

The effect of boron on the amount and type of carbides in chromium white irons

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Abstract: The effect of boron, in the amounts of 0.26, 0.39, and 0.59 wt.%, on the volume fraction and structure of carbides in Cr white irons was examined. It was demonstrated that the addition of boron can change the microstructural characteristics of white iron containing about 13 wt.% Cr. With increasing boron content, the volume fractions of M_3C carbide increase, but the volume fraction of M_7C_3 carbide remains unchanged. The addition of boron tends to produce hard borides and/or borocarbides. It also prevents the formation of pearlite, which results in alloys possessing good wear resistance.

Keywords: chromium white iron, boron, carbides, borocarbide.

INTRODUCTION

The metal matrix plays a key role in the behaviour of high chromium white irons known as wear resistant materials under conditions of strong loading, whereas in other cases the behaviour of these materials depends on the type, fraction, size and morphology of the carbide phase.^{1,2} Carbide, or cementite, is an extremely hard, brittle compound of carbon with either iron or strong carbide forming elements, such as chromium, vanadium or molybdenum. Massive amounts of carbides increase the wear resistance of cast iron, but make it brittle and very difficult to machine. Dispersed carbides in either lamellar or spherical forms play an important role in providing strength and wear resistance in as-cast pearlitic and heat-treated irons.

Depending on the chemical composition of a particular high chromium white iron, its structure may contain M_7C_3 , M_3C and $M_{23}C_6$ carbides. Since their chemical and morphological characteristics differ, the exploitation properties of the white cast iron depend on the type of carbide prevailing in the structure.^{3–5} For this reason all the recent investigations, aimed at controlling and improving the exploitation properties of high chromium white irons were directed at studying the changes in the carbide phases as a function of the present alloying elements.^{6–9}

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Boron is interesting as an alloying element in chromium white irons. It is more known as a microalloying element of steel, where it is applied in the amounts of several tens to several hundreds of ppm-s. There, its role is to ensure the necessary hardenability of austenite. However, since the application of carbidizing elements has become popular in the investigation practice of improving the properties of chromium white irons properties, it became normal to perform experiments with boron, bearing in mind its properties, especially the structural and electrochemical ones.

Nevertheless, there are only a few published results concerning the influence of boron on the structure and properties of chromium white irons. The aim of the investigations carried out so far was to explore the influence of boron on the structure and wear resistance of white iron up to 0.4 mass % in 13Cr-4Mn alloy (the examinations were performed on bar-shaped samples of dimensions 12×12×60 mm)¹¹ and 0.11–1.26 mas % in 17Cr-2.7 C-0.7Mo alloy (the examinations were performed on rod-shaped samples of diameter 20 mm).¹²

The results of these examinations showed that boron changes the thermodynamic conditions of the formation of the carbide nucleus, and that it especially favours the formation of M₃C and M₂₃C₆ carbides in the structure of chromium white irons. Apart from the formation of these carbides, boron also ensures high hardenability, *i.e.*, the transformation of austenite into martensite. Such a structure ensures good abrasion wear resistance, but simultaneously causes brittleness. The dimensions and morphology of the examined samples were such that they enabled high cooling rates, compared with the much larger cross sections that are of great interest concerning the application of these materials, such as, for example, 'digging teeth'. Thus, the aim of this work was to examine the influence of boron in the amount of 0.26, 0.39 and 0.59 wt.% on the volume fraction and type of carbides present in the structure of 13Cr-2.3C chromium white irons, under much smaller cooling rates, which are achieved in samples of much larger cross sections.

EXPERIMENTAL

The chemical compositions of the examined alloys are given in the Table I.

TABLE I. Chemical compositions of the examined alloys

No	Contents of alloying elements/wt.%									
	C	Si	Mn	P	S	Cr	Ni	Mo	V	B
1	2.19	0.65	2.50	0.018	0.036	13.26	0.29	0.35	0.20	0.00
2	2.20	0.73	2.66	0.012	0.029	12.89	0.14	0.37	0.21	0.26
3	2.25	0.66	2.87	0.016	0.029	13.30	0.30	0.43	0.21	0.39
4	2.39	0.53	1.58	0.019	0.027	13.24	0.28	0.31	0.18	0.59

Alloy No. 1 is the basic alloy, and the alloys No. 2, 3 and 4 contain boron in the amount of 0.26, 0.39 and 0.59 %, respectively. The contents of other alloying elements were approximately the same for all the examined alloys, as can be seen from Table I.

The examined alloys were melted in a 50 kg medium frequency induction furnace, and cast in moulds prepared by CO₂ technology with the morphology of digging teeth as shown in Fig. 1. The examined samples were cut out from such castings, at positions where the thickness of the teeth was approximately 50 mm.



Fig 1. –Digging tooth– The casting from which the test samples were cut out.

For optical metallography, the samples were ground, polished to a 1/4 mm diamond finish, and then etched with picric acid solution (1 g) in distilled water (100 ml) with methanol (5 ml).

The total volume fraction and type of carbides present in the structure of the examined alloys were determined by a Siemens D500 diffractometer with Ni-filtered $\text{CuK}\alpha$ radiation. The volume fraction of carbides was determined from the ratio of the diffraction maximum intensity belonging to a particular phase and total diffraction maximum intensity of all the existing phases. In this experiment, there were two structural constituents – carbide phases and metal matrix, so the volume fraction of the carbide phase was determined according to the following formula:

$$\% C = I_1 / (I_1 + I_2).$$

where: I_1 – is the diffraction maximum intensity corresponding to the examined carbide phases and I_2 – is the diffraction maximum intensity that belongs to the metal matrix.

The peak area was used as the intensity measure. For phase identification and measurement of the peak area, the program DIFRAC AT[®] was used. The scanning rate was 2.5°/min.

In order to confirm independently the results obtained by the X-ray diffraction analysis, the following additional experiments were carried out:

1. To determine the type of carbides, selective etching of the samples in the Murakami reagent was performed.^{7,13}

2. To determine the total volume fraction of carbides, as well as the volume fraction of each type of eutectic carbide, quantitative analysis was performed using an automatic Leica Q500MC analysis system.

The microhardness of the metal matrix and eutectic carbides was measured under a load of 0.49 N (0.05 kg) on a Leitz microscope.

RESULTS

Microstructure of examined alloys

The microstructures of the examined alloys are shown in Fig. 2. Detailed analysis confirmed that the structure obtained in this investigation is typical for chromium white cast iron. The base alloy (No. 1) is characterized by the presence of primary austenitic dendrite and a eutectic that consists of eutectic carbides and eutectic austenite. The structure of the other alloys also consists of a primary phase and an eutectic, but the following differences can be noticed:

– With increasing boron content, the dendritic structure slowly disappears, while the primary phase obtains the form of isolated islands surrounded by the eutectic (Fig. 2 – c, e, g).

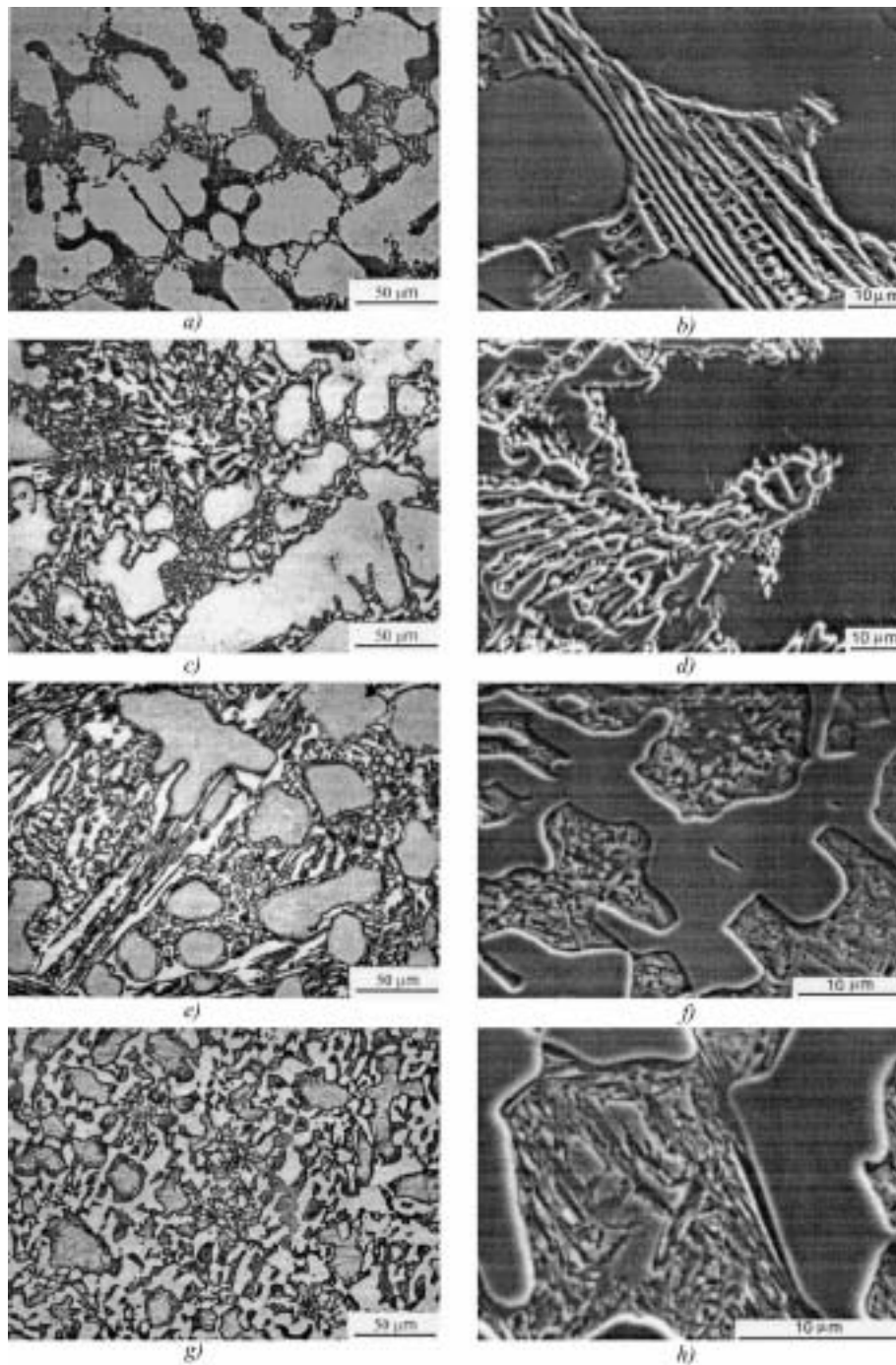


Fig. 2. Microstructure: a), b) – alloy No. 1; c), d) – alloy No. 2; e), f) – alloy No. 3; g), h) – alloy No. 4 (a, c, e, g – optical microphotographs; b, d, f, h – SEM).

– In the presence of boron, the primary phase becomes a mixture of austenite and martensite. The degree of martensite transformation increases with increasing boron content. The development of this transformation can be seen on the SE microphotographs (Fig. 2 – d, f, h).

X-Ray diffraction analysis of the examined alloys

X-Ray diffractograms of the alloys No. 1, No. 2 and No. 4 are presented in Fig. 3a – c.

Looking at the diffractograms in Fig. 3, it can be noticed that the diffractograms of the alloys No. 1 and No. 2 are very similar and clear. This is the consequence of good crystallization of the structural phases.

On the diffractogram No. 1, the peaks labeled with A belong to austenite (diffraction cards 23–298)*. Apart from austenite, two types of eutectic carbides have been detected in the structure of basic alloy (alloy No. 1 in Table I):

- $(\text{Cr,Fe})_7\text{C}_3$ (diffraction card 5-720) peaks labeled with *, and
- Fe_3C (diffraction card 35-772) peaks labeled with o.

By measuring the area under the highest peak, which belongs to austenite, positioned at the angle $2\theta = 50.191$ and the area under the highest peak, which belongs to the carbide, positioned at the angle $2\theta = 45.091$, the volume fraction of carbide alloy No. 1 is obtained and its value is approximately 9%. The rest up to 100% is the volume fraction of austenite (primary and eutectic).

According to the diffractogram belonging to alloy No. 2 (Fig. 3b), the austenite (peaks labeled with A), the carbide $(\text{Cr,Fe})_7\text{C}_3$ (peaks labeled with *) and carbide Fe_3C (peaks labeled with o) also constitute to the structure of this alloy.

Proceeding with the calculations in the same way as for alloy No. 1, *i.e.*, by measuring the area under the highest peak which belongs to austenite (detected at $2\theta = 43.374$) and the area under the highest peak that belongs to the carbide (detected at $2\theta = 44.450$), the volume fraction of carbide in alloy No. 2 is obtained to be 20.5% (see Table II).

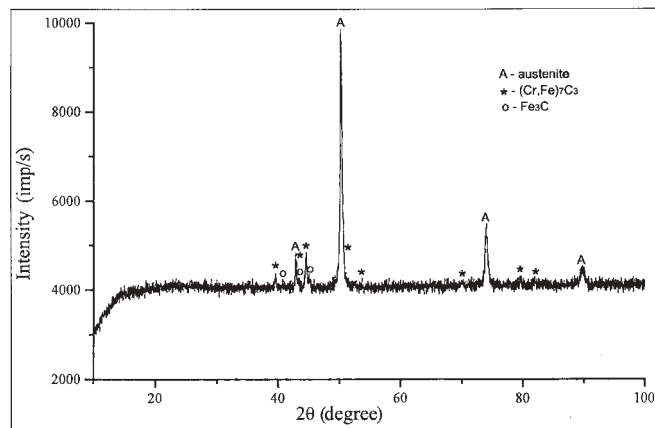
TABLE II. Results of quantitative microstructure analysis

No.	Volume fraction of the structural phases/vol.%				
	M*	EC*			X-Ray diffraction
		$\text{M}_7\text{C}_{3\text{eut}}$	$\text{M}_3\text{C}_{\text{eut}}$	EC_{total}	
				Quantitative analysis	
1	86.75	13.25	–	13.25	9.0
2	80.04	17.47	2.49	19.96	20.5
3	75.23	NE*	NE	24.77	NE
4	48.73	16.25	35.02	51.27	47.4

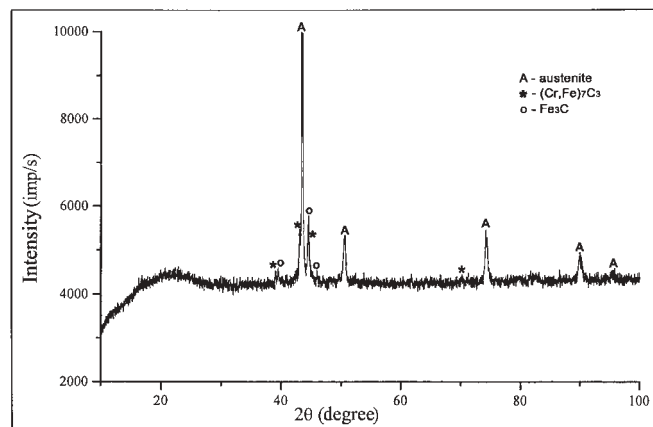
*M-metal matrix; EC-eutectic carbides; NE-no examined

The diffractogram which belongs to alloy No. 4 is different from the previous two. Due to the presence of a greater number of phases, the number of diffraction lines is much

* JCP data base



a)



b)

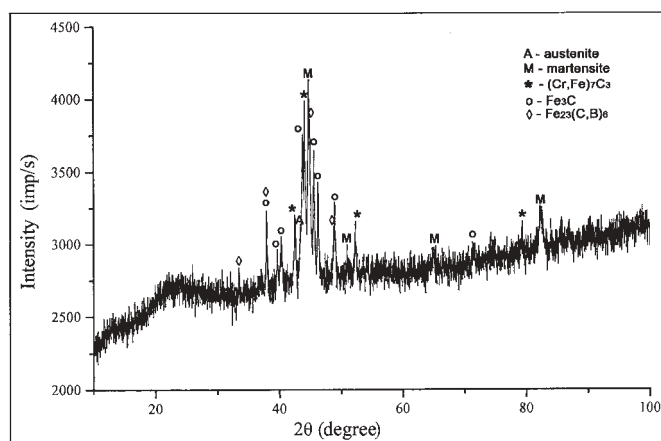


Fig. 3. X-Ray diffractograms of: a) alloy No. 1; b) alloy No. 2; c) alloy No. 4.

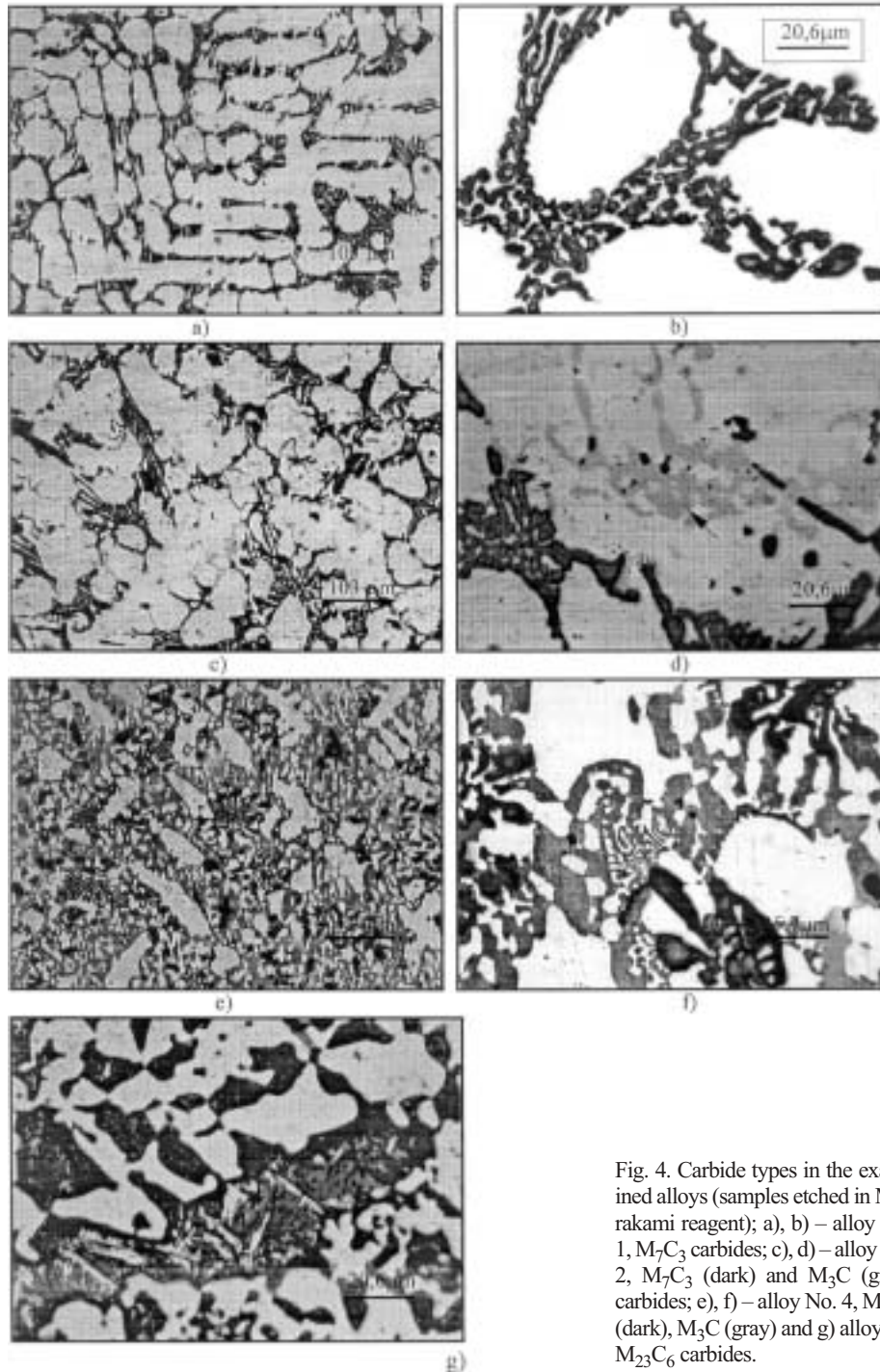


Fig. 4. Carbide types in the examined alloys (samples etched in Murakami reagent); a), b) – alloy No. 1, M_7C_3 carbides; c), d) – alloy No. 2, M_7C_3 (dark) and M_3C (gray) carbides; e), f) – alloy No. 4, M_7C_3 (dark), M_3C (gray) and $M_{23}C_6$ carbides.

larger which makes this diffractogram much more complex, compared with the diffractograms of alloys No. 1 and No. 2.

The peaks labeled with M belong to martensite. The peak labeled with A belongs to austenite, the peaks labeled with * belong to the $(\text{Cr, Fe})_7\text{C}_3$ carbide, the peaks labeled with o belong to the Fe_3C carbide and the peaks labeled with \diamond belong to the $\text{Fe}_{23}(\text{C, B})_6$ secondary carbide (diffraction card 12-570).

By measuring the area under the highest peak which corresponds to the metal matrix (in this case it is the peak that arising from martensite) detected at an angle $2\theta = 44.758$ and the area under the highest peak that belongs to the carbide phase, detected at $2\theta = 44.070$, the volume fraction of the carbide phase in alloy No. 4 was determined to be 47.4 %.

Quantitative analysis of the structural phases

Additional carbide type identification was performed by selective etching of the samples of the examined alloys in Murakami reagent (Fig. 4). Using the same alloys, the volume fraction of each eutectic carbide types was detected (Table II), by measuring the segments produced by the test lines on the examined phases. The structure of alloy No. 1 etched by Murakami reagent is presented in Fig. 4a and b. Only the M_7C_3 carbide in an amount of 13.25 % is present.

On the microphotograph of alloy No. 2 (Fig. 4c and d), the presence of two carbide types (dark phase – M_7C_3 and gray phase indicated by the dark arrow in Fig. 4d – M_3C) can be noticed. The volume fraction of the carbide phase in alloy No. 2, obtained by measuring the segments produced by the test lines on the examined phase, is 19.96 % (17.47 % – M_7C_3 and 2.49 % – M_3C , Table II). This result is absolutely in accordance with the result obtained by X-ray diffraction analysis, where a value of 20.5 % was obtained.

Bearing in mind the great similarity between alloy No. 2 and alloy No. 3 detected during the examination of the microstructural and mechanical properties, in order to reduce the number of tests, the volume fraction of each particular type of eutectic carbides in the third alloy was not analyzed. Only the total quantity of carbide phase was calculated to be 24.77 % (see Table II).

Finally the presence of three types of carbides: eutectic M_7C_3 (dark phase – Fig. 4e and f) and M_3C (gray phase – Fig. 4e and f) and secondary M_{23}C_6 (small dark lines in the gray phase (metal matrix) – Fig. 4g) were detected. In this alloy, the total carbide volume was 51.27 % (Table II), which is in accordance with the results obtained by X-ray diffraction analysis, where a volume of 47.4 % was determined.

From X-ray diffraction analysis and selective etching, it was concluded that the eutectic M_7C_3 and M_3C carbides are present in the structure of all the alloys. In alloy No. 4, apart from eutectic carbides, secondary M_{23}C_6 carbides are also present (Fig. 3c and Fig. 4g).

Microhardness of the structural phases

The results of the measurement of the microhardness are given in Table III. As can be seen from Table III, increasing the boron content from 0 to 0.59 % causes the metal matrix

microhardness to increase from 428 to 640 HB, and the microhardness of the eutectic carbides to increase from 992 to 1645 HB. It can also be noticed that at lower boron contents, the rate of increase of the microhardness is low, whereas in the fourth alloy with the maximal boron content the microhardness had increased drastically.

TABLE III. Results of the microhardness of the structural phases

No.	Microhardness of the structural phases	
	Metal matrix	Eutectic carbide
1	428	992
2	434	1041
3	486	1076
4	640	1645

DISCUSSION

The experimental results presented in this paper show clearly that boron has a significant influence on the microstructure of chromium white irons. This fact is primarily reflected in the change of the ratio of carbide and/or boron-carbide phases present in the examined alloys. With increasing boron content, the volume fractions of the M_3C carbide and/or $M_3(C,B)$ boron-carbide increase significantly. This clearly demonstrates the capability of boron to create complex carbides and/or boron-carbides in chromium white irons.

Besides the change of the volume fractions of the carbide and/or boron-carbide phases, with the increasing boron contents the type of carbides that prevails in the structure of the examined alloys also changes. In the basic alloy (No. 1 – Table I), apart from the prevailing M_7C_3 carbide, the eutectic carbide M_3C is also present. The amount of the M_3C carbide is very small and it is detected only qualitatively by X-ray diffraction analysis, but not quantitatively by stereological analysis.

With increasing boron content, the volume fraction of some eutectic carbides changes slowly, so the fraction of the M_7C_3 carbide in the second alloy with 0.25 % B was slightly increased and remained at the same value even with further increasing of the boron content, whereas the fraction of the M_3C carbide increases constantly with increasing boron content and achieves a value of 35.02 % in alloy No. 4.

Generally speaking, the addition of boron in the examined alloys causes the following:

- The fraction of the M_7C_3 carbide remains practically unchanged;
- The fraction of the M_3C carbide increases significantly;
- The microhardness of the prevailing eutectic carbide in alloy No. 4 with 0.59 % B also increases significantly;
- Only in alloy No. 4 with 0.59 % B do the secondary $M_{23}C_6$ carbides appear. By diffraction analysis, it was shown that these carbides are $M_{23}(C,B)_6$ carbides.

If the assertion from the literature that boron influences the structure of the chromium white irons^{11,12,14} where $M_3(C,B)$ and $M_{23}(C,B)_6$ carbides have also been detected is

taken into account, it is logical to conclude that the boron embeds itself into the crystal lattices of the M_3C and $M_{23}C_6$ carbides, but not into the crystal lattice of the M_7C_3 carbide. Thus, the complex $(Fe,Cr)_3(C,B)$ and $(Fe,Cr)_{23}(C,B)_6$ carbides are created. This would practically mean that boron substitutes a certain number of carbon atoms in the eutectic M_3C carbide. The atoms of carbon replaced by boron are transferred into the rest of the melt, ensuring an increase of the saturation of the melt in carbon. These are thermodynamic conditions for the formation of a greater number of the nuclei of carbide particles that will, after solidification, ensure an increase of the fraction of the carbide phase in the alloy.

The supposition that the atoms of boron substitute the atoms of carbon is related with the similarity of the radii of the atoms of boron and carbon, as well as the significant electronegativity of boron, which ensures good conditions for the formation of strong bonds between the atoms of boron and the surrounding atoms of carbon. Such strong bonds ensure extremely high hardness of the newly created carbides, which was demonstrated by measuring the microhardness of the structural phases (Table III).

The newly created eutectic carbide could have the formula $(Fe,Cr)_3(C_xB_y)$. If it is assumed that all the boron (0.59 %) embeds itself into the lattice of the M_3C carbide, then for the 35.02 % of the M_3C carbide present in alloy No. 4 (Table II), by stoichiometric calculation, the value $y_{max} = 0.5$ is obtained.

However, the whole amount of the boron, at least in alloy No 4, will not really be embedded into the lattice of the M_3C carbide because in that alloy the presence of secondary $M_{23}(C,B)_6$ carbides has already been detected by X-ray diffraction analysis. Besides, bearing in mind the significant hardenability with increasing boron content, most probably a part of the total amount of boron remains in the solid solution. This means that for alloy No 4 $y_{max} < 0.5$.

CONCLUSIONS

1. In 13Cr–2.3C chromium white irons, boron in amounts up to 0.39 % has a slight tendency to form complex boron-carbides. Further increasing of the boron content, up to 0.59 %, significantly increases this tendency of boron.
2. In the structure of the basic Fe–Cr–C alloy, M_7C_3 carbides prevail. A small quantity of M_3C carbides is also present. By increasing the boron content from 0.26 to 0.59 % the amount of M_3C carbide increase from 2.49 to 35.02 %, while the volume fraction of the M_7C_3 carbides remains unchanged. Secondary $M_{23}C_6$ carbides appear in the structure of alloy No. 4.
3. It is suggested that boron resides on carbon sublattice sites, *i.e.*, it embeds itself into the lattice of the M_3C eutectic carbide and the $M_{23}C_6$ secondary carbide, probably forming complex compounds of the type $M_3(C,B)$ and $M_{23}(C,B)_6$.

ИЗВОД

УТИЦАЈ БОРА НА КОЛИЧИНУ И ВРСТУ КАРБИДА У ХРОМНИМ БЕЛИМ ГВОЖЂИМА

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У раду је испитиван утицај бора, у количини од 0,26, 0,39 и 0,59 теж.%, на запремински удео у структури карбида присутних у хромним белим гвожђима са око 13 теж. % Cr. Показало се да се додатком бора мењају микроструктурне карактеристике испитиваних белих гвожђа. Са повећањем садржаја бора повећава се запремински удео M_3C карбида док запремински удео M_7C_3 карбида остаје непромењен. Присуство бора обезбеђује стварање тврдих борида и/или боркарбида, али и спречава стварање перлита, што ове легуре чини отпорним на хабање.

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