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INFLUENCE OF BORON MODIFICATION AND COOLING CONDITIONS DURING SOLIDIFICATION ON STRUCTURAL AND PHASE STATE OF HEAT- AND WEAR-RESISTANT WHITE CAST IRON

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ABSTRACT

The paper is devoted to examination of the effect of boron modification and temperature conditions for metal cooling in a mould on phase composition, morphology and chemical composition of structural components of heat- and wear-resistant white cast iron of Fe–C–Cr–Mn–Ni–Ti–Al–Nb system. The phase composition of the metallic base changed from the dual-phase (α - and γ -phases) to the completely single-phase (γ -phase). Boron modification influenced on the type of secondary carbides, while secondary hardening in a mould occurs owing to extraction of dispersed niobium carbides (without boron, but owing to chromium carbides). The structure of modified cast iron is presented by the primary complex carbides (Ti, Nb, Cr, Fe) C, as well as by solid solution dendrites, eutectics and secondary carbides MC. Boron addition changes the chemical composition of primary carbides with decrease of niobium content from 44 to 2% and increase of titanium content from 24 to 65%; content of eutectic carbides rises as well. As for hypereutectic carbides, they are characterized by increase of Fe content and lowering of Cr content. Parameters of the primary phases (MC carbides and solid solution dendrites) were investigated using the methods of quantitative metallography. The special technique of Thixomet PRO image analyzer was used for evaluation of the F form factor which is the criterion of compatibility of the primary phases. The following parameters were used in this work as the parameters of dendrite structure: dispersity of the dendrite structure (δ), volumetric part of dendrites (V), distance between the axes of second order dendrites (λ_2), form factor (F), average dimensions of dendrites — square (S), length (l) and width (β). Of the suggested characteristics (parameters) allowed not only to provide quantitative evaluation of the dendrite structure, but also to determine modification degree as relative (in %) variation of the each criterion in modified cast iron in comparison with non-modified iron. Quantitative relation between modification degree and crystallization conditions were established as well.

Key words:

heat- and wear-resistant white cast iron, modification, temperature conditions of metal cooling in a mould, structure, phase composition, chemical composition, secondary hardening in a mould, phase parameters, form factor, modification degree.

Introduction

Examination of the effect of boron modification and temperature conditions of metal cooling in a casting mould on phase composition, morphology and chemical composition of the structural components of heat- and wear-resistant white cast iron has large practical importance [1, 2, 8–13]. It is known that morphology of the primary phases (solid solution dendrites and carbides) as well as eutectics has substantial effect on mechanical and special properties of the alloys (e.g. wear resistance, scale resistance, growth resistance) [1–7, 14–20]. Optimal values of these parameters are achieved at definite relations between sizes and form of the alloy structural components.

Complex alloyed white cast iron is a prospective heat- and wear-resistant material where stability of the structure and properties in the work are among the main advantages for choosing this material.

Heat- and wear-resistant cast iron is characterized by special structure, complicated chemical and phase compositions. Complex alloying creates the conditions for forming the multi-phase structure containing of primary carbides and solid solution dendrites, eutectics and secondary carbides. Efficiency of multi-phase microstructure in oxidation and abrasive wear resistance depends on morphology of the phases, their quantity and chemical composition; type, dispersity

and character of hardening phase distribution (primary, eutectic and secondary carbides) [3–7]. Single-phase structure of cast iron metallic base is considered to be the most suitable for the conditions of high-temperature oxidation. Phase composition of this base depends on chemical composition of the alloy and thermal-kinetic conditions of crystallization. If the metal base is multi-phase, large amount of defects of different nature is originated in the forming oxide films. It leads to cracking of these films, lowering of their protective function during operation and to complete destruction of product surface.

This investigation is aimed on examination of the effect of boron additives and cooling conditions of the alloys in a mould on phase composition of cast iron, chemical composition of the phases, as well as on structure and parameters of structural components.

Material and technique of the investigations

Complex alloyed white cast iron of Fe–C–Cr–Mn–Ni–Ti–Al–Nb system [21, 22] modified by boron in the amount 0.005%; 0.01%; 0.02%; 0.03% was the material in this investigation. The alloys were molten in the IST-006 induction furnace with basic lining and then cast in different mould types: dry and wet sand-loam moulds (SLM) and block mould. Cooling rate made 3–10 °/min in the crystallization interval for the dry SLM, 8–12 °/min for the wet SLM and up to 30 °/min for the iron block mould.

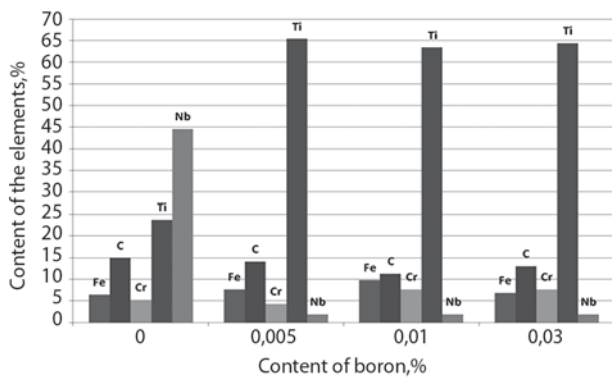


Fig. 1. Content of carbides (Ti, Nb, Cr, Fe)C

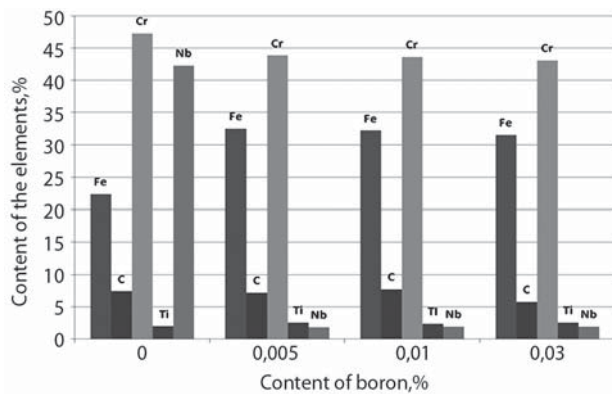


Fig. 2. Chemical composition of eutectic carbides M₇C₃ depending on boron content

Chemical composition of the samples was determined using Baird emission spectrometer and OBLF QSG 750 spectrometer.

Iron structure and phase composition were examined using metallographic method (light microscope MEIJI 2700) and X-ray method (diffractometer DRON-UM1 with co-

balt K α emission). Quantitative metallographic analysis was conducted using Thixomet PRO image analyzer. Chemical composition of the alloy phase components was determined with scanning electronic microscopes TESCAN VEGA II XMU using electron microprobe analyzers.

Obtained results and their discussion

Cast iron phase composition presents (in initial state, without boron additives) α -phase (ferrite), γ -phase (austenite), M₇C₃ carbides and MC carbides. MC carbides are crystallized at first from melt during solidification of white cast iron, then solid solution dendrites are crystallized, and afterwards the consequent eutectic reaction occurs with forming of austenite-chromium-carbide eutectics [18, 19].

The structure of initial cast iron consists of superfluous complexes of niobium carbide and titanium (Nb, Ti)C, solid solution dendrites, eutectics and M₇C₃ secondary carbides. The results of X-ray structural analysis have displayed that boron addition has led to variation of the phase composition of the metallic base from the dual-phase (α - and γ -phases) to the completely single-phase (γ -phase). The structure of modified cast iron contains primary complex titanium carbides, austenite dendrites, eutectics and NbC secondary carbides.

Boron modification influenced on the type of secondary carbides, and secondary hardening in the mould occurs owing to extraction of dispersed complex niobium carbides (without boron, but owing to chromium carbides).

Electronic microprobe analytical investigations have shown that primary carbides are the complex ones — (Ti, Nb, Cr, Fe)C, while boron additives vary the chemical composition of carbides: niobium content decreases from 44 to 2% and titanium content increases from 24 to 65% (see fig. 1).

Boron addition also leads to variation of the chemical composition of eutectic carbides and increase of boron additives is accompanied by rise of Fe content in eutectic carbides, while amount of niobium and chromium in these carbides decreases (see fig. 2).

Carbides (Ti, Nb, Cr, Fe)C are located mainly in inter-axial space of austenite dendrites. Parameters of the primary carbide phase of cast iron have been examined (see tab. 1). The special technique of Thixomet PRO image analyzer was used for evaluation of the F form factor which is the criterion of compatibility of the primary phases. The form factor, or compatibility factor *F* is the relation between the perimeter of carbide particles and their square. Carbide particles with strongly developed surface and, respectively, strong input of its perimeter, are characterized by less form factor in comparison with compact form carbides. The larger is *F*, the most compact are carbides. The form of carbide inclusions with *F* \geq 0.6 is close to a ball-type form.

No. of sample	Type of form	Parameters of carbide phase MC					
		Volumetric part V, %	Length L, μ m	Square S, μ m ²	Distance between carbides, μ m	Average diameter, μ m	Form factor <i>F</i>
1**	dry*	3.38	3.45	16.4	96	11.2	0.49
	wet	4.9	3.20	12	88	9.8	0.50
	bl. md	5.4	1.31	4.5	28	8.5	0.55
2	dry	3.06	2.35	1.2	157	4.88	0.58
	wet	4.30	1.99	4.45	159.7	3.6	0.60
	bl. md	4.26	1.02	0.9	89.3	2.4	0.65
3	dry	2.90	2.07	4	229.9	4.75	0.60
	wet	3.73	1.92	3.04	248.5	2.23	0.66
	bl. md	3.94	0.99	0.92	136.7	1.8	0.67
4	dry	2.61	1.52	2.58	253	4.30	0.63
	wet	4.22	1.27	1.56	148.7	2.01	0.65
	bl. md	4.11	0.901	0.78	108.6	1.57	0.65
5	dry	3.17	1.53	2.83	174.2	4.64	0.60
	wet	4.34	1.35	2.13	138.2	2.45	0.60
	kok	4.6	1.10	1.63	81.7	1.98	0.64

* Тип формы: dry — dry SLM; wet — wet SLM, bl. md — block mould.
 **Numbers of samples: 1 — 0% B; 2 — with 0.005% B; 3 — with 0.01% B; 4 — with 0.02% B; 5 — 0,03% B.

Increase of the cooling rate during solidification varies the form and size of carbides. Carbides (Nb, Ti, Cr, Fe)C become less branched, their dispersity and compatibility increase.

Rise of boron content in cast iron up to 0.01–0.02% leads to decrease of MC carbides amount (by 5–7%); square and diameter of carbides also reduce in average by 2 times (in dry SLM) and by 2–4 times (in a block mould) (see tab.1).

Liquid is enriched by boron during the primary crystallization, while boron surface active atoms are adsorbed on crystal surfaces with forming of adsorbing films that hamper diffusion of atoms to crystal surfaces and retard their growth. The alloy is overcooled with consequent forming of fine-dispersed structure during crystallization. The form of primary carbides varies from branched to compact one, and the form factor F (without boron additives) makes 0.49–0.55 in different form types. Rise of boron content and cooling rate during crystallization causes increase of the form factor F that is equal to 0.60–0.67 at boron addition 0.01–0.02%.

Positive effect of modification on parameters of carbides (Nb, Ti, Cr, Fe)C is observed after boron addition up to 0.02%. Introduction of large amount of modifier in the composition leads to enlargement and growth of carbides and reduction of the form factor, i.e. to structure coarsening. Thereby decrease of the modifying effect occurs and over-modification of “ageing” of the modifying effect takes place.

Austenite dendrites of different morphology are forming during solidification of cast iron, depending on the cooling conditions and boron additives. The following parameters (see **tab. 2**) were investigated in this work as dendrite structure characteristics: dispersity of the dendrite structure (δ), volumetric part of dendrites (V), distance between the axes of second order dendrites (λ_2), form factor (F), average dimensions of dendrites — square (S), length (ℓ) and width (β).

Dispersity of the dendrite structure δ is determined by total amount of axial and inter-axial areas in the length unit. Calculation of dendrites width β includes measurements of dendrite axes of low orders, and variation of their sizes determines variation of the dendrite structure in general.

Proposed parameters allow to conduct the quantitative evaluation of the cast iron dendrite structure depending on the conditions of crystallization and boron additives. It is expedient to use these parameters when any of the crystallization factors (cooling rate, modifying additives) is subjected to variation. Quantitative evaluation of the dendrite structure makes it possible not only to compare relative effect of different factors, but also to find the rational limits of usage of any factor. Usage of the suggested factors allows to evaluate quantitatively the dendrite structure and to determine the modification degree as well, i.e. to reveal relative (in %) variation of each criterion in modified cast iron in comparison with non-modified cast iron.

Determination of the modification degree is considered useful in several cases, e.g. for establishment of the possible quantitative relations between modification degree and crystallization conditions.

Table 2. Parameters of dendrite structure

No. of sample	Type of form	$S, \mu\text{m}^2$	$\ell, \mu\text{m}$	$\beta, \mu\text{m}$	$V, \%$	$\lambda_2, \mu\text{m}$	F	$\delta, 1/\mu\text{m}$
1	dry	2456	232	9.47	47	5.6–6.8	0.26	0.16
	wet	1893	195	9.10	45	4.8–5.6	0.26	0.19
	bl. md	89	41	2.21	44.6	1	0.28	1.0
2	dry	2416	201	9.15	44.5	5.2–7.1	0.28	0.16
	wet	1831	191	9.38	46.8	5,4	0.3	0.18
	bl. md	85	38,8	2.10	40	0.9	0.32	1.1
3	dry	1912	198	9.18	44.6	4.9–6.3	0.29	0.19
	wet	1714	185	8.95	45.6	2.8–3.2	0.3	0.33
	bl. md	36	19	1.89	37	–	0.33	–
4	dry	1581	130	10.50	45	2.5–3.8	0.34	0.18
	wet	1568	92	9.58	51	3.2	0.35	0.31
	bl. md	35	17	1.70	39	–	0.50	–
5	dry	1316	180	10.90	46	2.5–4.5	0.34	0.17
	wet	1718	132	9.84	47.2	4.1	0.39	0.24
	bl. md	77	32	2.27	41.8	–	0.45	–

Thus, relative variation of β parameter after addition of 0.01% of boron makes 3.1; 9.0 and 23.1% in dry and wet SLM and in the block mould correspondingly. Modification degree of the ℓ parameter after addition of 0.02% of boron makes 44.0; 52.8 and 58.5%. The degree of influence of the cooling rate without boron additions makes 15.9–78.9% on the ℓ parameter and 3.91–75.7% on the β parameter.

The volumetric part of austenite dendrites does not vary during modification, but it decreased by 20% in average with rise of the cooling rate of casting in the block mould.

Examinations of the morphology of eutectics and eutectic carbides have displayed that increase of boron additives provides decrease of the sizes of eutectic carbides and eutectic colonies, as well as growth of their amount in all form types. As soon as the cooling rate of casting in the block mould increases, the sizes of primary carbides, austenite dendrites reduce and volumetric part of eutectics rises (see **fig. 3**).

The volumetric part of eutectics increases from 51 to 65% in comparison with the casting center, while the volumetric part of austenite dendrites decreases from 48 to 35%. Austenite dendrites constitute in this area the separate and almost equiaxial non-branched grains. Length of this area is the larger, the higher is the cooling rate of casting in the block mould. Forming of dendrites of higher order is observed during examination of dendrites morphology variation deep inside a casting. In the center equiaxial dendrites prevail again. Boron addition in the alloy leads to retarding of forming the branches of higher order and dendrites get more compact and round form that is uniformly distributed and encircled by eutectics.

Conclusions

1. The effect of boron modification on phase composition and structure of heat- and wear-resistant white cast iron of Fe–C–Cr–Mn–Ni–Ti–Al–Nb system is displayed. It is shown that the phase composition of the metallic base changed from the dual-phase (α - and γ -phases) to the completely single-phase (γ -phase). The structure of modified cast iron is presented by the primary complex titanium carbides,

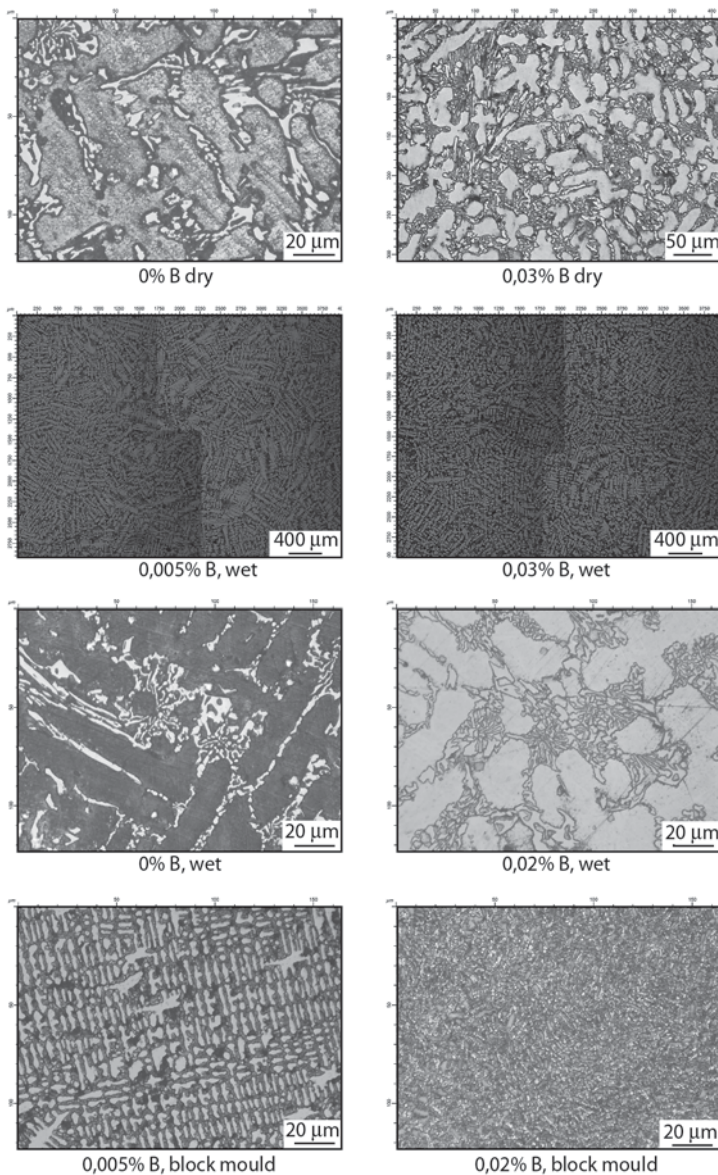


Fig. 3. Panoramic images of structures of cast iron after casting in different mould types, before and after boron modification

solid solution dendrites, austenite-chromium-carbide eutectics and secondary carbides NbC.

2. Boron addition changes essentially the chemical composition of primary and eutectic carbides: niobium content decreases substantially from 44 to 2% and titanium content in primary carbides (Nb, Ti, Cr, Fe)C increases from 24 to 65%. As a result, austenite is oversaturated by niobium, and secondary hardening in the mould occurs owing to extraction of dispersed NbC carbides.

3. The following parameters of primary phases (MC carbides and solid solution dendrites) were investigated by the methods of quantitative metallography: form factor (F), that is a criterion of compatibility of primary phases; dispersity of the dendrite structure (δ); volumetric part of dendrites (V); distance between the axes of second order dendrites (λ_2); average dimensions of dendrites — square (S), length (ℓ) and width (β). Usage of the suggested characteristics (parameters) allowed not only to provide quantitative evaluation of

the dendrite structure, but also to determine modification degree as relative (in %) variation of the each criterion in modified cast iron in comparison with non-modified iron. Quantitative relation between modification degree and crystallization conditions were established as well.

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DESTRUCTION MECHANISM OF CASTING GRAPHITE IN MECHANICAL ACTIVATION

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ABSTRACT

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Key words:

graphite, mechanical activation, destruction, plastic deformation, slipping plane, twinning, cast iron, burn-in, non-stick coating.

Development of the technologies allowing to improve the quality of initial materials is considered as the actual problem of casting and foundry production at present time. This tendency is connected with working and depletion of existing and operating deposits. Natural graphites are subjected to crushing, comminution, concentration and other operations during their preparation. Each of these operations is realized using special equipment, and their transition to the higher technological level requires additional expenses. Thereby, mechanical activation seems to be the most prospective method that does not need to include additional equipment in the technological chain of materials preparation. This process is accompanied by varying of crystal lattice energy in the processing material and is connected with forming of different structural defects (such as dislocations and vacancies), leading to forming of the new separation surfaces. The energy is reserved in such way and then it is spent for strengthening of chemical and physical-mechanical reactions during consequent fabrication of products (including non-stick coatings) on the base of activated materials, and it was proved convincing in the works. Many investigations in this field have examined only varying of parameters depending on activation time, without any discussion about the destruction mechanism of the particles. This work was aimed on examination of the destruction mechanism of natural graphite during mechanical activation from the point of view of crystallography. Natural crystalline graphite from Zavalyevskoe deposit has been chosen for investigations. The destruction mechanism has been studied on large oval graphite plates with maximal diameter 1.5 mm. Graphite activation was realized in the AGO-2 mill of planetary-centrifugal type. The activation procedures are discussed in the paper. Metallographic analysis via transmission electronic microscope UEVM-100K was used for determination of the mechanism of crack origination in graphite particles.

Natural crystalline graphite from Zavalyevskoe deposit containing of oval graphite plates with maximal diameter 1.5 mm and small particles (about 10%) with more complicated and elongated form has been chosen for investigations. Size and total surface of particles, their distribution on fractions has been determined by the method of light laser screening in Novosibirsk institute of solid state chemistry and mechanochemistry on PRO-7000 unit.

The form and micro-shape of particles has been determined using transmission electronic microscope UEVM-100K. It was established that destruction of particles during graphite mechanical activation occurs via the mechanism similar to destruction during usual forging. At the same time it was noted that two main types of plastic deformation (slipping and twinning) are observed in mechanical activation owing to strong deformation of graphite crystals under the effect of balls. Fracture planes coincide with slipping planes, while fracture is caused by the defined stress value perpendicular to the fracture surface.

Introduction

Creation of the technologies, allowing to improve the properties of initial materials, and fabrication of non-stick coatings on the base of these materials, allowing to improve quality of cast products, remains the actual problem of casting production at present time [1–3].

Carbon-containing materials, i.e. natural graphites are subjected to crushing, comminution, concentration etc. operations during their preparation [4–8]. Each of these technological stages is conducted using special equipment, and their transition to the higher technological level requires additional energy consumption and labour efforts [9–12].

Mechanical activation is considered as one of the most prospective methods that does not need introduction of additional equipment in the technological chain for materials preparation [11, 13–16].

Usage of this technology is accompanied by varying of crystal lattice energy of the processing material; it can be connected with forming of different defects of the structure (dislocations, vacancies) that result in forming of the new separation surfaces [11, 16–19]. Energy reserved in such way is consumed on increase of chemical and physical-mechanical reactions during consequent manufacture of products, i.e. non-stick coatings, on the base of activated material.

The paper [20] presents the results of examination of the effect of time activation on geometrical parameters of natural crystalline graphite. It was displayed in this case that the most