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The effect of boron on the stereological characteristics of the structural phases present in the structure of the 13% Cr white iron

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In this paper, the results of the examination of the effect of boron, in the amounts of 0.26, 0.39 and 0.59 wt%, on the stereological characteristics of the structural phases present in the structure of 13%Cr–2.3%C white iron, are reviewed. The examined stereological characteristics were: volume fraction of phases, dendrite arm spacing-DAS and size of eutectic carbides.

It has been concluded that with the increasing of boron content, the volume fraction of the matrix of austenite partially transformed into martensite decreases, whereas the volume fraction of the eutectic carbides increases. The increasing of the boron content also decreases the value of DAS, but at the same time the eutectic carbides become coarser.

1. Introduction

The properties of the most often used hypoeutectic and eutectic chromium white irons—wear resistant materials—depend directly on the stereological characteristics of the structural phases present in these alloys. Their structure consists of the matrix of austenite or mixture of austenite and martensite, and the eutectic carbides [1]. The main stereological characteristics of the structural phases are volume fractions, their size and dendrite arm spacing—DAS.

Apart from the working conditions in which the chromium white irons are applied (the abrasive properties, stresness, etc.), taking into account the stereological characteristics of the structural phases present in these materials facilitates significantly the estimation of their exploitation behaviour. For example, taking into account the volume fractions ratio of the structural phases present in the chromium white irons it is possible, at least partially, to estimate their wear resistance and toughness—the properties relevant for the wear resistant materials. However, if the dendrite arm spacing (which is used as the parameter for the quantitative estimate of the alloy's structure fineness) is also determined, as well as the size of the structural phases, than the picture is much clearer. For the wear resistant materials the size of eutectic carbides is the most important. Big carbides in the structure of chromium white irons ensure good wear resistance but at the same time make them brittle and difficult to machine. Thus the presence of fine, dispersed carbides in the structure of the chromium white irons is desirable.

The ways to change the structural characteristics of the structural phases are: alloying, changing the solidification conditions or applying thermal treatment [2–15].

In this paper, the results of the examination of the effect of boron on the stereological characteristics of the structural phases present in the 13%Cr–2.3%C white iron, are given.

There are few published results concerning the influence of boron on the structure and properties of chromium white irons. The aim of the investigation 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 the 13Cr-4Mn alloy [7], up to 0.6 mass% in the 28Cr-2.4C [8] and 0.11–1.26 mass% in the 17Cr-2.7C-0.7Mo alloy [15]. In all the cases mentioned above, the examinations have been performed at great cooling rates. The results given in this paper have been obtained in the examination of influence of boron up to 0.59% on the structure and wear resistance of 13Cr-2.3C chromium white irons, under much lower cooling rate, achieved in the samples of much larger cross-sections. The examination results confirmed that significant improvement of wear resistance of these alloys was obtained at the boron content of 0.59%.

2. Experiment

Chemical compositions of the examined alloys are given in Table I.

The alloy No. 1 is the basic alloy, and the alloys No. 2, 3 and 4 contain boron in the amounts of 0.26, 0.39 and 0.59%, respectively. The contents of other

TABLE I Chemical compositions of the examined alloys

No.	C	Si	Mn	P	S	Cr	Ni	Mo	V	B
	Contents of alloying elements, mass%									
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

alloying elements were approximately the same for all the examined alloys, which can be seen in the Table I.

The examined alloys were melted in a 50 kg medium frequency induction furnace, and cast in moulds prepared by CO_2 technology with the morphology of digging teeth. The examined samples were cut out from such castings, at positions where the thickness of the teeth was approximately 50 mm.

For optical metalography, the samples were ground, polished to a 1/4 μm diamond finish, and than etched with picric acid solution (1 g) in distilled water (100 ml) with metil-alcohol (5 ml). The plane of polish was perpendicular to the direction of heat loss. Those samples were analyzed by the automatic LEICA Q500MC analysis system in order to examine stereological parameters of the structural phase—volume fraction of primary austenite in the base alloy and mixture of primary austenite and martensite in the rest of the alloys and eutectic carbides, (volume fraction of eutectic austenite, which in the presence of boron also partially transformed to martensite, is calculated as a rest up to 100%), dendrite arm spacing—DAS and the size of eutectic carbides—L. All the data have average values of 100 visual areas.

3. Results

3.1. Microstructure of examined alloys

Microstructures of examined alloys are presented in the Fig. 1.

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

- With the increase of boron content, the dendrite structure slowly disappears, while the primary phase gets the form of isolated islands surrounded by eutectic cells (Fig. 1c, e, and g).
- In the presence of boron, the primary phase becomes the mixture of austenite and martensite. The degree of martensite transformation increases with the increase of the boron content. The flow of this transformation can be seen on the SE microphotographs (Fig. 1d, f, and h).

3.2. Volume fraction of structural phases

The volume fractions of the structural phases present in the examined alloys versus the boron content are given in the Table II.

TABLE II Results of quantitative microstructure analysis

	Volume fraction of structural phases, vol%						
			EC[a]				Eutectic carbide size
No.	PP[a]	EA[a]	M_7C_3	$M_3(C,B)$	Σ	DAS (μm)	(μm)
1	69	17	13	–	13	31	3
2	62	18	17	2	19	28	4
3	56	19	–	–	25	28	4
4	30	19	16	35	51	22	9

[a] PP-primary austenite in alloy 1 and mixture of austenite and martensite in alloys 2, 3 and 4; EA-eutectic austenite in alloy 1 and mixture of austenite and martensite in alloys 2, 3 and 4; EC-eutectic carbides.

As it can be seen, the increasing of the boron content in the alloy from 0 to 0.59% causes the decreasing of the volume fraction of the primary austenite partially transformed to martensite from 69 to 30 vol%, as well as the increasing of the volume fraction of the eutectic carbides from 13 to 51 vol%. Having in mind the fact that two types of eutectic carbides are present in the structure of examined alloys—M_7C_3 and M_3C (Fig. 2), it was observed that in the presence of boron only the volume fraction of the M_3C carbide increases, whereas the increase of the volume fraction of the M_7C_3 carbide is very small and can be considered insignificant (Table II) [16]. At the same time, the increasing of the volume fraction of the eutectic austenite, which is also partially transformed to martensite from 17 to 19 vol% can be considered insignificant.

3.3. Dendrite arm spacing—DAS

The results obtained by the measuring of the dendrite arm spacing—DAS are also given in the Table II. The reduction of the values of DAS from 31 to 22 μm as the result of adding 0.59% of boron shows that boron plays the role of "modifier", i.e., it makes the structure finer.

The effect of boron on the distribution of the secondary dendrite arm spacing, as well as on total interval of the distribution of dendrite segments values, is showed on the Figs 3 and 4.

By analysis of the Figs 3 and 4 it can be concluded that the dispersion of values of dendrite arm spacing decreases by the increasing of boron content in the alloy, and in the alloy No. 4 it is the smallest. In that alloy, 63% are the dendrites, whose size is in the range from 10 to 30 μm, where 42% are the dendrites, whose size is in the range from 10–20 μm. In the alloy No. 1, 50% are the dendrites, whose size is in the range 10–30 μm. However, in this alloy, the dendrites, whose size is in the range from 20–30 μm are present in greater quantity—26%. In the alloy No. 2, the fraction of the dendrites, whose size is in the range from 10 to 30 μm is 50% (27% are the dendrites, whose size is in the range 10–20 μm), and in the alloy No. 3 the fraction of the dendrites, whose size is in the range from 10 to 30 μm is 48% (28% are the dendrites, whose size is in the range from 10 to 20 μm).

In the Figs 3 and 4 it can also be seen that the width of the total interval of dispersion of dendrite segments values becomes smaller with the increasing of the boron content.

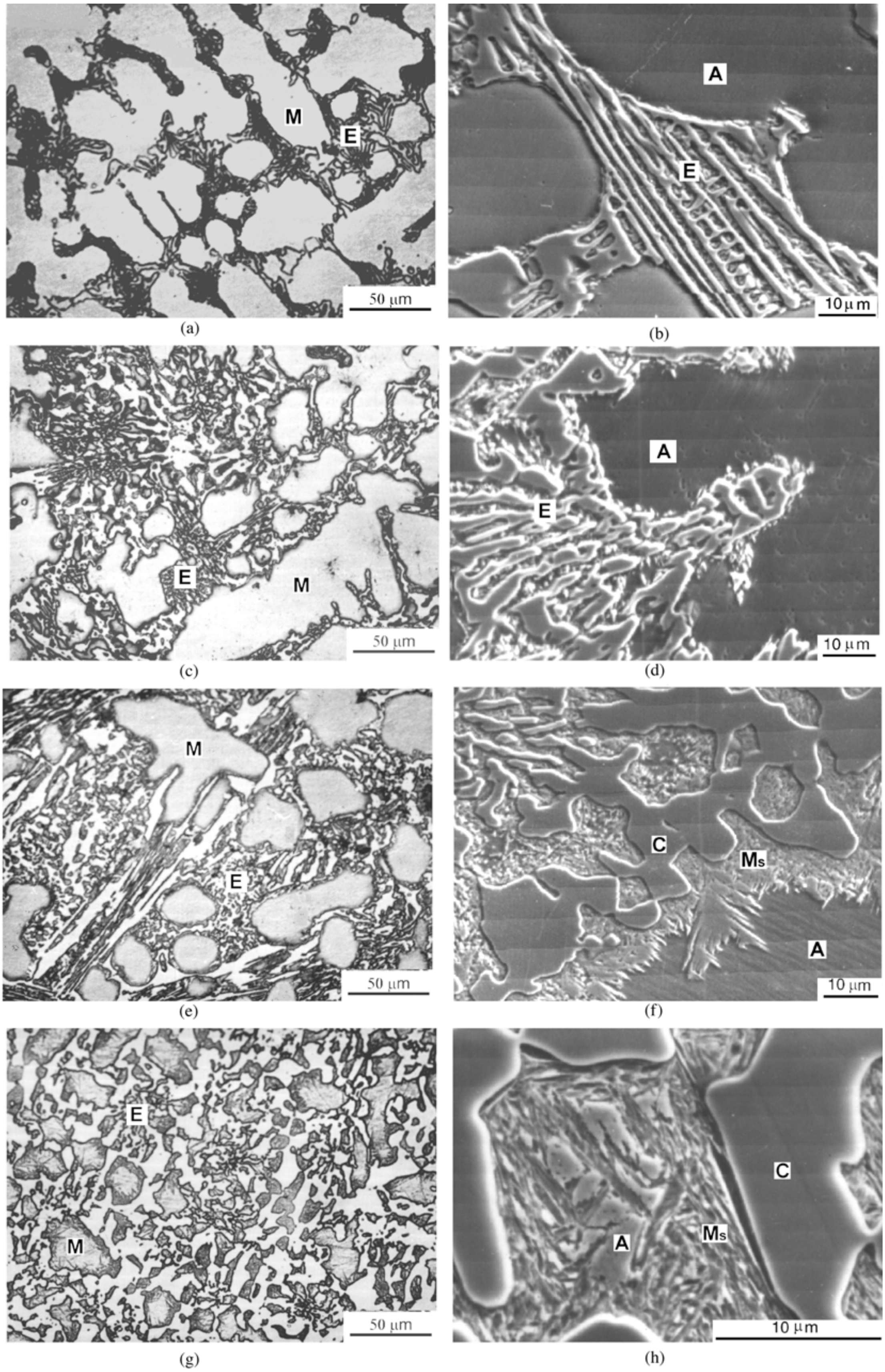


Figure 1 Microstructure: (a), (b)-alloy 1; (c), (d)-alloy 2; (e), (f)-alloy 3; (g), (h)-alloy 4; (a, c, e, g-OM; b, d, f, h-SEM); M-matrix (austenite in alloy 1 and mixture of austenite and martensite in the alloys 2, 3 and 4), C-eutectic carbide, E-eutectic, A-austenite, Ms-martensite.

3.4. Size of eutectic carbides

In the Table II, the size of eutectic carbides versus boron content in the alloy is given. It is evident that with the increasing of the boron content, the size of eutectic carbides also increases.

In the Fig. 5a it can be seen that in the structure of the alloy No. 1, the carbides whose size is in the range from 1 to 3 μm constitute the greatest fraction. The quantity of carbides whose size is in the range 1–2 μm is somewhat greater than

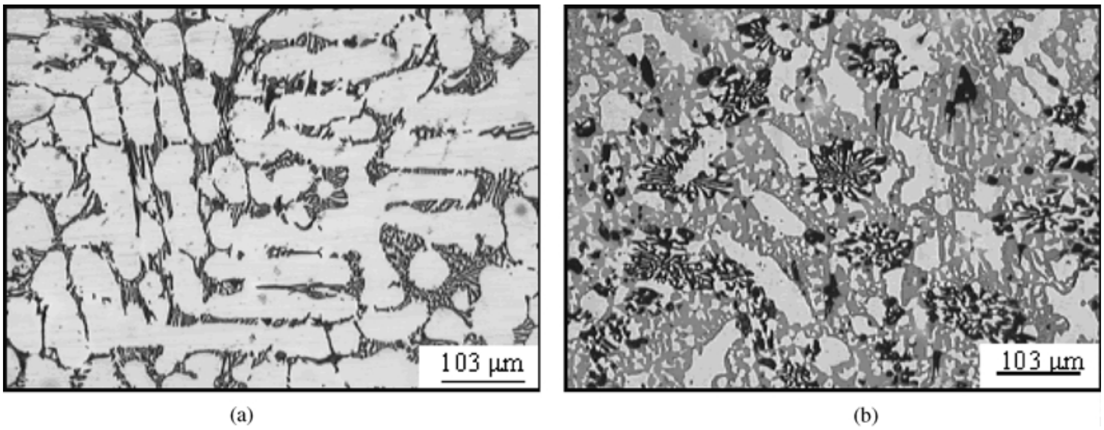


Figure 2 Types of eutectic carbides in examined alloys (samples etched in the Murakami reagent): (a) alloy 1—M_7C_3 carbides (dark phase); (b) alloy 4—M_7C_3 carbides (dark phase) and M_3C carbides (gray phase).

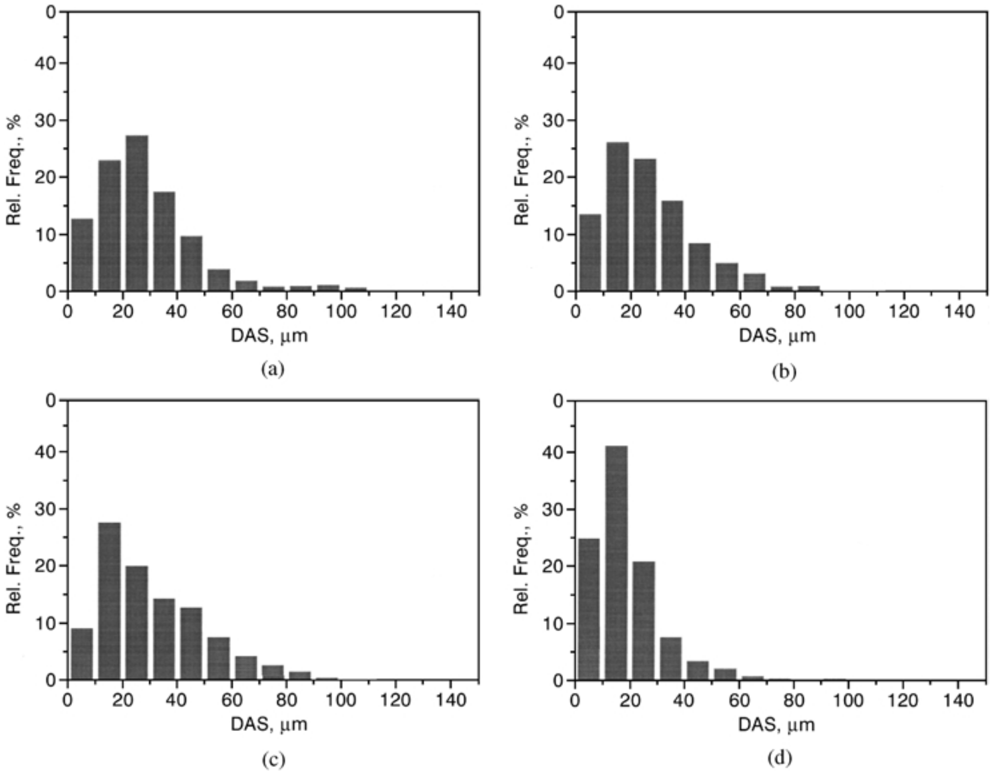


Figure 3 Histograms of the distribution of dendrite arm spacing versus boron content in the alloy: (a)—alloy 1; (b)—alloy 2; (c)—alloy; 3 (d)—alloy 4.

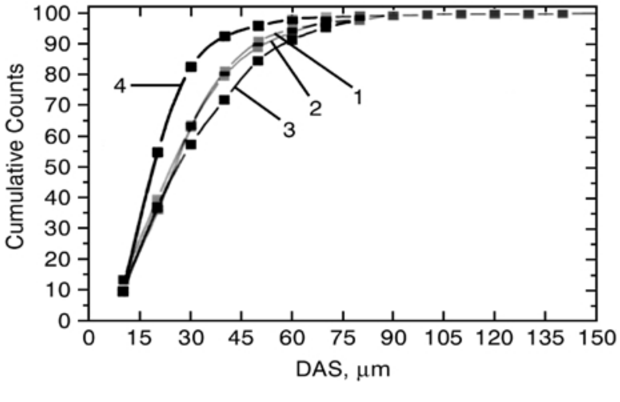


Figure 4 Cumulative curves of the distribution of dendrite arm spacing versus boron content in the alloy: 1-alloy 1; 2-alloy 2; 3-alloy 3 and 4-alloy 4.

the quantity of carbides whose size is in the range 2–3 μm.

In the alloy No. 2 (Fig. 5b) the carbides, whose size is in the range 1–3 μm also constitute the greatest fraction. However, in this alloy the carbides, whose size is in the range 2–3 μm are present in somewhat greater quantity. In the structure of the alloy No. 3 (Fig. 5c) the carbides, whose size is in the range 1–2 μm prevail again, whereas in the alloy No. 4 (Fig. 5d) the carbides become coarser. In that alloy, the carbides, whose size is in the range 2–4 μm are present in the greatest quantity. The carbides, whose size is in the range 1–2 μm are present in small quantity (8%), and the rest are the carbides, whose size is greater than 4 μm.

With the change of the carbides size, the degree of their dispersion also changes. In the Fig. 6 that change is demonstrated. It can be seen that the total interval of dis-

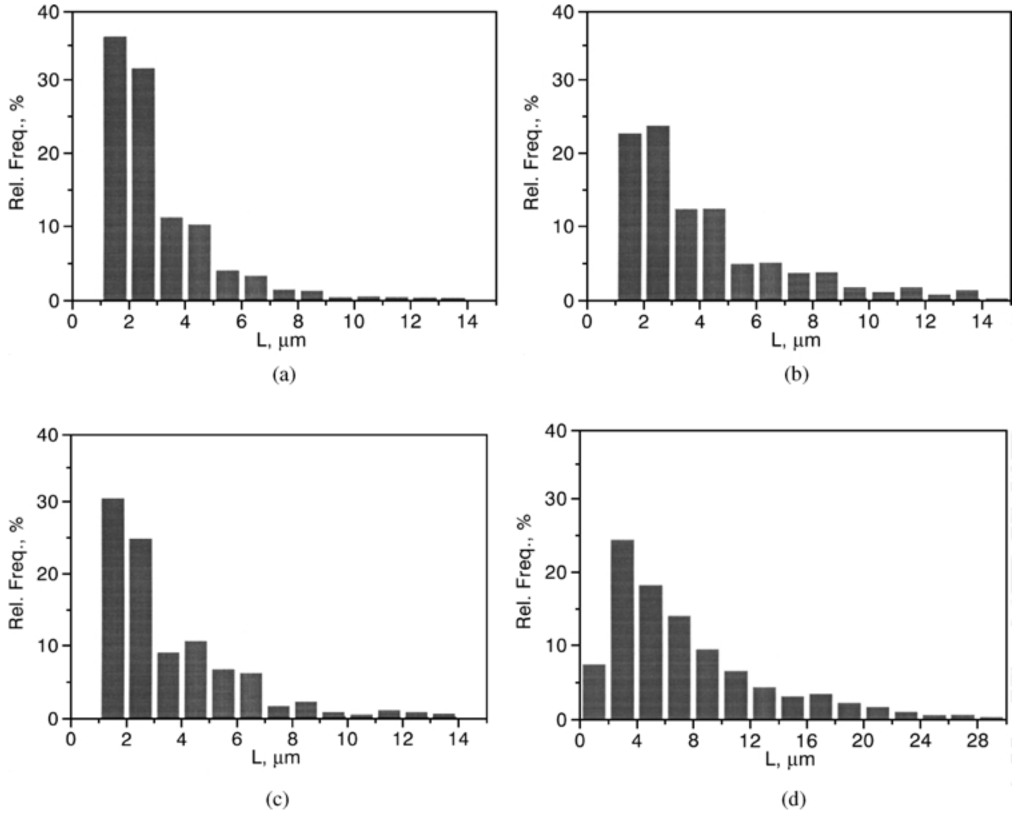


Figure 5 Histograms of the distribution of eutectic carbides size versus boron content in the alloy: (a)—alloy 1; (b)—alloy 2; (c)—alloy 3 and (d)—alloy 4.

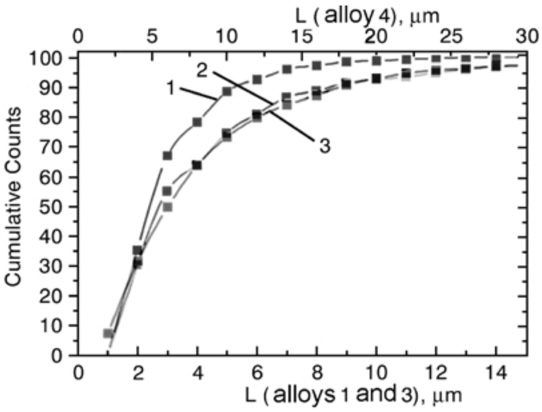


Figure 6 Cumulative curves of the distribution of eutectic carbides size versus boron content in the alloy: 1-alloy 1; 2-alloy 3; 3-alloy 4.

persion of the carbide segments values becomes wider with the increasing of the boron content in the alloy.

4. Discussion

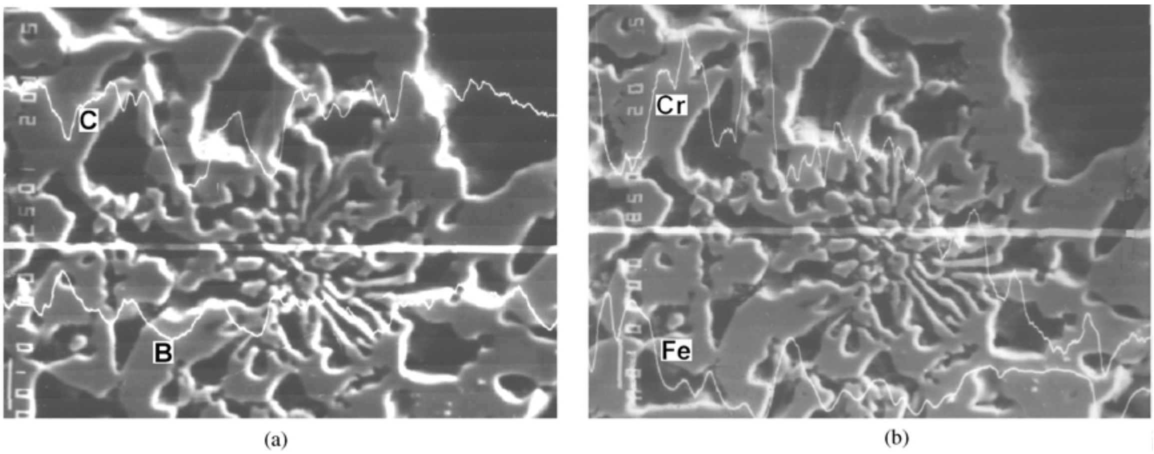
The basic alloy, which was the subject of the examination, belongs to the group of hypoeutectic Fe-Cr-C alloys. It is a two-component alloy whose structure is made of the austenite matrix and the eutectic cells, which consist of the eutectic austenite and the eutectic carbides.

By the examining of the stereological characteristics of the structural phases present in the alloys, it was concluded that significant changes in the structure of the basic alloy took place because of the presence of boron. Those changes include the change of the structure phases volume fractions. The fraction of the primary austenite partially transformed to martensite decreases and that of the eutectic carbides increases (Table II). That means that during the solidification of the primary austenite, in the rest of the melt in the presence of boron, the thermodynamic and concentration conditions for the formation of stable eutectic carbides are met earlier. It can be observed in the Fig. 7 that in that case the atoms of boron embed themselves in the lattice of the eutectic carbides.

The significant increase of the volume fraction of the M_3C carbide (compared with the volume fraction of the M_7C_3 carbide) leads to the conclusion that the atoms of boron embed themselves in the crystal lattice of the M_3C carbide. In such a way, the M_3C carbide in the presence of boron becomes extremely hard and stable boro-carbide $(Fe,Cr)_3(C,B)$. The supposition that the boron atoms substitute a part of the carbon atoms in the M_3C carbide is based on the similarity of the radii of boron and carbon atoms, as well as strong boron electronegativity, which facilitates the formation of strong bonds between boron atoms and surrounding carbon atoms. Such strong bonds provide to the newly formed $(Fe,Cr)_3(C,B)$ boron carbide extremely high stability, which can also be concluded on the basis of the microhardness value (Table III).

Such hard carbides together with significant quantity of martensite provide very good wear resistance to alloy 4 (Table IV) but at the same time this alloy became very brittle.

By stechiometric calculus it was concluded that the quantity of 0.59% of boron was enough to form eutectic $(Fe,Cr)_3(C,B)$ carbides in the quantity that was detected.



(a) (b)

Figure 7 Distribution of (a) C and B and (b) Cr and Fe in the carbide phase of the alloy 4 (deep etched sample).

The change of the volume fractions of the structural phases directly effects on their size. In the basic alloy where the volume fraction of the primary austenite is 69%, there is enough room for the formation of the austenite dendrites and they grow up freely in the heat loss direction. However, in the alloys that contain boron, the presence of greater quantity of eutectic carbides "mechanically" limits the growth of dendrites of the primary phase, changing the direction of their growth or even stopping it. Thus, in the alloys that contain boron, the primary phase looses its dendrite shape and it appears as a set of isolated islands separated by eutectic cells. In other words, the primary phase becomes finer, which is proven by results of measuring of dendrite arm spacing—DAS (Table II).

As for the carbides size, by the quantitative microstructure analysis it was concluded that by the increasing of the boron content in the alloy, the carbide phase gets coarser (Table II). This practically means that with the increasing of the boron content in the alloy, the number of critical nuclei of the carbide phase increases, and at the same time the carbides grow more intensively as well. Such a conclusion is correlated with the examination results of the distribution of eutectic carbides size.

TABLE III Results of microhardness of structural phases

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

TABLE IV Results of abrasion wear resistance

No.	Mass loss (g)	Volume loss (mm^3)
1	0.15	19.09
2	0.20	26.18
3	0.12	15.79
4	0.07	9.48

5. Conclusions

The presence of boron in 13% chromium white irons implies the following:

1. Greater volume fraction of eutectic carbides in the alloy's structure and the reduction of the volume fraction of the primary phase at the same time.
2. Size reduction of dendrite arms and consequently finer and more disperse structure of the matrix.
3. Less dendrites in the primary phase.
4. Coarser eutectic carbides.

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