

Research article

The influence of cooling rate on the structure and properties of castings of hypereutectic high-chromium cast iron when they are modified with B, Bi, Sb, Sn, Ca

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Abstract: The article presents the results of a study of the influence of B, Bi, Ca, Sn, and Sb additives on the structure, composition, and properties of individual phases and mechanical properties of castings made of hypereutectic high-chromium cast iron (HCCI), similar in composition to G-X300CrMo27-1 cast iron. Additives of these elements were introduced into the melt before cooling at an amount of 0.2 wt.%. The ingots were obtained at a melt cooling rate in the crystallization range of 0.083–0.116 °C/s and at 4.67–5 °C/s. When studying the structure, the parameters and proportion of primary carbides, and the proportion of eutectic carbides were determined and a description was given of the change in the austenitic matrix. Using microprobe analysis and microhardness measurements, changes in the composition and hardness of primary, eutectic carbides and the matrix were determined. Hardness HV, bending strength, and abrasive wear resistance were determined. It has been shown that depending on the cooling rate, the effect of these additives on the structure and properties of castings changes. The mechanism of influence of these elements on the process of crystallization of primary carbides in HCCI is considered. Based on the data obtained, it is proposed to use Ca as a modifying additive when producing castings from HCCI of a hypereutectic composition under slow cooling conditions, and B under fast cooling conditions. This makes it possible to increase the wear resistance of castings.

Keywords: hypereutectic high chromium iron; high chromium cast iron; modifier; abrasive wear resistance; carbide $(\text{Cr,Fe})_7\text{C}_3$

1. Introduction

High-chromium cast irons (HCCI), due to their high wear resistance, are widely used for the manufacture of parts intended for mining, metallurgical, and cement equipment. An increase in the service life of such parts can significantly reduce the economic costs of mining, metallurgical, and processing enterprises [1].

The improved wear resistance of HCCI is achieved by a combination of the structure and properties of the phases that form these alloys. These cast irons are a martensitic matrix with inclusions of Me_7C_3 , Me_{23}C_7 carbides after austenitization and quenching [2]. It is known that the wear resistance of cast iron improves with increasing dispersion of the carbides included in their composition, and with an increase in the proportion of carbides [3]. Meanwhile, the eutectic point is at a carbon concentration of 3.2–3.4 wt.% according to the phase diagram of Fe-Cr-C [4], with a Cr content of 18–28 wt.%. Accordingly, when the alloy contains a higher amount of carbon, it becomes hypereutectic. In this case, primary chromium carbides $(\text{Cr,Fe})_7\text{C}_3$ appear in the structure. The crystals of this compound have an acicular shape and are significantly larger in size than precipitates of eutectic carbides. The size of such crystals increases significantly with a decrease in the crystallization rate [5,6]. The tendency of $(\text{Cr,Fe})_7\text{C}_3$ carbide to transcrystallization significantly worsens the mechanical properties of castings from these cast irons. For this reason, hypereutectic chromium cast irons can be considered promising if dispersed crystals of primary $(\text{Cr,Fe})_7\text{C}_3$ carbides are formed. When these alloys are cast in sand molds with a refrigerator, in graphite or steel molds, a fine-grained structure can be achieved near the heat-removing surface. However, as one moves away from such a surface, a significant increase in the size of primary carbides occurs [7], as a result of which the mechanical properties over the cross section of the casting differ significantly [8], and this is undesirable. In this regard, it becomes necessary to exert a volumetric effect on the crystallizing melt for casting large castings from hypereutectic chromium cast irons. The review paper [9] considers various methods of volumetric action on hypereutectic high-alloy chromium cast irons. One of these methods of effect is the introduction of modifying additives. This method is widely used in industry for the production of castings from steels, cast irons, and non-ferrous metal alloys.

There are works to study the influence of modifying additives such as B additives [10,11], rare earth elements—Ce, La, Y [12–17], and carbide-forming elements such as Ti [18,19], W [20,21], V [22,23], Nb [24,25], Mo [26]; which do not form metal carbides—Cu [27], Si [28] and complex modifying additives [3,13], on the structure and properties of HCCI castings. These elements, dissolving in the melt, have a different effect on the crystallization process of hypereutectic HCCI, as a result of which the properties of the castings change. The sources cited to indicate that the addition of some of these elements can affect the size of the primary carbide $(\text{Fe,Cr})_7\text{C}_3$ without affecting their morphology. At the same time, there is a change in mechanical properties and wear resistance. At the same time, there are also contradictions when some authors describe an increase in the characteristics of alloys with the introduction of certain additives while others indicate the absence of effect or even deterioration of properties. This is probably due to the difference in the conditions of the experiments and, in particular, in connection with the difference in the cooling rate of the castings in the

crystallization interval. At the same time, an increasing number of publications describe an increase in the characteristics of alloys with the addition of complex modifiers. The most interesting results were obtained by adding a complex of modifying (N + Ti + V + REE (rare earth elements)-Mg) additives to hypereutectic HCCI by the authors of [3]. As a result, they were able to reduce the size of the primary Me_7C_3 carbide by 60 %. It resulted in a 75 % increase in wear resistance in dry sliding conditions and 98.1 % in corrosive wear conditions. The authors of this work believe that the refinement of the primary carbide Me_7C_3 can be explained by two mechanisms: (1) refinement due to heterogeneous nucleation of TiC and VC and (2) due to the adsorption of a combination of elements—N, Ti, and V on the preferred growth surface of Me_7C_3 (0001).

Besides, the direction of modification of hypereutectic HCCIs with inoculants added to the melt in the form of refractory particles of TiC [29], TiAlB [15,30], B_4C [31], and rare earth oxides [30,31] are of great interest. A noticeable decrease in the size of primary carbides and an increase in mechanical properties and wear resistance were achieved under laboratory conditions, with the introduction of such powders. However, these modifiers are considered unreliable since the uniform distribution of powders in the melt is very difficult under industrial conditions [9].

An analysis of these and other scientific papers on the problem of how to modify the structure of hypereutectic HCCI indicates that no effective modifying additives have been found at present that could significantly affect the morphology and size of primary carbides and especially in large-sized castings. Also, the mechanism of the effect of various elements on the growth of precipitates of primary carbide $(\text{Cr,Fe})_7\text{C}_3$ is not completely clear. This problem is also pointed out by the authors of the review article [9]. Since HCCIs are multicomponent, the mechanism of the effect of additionally introduced additives can be diverse. Besides additional alloying of the phases that form cast iron, it is possible to separate new phases and adsorb them on the surface of growing grains and local supercooling of the melt. New carbides are formed with the introduction of carbide-forming elements, as a result, the distribution of carbon changes, and the proportion of primary carbide $(\text{Cr,Fe})_7\text{C}_3$ decreases. These and other possible mechanisms for modification of the HCCI structure are described in [9].

Very encouraging results on the modification of the structure of low-chromium cast iron of eutectic composition were shown by the addition of Bi under conditions of use in complex modifiers, including RE [32]. It was found that Bi, along with RE, is localized at the carbide/austenite interface which slows down growth. It suggested that the modification mechanism is based on the fact that the accumulation of Bi and RE atoms near the surface of the carbide plate reduces the temperature of the local solid/liquid equilibrium that slows down its growth.

Sn and Sb in gray cast iron promote the formation of finer lamellar pearlite [33,34]. The papers [34,35] describe the effect of the addition of these elements on the shape of graphite precipitates in gray cast iron. It was shown in [36] that the addition of 0.045 wt.% Sn together with 0.15 wt.% Nb to the composition of gray cast iron contributes to an increase in its wear resistance.

The effect of small B additives on the structure and properties of chromium cast irons is also of practical interest. It is believed [37] that B reduces the solubility of C in austenite, causing higher precipitation of C, hence increasing the number of nuclei before eutectic precipitation of carbide. The authors of [38] described the effect of boron additions from 0.18 to 1.25 wt.% B on the structure and properties of eutectic HCCI. They showed that the maximum level of strength and wear resistance of castings is achieved at a content of 0.23 wt.% B (0.1%–0.3%). The structure of cast iron becomes hypereutectic with an increase in the boron content to 1.25 wt.% while the hardness increases and the impact strength decreases. At the same time, the article [39] shows a positive effect of significantly

higher boron concentrations on the hardness and impact toughness of castings from white cast irons containing 4 wt% Cr. At the same time, it was pointed out in [40] that even small boron impurities increase the hardness but decrease the impact strength of HCCI.

Despite the significant development of research aimed to find effective structure modifiers for hypereutectic HCCI, industrially used modifying additives for these cast irons have not yet been developed. At the same time, taking into account that castings from hypereutectic HCCI are characterized by a higher corrosion and wear resistance compared to widely used hypoeutectic HCCI [41], it makes further research aimed to find more efficient and economical ways to modify the structure of such cast irons relevant.

In this regard, it is necessary to study further the effect of various additives on the structure and properties of castings obtained under various cooling conditions to develop effective methods intended to modify hypereutectic HCCI. There is a need to expand understanding of the mechanism by which such additives affect the HCCI crystallization process. Bi, Ca, Sn, Sb, and B are more readily available for industrial use. The presence of evidence for the positive effect of small additions of these elements on the structure and properties of hypereutectic HCCI makes it important to continue research to clarify their effect under crystallization conditions that reproduce the production of thin-walled and thick-walled castings.

The aim of the research was to study the effect of B, Bi, Sb, Sn, and Ca additives in an amount of 0.2 wt.% on the structure and properties of ingots from hypereutectic cast iron of G-X300CrMo27-1 Grade under the conditions of its crystallization at a cooling rate of 4.6–5 °C/s and 0.08–0.11 °C/s. This work is a continuation of a similar work [14], in which the influence of small REE additives on the structure and properties of cast iron of a similar composition was studied.

2. Materials and methods

Two series of experiments were carried out with a hypereutectic cast iron alloy with a similar composition to the G-X300CrMo27-1 brand, but with increased chain voltage up to 4.1–4.2 wt.% (Table 1) for a standard increase in the proportion of primary carbides $(\text{CrFe})_7\text{C}_3$ in casting conditions. The effect of B, Sb, Bi, Ca, and Sn separately on the structure and mechanical properties of castings was assessed as part of the experiments. Additives of these metals in the amount of 0.2 wt.% were introduced into the melt at a temperature of 60–80 °C above the liquidus line and held for 5 min. This introduction mode for a modifying additive and holding the melt simulates the conditions of out-of-furnace modification. In the experiments, we tried to reproduce the conditions of crystallization in the production of large-sized thick-walled castings in sand casting molds and under the conditions to obtain castings in a chill mold. Accordingly, in the first series of experiments, the cooling rate during crystallization was 0.083–0.116 °C/s while the melt remained in an alundum crucible in the furnace. In the second series of experiments, the melt was poured into a graphite mold and obtained an ingot $\varnothing 24$ and 300 mm long. In this case, the melt cooling rate in the crystallization interval was 4.6–5 °C/s. In the first and second series of experiments, tests were carried out on a pre-melted alloy according to the method and using charge materials described in the article [14]. The conditions for obtaining samples in series 1 and 2 of the experiment reproduced the conditions described in [14].

Bi, Sb, and Sn were introduced into the melt in the form of pure elements (99.999 wt.% of the main component). B was introduced in the form of FeB ferroalloy with a concentration of 23 wt.% B.

Ca was introduced in the form of silicocalcium SC20 ferroalloy with a calcium concentration of 20 wt.%. In the case of ferroalloys, the required weight was calculated from the content of Ca and B. The obtained ingots were not subjected to destabilizing annealing and other types of heat treatment. The structure and properties of ingots after modification were compared with unmodified ingots (WMA). These ingots were obtained under identical conditions.

Table 1. Composition of chromium cast iron samples.

Alloy	Chemical composition, wt.%									
	Fe	Cr	C	Mo	Ni	Mn	Si	P	S	Ti
G-X300CrMo27-1	rest	23–28	3–3.5	1–2	≤1.2	0.5–1.5	0.2–1	≤0.1	≤0.06	-
HCCI used in experiments	rest	23–24	4.1–4.2	0.5–1	0.2–0.3	0.7–0.8	0.8	0.02	0.04	0.13

The distribution of modifying additives and the composition of the phases were studied with samples without preliminary etching of the structure on a Jeol JXA-8230 microprobe analyzer using energy dispersive spectroscopy (EDS) and wadedispersive spectroscopy (WDS) microanalysis systems. Since boron is identified by these methods only at its high concentrations, the potentiometric titration method was used to determine its content in the composition of carbides and the matrix. To do this, the samples were dissolved at room temperature in a solution of 100 mL HCl + 7 mL H₂SO₄ + 30 g CuSO₄ for a within 30 days. As a result, the matrix was dissolved, and the carbides settled on the bottom. The carbide powders thus obtained were repeatedly washed with distilled water. The analysis of cast iron and carbides made it possible to establish the content of boron in them.

The study of the microstructure, measurement of hardness and microhardness, wear resistance tests with determination of relative wear resistance were carried out according to the methods described in [14].

3. Results

3.1. Alloy microstructure analysis

The study of the microstructure of ingots obtained at a cooling rate in the crystallization range of 0.083–0.116 and 4.67–5 °C/s showed that their structure is characteristic of hypereutectic high-chromium wear-resistant cast irons (Figures 1 and 2). The structure is formed by needle-shaped primary carbide precipitates (FeCr)₇C₃, eutectic carbides (FeCr)₇C₃ of different morphology, and an austenitic matrix. Austenite is partially precipitated in the dendritic form at a cooling rate of 4.67–5 °C/s (Figure 2). At a cooling rate of 0.083–0.116 °C/s, part of the austenite undergoes decomposition with the formation of martensite and pearlite. Martensite precipitates predominantly at the interface between carbides and austenite. Pearlite begins to form in the center of the austenite grains. The reason for it is the uneven distribution of elements over the cross section of the austenitic matrix between carbide precipitates.

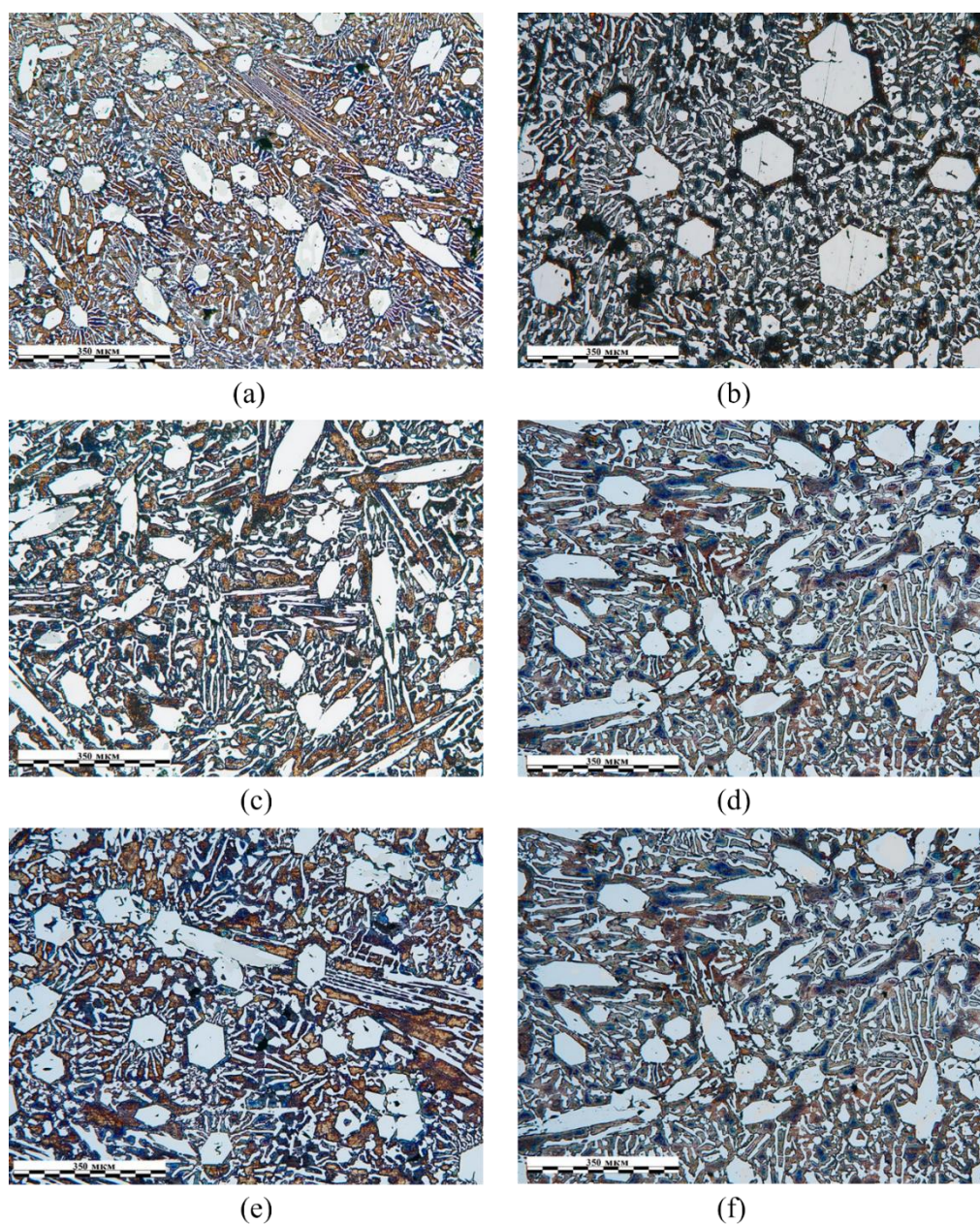


Figure 1. Effect of additives of 0.2 wt.% Bi, B, Ca, Sn and Sb on the microstructure of HCCI ingots obtained at a cooling rate 0.083–0.116 °C/s($\times 150$): (a) WMA; (b) B; (c) Ca; (d) Bi; (e) Sn; (f) Sb.

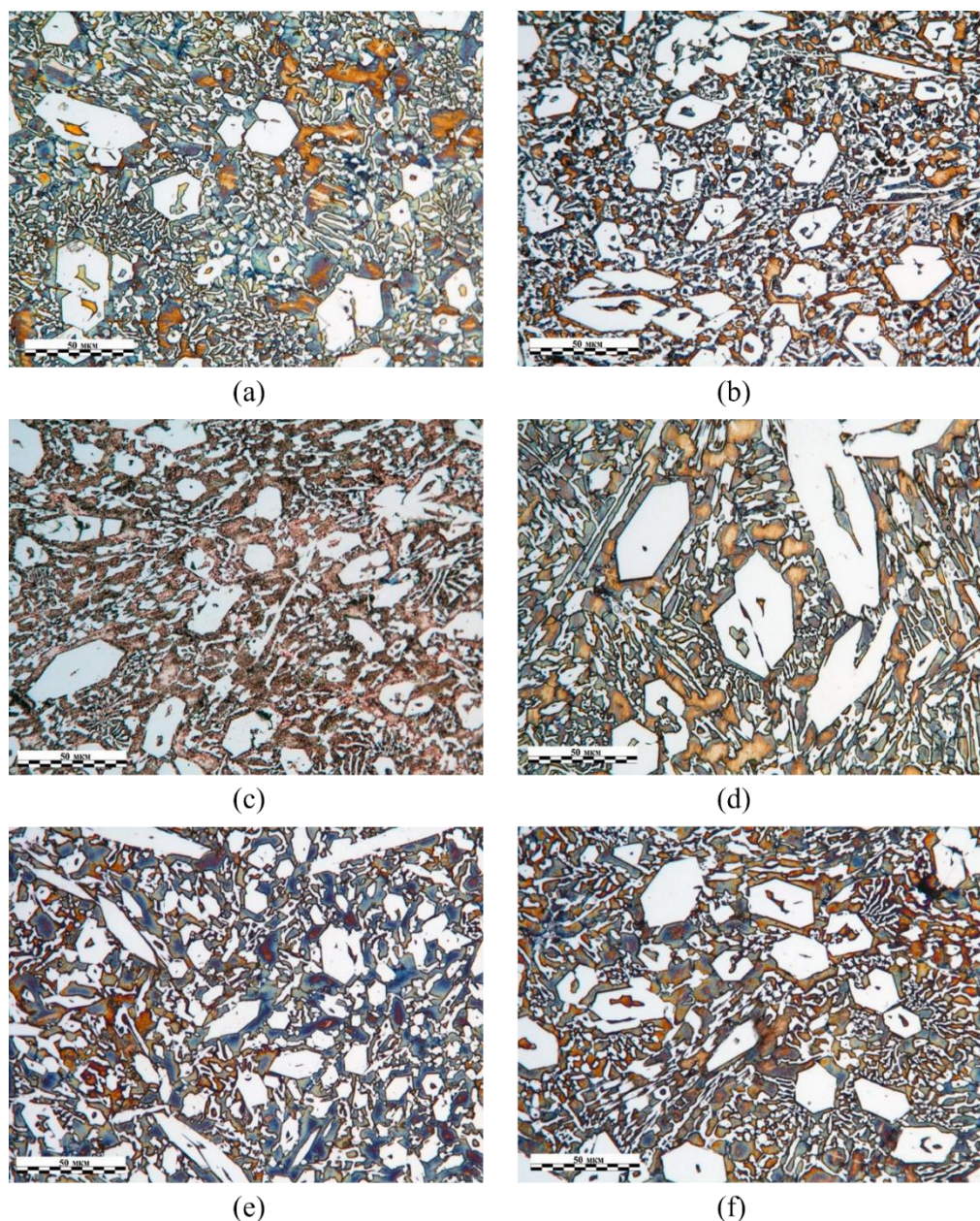


Figure 2. Effect of additives of 0.2 wt.% Bi, B, Ca, Sn and Sb on the microstructure of HCCI ingots obtained at a cooling rate 4.67–5 °C/s ($\times 750$): (a) WMA; (b) B; (c) Ca; (d) Bi; (e) Sn; (f) Sb.

It was found that the introduction of modifying additives (Bi, B, Ca, Sn and Sb) does not have a significant effect on the morphology of primary and eutectic carbides. In ingots obtained at a cooling rate of 0.083–0.116 °C/s, the proportion of eutectic carbides is 20–23 vol.%, and primary—14–19 vol.%. Bi and B additives have the greatest effect on the ratio of primary and eutectic carbides. Thus, the addition of Bi increases the proportion of eutectic carbides by ~2 vol.% and reduces the proportion of primary carbides by ~3 vol.%. The addition of boron increases the proportion of primary carbides by 2 vol.% and reduces the proportion of eutectic carbides by 1 vol.%. Additives of Ca, Sn, and Sb do not have a significant effect on the proportion of primary and eutectic carbides when compared with

an ingot without additives. In ingots obtained at a cooling rate of 4.67–5 °C/s, the proportion of eutectic carbides is 12.9–18.9 vol.%, and primary carbides—14.4–17.9 vol.%. In this case, the addition of boron reduces the proportion of eutectic carbides by ~2 vol.% and increases the proportion of primary carbides by ~3 vol.%. Additions of Ca and Sn increase the proportion of eutectic carbides by ~2 vol.% and reduce the proportion of primary carbides by ~2 vol.%. Bi addition does not have a significant effect on the proportion of primary and eutectic carbides when compared with an ingot without additives.

The introduction of Bi, Ca, Sn, and Sb additives leads to a decrease in the minimum cross-section of primary carbides by 6.7%–28.2% in ingots obtained at a cooling rate of 0.083–0.116 °C/s (Figure 3a). Under such crystallization conditions, the introduction of additive B causes an increase in the minimum cross-section of primary carbides by 49%. An increase in the minimum cross-section of a needle-shaped crystal leads to a significant increase in its cross-sectional area (by 290%) and a reduction in the total amount of precipitation of such carbides per unit volume of the ingot.

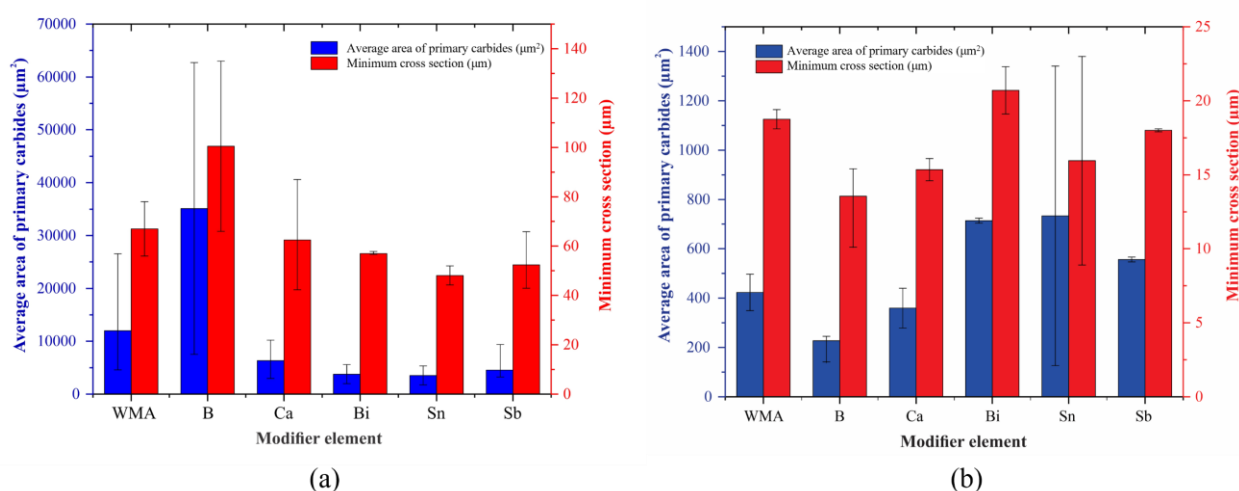


Figure 3. Effect of the modifying additive on the size of primary carbides $(\text{Fe,Cr})_7\text{C}_3$ in HCCI ingots obtained at different cooling rates: (a) 0.083–0.116 °C/s; (b) 4.67–5 °C/s.

Modifying additives have a different effect on the size of primary carbides in HCCI ingots obtained with a crystallization rate of 4.67–5 °C/s. Thus, the opposite effect is exerted by the introduction of B (Figure 3b) which results in a decrease in the minimum cross section of primary carbides by ~28%. At the same time, the additions of Bi, Sn, Sb, without significantly affecting the minimum cross section (+10%, –15% and –4%, respectively), lead to an increase in the cross-sectional area of primary carbides (by 69%, 73% and 32%, respectively) caused by the elongation of the needle-shaped crystals. The addition of Ca, as in the case of a low cooling rate, leads to a decrease in the minimum cross section and cross sectional area of primary carbides by 18% and 15% compared to the WMA sample.

Thus, the introduction of 0.2 wt % B, Ca, Bi, Sn, and Sb into the HCCI melt does not significantly affect the morphology of precipitates of primary and eutectic carbides $(\text{FeCr})_7\text{C}_3$ and on the degree of decomposition of austenite during the cooling of ingots. Depending on the cooling rate in the HCCI crystallization interval, the effect of B, Ca, Bi, Sn, and Sb additives on the size of primary carbide precipitates may differ. The effect of additive B changes most significantly with the cooling rate. The addition of this element during slow crystallization (0.083–0.116 °C/s) causes a significant increase in

the size of primary carbides in HCCI ingots. Under such crystallization conditions, the sizes of primary carbides are positively influenced by the additions of Ca, Bi, Sn, and Sb. At a high cooling rate (4.67–5 °C/s), a decrease in the size of primary carbides causes the introduction of B and Ca. Additives B, Ca Bi, Sn, and Sb refer to the proportions of primary and eutectic carbides. The most significant effect is exerted by the development of B, which does not depend on the cooling rate of the melt and leads to an increase in the proportion of primary carbides and a decrease in the proportion of eutectic carbides. To increase the proportion of eutectic carbides, the additions of Bi (at 0.083–0.116 °C/s), Ca, and Sn (at 4.67–5 °C/s) are introduced, while the proportion of primary carbides decreases. This indicates that when such measurements are carried out, a slight displacement of the eutectic point occurs.

3.2. Analysis of the content of the modifying additive in the composition of ingots and HCCI phases

Analysis of the composition of samples of HCCI ingots obtained in two cooling modes showed that the concentration of modifying Bi, Ca, Sb, and B additives in them differs from the specified one (Table 2).

Table 2. Actual concentration of modifying agents.

Experiment series number	Concentration. wt.%				
	B	Ca	Bi	Sn	Sb
1	0.159	0.151	not found	0.192	0.195
2	0.176	0.197	not found	0.171	0.120

A comparison of the phase composition of WMA castings obtained at two cooling rates indicates their differences (Tables 3–5). Thus, the content of Cr (by 1.2 at.%) and Mo (by 0.24 at.%) does not significantly decrease in primary carbides, while the content of Fe (by 1.0 at.%) and Mn (by 0.24 at.%) increases. The composition of eutectic carbides has changed more significantly. In particular, the content of Cr decreased (by 6.6 at.%) and the content of Fe (by 6.3 at.%) and Mn (by 0.42 at.%) increased. Besides, Ni was dissolved in eutectic carbides in small amounts under such cooling conditions. The content of Cr increased (by 3.0 at.%) and the content of Fe (by 2.4 at.%), Mn (by 0.3 at.%), Mo (by 0.22 at.%), and Si (by 0.19 at.%) in the composition of the austenitic matrix.

Microprobe analysis showed that the addition of 0.2 wt.% Ca, Bi, Sn, and Sb affects the composition of primary and eutectic (Tables 3 and 4). At the same time, modifying additives were not found in their composition. The addition of these elements leads to a decrease in the content of Cr, an increase in the content of C, Mn, and Fe in eutectic carbides. In primary carbides, the addition of Bi reduces the concentration of Cr and increases the concentration of Mn and Fe. The addition of Ca reduces the concentration of iron and slightly increases the concentration of carbon. Additions of Sn and Sb increase the concentration of Mn while the addition of Sb does not significantly reduce the concentration of Cr. The addition of 0.2 wt.% Ca, Bi, Sn, Sb to the composition of HCCI leads to a decrease in the concentration of Mn and Cr in the matrix (Table 5). An increase in the Si concentration in the HCCI composition with the addition of Ca is associated with the introduction of silicocalcium into the melt. In this case, there is no change in the composition of the carbides and no fluctuations in the content of elements across the cross-section of the austenitic matrix.

The addition of 0.2 wt.% Bi, Sn, Sb does not significantly affect the composition of the primary carbide under cooling conditions at a rate of 4.67–5 °C/s (2 series of experiments). The content of Cr

and C does not significantly decrease, and the content of Fe, Mn, and Mo increases with the introduction of an additive of 0.2 wt.% B in the composition of primary carbides. At the same time, fluctuations in the content of Fe and Cr increase significantly, which indicates an expansion of the concentration range of existence of the $(\text{FeCr})_7\text{C}_3$ phase. It indicates an expansion of the concentration range of the $(\text{FeCr})_7\text{C}_3$ phase existence when B is dissolved in it. The influence of additions of 0.2 wt.% Bi, Sb on the composition of eutectic carbides is similar to that observed in ingots obtained at a cooling rate of 0.083–0.116 °C/s. In particular, the introduction of these elements reduces the Cr, Mn concentration and increases the Fe concentration. The addition of 0.2 wt.% Sn under such cooling conditions does not affect the content of Cr, Fe but reduces the Mn concentration. The Mo content in eutectic carbides increases the Sn content and reduces the additions of Bi, Sb, and B. In ingots with an increase of 0.2 wt.% Bi, Sn, Sb, and B in the composition of eutectic carbides identified by Si. This distinguishes them from WMA samples and ingots obtained at low cooling rates. The austenite composition indicators are less good. Thus, B and Sb additives cause disrespect for Cr health. Additives of Bi, Sn, and Sb increase the concentration of Mn in the austenite composition. The addition of Sb increases the stability of Ni. The distribution of Sn and Sb in austenite is uneven, which indicates different changes in the sizes of these elements.

Table 3. Composition of primary carbides in HCCI ingots obtained at different cooling rates.

Modifying agent	Cooling rate, °C/s	Concentration, at. %				
		C	Cr	Mn	Fe	Mo
WMA	0.083–0.116	29.4 ^{+0.79} _{-0.91}	43.9 ^{+0.71} _{-0.42}	0.67 ^{+0.26} _{-0.34}	24.5 ^{+0.29} _{-0.48}	0.84 ^{+0.18} _{-0.19}
	4.67–5	29.6 ^{+0.45} _{-0.34}	42.8 ^{+0.13} _{-0.26}	1.1 ^{+0.85} _{-0.6}	25.5 ^{+0.18} _{-0.18}	0.6 ^{+0.12} _{-0.09}
Bi	0.083–0.116	29.6 ^{+1.4} _{-1.6}	41.9 ^{+2.9} _{-4.7}	1.1 ^{+0.11} _{-0.12}	26.1 ^{+3.15} _{-1.77}	0.7 ^{+0.51} _{-0.27}
	4.67–5	30.1 ^{+1.28} _{-1.3}	42.2 ^{+0.81} _{-0.84}	1.0 ^{+0.15} _{-0.18}	25.7 ^{+0.33} _{-0.25}	0.6 ^{+0.18} _{-0.14}
Sb	0.083–0.116	30.8 ^{+0.71} _{-1.16}	42.7 ^{+0.54} _{-0.58}	1.2 ^{+0.31} _{-0.20}	24.1 ^{+0.72} _{-0.35}	0.8 ^{+0.38} _{-0.45}
	4.67–5	28.6 ^{+0.44} _{-0.51}	43.2 ^{+0.22} _{-0.14}	0.9 ^{+0.01} _{-0.01}	26.2 ^{+0.31} _{-0.26}	0.6 ^{+0.25} _{-0.16}
Sn	0.083–0.116	29.1 ^{+0.69} _{-0.73}	43.8 ^{+0.36} _{-0.41}	1.2 ^{+0.11} _{-0.23}	24.7 ^{+0.40} _{-0.48}	0.8 ^{+0.14} _{-0.23}
	4.67–5	29.8 ^{+0.26} _{-0.16}	42.7 ^{+0.39} _{-0.26}	0.9 ^{+0.35} _{-0.2}	25.2 ^{+0.31} _{-0.28}	0.6 ^{+0.41} _{-0.21}
Ca	0.083–0.116	31.2 ^{+0.86} _{-0.53}	43.7 ^{+0.32} _{-0.45}	0.8 ^{+0.23} _{-0.26}	22.6 ^{+0.28} _{-0.38}	0.6 ^{+0.11} _{-0.27}
	4.67–5	-	-	-	-	-
B	0.083–0.116	29.0 ^{+1.24} _{-0.91}	44.3 ^{+0.43} _{-0.56}	1.0 ^{+0.51} _{-0.37}	24.5 ^{+0.61} _{-0.24}	0.8 ^{+0.61} _{-0.24}
	4.67–5	28.6 ^{+0.44} _{-0.51}	42.1 ^{+1.54} _{-1.08}	1.13 ^{+0.35} _{-0.24}	27.0 ^{+2.47} _{-2.46}	0.7 ^{+0.18} _{-0.08}

Table 4. Composition of eutectic carbides in HCCI ingots obtained at different cooling rates.

Modifying agent	Cooling rate, °C/s	Concentration, at. %						
		C	Cr	Mn	Fe	Mo	Si	Ni
WMA	0.083–0.116	29.1 ^{+1.01} _{-1.12}	42.3 ^{+1.35} _{-1.16}	0.88 ^{+0.2} _{-0.2}	26.4 ^{+1.1} _{-0.76}	0.97 ^{+0.6} _{-0.3}	-	-
	4.67–5	29.8 ^{+0.56} _{-0.71}	35.6 ^{+0.34} _{-0.35}	1.3 ^{+0.28} _{-0.33}	32.7 ^{+0.59} _{-0.51}	1.01 ^{+0.52} _{-0.34}	-	0.3 ^{+0.14} _{-0.1}
Bi	0.083–0.116	30.4 ^{+1.60} _{-1.76}	37.9 ^{+2.68} _{-2.05}	1.34 ^{+0.26} _{-0.24}	28.6 ^{+1.30} _{-1.13}	1.33 ^{+0.34} _{-0.65}	-	-
	4.67–5	29.4 ^{+0.48} _{-0.47}	34.9 ^{+0.14} _{-0.14}	1.02 ^{+0.27} _{-0.31}	33.6 ^{+0.85} _{-0.85}	0.77 ^{+0.19} _{-0.24}	0.6 ^{+0.14} _{-0.14}	0.4 ^{+0.22} _{-0.27}
Sb	0.083–0.116	31.7 ^{+1.72} _{-1.23}	38.1 ^{+1.67} _{-2.94}	1.19 ^{+0.15} _{-0.19}	27.6 ^{+0.93} _{-1.21}	1.2 ^{+0.45} _{-0.48}	-	-
	4.67–5	30.4 ^{+0.61} _{-1.1}	33.6 ^{+4.69} _{-5.31}	0.97 ^{+0.47} _{-0.32}	34.4 ^{+6.34} _{-5.87}	0.89 ^{+0.3} _{-0.16}	0.53 ^{+0.14} _{-0.2}	0.3 ^{+0.1} _{-0.19}
Sn	0.083–0.116	32.6 ^{+0.59} _{-0.98}	36.4 ^{+0.80} _{-1.33}	1.16 ^{+0.37} _{-0.29}	27.6 ^{+0.67} _{-0.51}	1.43 ^{+0.88} _{-0.44}	-	-
	4.67–5	30.2 ^{+1.5} _{-1.66}	31.0 ^{+6.70} _{-6.4}	1.17 ^{+0.49} _{-0.38}	36.2 ^{+8.99} _{-7.19}	1.13 ^{+0.57} _{-0.5}	0.3 ^{+0.18} _{-0.18}	0.4 ^{+0.15} _{-0.18}
Ca	0.083–0.116	32.6 ^{+0.59} _{-0.98}	36.4 ^{+0.8} _{-1.33}	1.16 ^{+0.37} _{-0.29}	27.6 ^{+0.67} _{-0.51}	1.50 ^{+0.81} _{-0.52}	-	-
	4.67–5	-	-	-	-	-	-	-
B	0.083–0.116	29.8 ^{+1.26} _{-1.38}	40.4 ^{+2.33} _{-1.35}	0.78 ^{+0.4} _{-0.31}	27.6 ^{+2.44} _{-2.16}	0.85 ^{+0.32} _{-0.33}	-	-
	4.67–5	26.6 ^{+0.66} _{-0.12}	29.6 ^{+1.5} _{-1.23}	1.01 ^{+0.27} _{-0.29}	41.4 ^{+0.98} _{-1.62}	0.93 ^{+0.35} _{-0.24}	0.5 ^{+0.12} _{-0.13}	0.4 ^{+0.2} _{-0.13}

Table 5. Matrix composition in HCCI ingots obtained at different cooling rates.

Modifying agent	Cooling rate, °C/s	Concentration, at. %							
		Si	Cr	Mn	Fe	Ni	Mo	Sb	Sn
WMA	0.083–0.116	2.61 ^{+0.94} _{-0.46}	10.3 ^{+1.32} _{-0.77}	1.28 ^{+0.55} _{-0.46}	85.5 ^{+0.43} _{-0.77}	1.47 ^{+0.19} _{-0.46}	0.91 ^{+0.36} _{-0.21}	-	-
	4.67–5	2.42 ^{+0.35} _{-0.37}	13.3 ^{+0.85} _{-1.43}	0.98 ^{+0.24} _{-0.14}	83.1 ^{+2.41} _{-1.4}	1.42 ^{+0.58} _{-0.22}	0.69 ^{+0.58} _{-0.28}	-	-
Bi	0.083–0.116	2.91 ^{+0.26} _{-0.23}	9.1 ^{+0.74} _{-1.79}	1.07 ^{+0.29} _{-0.21}	86.2 ^{+1.09} _{-0.52}	1.86 ^{+0.12} _{-0.12}	1.12 ^{+0.63} _{-0.44}	-	-
	4.67–5	2.91 ^{+0.26} _{-0.23}	13.14 ^{+0.684} _{-0.179}	1.3 ^{+0.1} _{-0.17}	82.5 ^{+0.3} _{-0.7}	1.38 ^{+0.27} _{-0.15}	0.68 ^{+0.27} _{-0.22}	-	-
Sb	0.083–0.116	2.91 ^{+0.26} _{-0.233}	9.1 ^{+0.74} _{-1.793}	1.07 ^{+0.29} _{-0.21}	86.2 ^{+1.09} _{-0.52}	1.86 ^{+0.12} _{-0.12}	1.12 ^{+0.63} _{-0.44}	0.17 ^{+0.36} _{-0.17}	-
	4.67–5	2.4 ^{+0.13} _{-0.38}	12.5 ^{+0.49} _{-0.67}	1.15 ^{+0.33} _{-0.28}	83.0 ^{+0.69} _{-0.61}	1.66 ^{+0.84} _{-0.33}	0.82 ^{+0.34} _{-0.25}	0.32 ^{+0.1} _{-0.32}	-
Sn	0.083–0.116	2.77 ^{+0.64} _{-0.45}	9.0 ^{+1.16} _{-0.95}	1.45 ^{+0.57} _{-0.22}	85.9 ^{+0.75} _{-1.03}	1.49 ^{+0.44} _{-0.31}	1.51 ^{+0.93} _{-0.81}	-	0.54 ^{+0.3} _{-0.13}
	4.67–5	2.59 ^{+0.75} _{-0.62}	14.2 ^{+0.05} _{-0.02}	1.31 ^{+0.1} _{-0.15}	81.5 ^{+0.09} _{-0.08}	1.4 ^{+0.13} _{-0.11}	0.61 ^{+0.34} _{-0.18}	-	0.47 ^{+0.1} _{-0.47}
Ca	0.083–0.116	5.06 ^{+1.17} _{-1.95}	9.5 ^{+1.37} _{-0.98}	1.15 ^{+0.32} _{-0.23}	82.9 ^{+0.3} _{-0.7}	1.72 ^{+0.5} _{-0.4}	1.05 ^{+0.51} _{-0.39}	-	-
	4.67–5	2.89 ^{+0.75} _{-0.6}	11.3 ^{+1.37} _{-2.29}	1.4 ^{+0.19} _{-0.31}	84.8 ^{+1.85} _{-1.09}	1.88 ^{+0.37} _{-0.41}	1.17 ^{+0.63} _{-0.51}	-	-
B	0.083–0.116	2.89 ^{+0.75} _{-0.6}	11.3 ^{+1.37} _{-2.29}	1.4 ^{+0.19} _{-0.31}	84.8 ^{+1.85} _{-1.09}	1.88 ^{+0.37} _{-0.41}	1.17 ^{+0.63} _{-0.51}	-	-
	4.67–5	2.66 ^{+0.33} _{-0.61}	12.2 ^{+1.09} _{-0.81}	0.96 ^{+0.06} _{-0.06}	83.3 ^{+0.7} _{-0.99}	1.47 ^{+0.17} _{-0.09}	0.49 ^{+0.37} _{-0.18}	-	-

Thus, the concentration of these additives in the composition of the melt changes with the introduction of 0.2 wt.% B, Ca, Bi, Sn, and Sb into cast iron melts during their holding and cooling. Thus, the Bi concentration decreases to almost 0%. The concentrations of Sn, Ca, B, and Sb decrease to a lesser extent. It indicates intense evaporation of Bi and less intense evaporation of Ca. This is explained by the fact that these elements do not dissolve in liquid iron and have a high vapor pressure at the fusion temperature [42]. Confirmation of the possibility of separating small impurities from the melt due to differences in vapor pressure in a vacuum are the results of [43]. Sb and Sn, according to state diagrams Fe-Sb and Fe-Sn, form solid and liquid solutions with iron which slows down their evaporation. In addition, the minimal change in Sn concentration is explained by its low vapor pressure, which, according to the data given in [43], is (10^{-1} mmHg at 1372 °C). Boron is characterized by low

vapor pressure but at the same time, being a deoxidizer, it can evaporate from the melt surface in the form of boron oxide.

The introduction of Ca, Bi, Sn, and Sb additives into HCCI results in a change in the composition of primary and eutectic carbides, as well as in the matrix. In this case, only Sn and Sb form solid solutions with austenite; in other cases, these elements do not form compounds and solid solutions with HCCI phases.

3.3. Microhardness of phases, hardness and strength of HCCI ingots after modification

The introduction of 0.2 wt.% B, Ca, Bi, Sn, Sb causes a decrease in the hardness of HCCI ingots obtained at a cooling rate of 0.083–0.116 °C/s (Figure 4). The greatest decrease occurs from the introduction of B (by ~14%) and Bi (by ~5.7%). An analysis of the measurement results for the microhardness of individual phases of ingots after a modification indicates that the additions of B, Sn, and Ca cause an increase in the microhardness of primary carbides by 4.7%, 2.5%, and 4.1%, respectively (Figure 5a), and the addition of Sb leads to a decrease in their microhardness by 3.1%. The addition of Bi increases the microhardness of eutectic carbides by 4.5% while the additions of B, Sn, and Sb decrease it by 15.7%, 8.8%, and 6.0%. The microhardness of austenite is increased only by the additions of Sn and Ca by 2.6% and 3.2% while the additions of B, Sb, and Bi reduce it by 6.3%, 9.9%, and 8.3%, respectively (Figure 5a). Thus, only the addition of Ca has a positive effect on the microhardness of primary carbides and austenite and practically does not affect the microhardness of eutectic carbides. Additives—B, Bi, Sn, and Sb adversely affect the microhardness of one or more phases of cast iron castings obtained at a cooling rate of 0.083–0.116 °C/s.

At a cooling rate of ingots of 4.67–5 °C/s, the addition of B, Ca, Bi, Sn, and Sb causes an increase in the hardness of HCCI (Figure 4). The most significant increase is caused by additions of B (by ~8.7%) and Ca (~5.7%). However, the measurement of the microhardness of primary carbides showed that only Bi additives increase it by ~1.7%. Additives—B, Ca, Sn, Sb reduce the microhardness of primary carbides by 5.5%, 3.8%, 8.1%, and 11.0%, respectively (Figure 5b). The increase in the hardness of castings obtained at this cooling rate may be caused by an increase in the hardness of the matrix and eutectic carbides. The strength of castings obtained at a cooling rate of 4.67–5 °C/s, after the introduction of Ca and Bi additives, increases by ~20% and ~3.5%, respectively (Figure 6). With the introduction of B, Sn, and Sb, the strength of castings decreases by ~12.0%, 5.5%, and 5.9%, respectively.

Thus, the introduction of 0.2 wt.% B, Ca, Bi, Sn, and Sb additives into the HCCI melt has a different effect on the mechanical properties of ingots crystallized with different cooling rates. A general decrease in hardness is observed with the introduction of all additives at a low cooling rate (0.083–0.116 °C/s). In this case, only the addition of Ca increases the hardness of the primary carbides and the matrix. Ca and Bi additions increase the hardness and strength of the casting at a high cooling rate (4.67–5 °C/s). In the case of Ca, this can be explained by an increase in the proportion of eutectic carbides and a decrease in the proportion and size of primary carbides in the structure of the castings. The addition of Bi does not significantly increase the microhardness of primary carbides.

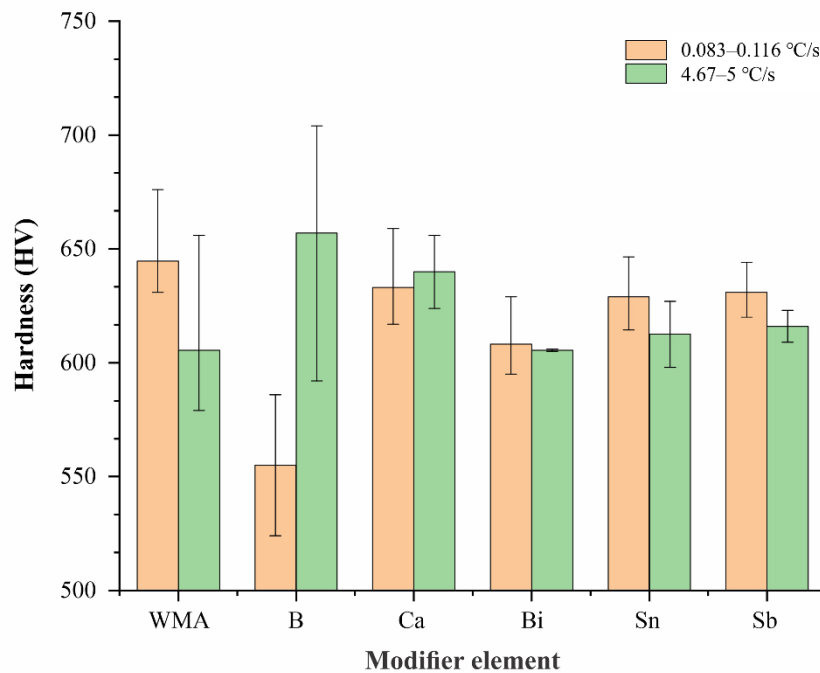


Figure 4. Effect of the modifying additive on the hardness of HCCI ingots obtained with different cooling rates.

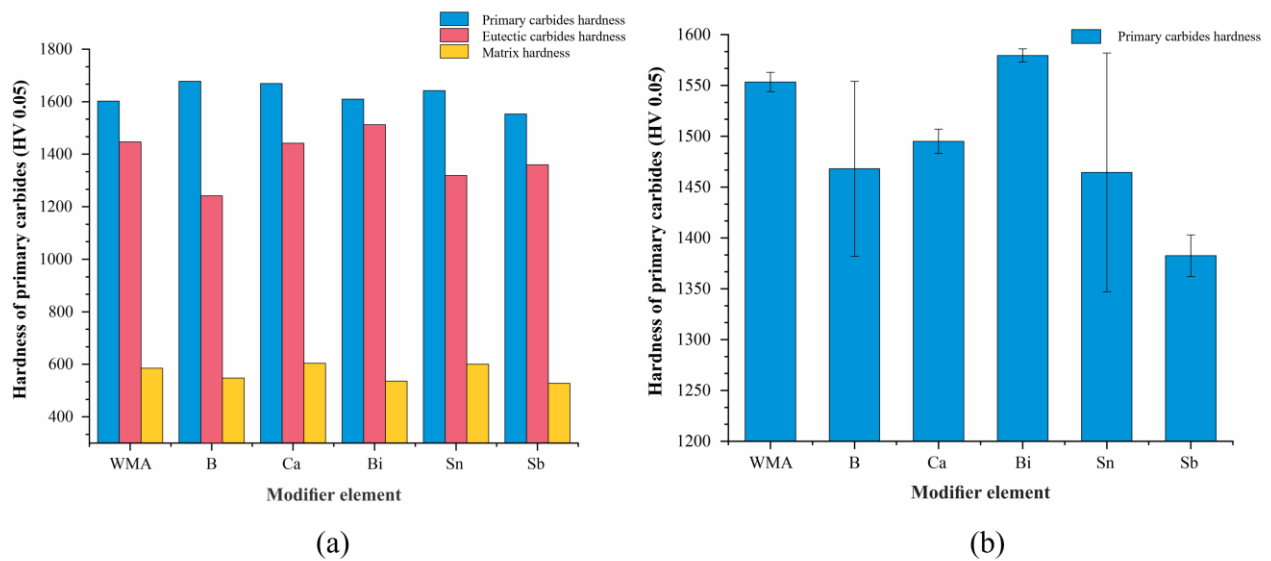


Figure 5. Effect of the modifying additive on the microhardness of phases in HCCI ingots obtained at a cooling rate: (a) 0.083–0.116 °C/s; (b) 4.67–5 °C/s.

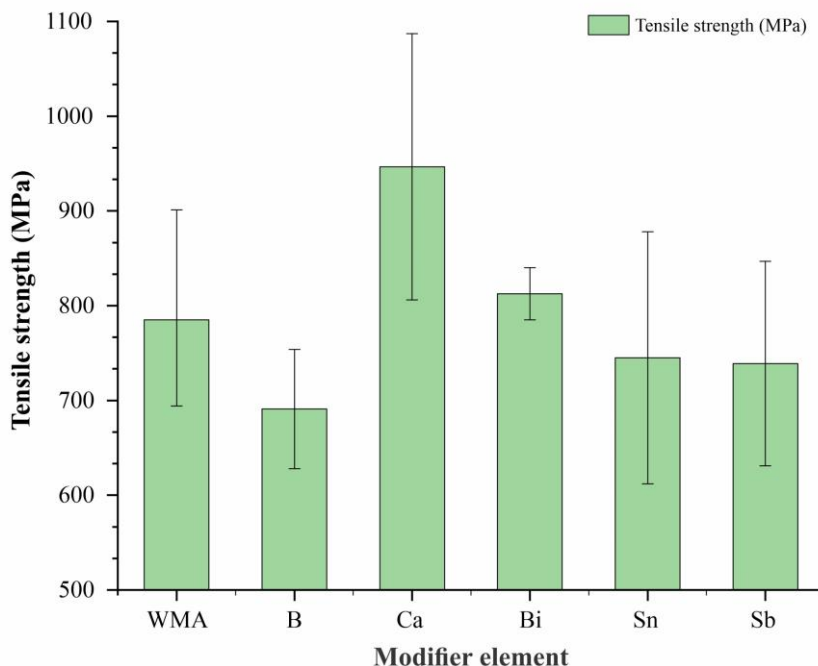


Figure 6. Effect of the modifying additive on the tensile strength of HCCI ingots obtained at a cooling rate of 4.67–5 °C/s.

3.4. Tribo testing of HCCI ingots modified with various elements

The B, Ca, Bi, Sn, and Sb additives have a different effect on the wear resistance of HCCI ingots obtained with different cooling rates by analogy with the effect on the structure and mechanical properties. Thus, the addition of B significantly (by 153%) increases the wear rate at low cooling rates of 0.083–0.116 °C/s (Figure 7). Ca, Bi, Sn, and Sb additives reduce the wear rate by ~47%, 26%, 56%, and 53%, respectively. The study of the wear surface structure showed that the wear of samples with the addition of Ca, Bi, Sn, and Sb develops more intensively in the eutectic regions. Primary carbides wear out mainly with the formation of chips (Figure 8a). Samples with additive B wear similarly but with the destruction of large primary carbides.

Castings obtained at a high cooling rate (4.67–5 °C/s) are characterized by opposite wear resistance. When B is added, the wear rate is reduced by ~20% (Figure 7). When Ca, Bi, Sn, and Sb are added, the wear rate increases by ~81%, 14%, 69%, and 162%, respectively. The wear surface study showed that the wear of the eutectic and primary carbides occurs more evenly in comparison with the samples obtained at a low cooling rate. However, eutectic wear prevails over primary carbides and develops more significantly in samples with additions of Ca, Bi, Sn, and Sb in comparison with the original sample and with a sample with B addition. The wear of primary carbides in such samples occurs without chips and cracks (Figure 8b).

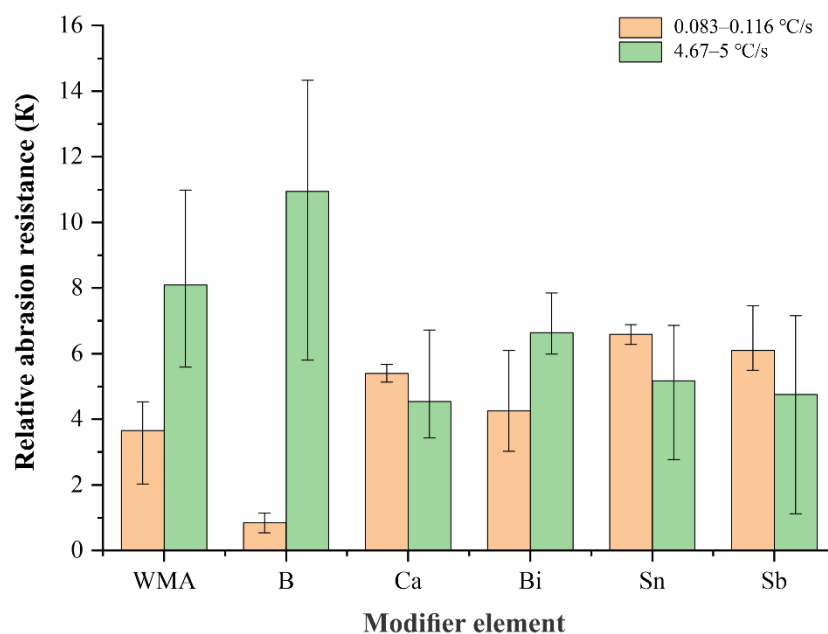


Figure 7. Effect of modifying additive on wear resistance of HCCI ingots produced at different cooling rates.

Thus, the effect of modifying B, Ca, Bi, Sn, and Sb additives on the wear resistance of castings, changes significantly depending on the cooling rate of ingots during crystallization. So, Ca, Bi, Sn, and Sb render a positive effect on the wear resistance of ingots obtained at a low cooling rate. At a high cooling rate of the ingots, only the B additive increases the wear resistance.

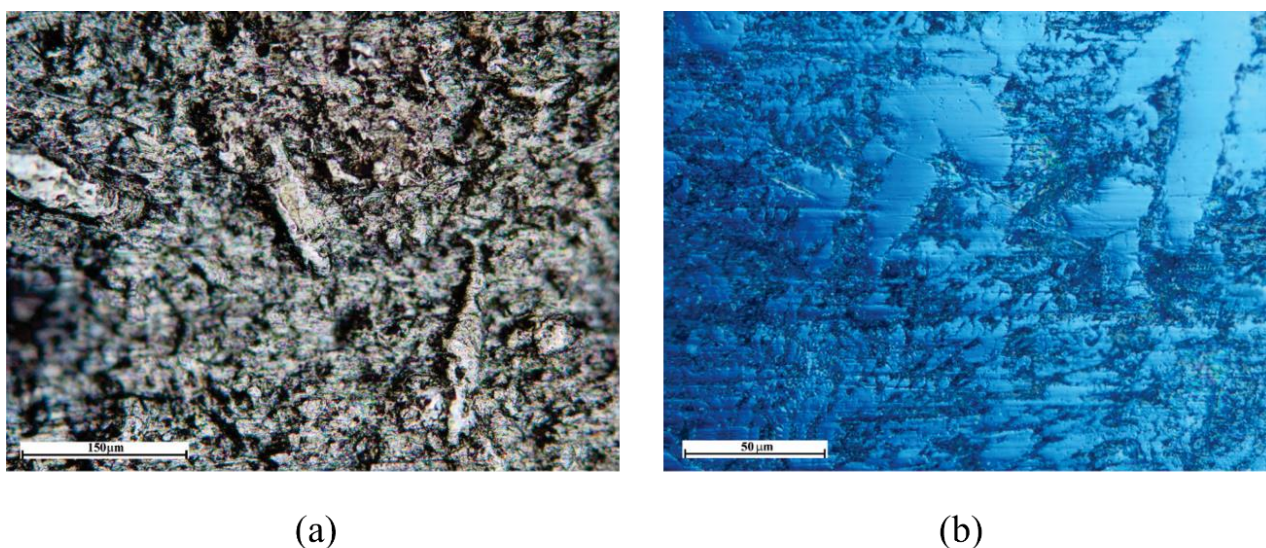


Figure 8. Effect of the modifying additive on the microhardness of phases in HCCI ingots obtained at a cooling rate: (a) 0.083–0.116 °C/s; (b) 4.67–5 °C/s.

4. Discussion

Table 6 summarizes the results described above on the effect of additives of 0.2 wt.% B, Ca, Bi, Sn, Sb on the structure and properties of hypereutectic HCCI ingots obtained at two cooling rates.

Table 6. Changes in the structure, composition, and microhardness of phases and mechanical properties of ingots modified with 0.2 wt.% of various additives and obtained at different speeds (↑: increase in indicator; ↓: decrease in indicator; uv: unchanged value; highlighted in green (↓↑): improving characteristics; highlighted in red (↑↓): deteriorating characteristics).

Modifying additive	B	Bi	Ca	Sn	Sb
Cooling rate 0.083–0.116 °C/s					
Proportion of primary carbide	↑	↓	uv	uv	uv
Proportion of eutectic carbide	↓	↑	uv	uv	uv
Average minimum cross-section of primary carbides	↑	↓	↓	↓	↓
Average cross-sectional area of primary carbides	↑	↓	↓	↓	↓
Content of elements in the composition of primary carbides	Not changed	Cr↓, Mn↑, Fe↑	C↑, Fe↓	Mn↑	Mn↑, Cr↓
Content of elements in the composition of eutectic carbides	-	Cr↓, C↑, Fe↑, Mn↑	Cr↓, C↑, Fe↑, Mn↑	Cr↓, C↑, Fe↑, Mn↑	Cr↓, C↑, Fe↑, Mn↑
Content of elements in the matrix (austenite)	-	Cr↓, Mn↓	Si↑, Mn↓	Cr↓, Mn↓	Cr↓, Mn↓
Microhardness of primary carbides	↑	uv	↑	↑	↓
Microhardness of eutectic carbides	↓	↑	uv	↓	↓
Matrix microhardness	↓	↓	↑	↑	↓
Hardness HV	↓	↓	↓	↓	
Tensile strength					↓
Relative wear resistanc	↓	↑	↑	↑	↑
Cooling rate 4.67–5 °C/s					
Proportion of primary carbide	↑	uv	↓	↓	uv
Proportion of eutectic carbide	↓	uv	↑	↑	uv
Average minimum cross-section of primary carbides	↓	↑	↓	↓	↓
Average cross-sectional area of primary carbides	↓	↑	↓	↑	↑
Content of elements in the composition of primary carbides	Cr↓, C↓, Fe↑, Mn↑, Mo↑	uv	-	uv	uv
Content of elements in the composition of eutectic carbides	Mo↓, Si↑	Cr↓, Mn↓, Si↑	Fe↑, Mo↓	Mn↑, Si↑	Mo↑, Cr↓, Mn↓, Si↑
Content of elements in the matrix (austenite)	Cr↓	Mn↑	-	Mn↑	Cr↓, Ni↑, Mn↑
Microhardness of primary carbides	↓	↑	↓	↓	↓
Microhardness of eutectic carbides	-	-	-	-	-
Matrix microhardness	-	-	-	-	-
Hardness HV	↑	↑	↑	↑	↑
Tensile strength	↓	↑	↑	↓	↓
Relative wear resistanc	↑	↓	↓	↓	↓

The B, Bi, Ca, Sn, and Sb additives considered in this article should be distinguished by their interaction with the HCCI components. For example, it is known that Bi and Ca do not form liquid and solid solutions with iron which precludes their dissolution in austenite and, at high concentrations, can lead to melt separation. Sn with Fe and Cr forms monotectics and limited solid solutions. Sb is infinitely soluble in iron melt and form solid solutions with austenite. B is highly soluble in iron melt but practically does not form solid solutions with austenite. Bi, Sn and Sb are not carbide forming elements. Accordingly, they cannot form new carbides in the HCCI structure but they can potentially dissolve in the primary and eutectic carbide $(\text{FeCr})_7\text{C}_3$ in very small amounts. Ca and B are carbide forming elements. It is known that B forms solid solutions with carbide $(\text{FeCr})_7(\text{C,B})_3$ [44] and is also soluble in other carbides [45]. The formation of CaC_2 does not occur when calcium is dissolved in cast iron melts, since it is known that CaC_2 decomposes into Ca and C when introduced into the melt which makes it possible to use it as a refining additive [46].

The experimental results presented in this article show that B, Bi, Ca, Sn, and Sb additions affect both the structure and properties of hypereutectic HCCI. However, depending on the cooling rate of the ingots in the crystallization interval, the effect of these additives varies significantly. In hypereutectic HCCI ingots obtained under conditions of low cooling rate, with the introduction of Bi, Ca, Sn, and Sb additives, the sizes of primary carbides $(\text{FeCr})_7\text{C}_3$ decrease. Obviously, this is because these elements do not dissolve in carbides. As a result, during crystallization, these elements, accumulating at the solid/liquid interface, cause a change in equilibrium which leads to a slowdown in the growth of carbides, and a reduction of their size. In addition, in the case of introducing Bi, the crystallization process is affected by the mechanism of local supercooling caused by its evaporation. It is confirmed by the absence of Bi in the composition of the ingots obtained at both cooling rates. Despite the lack of solubility of Bi, Ca, Sn, and Sb in $(\text{FeCr})_7\text{C}_3$, their introduction causes a change in the elemental composition of both primary and eutectic carbides. A decrease in the content of Cr and an increase in the content of C, Mn, and Fe in eutectic carbides, as well as an increase in the proportion of such carbides, indicate the removal of the eutectic point from the iron angle of the phase diagram. This is also indicated by the decrease in the proportion of primary carbides discovered during the studies. Besides, the introduction of these elements into the composition of HCCI leads to a decrease in the concentration of Mn and Cr in the matrix. Since it is known that the hardness of $(\text{FeCr})_7\text{C}_3$ carbides increases with an increase in the Cr concentration in them, the observed decrease in microhardness is explained by a decrease in the concentration of this element. The different effect of modifying elements on the hardness of the matrix is associated both with a change in its composition and with a different proportion of austenite decomposition. This effect, as well as a decrease in the size of primary carbides and a change in the composition and ratio of primary and secondary carbides caused by the introduction of Bi, Ca, Sn, and Sb additives, can explain the increase in the abrasive wear resistance of HCCI ingots obtained under slow cooling conditions.

When Ca is used as a modifying additive, this element is not found by microprobe analysis in the composition of the matrix and carbides. However, in X-ray fluorescence analysis, especially of samples prepared (cut and polished) without the use of water cooling, Ca is clearly identified. As mentioned above, Ca does not form solid solutions with austenite. It suggests that it is washed out from the surface of the section during its preparation upon contact with water.

More elongated primary acicular crystals of carbide $(\text{FeCr})_7\text{C}_3$ are precipitated during the crystallization of hypereutectic HCCI ingots with additions of Bi, Sn, and Sb under conditions of accelerated cooling (4.67–5 °C/s). Since the minimum cross section of primary carbides after the

introduction of such additives under these crystallization conditions does not change, the effect of the accumulation of these elements at the solid/liquid contact boundary should be excluded. Consequently, the addition of these elements reduces the number of crystallization centers and (or) limits the growth of individual nuclei under conditions of melt supercooling. The observed decrease in the size of primary carbides in Ca-modified HCCI ingots can be associated with both additional alloying with silicon and the precipitation of refractory CaC_2 particles in the melt bulk but it requires additional studies. So, the effect of silicon was investigated by the authors of [47]. They report an improvement in the structure and state that Si inhibits the growth of carbide. However, it was found in [37,48] that Si reduces the nucleation process, does not affect the growth of carbide, and leads to a coarser structure.

A relatively small increase in the hardness of ingots ($\sim 5.7\%$ in case of Ca) after the introduction of Ca, Bi, Sn, and Sb additives into them and a slight decrease in the microhardness of primary carbides (in the case of Ca, Sn, Sb) and strength (in the case of Bi, Sn, Sb) also confirms that these elements do not significantly affect the crystallization process under such cooling conditions ($4.67\text{--}5^\circ\text{C/s}$). Since the addition of Bi caused the melt to boil under a vacuum, this could refine the melt from non-metallic inclusions. This led to an increase in the hardness of the primary carbides $(\text{FeCr})_7\text{C}_3$ but increased their size due to a decrease in crystallization centers. The increase in the strength of the Ca-modified ingots is most likely due to the hardening of the matrix caused by co-doping with Si. The decrease in wear resistance after the introduction of Ca, Bi, Sn, and Sb is obviously associated with both an increase in the cross-sectional area of primary carbides and a change in the properties of the matrix.

The conducted studies have shown that, unlike Ca, Bi, Sn, Sb, additive B dissolves in carbides $(\text{FeCr})_7\text{C}_3$. However, considering that B does not dissolve in the γ -phase, the actual content of this element in carbides is significantly lower than expected. This is probably due to melt deoxidation and evaporation of B_2O_3 oxide. The effect of B additives on the structure and properties of HCCI changes significantly with the change in the cooling rate during the crystallization of the ingot. There is a significant increase in the size of primary carbides in the alloy and an increase in their microhardness but the hardness and wear resistance of the alloys decrease at a low crystallization rate ($0.083\text{--}0.116^\circ\text{C/s}$). A decrease in the size of primary carbides and a decrease in their microhardness are observed with an increase in the cooling rate to $4.67\text{--}5^\circ\text{C/s}$, on the contrary, while the bending strength of the castings decreases, and the hardness and wear resistance increase. It allows us to conclude that B has a significant effect on the crystallization process. First, B dissolves in carbide $(\text{FeCr})_7\text{C}_3$, as a result, regardless of the cooling rate, it causes an increase in its proportion. But since the proportion of eutectic carbides decreases with an increase in the cooling rate, it may indicate the overcooling of the melt. It led to a shift of the eutectic point towards Fe. Since B reduces the solubility of C in austenite [37], at a low cooling rate, it causes a decrease in the strength of the matrix and, as a consequence, a decrease in the hardness of the ingot. In this case, under conditions of slow cooling, there is no significant shift of the eutectic point but an increase in the hardness of primary carbides indicates their higher alloying degree.

Thus, a significant change in the effect of additions of 0.2 wt.% B, Bi, Ca, Sn, and Sb on the structure and properties of hypereutectic HCCI ingots was found, depending on the cooling rate in the crystallization interval. Obviously, it is due to a change in the mechanism of action of these additives depending on the supercooling degree of the melt. This indicates the need for prudent use of additives of such elements to modify HCCI castings. Meanwhile, since HCCIs are widely used in the production of large-sized sand castings, the problem to improve their performance is very serious. In this regard, the positive effect of Bi, Ca, Sn, and Sb additions on the structure and properties of ingots cooled at a rate of $0.083\text{--}0.116^\circ\text{C/s}$, described in this article, is of interest for further verification when these

castings are obtained. Particularly noteworthy is the addition of Ca also considered as a refining one. The need for refining HCCI cast irons is justified by the use of a large proportion of scrap in their production and, as a result, by contamination with non-metallic particles [49].

5. Conclusions

The addition of 0.2 wt.% B, Bi, Ca, Sn, and Sb to the melt of hypereutectic HCCI does not have a significant effect on the morphology of primary and eutectic carbides $(\text{FeCr})_7\text{C}_3$ in ingots obtained at a cooling rate in the crystallization range of 0.083–0.116 and 4.67–5 °C/s. Depending on the cooling rate, the degree of influence of these additives on the size of primary carbides, the proportion of primary and eutectic carbides, the composition of phases, and the mechanical properties of castings changes.

In the case of cooling the HCCI melt at a rate of 0.083–0.116 °C/s with the introduction of Bi, Ca, Sn, and Sb additives that do not form carbides and are limitedly soluble in the melt (Bi, Ca, Sn), a decrease in the size of primary carbides $(\text{FeCr})_7\text{C}_3$ is noted, change in phase composition. The mechanism of influence of such elements is associated with their accumulation in the melt near the crystallization front and, as a consequence, with a change in equilibrium. In addition, Bi and Ca are inoculants due to their high vapor pressure. The introduction of these elements leads to a decrease in the hardness of HCCI but to an increase in their relative wear resistance.

At a cooling rate of 4.67–5 °C/s of an HCCI melt with additions of 0.2 wt.% Bi, Sn, and Sb, a decrease in the size of primary carbides does not occur. The addition of Ca reduces the size of primary carbides and, along with the addition of Sn, increases the proportion of eutectic carbides and reduces the proportion of primary carbides. At such a cooling rate, a large number of crystallization centers appear, which naturally increases the total surface area of the carbides near the crystallization front. As a result, the required concentration of these elements is not achieved, which could lead to a slowdown in their growth. The Ca addition probably creates additional crystallization centers. Ingots obtained with the addition of these elements are characterized by greater hardness, but less resistance to abrasive wear.

Boron dissolves in primary and eutectic HCCI carbides to form the compound $(\text{FeCr})_7(\text{C,B})_3$. As a result, the proportion of eutectic carbides decreases and the proportion of primary carbides increases. This, in the case of ingots obtained at a cooling rate of 0.083–0.116 °C/s, causes a sharp decrease in all mechanical properties. In hypereutectic HCCI modified with boron, at a melt cooling rate of 4.67–5 °C/s, additional crystallization centers are formed, which leads to the precipitation of more dispersed primary carbides. This, as well as an increase in hardness, leads to an increase in the abrasive wear resistance of castings.

Based on the data obtained, it is proposed to use 0.2 wt.% Ca as modifying additives when producing castings from HCCI of hypereutectic composition under slow cooling conditions, and 0.2 wt.% B under rapid cooling conditions.

Use of AI tools declaration

The authors declare they have not used Artificial Intelligence (AI) tools in the creation of this article.

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Conflicts of interest

The authors declare no conflict of interest.

References

1. Studnicki V, Dojka R, Gromczyk M, et al. (2016) Influence of titanium on crystallization and wear resistance of high chromium cast iron. *Arch Foundry Eng* 16: 117–123. <https://doi.org/10.1515/afe-2016-0014>
2. Liu Y, Liu W, Yang P, et al. (2023) Microstructure evolution and hardness of hypereutectic high chromium cast iron after tempering. *J Mater Eng Perform* <https://doi.org/10.1007/s11665-023-08197-6>
3. Gong L, Fu H, Yang P, et al. (2023) Refinement of primary carbides and improvement of wear resistance of hypereutectic high chromium cast iron after modification. *J Mater Res Technol* 24: 5724–5742. <https://doi.org/10.1016/j.jmrt.2023.04.176>
4. Inden G (1990) Phase equilibria in iron ternary alloys, In: Raynor GV, Rivlin VG, *The Institute of Metals*, London: Wiley. <https://doi.org/10.1002/adma.19900020118>
5. Panichkin A, Kenzhegulov A, Mamaeva A, et al. (2023) Effect of carbon and cooling rate on the structure of hypereutectic high chromium cast iron in the cast state and after heat treatment. *J Compos Sci* 7: 483. <https://doi.org/10.3390/jcs7120483>
6. Panichkin A, Wieleba W, Kenzhegulov A, et al. (2023) Effect of thermal treatment of chromium iron melts on the structure and properties of castings. *Mater Res Express* 10: 086502. <https://doi.org/10.1088/2053-1591/acead7>
7. Yang D, Lei T (2012) Investigating the influence of mid-chilling on microstructural development of high-chromium cast iron. *Mater Manuf Process* 27: 919–924. <https://doi.org/10.1080/10426914.2011.602793>
8. Laird G, Dogan ÖN (1996) Solidification structure versus hardness and impact toughness in high-chromium white cast irons. *Int J Cast Metal Res* 9: 83–102. <https://doi.org/10.1080/13640461.1996.11819648>
9. Jain A, Chang H, Tang X, et al. (2021) Refinement of primary carbides in hypereutectic high-chromium cast irons: A review. *J Mater Sci* 56: 999–1038. <https://doi.org/10.1007/s10853-020-05260-8>

10. Chung R, Tang X, Li D, et al. (2013) Microstructure refinement of hypereutectic high Cr cast irons using hard carbide-forming elements for improved wear resistance. *Wear* 301: 695–706. <https://doi.org/10.1016/j.wear.2013.01.079>
11. Purba R, Shimizu K, Kusumoto K, et al. (2022) Effect of boron addition on three-body abrasive wear characteristics of high chromium based multi-component white cast iron. *Mater Chem Phys* 275: 125232. <https://doi.org/10.1016/j.matchemphys.2021.125232>
12. Zhi X, Xing J, Fu H, et al. (2009) Effect of fluctuation, modification and surface chill on structure of 20%Cr hypereutectic white cast iron. *Mater Sci Technol* 25: 56–60. <https://doi.org/10.1179/174328407X245139>
13. Zhao W, Liu Z, Ju Z, et al. (2008) Effects of vanadium and rare-earth on carbides and properties of high chromium cast iron. *Mater Sci Forum* 575: 1414–1419. <https://doi.org/10.4028/www.scientific.net/MSF.575-578>
14. Panichkin A, Uskenbayeva A, Kenzhegulov A, et al. (2023) Assessment of the effect of small additions of some rare earth elements on the structure and mechanical properties of castings from hypereutectic chromium white irons. *AIMS Mater Sci* 10: 517–540. <https://doi.org/10.3934/matensci.2023029>
15. Guo Q, Fu H, Guo X, et al. (2022) Microstructure and properties of modified as-cast hypereutectic high chromium cast iron. *Materialwiss Werkst* 53: 208–219. <https://doi.org/10.1002/mawe.202100183>
16. Liu W, Jin T, Li S, et al. (2022) Microscopic study of carbide precipitation during heat treatment of 35Cr–4C high chromium cast iron. *Trans Indian Inst Met* 75: 3017–3028. <https://doi.org/10.1007/s12666-022-02690-7>
17. Shi Z, Shao W, Rao L, et al. (2021) Effects of Y dopant on mechanical properties and electronic structures of M_7C_3 carbide in Fe-Cr-C hardfacing coating. *Appl Surf Sci* 538: 148108. <https://doi.org/10.1016/j.apsusc.2020.148108>
18. Huang Z, Xing J, Zhi X, et al. (2011) Effect of Ti addition on morphology and size of primary M_7C_3 type carbide in hypereutectic high chromium cast iron. *Mater Sci Technol* 27: 426–430. <https://doi.org/10.1179/026708309x12601952777666>
19. Ding H, Liu S, Zhang H, et al. (2016) Improving impact toughness of a high chromium cast iron regarding joint additive of nitrogen and titanium. *Mater Design* 90: 958–968. <https://doi.org/10.1016/j.matdes.2015.11.055>
20. Kopycinski D, Piasny S (2012) Influence of tungsten and titanium on the structure of chromium cast iron. *Arch Foundry Eng* 12: 57–60. <https://doi.org/10.2478/v10266-012-0011-3>
21. Lv Y, Sun Y, Zhao J, et al. (2012) Effect of tungsten on microstructure and properties of high chromium cast iron. *Mater Design* 39: 303–308. <https://doi.org/10.1016/j.matdes.2012.02.048>
22. Radulovic M, Fiset M, Peev K (1994) Effect of rare earth elements on microstructure and properties of high chromium white iron. *Mater Sci Technol* 10: 1057–1062. <http://dx.doi.org/10.1179/mst.1994.10.12.1057>
23. Mampuru L, Maruma M, Moema J (2016) Grain refinement of 25 wt% high-chromium white cast iron by addition of vanadium. *J South Afr Inst Min Metall* 116: 969–972. <http://dx.doi.org/10.17159/2411-9717/2016/v116n10a12>
24. Nofal A, Reda R, Ibrahim K, et al. (2011) Structural refinement of 15% Cr-2% Mo white irons. *Key Eng Mater* 457: 231–236. <https://doi.org/10.4028/www.scientific.net/KEM.457.231>

25. Zhi X, Xing J, Fu H, et al. (2008) Effect of niobium on the as-cast microstructure of hypereutectic high chromium cast iron. *Mater Lett* 62: 857–860. <https://doi.org/10.1016/j.matlet.2007.06.084>
26. Yamamoto K, Inthidech S, Sasaguri N, et al. (2014) Influence of Mo and W on high temperature hardness of M_7C_3 carbide in high chromium white cast iron. *Mater Trans* 55: 684–689. <https://doi.org/10.2320/matertrans.FM2014801>
27. Gong LQ, Fu HG, Zhi XH (2023) Microstructure and properties of Cu-bearing hypereutectic high chromium cast iron. *Mater Charact* 195: 112546. <https://doi.org/10.1016/j.matchar.2022.112546>
28. Bedolla-Jacuinde A, Rainforth MW, Mejía I (2013) The role of silicon in the solidification of high-Cr cast irons. *Metall Mater Trans A* 44: 856–872. <https://doi.org/10.1007/s11661-012-1434-8>
29. Fu H, Wu X, Li X, et al. (2009) Effect of TiC particle additions on structure and properties of hypereutectic high chromium cast iron. *J Mater Eng Perform* 18: 1109–1115. <https://doi.org/10.1007/s11665-008-9330-5>
30. Yilmaz S, Teker T (2016) Effect of TiBAl inoculation and heat treatment on microstructure and mechanical properties of hypereutectic high chromium white cast iron. *J Alloys Compd* 672: 2016 324–331. <https://doi.org/10.1016/j.jallcom.2016.02.125>
31. Kopyciński D (2013) *The Inoculation of White Cast Iron*, Hoboken: Wiley. <http://dx.doi.org/10.1002/9781118663547.ch75>
32. Bedolla-Jacuinde A, Aguilar SL, Hernández B (2005) Eutectic modification in a low-chromium white cast iron by a mixture of titanium, rare earths, and bismuth: I. Effect on microstructure. *J Mater Eng Perform* 14: 149–157. <https://doi.org/10.1361/10599490523300>
33. Wang MY, Huang Y, Lin YX (2012) Effect of trace Sn on microstructure and properties of gray cast iron. *Zhuzao/Foundry* 61: 17–24.
34. Theuwissen K, Lacaze J, Laffont L, et al. (2012) Effect of Ce and Sb on primary graphite growth in cast irons. *Trans Indian Inst Met* 65: 707–712. <http://dx.doi.org/10.1007/s12666-012-0203-0>
35. Lacaze J, Valle N, Theuwissen K, et al. (2013) Redistribution and effect of various elements on the morphology of primary graphite in cast iron. *Adv Mater Sci Eng* 63: 638451. <https://doi.org/10.1155/2013/638451>
36. Li QG, Zhang Y, Zhang YN, et al. (2020) Influence of Sn and Nb additions on the microstructure and wear characteristics of a gray cast iron. *Appl Phys A* 126: 282. <https://doi.org/10.1007/s00339-020-03468-8>
37. Ma N, Rao Q, Zhou Q (1990) Effect of boron on the structures and properties of 28% chromium white cast iron. *Trans Am Foundry Soc* 98: 775–781.
38. Kaleicheva J, Kirov K, Mishev V, et al. (2021) Microstructure and properties of high chromium white cast irons alloyed with boron. Environment Technology Resources Proceedings of the International Scientific and Practical Conference, 137–141.
39. Chen X, Li Y, Zhang H (2011) Microstructure and mechanical properties of high boron white cast iron with about 4 wt% chromium. *J Mater Sci* 46: 957–963. <https://doi.org/10.1007/s10853-010-4840-6>
40. Nurjaman F, Sumardi S, Shofi A, et al. (2016) Effect of molybdenum, vanadium, boron on mechanical properties of high chromium white cast iron in as-cast condition. *AIP Conf Proc* 1711: 020005. <https://doi.org/10.1063/1.4941614>
41. Gong L, Fu H, Zhi X (2023) Corrosion wear of hypereutectic high chromium cast iron: A review. *Metals* 13: 308–314. <https://doi.org/10.3390/met13020308>

42. Volodin V, Tuleushev Y, Burabaeva N, et al. (2020) Thermodynamics of solutions and azeotropy in zinc–calcium melts. *Russ J Inorg Chem* 65: 1069–1076. <https://doi.org/10.1134/S0036023620070232>
43. Geiger F, Busse C, Loehrke R (1987) The vapor pressure of indium, silver, gallium, copper, tin, and gold between 0.1 and 3.0 bar. *Int J Thermophys* 8: 425–436. <https://doi.org/10.1007/BF00567103>
44. Wu Z, Cheng P, Fu G (2014) Effect of quenching temperature on microstructure and properties of Fe–Cr–B–Al alloy. *Trans Mater Heat Treat* 35: 34–37.
45. Tomovic-Petrovic S, Marković S, Zec S (2002) The effect of boron on the amount and type of carbides in chromium white irons. *J Serb Chem Soc* 67: 697–707. <https://doi.org/10.2298/JSC0210697T>
46. Chen Z, Liu M, Ma G, et al. (2023) Removal of residual element antimony from molten steel by CaC₂-containing refining slag. *Metals* 13: 441. <https://doi.org/10.3390/met13030441>
47. Han FS, Wang CC (1989) Modifying high Cr–Mn cast iron with boron and rare earth–Si alloy. *Mater Sci Technol* 5: 918–924. <https://doi.org/10.1179/mst.1989.5.9.918>
48. Shen J, Zhou QD (1988) Solidification behaviour of boron-bearing high-chromium cast iron and the modification mechanism of silicon. *Cast Met* 1: 79–85. <https://doi.org/10.1080/09534962.1988.11818951>
49. Panichkin AV, Korotenko RY, Kenzhegulov AK, et al. (2022) Porosity and non-metallic inclusions in cast iron produced with a high proportion of scrap. *Complex Use Miner Resour* 4: 68–76. <https://doi.org/10.31643/2022/6445.42>



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