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Microstructure and mechanical properties of high boron white cast iron with about 4 wt% chromium

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Abstract The microstructure and mechanical properties of high boron white cast irons with about 4 wt% chromium before and after treating with rare earth magnesium alloy were studied in this article. The experimental results indicate that the cast irons comprise a dendritic matrix and interdendritic eutectic borides M_2B and $M'_{0.9}Cr_{1.1}B_{0.9}$ that distributed in the form of continuous network in as-cast condition. The matrix is made up of fine pearlite in the alloys with and without modification, but the grain size of the matrix is decreased greatly after modification. After water quenching at 1,303 K and tempering at 473 K, the matrix of the alloy mostly changes to lath-type martensite. For the alloy without modification the boride morphology remains almost unchanged after heat treatment. And a secondary precipitation of $M_{23}(C,B)_6$ compound appears in the central region of dentritic matrix grains. The morphology of the eutectic borides is changed to the form of isolated blocks after heat treatment and there is only little intragranular $M_{23}(B,C)_6$ particles in the matrix are found in the alloy modified with rare earth magnesium alloy. The modification by rare earth magnesium alloy can refine the primary austenite and the eutectic borides. Combined with a high austenitizing temperature the modification can improve the morphology of the borides which results in the improvement of toughness and tensile strength.

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Introduction

In the course of the development of wear-resistant materials, a better combination of toughness and hardness is a concerned problem all the time. The invention of high chromium white cast iron was considered a breakthrough. However, the high chromium white cast iron is still a kind of brittle material that cannot meet the demand of serious work conditions. Niu et al. [1] developed an oriented high-chromium cast iron bars reinforced Hadfield steel matrix composite. The development of austempered ductile cast iron (ADI) that has a fine duplex matrix microstructure of bainitic ferrite and retained austenite (ausferrite) is another milestone of the development of wear-resistant materials and still a world wide research interest so far [2, 3]. However, owing to the intrinsic solidification procedure and structural characteristics of ADI, its application in some areas has been greatly limited.

High boron white cast iron is a kind of new wear-resistant material, which with boron substituting for carbon in cast iron composition and eutectic borides substituting for eutectic carbides in microstructure as the hard wear-resistant phase [4, 5]. Boron is a neighboring element with carbon in the periodic table. However, it behaves absolutely different from carbon when added as an alloying element in steel. The solubility of boron in iron is remarkably low, either in austenite (0.02 wt% at 1,149 °C) or in ferrite (lower than 0.0004 wt% below 700 °C) [6], compared with relatively high carbon solubility of 2.11 wt% (at 1,148 °C) in austenite and 0.0218 wt% (at 727 °C) in ferrite [7], which makes boride form when boron addition is more than its solubility in ferrous alloy [8, 9]. Compared with carbides, borides have higher hardness and heat stability [10], which put borides the potentials to be a kind of good wear-resistant phases. Some studies and application cases that taking borides containing alloys as wear-resistant materials have been reported [11–14]. The marked advantage of high boron white cast iron is that the matrix and the borides amount could be controlled, respectively, by carbon and boron content, as a result, strengthening and toughening matrix and adequate volume percentage of borides could be get simultaneously. The advantage of high boron white cast iron can make it possible to design the microstructure that we need. However, the literature [15] have shown that high boron white cast iron is still a brittle material with relatively low toughness for the continuos network of borides in the matrix. The morphology of eutectic borides are in the form of fish-bone type, beehive type, and screen-mesh type. One of the attempts to increase the toughness of the high boron white cast iron was to treat with modifier such as the rare earth magnesium alloy [16].

The aim of this study is to investigate the microstructure and mechanical properties of high boron white cast irons with about 4 wt% chromium before and after treating with rare earth magnesium alloy, and to develop a practical method for improving the toughness of this alloy.

Experimental procedures

The chemical composition of the high boron white cast irons with about 4 wt% chromium are shown in Table 1.

The high boron white cast irons with about 4 wt% chromium were melted in a 100 kg capacity medium-frequency coreless induction furnace with siliceous lining, with charge materials of steel scrap, graphite, Fe–B, Fe–Mn, Fe–Cr, Fe–Si master alloys and copper. As boron is an active element, oxygen and nitrogen in the melt should be effectively removed first to ensure the yield of boron. Aluminum wire and Fe–Ti master alloy were added to remove oxygen and to fix nitrogen before Fe–B alloy was added. The melt was superheated to 1,600 °C. After holding at the temperature for 5 min, alloy A was poured into Y blocks directly and alloy B was modified with rare earth magnesium alloy (RE8Mg5Si40) and then was poured into Y blocks. The rare earth magnesium alloy (0.5% addition) was placed in the bottom of ladle and covered with thin iron sheet before pouring.

All samples were cut from the lower part of the Y blocks. The heat treatment of samples was carried out in an electrical resistance furnace. The heat treatment process was made according to the author's former research on high boron cast irons [17]. The samples were held at 1,303 K for 3 h, quenched in water at room temperature, and then tempered at 473 K for 1 h. The samples after the heat treatment were polished using 0.25 μm diamond paste. The microstructures of the austempered samples were examined on an Neophot 32 optical microscope (OM) and a FEI Quanta 200 FEG scanning electron microscope (SEM) equipped with energy dispersive X-ray spectrometer (EDX) using an accelerating voltage of 15 kV after etching with 3% nital solution. The specimens for transmission electron microscope (TEM) were sliced into 0.5-mm thick plate and subsequently ground down to a thickness of 50 μm on a wet 800 grit silicon carbide abrasive paper. The specimens were punched into diameter 3 mm foils. These foils were finally electropolished in a twin-jet electro-polisher, at room temperature, at 30–35 V and 50–70 mA using a standard chromium trioxide–acetic acid solution. The deformation microstructure were examined in a JEOL JEM-2011 transmission electron microscope operated at 100 kV. X-ray diffraction analysis was performed on a D/max-RB X-ray diffractometer (XRD) to determine the borides type after heat treatments. The specimens were scanned using Cu K_α radiation at 40 kV and 300 mA. The scanning rate (2θ) was $1^\circ\ \mathrm{min}^{-1}$.

After the heat treatment, standard tensile test specimens (Ø 10 × 110 mm) and standard Mesnager U-notch samples (10 × 10 × 50 mm with a 2-mm U notch) were machined from the Y blocks. Tensile tests were carried out on a hydraulic servo controlled MTS 810 test machine at room temperature. The yield and tensile strength were calculated from the load versus displacement plots on an X–Y recorder. Tensile strength and yield strength values reported in this article are averages of three tests. Impact tests were done using an 150-J capacity machine at room temperature. Hardness tests were made on samples machined from the Mesnager samples. The impact toughness values reported are the averages of three tests. Hardness and microhardness were tested on a Rockwell hardness machine. For hardness test, a sufficient step between these marks must be selected to minimize the interaction of the plastically deformed zones and the step between two marks of indentation is larger than 5 mm. Five readings were taken on each sample in a random way and the average of them is reported.

Table 1 The chemical composition of two high boron white cast irons (wt%)

Alloy	B	C	Si	Mn	Cr	P	Ti	S	Mg	Ce	La	Fe
A	1.56	0.37	0.79	1.07	4.24	0.018	0.048	0.014	–	–	–	Balance
B	1.61	0.35	0.83	1.06	4.13	0.020	0.43	0.016	0.012	0.016	0.018	Balance

Results and discussion

As-cast microstructure

The as-cast microstructures of high boron white cast irons with about 4 wt% chromium before and after treating with rare earth magnesium alloy are shown in Fig. 1. It can be seen from Fig. 1 that the high boron white cast irons comprise a dendritic matrix and an interdendritic eutectic compound that distributed in the form of continuous network (Fig. 1a, c). However, there are some broken necks between the borides in alloy B modified with rare earth magnesium alloy. The matrix of both alloys is made up of fine pearlite (Fig. 1b, d). By comparing the grain size of matrix in alloy A and alloy B, it is decreased greatly in alloy B (Fig. 1a, c), which means that the modification with rear earth magnesium alloy can refine the primary austenite of the alloy. As a result, the borides are distributed evenly and the size of the borides is decreased as well. Rare earth elements and magnesium are strong constitutional supercooling promoting elements [18, 19], which are easy to aggregate in the melt around the primary austenite and leads to great undercooling. The behavior of rare earth elements and magnesium is beneficial to the refinement of dendritic austenite, and as a result, the eutectic region becomes smaller and leads to the refinement of eutectics. Moreover, rare earth elements are surface active materials, so they can interact with C, N, S, and O in the steel and form high melting point compounds, such as La_2O_3, Ce_2O_3, Ce_2O_2S, etc. These high melting point compounds can serve as heterogeneous nuclei of austenite in the melt [20–22].

According to the former research, the eutectic compound in the high boron cast irons with low or no chromium addition [16] is in M_2B type, where M represents iron, chromium, or manganese. When about 4 wt% of chromium is added, the eutectic compound in a chemical formula of $M'_{0.9}Cr_{1.1}B_{0.9}$ in high boron white cast irons appears in accordance with the XRD pattern (Fig. 2), where M′ stands for manganese in terms of the EDX spectra of the borides (Fig. 3). The higher chromium content, the more eutectic compound in chemical formula of $M'_{0.9}Cr_{1.1}B_{0.9}$. TEM analysis (Fig. 4) also show that the borides has a crystal structure of $M'_{0.9}Cr_{1.1}B_{0.9}$.

Figure 5 illustrates the energy dispersive X-ray spectrometer of pearlite in the matrix. In Fig. 3, there is no carbon or silicon peak in the EDX spectra of the eutectic compound contrary to Fig. 5. This means that carbon and silicon are mainly dissolved in the matrix and boron is mostly dissolved in the matrix. The character of elements

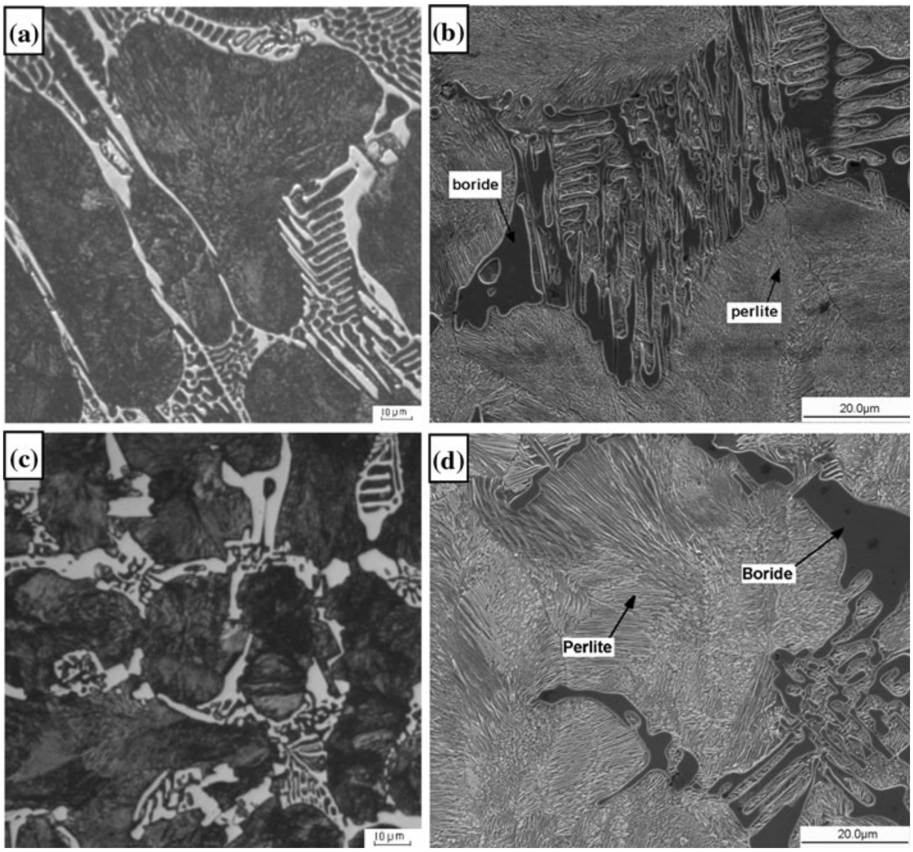

Fig. 1 As-cast microstructure of high boron white cast irons with about 4 wt% chromium **a** optical microscope micrograph of alloy A, **b** SEM micrograph of alloy A, **c** optical microscope micrograph of alloy B, and **d** SEM micrograph of alloy B

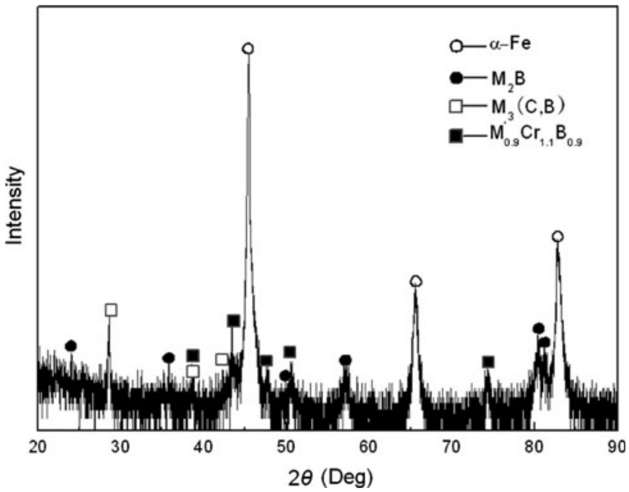

Fig. 2 X-ray diffraction pattern of as-cast alloy A

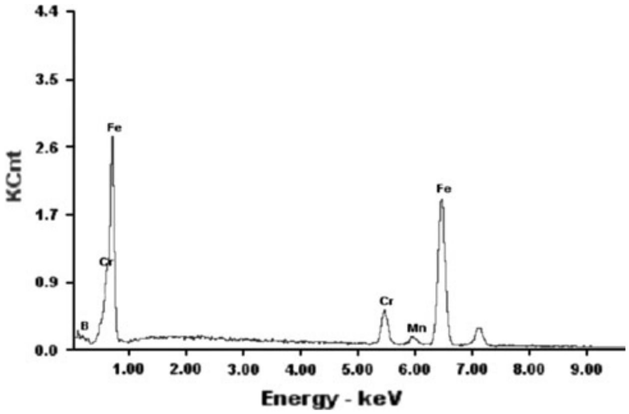

Fig. 3 Energy dispersive X-ray spectrometer of the borides alloy A

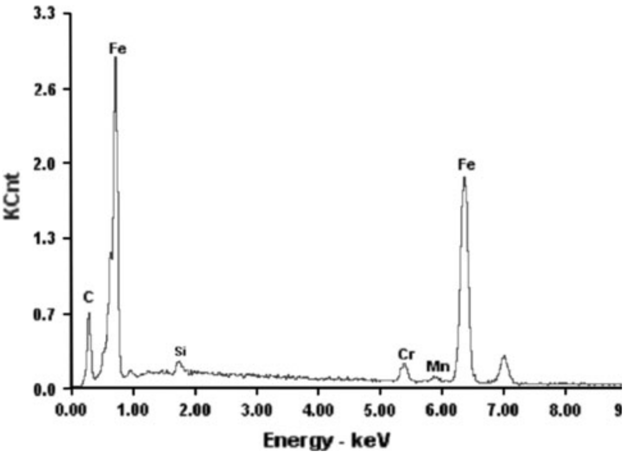

Fig. 5 Energy dispersive X-ray spectrometer of pearlite in alloy A

distribution in high boron white cast iron indicates that the boron mainly forms borides and carbon content determines the matrix.

Microstructure after heat treatment

The scanning electron microscopy microstructures of the high boron white cast irons with about 4 wt% chromium before and after treating with rare earth magnesium alloy after heat treatment are shown in Fig. 6.

After heat treatment, the matrix of alloy A without modification is changed from pearlite to lath-type martensite, and the morphology of the borides is still distributed in the form of continuous network (Fig. 6a). Except for the

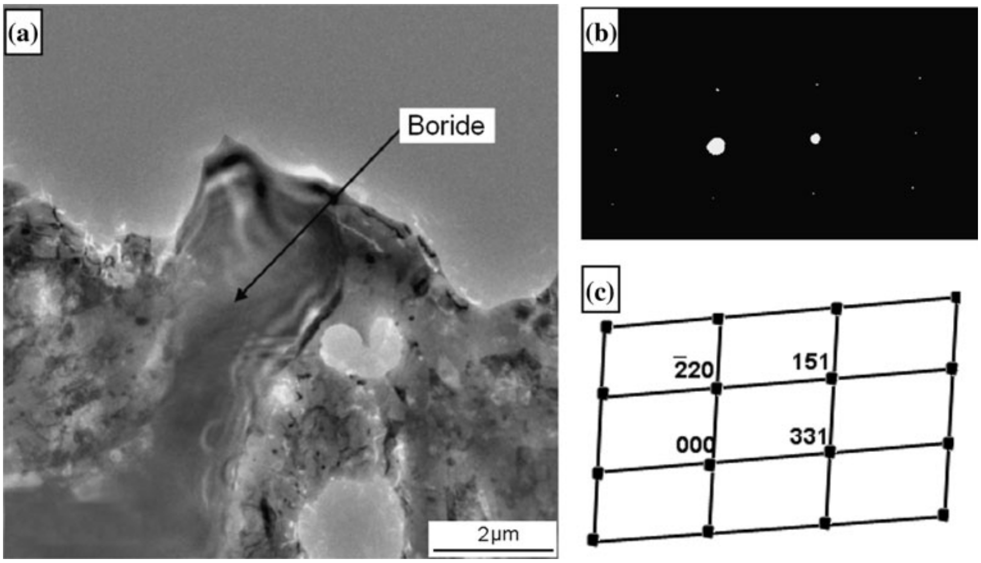

Fig. 4 Borides in formula of $M'_{0.9}Cr_{1.1}B_{0.9}$, $Z = [11\bar{6}]$ in alloy A, **a** bright field image of transmission electron microscopy, **b** corresponding diffraction pattern, and **c** interpretation of diffraction pattern

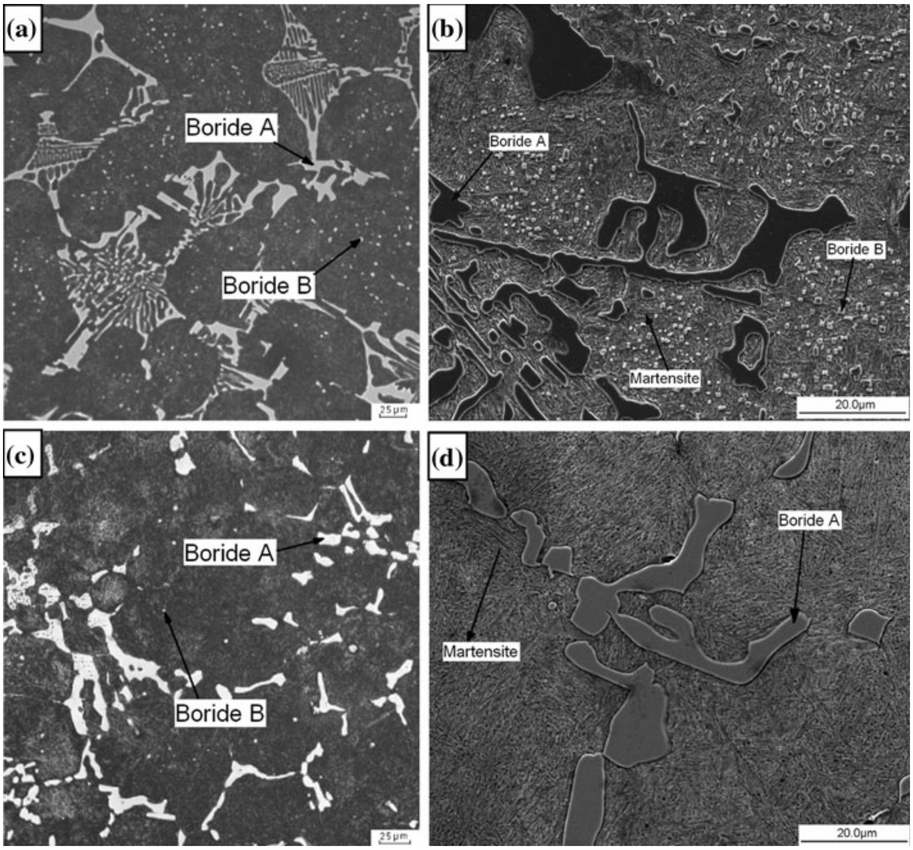

Fig. 6 Scanning electron microscopy microstructures after heat treatments of high boron white cast irons with about 4 wt% chromium **a** optical microscope micrograph of alloy A, **b** SEM micrograph of alloy A, **c** optical microscope micrograph of alloy B, and **d** SEM micrograph of alloy B

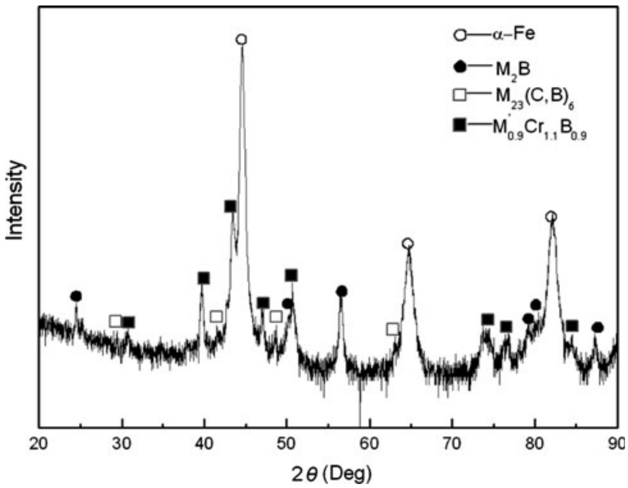

Fig. 7 X-ray diffraction pattern of alloy A after heat treatment

eutectic compounds (boride A in Fig. 6b) in the chemical formula of M_2B and $M'_{0.9}Cr_{1.1}B_{0.9}$, there has a lot of particles appears in the central region of dendritic matrix grains in alloy A. XRD (Fig. 7) and TEM analysis (Fig. 8) show that these particles (boride B in Fig. 6b) has a crystal structure of $M_{23}(B,C)_6$, where M may be iron, chromium, and manganese in terms of the EDX spectra of the borides (Fig. 9). Those secondary precipitated particles form during austenitizing at high temperature. Furthermore, XRD analysis has shown that there is no cementite precipitated in the structure.

The matrix of alloy B is also changed to lath-type martensite after heat treatment. However, it is very different with the alloy A, the morphology of the borides in alloy B modified with rare earth magnesium alloy is changed to the form of isolated blocks. And there is only little intragranular $M_{23}(B,C)_6$ particles (boride B in Fig. 6c) in the matrix are found in alloy B. The results indicated that the modification combined with a higher austenitizing temperature can improve the morphology of the borides. Moreover, the modification can retard the precipitation of the $M_{23}(B,C)_6$ particles in the matrix.

As we know, boron is easy to segregate by means of equilibrium or non-equilibrium style [23–26]. Non-equilibrium segregation is a dynamic process, which is quench-induced segregation [25]. Equilibrium segregation is a thermodynamics process, which only depends on the heating temperature and can be accounted by theories of solute drag [27]. The precipitation of the secondary $M_{23}(B,C)_6$ borocarbides is in the form of equilibrium segregation. Guo [11] considered that the diameter of chromium is larger than that of iron, it would enlarge the crystal lattice parameter as chromium is dissolved in iron by means of substitution. The dissolved boron would segregate to the grain boundary, and

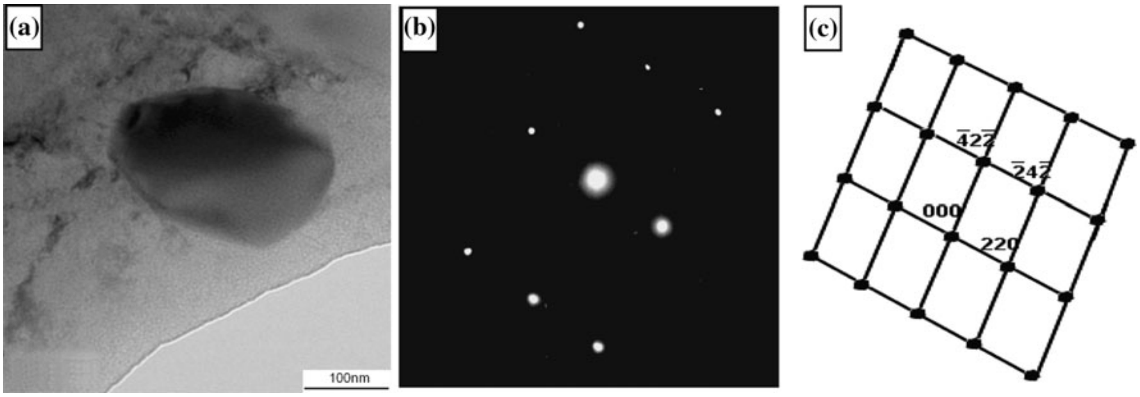

Fig. 8 Secondary precipitated borocarbides in formula of $M_{23}(B,C)_6$, $Z = [\bar{1}13]$ in alloy A after heat treatment, **a** bright field image of transmission electron microscopy, **b** corresponding diffraction pattern, and **c** interpretation of diffraction pattern

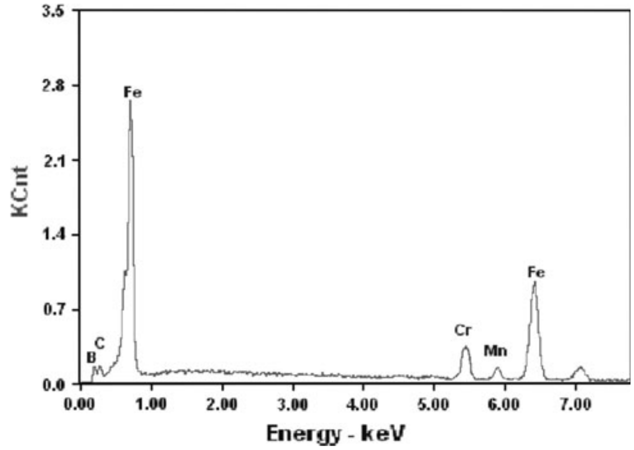

Fig. 9 Energy dispersive X-ray spectrometer of secondary precipitated borocarbides $M_{23}(B,C)_6$ in alloy A

the number of segregation raises with the increasing of temperature. Therefore, with the addition of chromium content, the matrix could dissolve more boron and results in the $M_{23}(B,C)_6$ borocarbides precipitation.

For alloy A, the primary austenite grains is large. The segregation of boron element at the primary austenite grain boundaries is low because it is required for boron element to diffuse a long distance form the central region of dentritic matrix grains to the grain boundaries. Consequently, the $M_{23}(B,C)_6$ borocarbides can precipitate in the matrix. Comparing with alloy A, alloy B modified with rare earth magnesium alloy has smaller primary austenite grains. The amount of segregation of boron element is high and thus results in a larger boron depleted zones appear adjacent to the boundaries. Hence, there has no enough boron dissolved in the matrix to precipitated in the form of $M_{23}(B,C)_6$ borocarbides.

Table 2 Mechanical properties of high boron white cat irons with about 4 wt% chromium

Alloy	Average as-cast hardness (HRC)	Mechanical properties after heat treatment		
		Average hardness (HRC)	Impact toughness (J cm^{-2})	Tensile strength (MPa)
A	32.5	58.5	4.0	412
B	32.9	59.0	11.2	656

Mechanical properties

The mechanical properties of high boron white cast irons with about 4 wt% chromium are listed in Table 2.

According to Table 2, there is no evident difference of as-cast hardness and hardness after heat treatment between the two alloys, but the impact toughness and tensile strength of alloy B are increased markedly, which is mainly due to the improvement of the borides' morphology from continuous network to the form of isolated distribution and the diminish of the grain size. Moreover, rare earth elements and magnesium can decrease the content of sulfur and oxygen, which can improve the purity of melt and be beneficial to the properties of alloy.

Conclusions

The microstructure and mechanical properties of high boron white cast iron with about 4 wt% chromium before and after treating with rare earth magnesium alloy were studied. The microstructure of the high boron white cast irons comprises a dendritic matrix and interdendritic eutectic M_2B and $M'_{0.9}Cr_{1.1}B_{0.9}$ that distributed in the form of continuous network in as-cast condition. The matrix is made up of fine pearlite in alloy A. There are some broken necks between the borides in alloy B after modification with rare earth magnesium alloy. The matrix is also made up of fine pearlite and the grain size of matrix is decreased greatly in alloy B in as-cast condition. After water quenching at 1,303 K and tempering at 473 K, the matrix of both alloys changes to lath-type martensite. The morphology of the borides is almost unchanged in alloy A. Except for the eutectic compounds in the chemical formula of M_2B and $M'_{0.9}Cr_{1.1}B_{0.9}$, there has a secondary precipitation of $M_{23}(C, B)_6$ appears in the central region of dentritic matrix grains in alloy A. It is very different with the alloy A, the morphology of the borides in alloy B modified with rare earth magnesium alloy is changed to the form of isolated blocks after heat treatment and there is only little intragranular $M_{23}(B,C)_6$ particles in the matrix are found. Modification with rare earth magnesium alloy can refine the primary austenite and the eutectic borides. High temperature heat treatment for high boron white cast irons with about 4 wt% chromium with modification is beneficial to granulate the borides and results in the improvement of toughness and tensile strength.

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