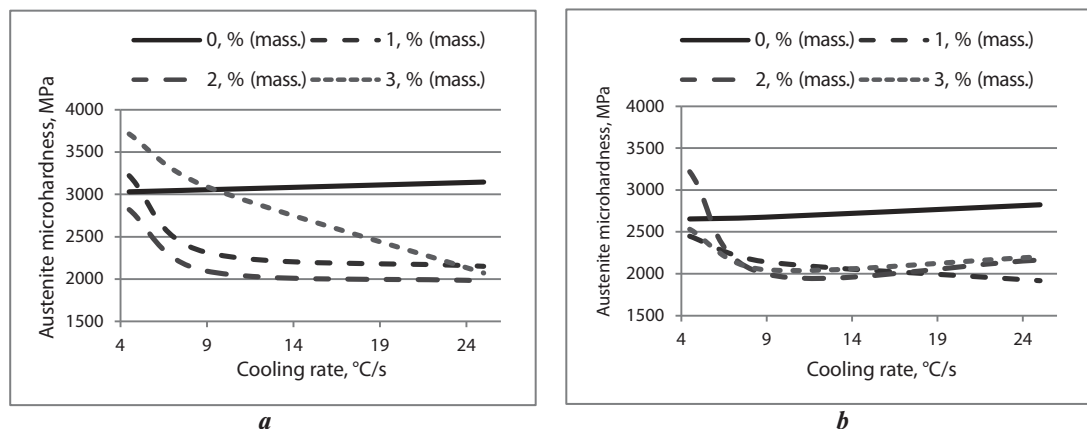*a*, *b*, *c* — in cast state; *d*, *e*, *f* — after quenching

Fig. 5. **Dependence of austenite microhardness on cooling rate during crystallization and alloying degree:**
a — in cast state; *b* — after quenching

Alloying of austenite steel by Ti–Ca–N alloying composition independently to its amount leads to harsh lowering of total amount of the carbide phase in the alloyed alloy in comparison with the basic alloy. Increase of cooling rate during crystallization from 4.5 to 25 °C/s has the effect on total amount of the carbide phase only for non-alloyed alloy, where amount of carbides alloyed by manganese decreases in monotonous mode from 4.2% to 2.1%.

Total amount of the carbide phase in alloyed alloys is in the range 1.3–1.5% independently on alloying rate and degree of the alloy (see fig. 4, *a*). It occurs owing to decrease of amount of carbides alloyed by manganese (see fig. 4, *b*)

and simultaneous increase of amount of titanium carbides by not more than 0.15% (see fig, 4, *c*).

Heating of the alloy to the temperature 1100 °C and holding at this temperature lead to dissolution of the carbide phase, while harsh cooling does not allow to realize the process of backward separation. Thereby total amount of the carbide phase (containing only carbides alloyed by manganese) in the basic alloy decreases by 0.4–2.4% depending on cooling rate of the alloy during crystallization. Total amount of the carbide phase in the alloyed alloys decreases from 1.3–1.5% to 0.3–1.2% depending on alloying degree and cooling rate of the alloy during crystallization (see fig. 4, *d*). At the same time amount of carbides alloyed by manganese
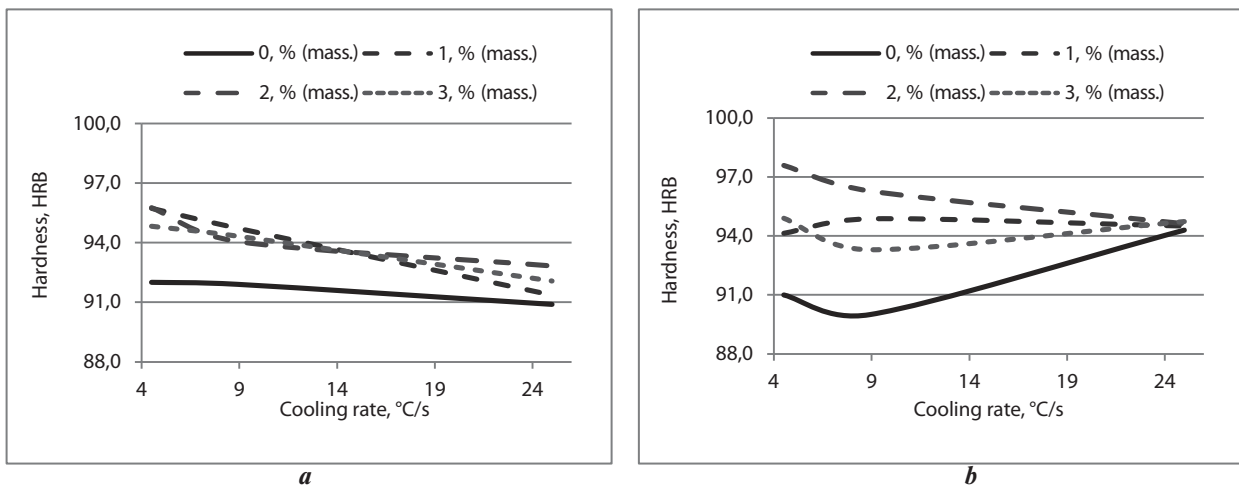
Fig. 6.   Dependence of hardness of examined steel on cooling rate during crystallization and alloying degree:
    a — in cast state; *b* — after quenching

decreases by 0.15−0.6% (see fig. 4, *e*), while amount of titanium carbide lowers by approximately 0.25% (see fig. 4, *f*).

Variation of amount of the carbide phase depending on cooling rate during crystallization, as well as variation of alloying degree of the alloy in cast state and dissolution of the carbide phase during heat treatment changes chemical composition of austenite, what is reflected on its microhardness (**fig. 5**).

Austenite microhardness of the basic alloy smoothly increases from 3030 to 3150 MPa in cast state with rise of cooling rate during crystallization of this alloy. Alloying by large amount of Ti−Ca−N alloying composition (more than 2%) leads to apparent growth of austenite microhardness only at low cooling rate during crystallization (4.5 °C/s). Rise of cooling rate during crystallization leads to decrease of austenite microhardness in average from 3000 to 2100 MPa, depending on alloying that has the effect on intensity of this decrease (see fig. 5, *a*). After heat treatment of castings, austenite microhardness decreases only in the basic alloy by 300−400 MPa in comparison with cast state. As for alloyed alloys, austenite microhardness does not vary after quenching and leaves on the level 2000 MPa (see fig. 5, *b*).

Austenite microhardness and total amount of the carbide phase in the structure of high-manganese steel determine the alloy hardness in general. Complex alloying of the austenite alloy leads to rise of its hardness in cast and quenched states (**fig. 6**).

However, the difference in hardness between the basic and alloyed alloys depends on cooling rate of the alloy during crystallization. If this rate increases from 4.5 to 25 °C/s in cast state, the difference makes from 3 to 1 HRB units respectively (see fig. 6, *a*). The quenched samples that have been cooled during crystallization with high rates have the same hardness independently on the fact and degree of alloying (see fig. 6, *b*).

All above-presented qualitative and quantitative parameters of microstructure have effect on the main operating properties of the high-manganese steel, such as abrasive and impact-abrasive wear resistance (**fig. 7**).

Introduction of Ti−Ca−N alloying composition in the alloy leads to harsh rise of its abrasive wear resistance by 1.4 times in comparison with the basic alloy (see fig. 7, *a*). After

quenching this difference is not so significant as in cast state (6−11%), but the coefficient of abrasive resistance of all alloyed steels is in the range 1.6−1.8 units (see fig. 7, *b*).

Dependence between impact-abrasive wear resistance of austenite steel and its alloying degree has more complicated mode in comparison with abrasive wear resistance. Increase of alloying degree at small cooling rates of castings decreases the coefficient of wear resistance of castings from 1.4 to 1.0 units in the temperature interval of crystallization (4.5 °C/s). If cooling rate during crystallization makes about 9 °C/s, the coefficient of impact-abrasive wear resistance of all alloyed (from 1 to 3%) castings is equal to one unit, what is smaller by 25% in comparison with castings having basic composition. Additional increase of cooling rate during crystallization in the basic alloy and in the alloy with 1.0% of alloying composition finalizes in lowering of impact-abrasive wear resistance. At the same time the alloys with 2 and 3% of alloying composition are characterized by increase of this wear resistance if cooling rates of castings during crystallization are equal (see fig. 7, *c*).

Essential increase of the coefficient of impact-abrasive wear resistance up to 1.5−1.8 units of the alloys alloyed by alloying composition in the amount 1% and 2% occurs after heat treatment depending on cooling rate during crystallization. Rise of the coefficient o wear resistance from 1.0 to 1.6 units takes place in the alloy alloyed by alloying composition in the amount 3% on the condition that cooling rate during crystallization is equal to 4.5 °C/s. Increase of cooling rate leads to gradual decrease of the difference between impact-abrasive wear resistance in cast and quenched states for the alloys with maximum alloying (3%). The coefficient of impact-abrasive wear resistance of the basic alloy leaves on the level of cast state in the whole range of cooling rates during crystallization (see fig. 7, *d*).

Discussion of the results

Introduction of Ti−Ca−N alloying composition in chemical composition of the high-manganese austenite steel leads to variation of its microstructure, mechanical and operating properties.
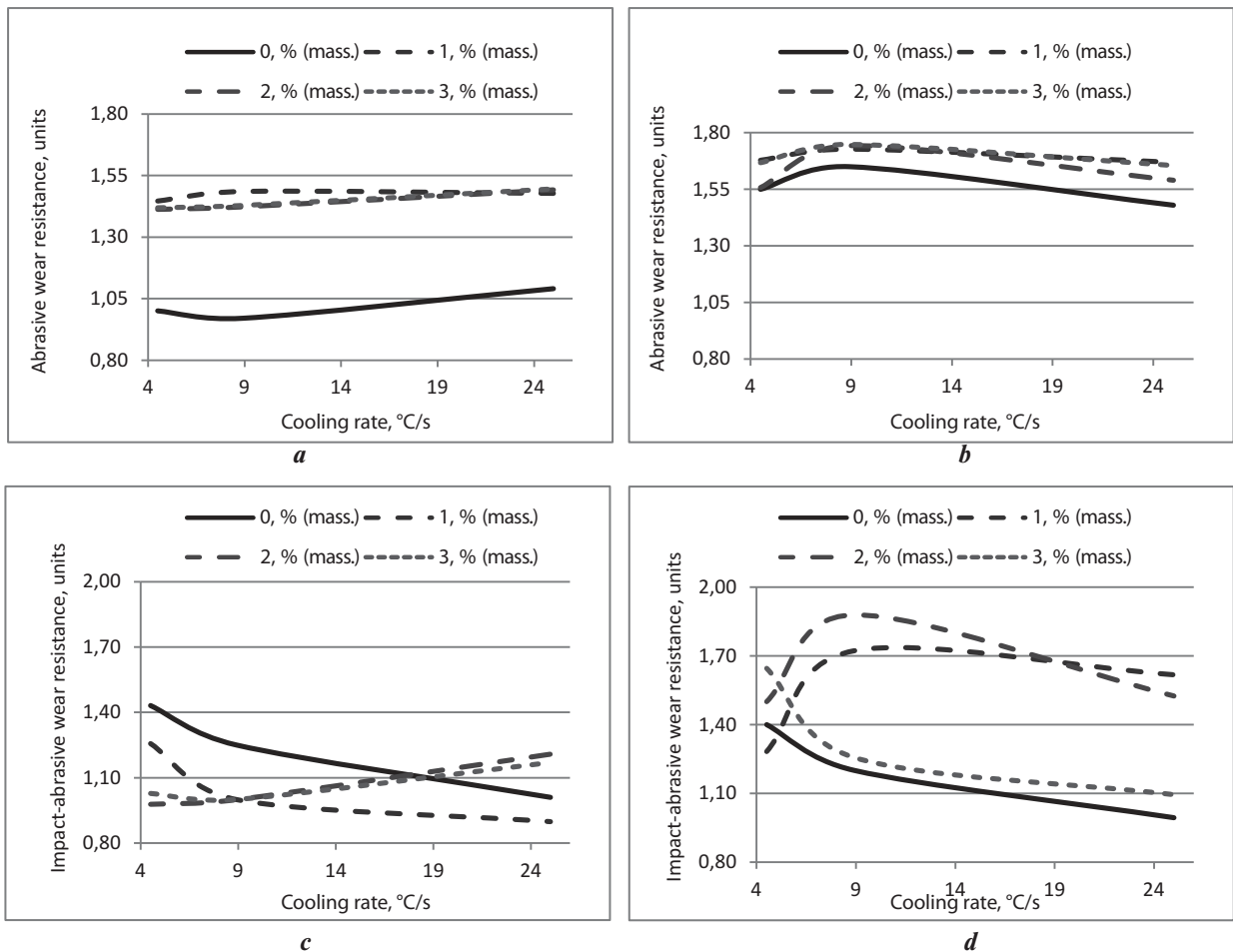
Fig. 7. Dependence of abrasive (*a, b*) and impact-abrasive (*c, d*) wear resistance of austenite steel on cooling rate of castings during crystallization and on alloying degree: *a, b* — in cast state; *c, d* — after quenching
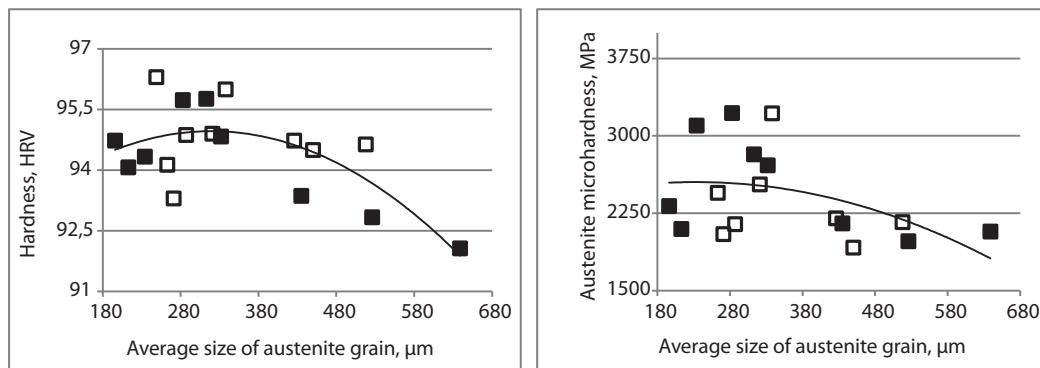

Fig. 8. Dependence of hardness (*a*) and austenite microhardness (*b*) on the average austenite grain size: ■ — in cast state; □ — after quenching

Titanium has large sensitivity to carbon than manganese and iron, and reacts with them. As a result of this reaction, dispersed carbides are forming [15]; they extract mainly in the center of austenite grains. At the same time decrease of the amount of phosphide eutectics, extracting during steel crystallization [16] is observed. In its turn, this eutectics impedes increase of austenite grains. Thereby alloying of the high-manganese steel by Ti–Ca–N alloying composition increased the tendency to growth of austenite grains. This effect strengthens with increase of the amount of alloying composition and

cooling rate of the alloy during crystallization. At the same time extracted dispersed titanium carbides impedes increase of austenite grains during heat treatment. Being more resistant to high-temperature effect in comparison with cementite alloyed by manganese, these carbides are saving in the structure in larger amount, thereby impeding increase of grain size.

Variation of the average austenite grain size of the high-manganese steel, alloyed by T–Ca–N alloying composition, is reflected on varying of such mechanical properties as hardness and microhardness (**fig. 8**).
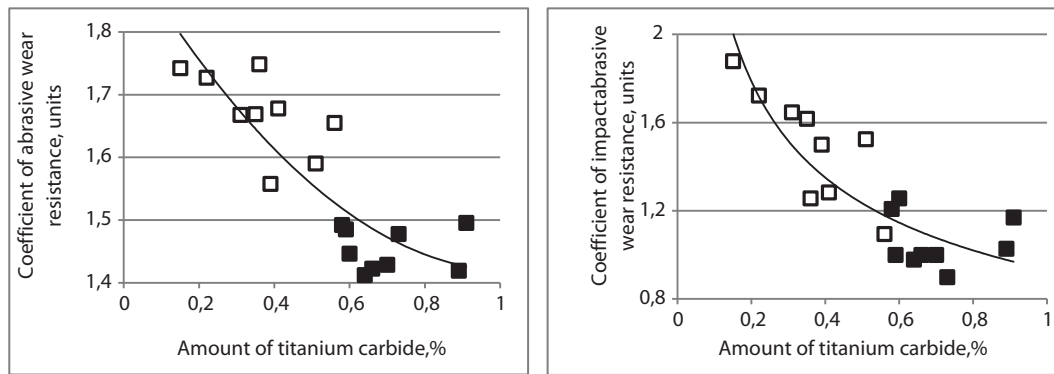
Fig. 9. Dependence of the coefficients of abrasive wear resistance (*a*) and impact-abrasive wear resistance (*b*) of austenite steel on the amount of titanium carbide in its structure:
■ — in cast state; □ — after quenching

Increase of the average austenite grain size in a complexly alloyed austenite steel leads to lowering of its microhardness and hardness of a casting in general.

Qualitative and quantitative parameters of the carbide phase also play the important role in forming of the basic operating properties of this steel, such as abrasive and impact-abrasive wear resistance. At the same time the most distinct relationship can be observed between these properties and the amount of titanium carbide in the alloy structure (**fig. 9**).

It can be concluded on the base of the above-presented relationships that dissolution of carbides and saturation of austenite by titanium lead to improvement of operating properties of the complex-alloyed high-manganese steel.

Conclusions

Alloying of the high-manganese steel by Ti−Ca−N alloying composition leads to decrease of the amount of phosphide eutectics and cementite alloyed by manganese in the structure. At the same time, dispersed titanium carbides appear in the structure.

Complex alloying of the austenite steel changes morphology of its carbide phase that extracts inside austenite and does not form solid net along the boundaries of its grains. The structure is now characterized by more large grain, at the same time increase of grains as a result of heat treatment is not observed.

Introduction of Ti−Ca−N alloying composition in the amount 1-2% in chemical composition of the high-manganese steel allows to improve its operating parameters after quenching and makes it possible to use it as a microalloying complex for rise of wear resistance of the components operating in the conditions of abrasive and impact-abrasive wear.

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