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WEAR RESISTANT HIGH BORON CAST ALLOY - A REVIEW

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Abstract. High boron cast alloy has attracted much attention as new kind of wear-resistant materials due to its low cost, high strength and toughness, and high wear resistance. This paper reviews research progress of wear resistant high boron cast alloy, including the alloy composition, fabrication, heat treamtment, improvement of boron morphology, wear properties, and application. At last, development direction and research emphasis on the high boron cast alloy are discussed.

1. INTRODUCTION

Abrasive wear resistant can substantially be improved by second phases embedded in a hard or soft matrix [1]. Conventional Fe-base wear-resistant materials take carbide as wear-resistant phase, such as high chromium cast iron and Ni-hard cast iron, which would consume a large amount of expensive alloying elements. In addition, high chromium white cast iron and Ni-hard cast iron are still a kind of brittle material, this fact restricts their application under serious work conditions. Therefore, it is important to develop a new type of wear-resistant materials that contains low amounts of expensive alloying elements and has good mechanical properties. Boron is an inexpensive material and is widely used in steel production [2,3]. In addition, borides usually possess very high hardness, which is widely used to increase the wear resistance of surface layer via the boriding process [4,5]. In recent years, boride is used as a hard phase in Fe alloys: high boron cast alloy, high boron white cast iron, Fe-B alloy, Fe-Cr-B alloy (Cr content varying from 5 wt.% to 15 wt.%), or Fe-C-B alloy, etc.

According to Fe-B phase diagram [6], see Fig. 1, boron has a very low solubility in iron (the maximum solubility in γ-iron is 0.02 wt.% and in α-iron is 0.0081 wt.%), which makes the formation of boride possible when boron is added in the iron melt. We can fabricate this alloy by adding more boron in Fe alloy; indeed, Fe_2B formation is preferable at boron content exceeding 0.0021 wt.%, see Fe-B phase diagram in Fig. 1. Lakeland [7] suggested the idea to use the boride as wear resistant skeleton and fabricated the high boron cast alloy for the first time. The matrix and wear-resistant phase here could be controlled by changing carbon and boron concentrations, this approach makes it possible to design the required microstructure. In addition, high boron cast alloy consumes relatively low amount of expensive alloying elements and has good abrasion resistance, large neutron capture cross section [8], corrosion resistance [9-12], etc.

This paper reviews research progress of wear resistant high boron cast alloy, including the alloy design, fabrication, heat treatment, improvement of boron morphology, wear properties and wear failure behavior, as well as the material applications.

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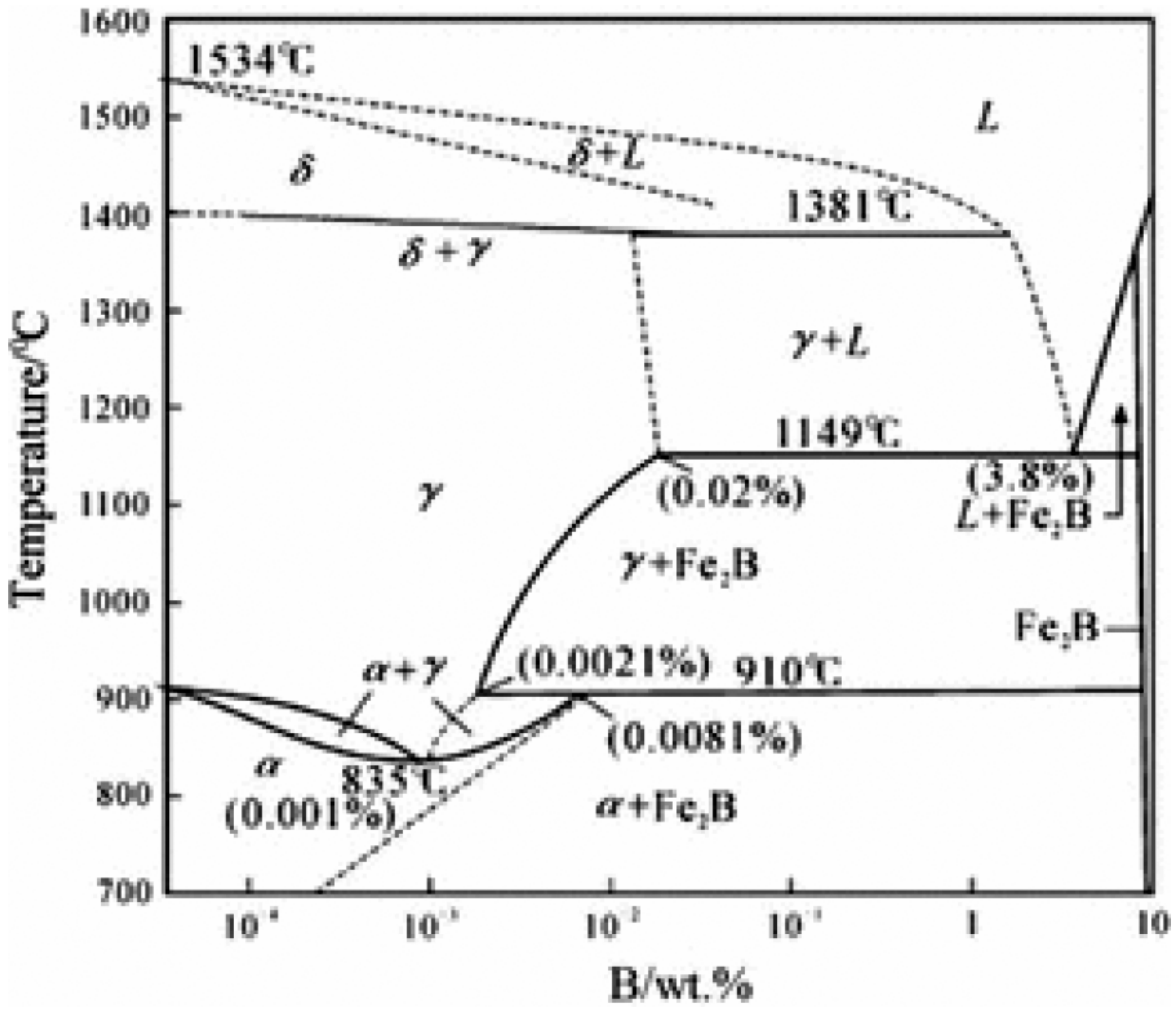

Fig. 1. Fe-B phase diagram, reprinted with permission from Jianjun Zhang // *Journal of Materials Engineering and Performance*, 20 (2011) 1658, © 2011 Springer.

2. HIGH BORON CAST ALLOY OVERVIEW

2.1. Composition design and solidification structure of high boron cast alloy

Lakeland performed a thorough experimental study of Fe-Cr-B alloy and tested its mechanical and wear properties. It was shown that Fe-Cr-B alloy exhibits excellent wear resistance and its hardness can change from HRC 22 to HRC 62. The chemical composition of the alloys used in the experiments of Lakeland is given in Table 1. This kind of high boron cast alloy has a high Cr content, while Ni, Mo, V, and Nb, etc. contents are low (see Table 1). Therefore, this kind of high boron cast alloy is usually called as Fe-Cr-B alloy.

The solidification microstructure of Fe-Cr-B alloy consists of a dendritic matrix and inter-dendritic M_2B borides, which constitute a three-dimensional networks surrounding the dendritic matrix [14]. The typical as-cast microstructures of the Fe-Cr-B cast irons are shown in Fig. 2 [15].

There exist a lot of reports describing Fe-Cr-B alloy fabrication and properties, see e.g. [16-18]. Guo and Kelly [16] reveal boron solubility in the as-cast and solution treated martensite of Fe-Cr-B cast alloy, containing ~1.35 wt.% of boron and 12 wt.% of chromium, as well as some other alloying elements. The significant microstructural variations after tempering at 750 °C for 0.5-4 h evident in comparison with the original as-cast and solution treated

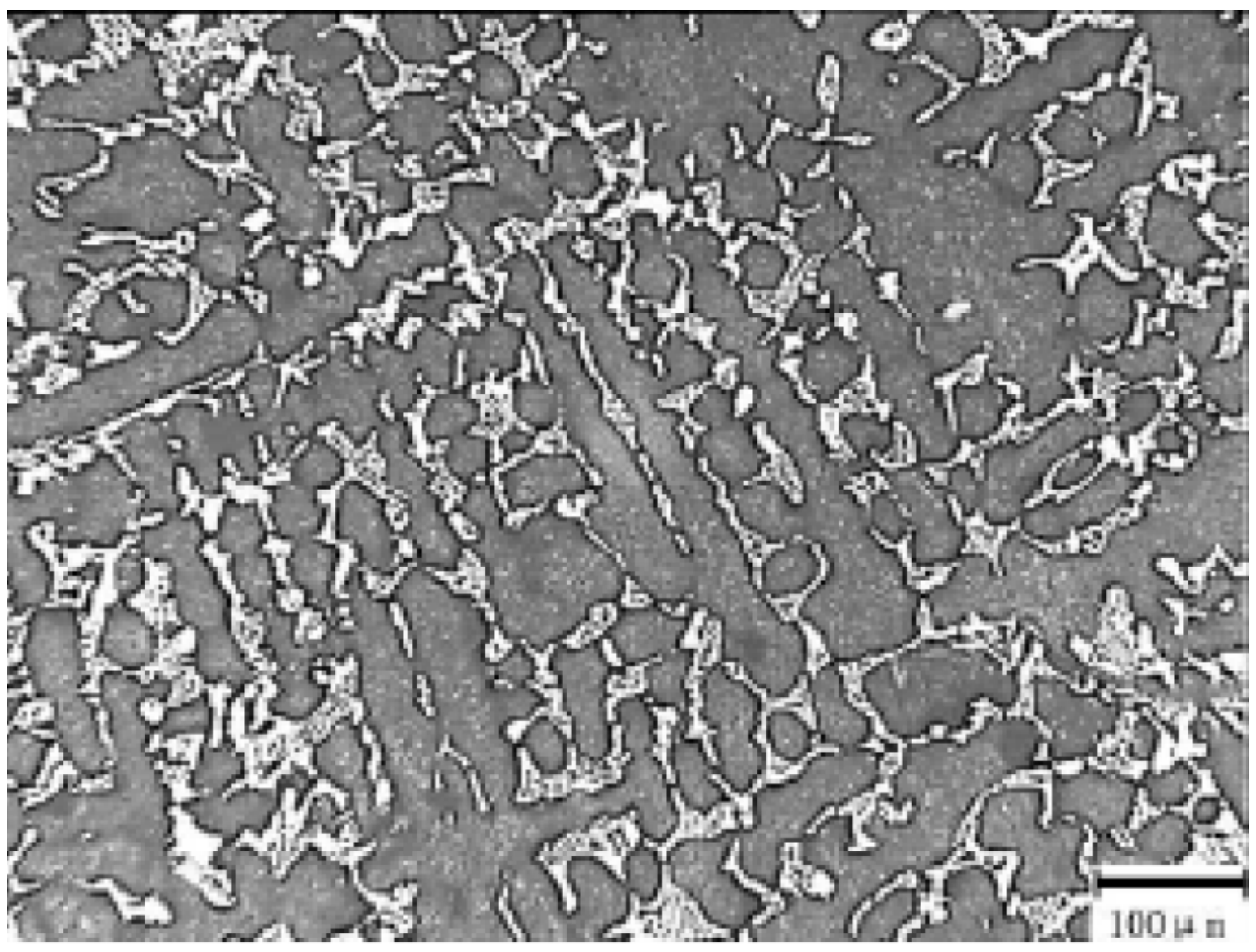

Fig. 2. The typical as-cast microstructures of the Fe-Cr-B cast alloy, reprinted with permission from Jianjun Zhang // Tribology Letters 44 (2011) 31, © 2011 Springer.

Table 1. Chemical composition of Fe-Cr-B alloy used (wt.%) manufactured and studied in [13], components added to Fe are listed.

Cr	B	Ni	Cu	C	Si	Mn	Mo	V	Nb
5-15	0.1-1.0	1.5-2	1-2	0.3-0.55	0.5-1.0	0.5-1.0	0.8-1.5	0.3-0.5	0.3-0.5

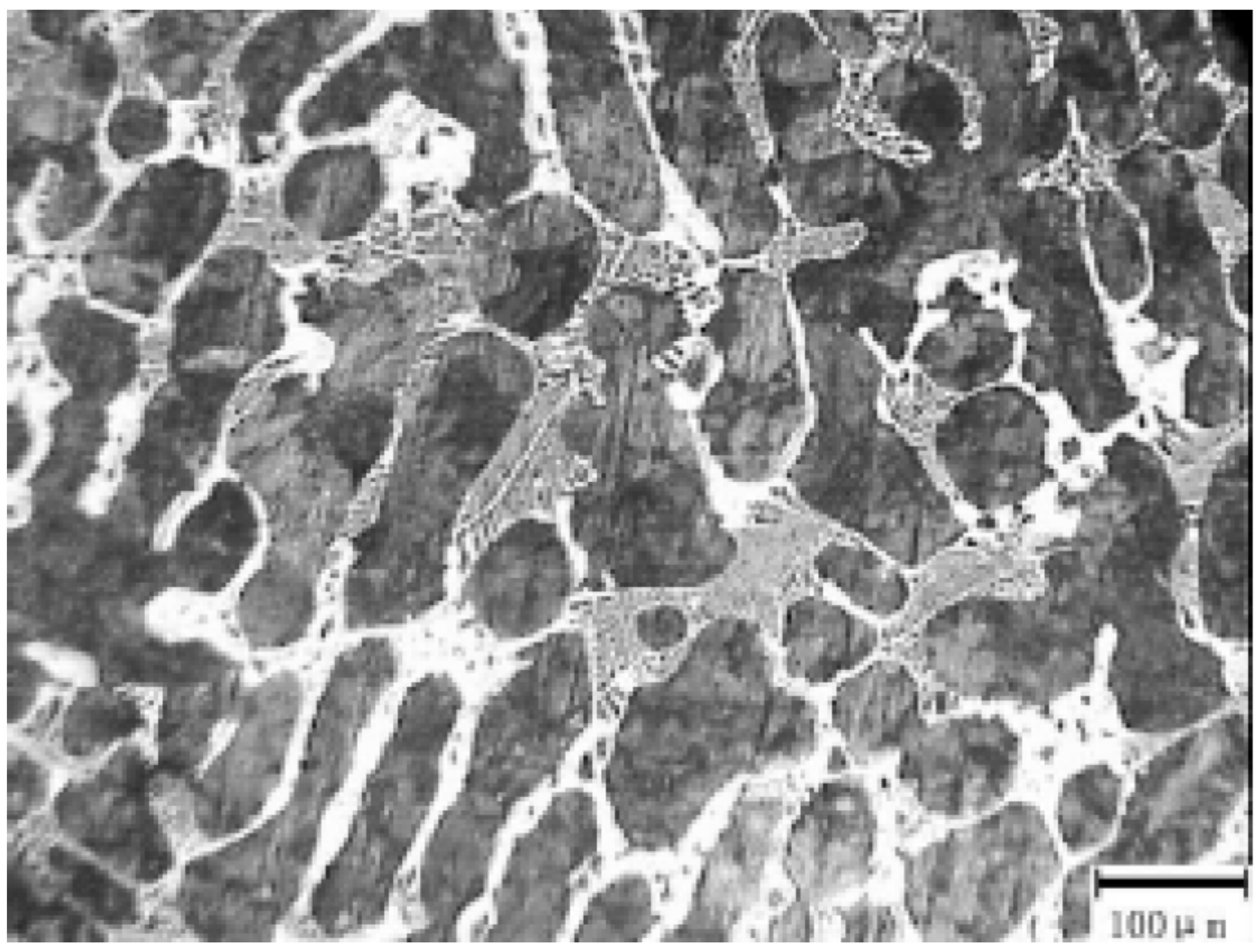

Fig. 3. The typical as-cast microstructures of the Fe-B alloy, reprinted with permission from Jianjun Zhang // Tribology Letters 44 (2011) 31, © 2011 Springer.

microstructures, indicated that the matrix consists of boron and carbon supersaturated solid solutions. The boron solubility detected by electron microprobe was lying between 0.185-0.515 wt.% for the as-cast martensite and 0.015-0.0589 wt.% for the solution treated martensite, this value is much higher than the value of 0.005 wt.% accepted for pure iron. This remarkable increase is thought to be associated with such metallic alloying element addition as chromium, vanadium, and molybdenum, which have atomic diameters larger than iron, and expand the iron lattice sufficiently to allow boron atoms to occupy the interstitial sites in iron lattice.

Chinese researchers innovated a new type high boron cast alloy. They reduced the Cr content down to ~ 2 wt.% (some alloys were manufactured even without Cr). The content of conventionally used alloying elements like Ni, Mo, V, Nb, etc. was also significantly reduced, sometimes down to zero, providing the reduction of the high boron cast alloy cost and, therefore, making it very interesting for industrial applications [19-22]. This type of high boron cast alloy is called Fe-B alloy. Fu et al. [19] reduced Cr content in the alloy, while Ni, Mo, V, Nb, etc. were not used at all. The alloy composition can be described as follows, wt.% added to Fe: 0.08-0.20 C, 2.2-4.0 B, 0.5-1.0 Si, 0.5-1.0 Mn, 0.5-2.0 Cr. The results of the structure investigation showed that the solidification microstructure of Fe-B alloy consists of Fe_2B, ferrite, and pearlite, boride is netlike distributed. After the heat treatment, matrix microstructure changes into martensite, the hardness increases up to 60 HRC, the impact toughness becomes higher than 10 J/cm^2, and the toughness higher than 30 MPa•m$^{1/2}$ is achieved. Thus, it was shown that the required properties of Fe-B alloy can be provided at low Cr content without additional alloying elements. The typical as-cast microstructures of the Fe-B alloy are shown in Fig. 3 [15]. Song [23] has systematically studied the Fe-B alloy varying carbon and boron content. Low carbon-low boron alloy (0.2-0.4% C, 1.0% B), medium carbon-alterable boron alloy (0.3-0.45% C, 0.5-3.0% B), and high carbon-high boron alloy (0.3-0.45% C, 0.5-3.0% B) were fabricated and studied. The methods of alloy melting process, solidification process for casting, heat treatment process, the structures and properties after heat treatment, wear-resistance and industry application of two-body abrasion and three-body wear have been investigated for these alloys. The effect of carbon and boron contents on boride and boron carbide formation in the high boron iron-based alloy can be described as follows. Under the certain boron content, boron carbide volume fraction increases with the increasing in carbon content, this increase is ~ 1 vol.% of formed boron carbide per each 0.1 vol.% of carbon content increase. Under the certain carbon content, boron content affect on boron carbide volume fraction is quite significant, it can be described by the following exponential curve y=7.078e$^{0.822x}$, where y is a forming boron carbide content and x – boron content.

Low carbon-low boron alloy was shown to posses low hardness, high impact toughness, and high fracture toughness. Changes in boron content in the medium carbon-alterable boron alloy resulted in significant changes in alloy macro-hardness after heat-treatment, impact toughness, and fracture toughness. The hardness of high carbon-high boron alloy was rapidly increased with the increase in carbon content, however, variations in carbon content slightly affect the impact toughness.

Some researcher added Ti to Fe-B alloy. Jiang [24] reported that the borides morphology was improved by such Ti adding, borides became disconnected, shorter, and dumpier, their distribution tended to spread. In these alloys, Ti mostly existed as TiC or TiB_2, TiC was mainly distributed on the grain boundaries or in the eutectic phases. The hardness of the boron-titanium cast Ferroalloy was increasing, while the impact toughness was reducing with the boron content increase. The increase in titanium content gives rise to allot hardness was reduction, while impact toughness was increasing here. It was shown that the hardness of Ti-containing Ferroalloy can be increased by carbon addition.

Liu et al. [25] have found that the addition of titanium can alter the solidification path of the Fe-B alloys, disrupt the formation of continuous grain-boundary Fe_2B network, and improve the mechanical properties of the alloys. When the titanium to boron ratio is 1:2, the microstructure becomes uniform with a mixed TiB_2-αFe morphology. This ternary Fe-B-Ti alloy exhibits balanced mechanical properties: yield strength, ultimate tensile strength, and elongation are 354 MPa, 552 MPa, and 4.0%, respectively. Additional rolling at 1223K enhances the alloy ductility, the increase can be ~16% or even more. It offers a great potential for the application of hard and malleable alloy.

It should be also mentioned that boron addition to stainless steel also improves the wear resistant, see results reported by Fu et al. [26-28]. It was shown that the borides do not decompose after the solution treatment at high temperature of 1050 °C, however, some part of borides dissolves into the matrix. This mechanism increases the boron solubility in the austenitic matrix and increases the hardness of stainless steel by 8.54%. The lifetime of transfer pipe for zinc liquid made from the high boron abrasive wear resistant stainless steel is 1.5-1.8 times longer than that of common stainless steel pipe [28].

2.2. Heat treatment of high boron cast alloy

Heat treatment plays an important role for the properties of high boron cast alloy, its microstructure and properties can be improved by quenching temperature and cooling method choice. Jiang et al. [29] studied the effect of quenching temperature on microstructure and hardness of high boron cast alloy. The as-cast matrix of high boron cast alloy consists of pearlite and ferrite. Quenching at 900~1100 °C did not significantly affect on the borides formation in the matrix. The micro-hardness of the matrix and macro-hardness were increased with the increase in quenching temperature. Under quenching at 900-1100 °C, the matrix completely transforms into the lath martensite having high strength and excellent toughness.

The effect of quenching temperature in the range from 900 to 1050 °C on the microstructure, mechanical properties, and abrasion resistance of modified high born cast steel containing 0.3 wt.% C, 3.0 wt.% B, and 0.072 wt.% Re was studied in [30]. It was stated that quenching at 900 °C resulted in structures containing a small amount of pearlite. The existence of pearlite led to poor hardness and wear resistance of modified high born cast steel. Quenching at temperatures between 900 and 950 °C resulted in the decrease in pearlite content and in the increase in hardness and abrasion resistance. The metallic matrix was completely transformed into the martensite during the quenching at 1000 °C; the modified high born cast steel had high hardness, tensile strength, impact toughness and excellent abrasion resistance. The hardness, tensile strength, and impact toughness of the modified high born cast steel were not significantly changed by the quenching at temperatures over 1000 °C. The increase in quenching temperature led to the transformation of borides from continuous to isolated shape and promoted the boride coarsening.

Fu et al. [31] investigated the solidification structures and mechanical properties of high boron cast alloy containing 1.4%-2.0% B and 0.4%-0.6% C at 950, 1000, and 1050 °C quenching temperatures and oil cooling. It was shown that solidification structures of Fe-B alloy consisted of such borides as Fe_2B, $Fe_3(C, B)$, and $Fe_{23}(C,B)_6$ and metallic matrix, such as martensite, pearlite and ferrite. The part of boride network here was broken; no new phases were detected after the quenching. The matrix transformed into the single martensite completely and the alloy hardness exceeds 55 HRC. The hardness of Fe-B alloy increases, while the impact toughness has no obvious change with the increase in the quenching temperature.

High boron cast alloy can be treated by water quenching, oil quenching, air quenching, and isothermal quenching. Liu [32] compared the effect of water quenching, oil quenching, and air quenching on the microstructure and properties of Fe-B alloy. The matrix of Fe-B alloy transforms into low hardness pearlite after the air quenching. After water cooling or oil cooling, the matrix of Fe-B alloy transforms into martensite, whose hardness is high. Since the amount of lath martensite produced by water cooling is higher than that formed after oil cooling, the hardness of samples after water cooling is higher than that produced by oil cooling. However, the impact toughness here is lower than in the samples produced using oil cooling. Feng et al. [33] performed similar experiments with analogous results. It was reported that the structure of Fe-B cast alloy changes from pearlite being prevailing, ferrite, and a small amount of martensite to martensite being prevailing with a small amount of pearlite. The hardness here increases with the increase in quenching cooling rate. In the case of water quenching, higher or lower quenching temperatures were not advantageous to obtain complete martensite matrix.

In order to improve the mechanical properties of Fe-B alloy, isothermal quenching method was adopted [34]. It was shown that the matrix transforms into bainite and netlike boride in Fe-B alloy and it was unchanged after isothermal quenching. Impact toughness of Fe-B alloy with bainite matrix was better than that of Fe-B alloy with martensite matrix. It should be noted that Fe-B alloy achieved excellent mechanical properties by isothermal quenching.

2.3. Improvement of boron morphology

High boron cast alloy possesses continuous networks of eutectic borides, which destroys the continuity of matrix and results in materials embrittlement. Several approaches were used to solve problems dealing with the low toughness of high boron cast alloy problem; such methods as heat treatment [35,36], rare earth (RE) modification [37,38], and semi-solid method [39] should be mentioned.

High temperature heat treatment can be used in white cast iron and high speed steel to improve the carbide morphology. However, high temperature heat treatment is not an effective way to improve the boride morphology. Fu [31] reported that the boride morphology improvement was not observed here after 1050 °C quenching. The use of high temperature heat treatment in order to break the boride network is difficult because boron has a very low solubility in iron (the maximum solubility in γ-iron is 0.02 wt.%).

Some rare earth metals have already been used in high boron cast alloy to improve the boron morphology. Fu et al. [37] studied the effect of rare earth and titanium additions on the microstructure and properties of Fe-B alloy. He discovered that the boride eutectic in the modified Fe-B alloy after the heat treatment exists in the form of a granular boride structure that appears to be isolated particles. The strength and toughness of the modified Fe-B alloy are higher than values typical for the unmodified Fe-B alloy. In particular, the impact toughness increases significantly and reaches 222.6 kJ/m^2 (80.5% increase). Liu et al. [38] used V, Ti, and RE-Mg as modification elements to improve the boride morphology. It was demonstrated that the matrix grain is decreased in size by half after such modification and the size of boride grains is also decreases. After the heat treatment, the boride network is broken up, this fact results in the further toughness improvement of the high boron iron-based alloy. Kuang et al. [40] added the RE-N in Fe-B-Ti alloy. After this modification, the grain and eutectic structure of Fe-B-Ti alloy were refined, the borides distribution is homogeneous. There are many obvious necking and broken net in the borides. Feng et al. [41] selected rare earth, titanium, and nitrogen as modification elements to improve the boride morphology. It was shown that the solidification structures of high boron cast alloy in this case were refined, structures distribution was uniform here. After the heat treatment, the boride in the high boron cast alloy turned into nodular and rod. The toughness of high boron alloy steel increases from 12-15 J/cm^2 to 28-32 J/cm^2, this increase is very significantly.

RE-Mg is adopted as a modification agent, which may improve the morphology and, as a result, increase the ductility by 34.6% after the heat treatment [42]. Shi [43] studied the effect of complex modification by RE-Mg on the structure and mechanical properties of Fe-B alloy. After the RE-Mg modification, lamellar carbon-boron compounds become shorter and thinner in the eutectic microstructure; necking and broken net appear in many positions, resulting in partial spheroidization of the borocarbide compounds. The hardness of Fe-B alloy increased after RE-Mg modification, and the impact toughness and wear resistance were significantly improved.

Yi [39] prepared the Fe-B alloy by semi-solid method. Compared with the coarse eutectic borides in the ordinary alloy, the eutectic boride structures in the semisolid alloy are greatly refined, see Fig. 4. These results demonstrated that the significant toughness improvement can not be obtained here because the method does not provide complete elimination of eutectic boride networks along grain boundaries. In our previous research, we have found that hot forging is the most effective method to improve the toughness of Fe-B alloy, this improvement can be assumed as being due to boride networks breaking [6,44]. The boride networks are broken down by hot forging and the matrix becomes continuous, see Fig. 5. Comparing the results shown by forged and unforged samples, one can conclude that the hardness of the forged samples slightly increases, while the toughness increase is quite significant (from 4 to 29.4 J/cm^2, [44]). Feng Li and Zhenghua Li [45] also adopted hot deformation for the improvement of the hard phase morphology and properties. The experimental results show that hot deformation can crush the continuous hard phase network in the alloy into gathered particles. Hot-rolling technology is used to improve the microstructure and mechanical properties [46], it results in great effects in microstructure and mechanical properties of the high boron Fe-B alloys. Hot rolling can disrupt the formation of the continuous grain-boundary Fe_2B network, refine the reinforcement particles, and eliminate the casting defects. The mechanical

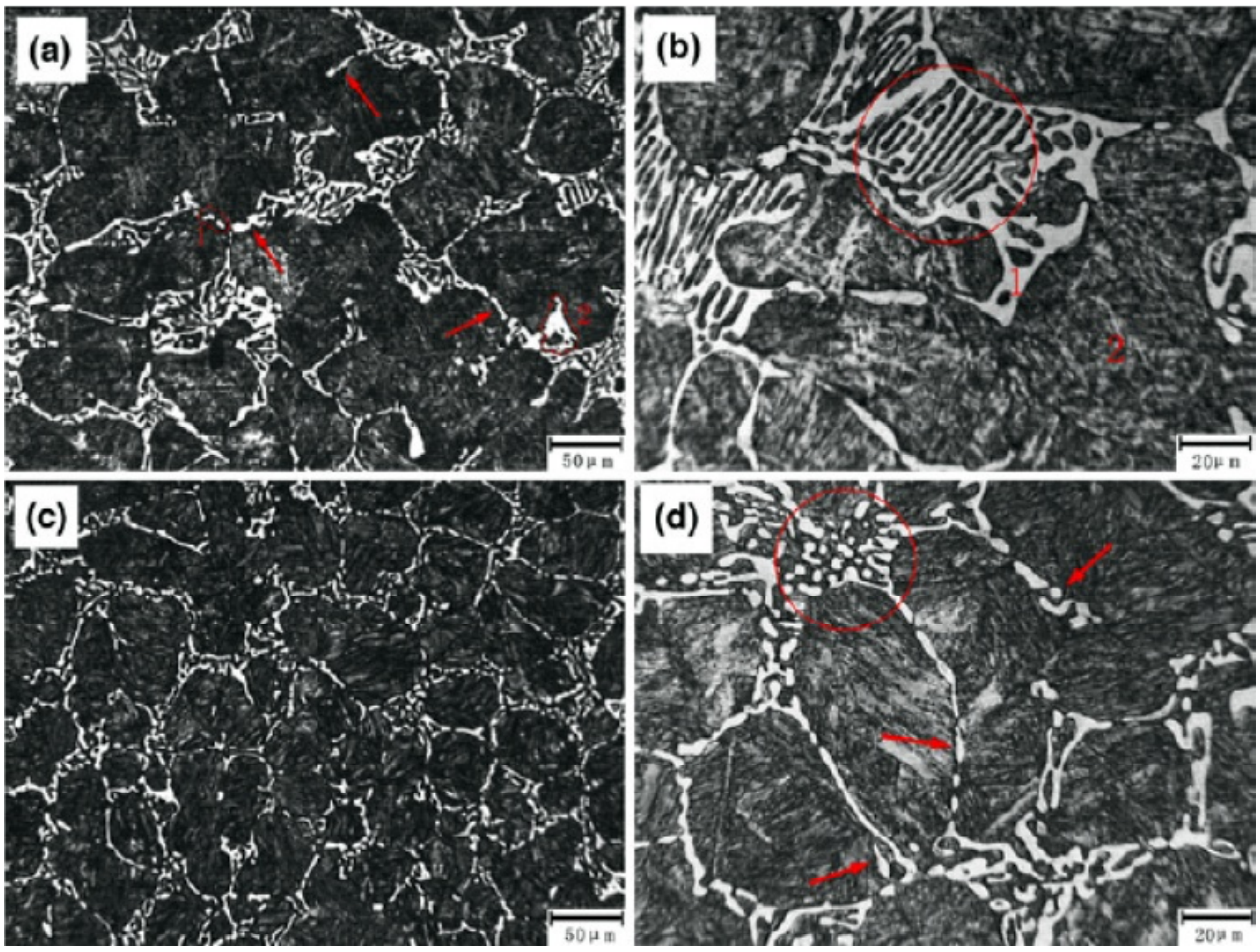

Fig. 4. Heat-treated structures of Ordinary and Semi-Solid: a, b showing 200 and 500 times magnification structures of Ordinary, respectively; c, d showing 200 and 500 times magnification structures of Semi-Solid, respectively, reprinted with permission from Dawei Yi // Tribology Letters 42 (2011) 67, © 2011 Springer.

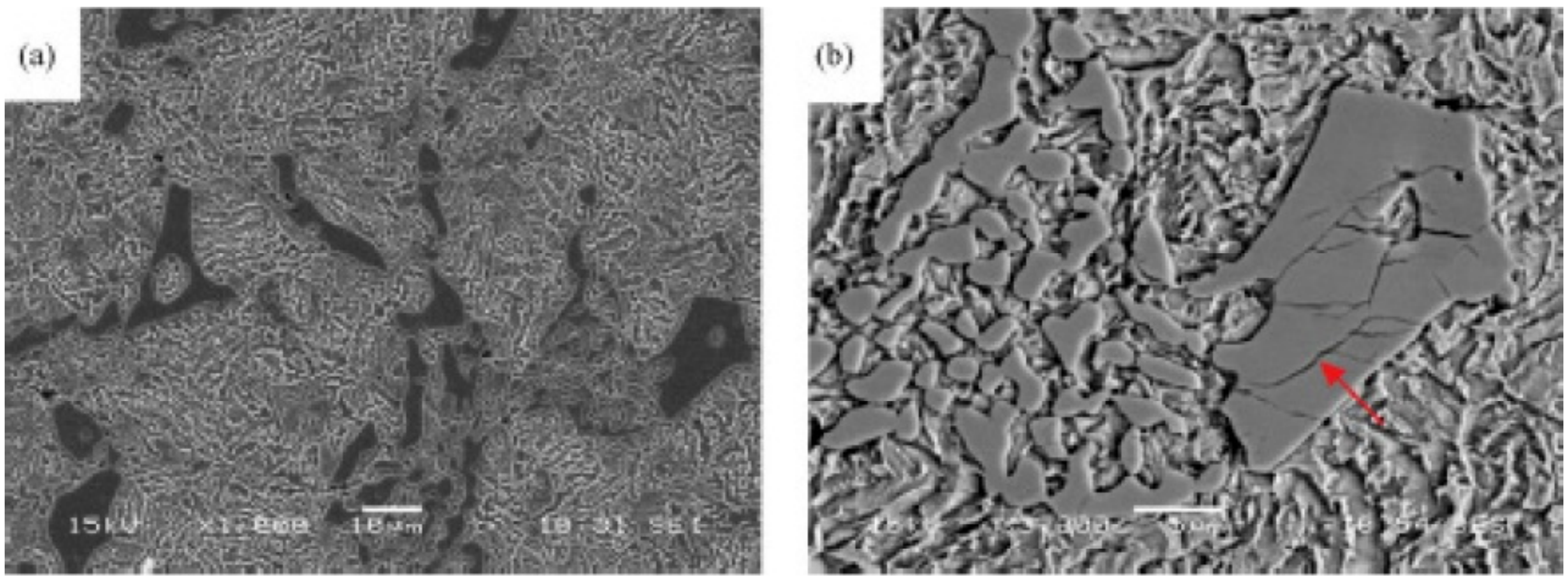

Fig. 5. Microstructure of high boron cast alloy after hot forging: (a) low magnification and (b) high magnification, reprinted with permission from Jianjun Zhang // Tribology Transaction 56 (2013) 461, © 2013 Taylor & Francis.

properties testing indicates that the yield strength is basically unchanged, but the tensile strength and elongation are improved greatly by hot rolling.

2.4. Wear properties of high boron cast alloy

It is assumed that boride is a wear skeleton of high boron cast alloy takes, this case duffers from conventional wear resistant materials with carbides as wear resistant skeleton. So, the study of high boron cast alloy boride wear resistance is a point of essential interest.

Fu et al. [19] reported the two-body wear properties of Fe-B alloy after heat treatment. It was shown that Fe-B alloy showed excellent abrasion resistance under pin-on-disk wear; its abrasion resistance exceeds that of Ni-hard white cast iron, GCr15, and Cr12MoV, and is close to the value reported for high chromium white cast iron. Song [47] researched wear resistance of Fe-B alloy under the two-body wearing, the wear resistance of Fe-B alloy was determined to be better than that of high chromium cast iron; it increased with the increase in boron content. As for the case of three-body impact wearing, the wear resistance of the alloy with boron con-

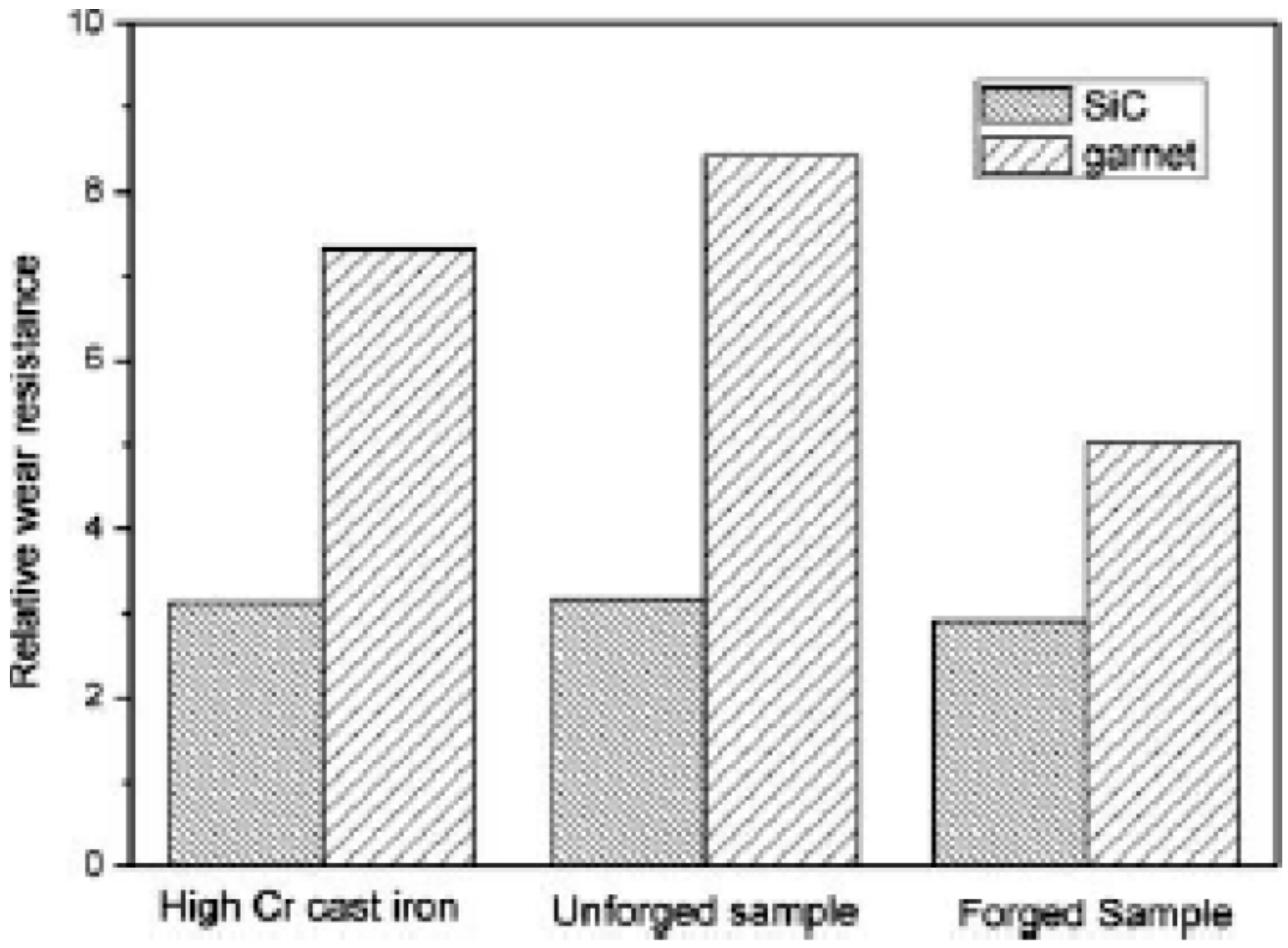

Fig. 6. Relative wear resistance of forged and unforged samples on different abrasives at a load of 50N, reprinted with permission from Jianjun Zhang // Tribology Transaction 56 (2013) 461, © 2013 Taylor & Francis.

tent less than 1.5% was showed to be higher than that of high chromium cast iron, while the wear resistance of the alloy with boron content exceeding 1.5% was slightly lower than that of high chromium cast iron. Huang [48] studied abrasive wear resistance and abrasive wear mechanisms of Fe-B alloy in three-body dead load or impact load grinding abrasion tests. Since the matrix of Fe-B alloy with low carbon and boron content is quite uniform, this alloy showed good abrasive wear resistance in these tests. However, the matrix of Fe-B alloy with high carbon and boron content contains a great amount of borides. These borides are easily cracking, therefore, the abrasive wear resistance of high carbon-high-boron Fe-B alloy is insufficient. Fu et al. [30] researched the effect of quenching temperature ranging from 900 to 1050 °C on the abrasion resistance of modified high born cast steel containing 0.3 wt.% C and 3.0 wt.% B. Impact abrasive measurements showed that the wear resistance of modified high boron cast steel can be significantly improved by quenching temperature increasing. However, the abrasive wear resistance begins to decrease when the quenching temperature exceeds 1000 °C.

Yi [39] compared the wear behavior of semi-solid Fe-B cast alloy and the ordinary Fe-B cast alloy under three-body abrasive wear test. The wear weight loss of semi-solid Fe-B cast alloy is lower than that of the ordinary Fe-B cast alloy because of the lower average boride area in semi-solid specimen. Some approaches describing the wear mechanisms for the low carbon Fe-B cast alloy under the different casting process are considered.

Our previous work reported the forging effect on the behavior of high boron cast alloy in two-body wear test [44]. In the two-body abrasion test, unforged Fe-B alloy exhibits excellent wear resistance; soft abrasive tends to give a higher wear resistance, see Fig. 6 [44]. When alloys are tested against very hard abrasives, the wear resistance of forged Fe-B alloy is similar to that of unforged Fe-B alloy; but in the case of soft abrasives, the wear resistance of forged Fe-B alloy is lower than that of unforged Fe-B alloy.

2.5. The application of high boron cast alloy

High boron cast alloy has a number of advantages: simple smelting process, low cost, good strength and toughness, and good abrasion resistance, so, its application potential is very high. As an example, Lakeland [49,50] patents on Fe-Cr-B cast irons application for the glass moulds and rolls production can be noted. Han-guang Fu [51] developed high boron cast alloy guide rolls, they were used as the

Table 2. Mechanical properties of Fe-Cr-B alloys studied in [13].

σ_b, MPa	σ_s, MPa	φ, %	δ, %	α_k, J·cm^{-2}	K_{IC}, MPa	HRC
450-850	350-555	1-2	0.5-1.5	8-15	25-35	22-62

finishing rolling stands of steel wire-rod rolling mills. The service life of cast boron steel guide rollers is 1.133 times higher than that of cast high chromium nickel alloy steel guide rolls and close to that of sintered carbide guide rollers. High-boron high-speed steel (HSS) has been developed as a cheap roll material [52]. The hardness of high-boron high-speed steel HSS roll is 66.5 HRC, and its impact toughness exceeds 13.1 J/cm^2. However, the manufacturing cost of high-boron HSS rolls is lower than that of hard alloy rolls produced by powder metallurgy, it is only 28% of that of powder metallurgy (PM) hard alloy rolls.

The application of high boron cast alloy for the hammer head, grinding roller, grinding ring, grinding ball, roller, and liner of high boron cast alloy were reported. The hammer heads possess excellent abrasion resistance, their service lifetime is more than three times longer than that determined for high manganese steel, it exceeds the service lifetime of the heads manufactured from medium chromium alloy steel and Ni-hard I by 55.8% and 41.9%, respectively [53]. High boron cast alloy hammer contains low amounts of alloying elements and it has rather simple production process, so, its production cost is close to that of high manganese steel and lower than that of medium chromium alloy cast steel and Ni-hard I by 40%. The wear resistant of high boron cast steel ball is close to that of high chromium white cast iron ball, while its production cost is 30% less than the cost of high chromium cast iron ball [54].

3. CONCLUSION

High boron cast alloy can be considered as a new type wear resistant material with the properties similar to chrome cast iron and Ni-hard cast iron. However, high boron cast alloy possess a number of advantages like simple smelting process, low cost, good strength and toughness, and good abrasion resistance. In addition, high boron cast alloy has a good large neutron capture cross section and corrosion resistance. However, the application of this material is limited by the absence of proper standard.

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