The microstructure evolution of boron-bearing high speed steel roll materials after casting and tempering was investigated. The results indicate that as-cast boron-bearing high speed steel consists of martensitic matrix, retained austenite and different borocarbides. The as-cast alloy has a hardness above 64 HRC, and the borocarbides distribute along the grain boundaries. After Re-Mg-Ti compound modification treatment, obvious necking and broken network appear in the grain boundaries. The hardness of boron-bearing high speed steel roll materials reduces gradually with the increase of tempering temperature. Under the same conditions, the toughness of the modified roll material is higher than that of the unmodified roll material. Wear tests show that the wear resistance of boron-bearing high-speed steel modified by Re-Mg-Ti compound modification treatment is better.

Keywords: Boron-bearing high speed steel rolls; Microstructure evolution; Modification treatment; Wear resistance

1. Introduction

With the development of steel rolling technology, the speed and automation of rolling mill have been continuously improved, and higher requirements have been put forward for the quality of rolls, especially the wear resistance, strength and toughness of rolls [1,2]. The new topic faced by roller developers is how to improve the performance of the roll and meet the needs of the rolling mill. In recent years, a great deal of researches have been done on roller materials [3-5], and breakthrough has been obtained in manufacturing new generation composite roll for high speed steel [6,7]. High speed steel composite rolls are a high-performance roll that the work layer and core part are combined by metallurgy. High speed steel with high hardness, especially good red hardness, wear resistance and hardenability is used as working layer of high-speed steel composite rolls. Forged steel with enough toughness, alloy cast steel, high-strength gray cast iron or high-strength nodular cast iron is used as core material of rolls [8,9]. At present, rolls used in hot rolling production line is dominant in the research and development of high speed steel rolls. The service life of high speed steel rolls for hot strip mill is several times than that of common rolls [10-12]. The incidental effect is to reduce the number of roll changing, increase usage counter, reduce inventory and decrease roll consumption and cost. At the same time, with the increase of the precision of rolled piece, free rolling can be realized. At present, the developing and using roll materials contain a large number of tungsten, molybdenum, vanadium, niobium, cobalt and other expensive alloy elements, which increases the production cost of roll and leads to poor market competitiveness. Under the background of resource exhaustion, it is extremely urgent to study the optimum alloying roll material and reduce roll consumption.

Boron is a cheap non-metallic element, and boron is abundant in china, while the resources of niobium and cobalt are scarce. At the same time, trace boron can improve the hardenability and harden-ability of steel [13,14]. The purpose of this study is to replace expensive alloying elements such as tungsten, molybdenum, vanadium, niobium and cobalt with cheap boron in high speed steel rolls, reducing the cost and increasing the properties of rolls. High-hardness boride is formed by reaction of boron and iron, which is beneficial to improving the wear resistance of rolls. The production cost of high-speed steel rolls is decreased and the grinding performance of rolls is improved by reducing substantially the vanadium content in high-speed steel rolls. The reduction of vanadium content can also significantly reduce the vanadium segregation in centrifugal casting, which will have a good effect on improving and stabilizing the properties of rolls.
2. Experimental

Boron-bearing high speed steel was melted in 50 kg alkaline medium frequency induction furnace. The ingredients comprised high speed steel scrap, scrap steel, pig iron, ferromolybdenum, ferrotungsten and ferrovanadium. After the metal charge was completely melted down in the induction furnace, ferrochromium was added. The ferrovanadium and ferroboron were added to the molten steel prior to tapping. Deoxidation was carried out during tapping by inserting aluminum wire into the ladle. After adjustments of the final chemical composition, the molten steel was tapped at 1503~1560°C. At 1460~1480°C the melted steel was molded by sand casting and was cast into 20 mm×20 mm×120 mm specimen. Then, the specimen was cut into respectively 20 mm×20 mm×20 mm and 10 mm×10 mm×55 mm by wire cutting to observe the structure and test the mechanical properties. The chemical composition of five different alloy melts are shown in Table 1. Alloy #1 falls to the left of the eutectic point of the Fe-C-B system. It’s a hypo-eutectic alloy. Alloys #2-5 are all from the hypereutectic region but with additional alloying elements. The tempering process of the sample is as follows: the samples were heated in a Therm craft XST-3-0-12-1V vacuum tube furnace protected by argon gas, with the heating temperature of 300°C, 400°C, 500°C, 530°C, and 560°C, respectively and the holding time of 200 min. And then, the samples were taken out and air-cooled to room temperature.

The microstructure was examined and analyzed using an Olympus BX-51 optical microscope and JSM-6510 scanning electron microscope. The phase composition was carried out on a Shimadzu XRD-7000 X-ray diffractometer with Cu-Kα radiation under 40 mA and 30 kV from 20°~80° at speed of 0.5°/min. The volume fraction of borocarbides was determined by image analysis. Macro hardness was tested by HR-150A Rockwell. The test load was 150 kgf. Seven points at different parts of the specimen were tested, and the maximum and minimum values were removed. The average value of remaining five points was macro hardness (HRC) value of the specimen. Micro hardness was measured using a MICROMET-5103 type digital microhardness tester. The load was 50 g and the loading time was 15 s. Seven points were similarly taken from each specimen, and the minimum and maximum values were also removed. The average value of the remaining five values was taken as the micro hardness (HV) value of the specimen. Wear resistance test was conducted in a ML-10 type pinon-disc wear tester under the test conditions: the speed of mill 60 rpm; abrasive paper grit 280# SiC waterproof; sample size Φ6.0 mm×25 mm; the feed rate of the specimen 4 mm/s; the starting radius 13 mm; the ending radius 103 mm; the wear distance 16.4 m; and the load 4.0 kg.

3. Results and discussion

3.1. Solidification structure of boron-bearing high speed steel roll material

Both alloy #1 and #2 were unmodified specimens. Solidification microstructures are shown in Fig. 1 and Fig. 2 respectively. It can be seen from metallographic and scanning electron microscopic that the as-cast structure of high speed steel rolls consists of α-Fe, borocarbides and a small amount of retained austenite. According to the phase diagram of Fe-B binary alloy, the maximum solid solubility of boron in the g phase is 0.02 wt.%, which leads to the enrichment of excess boron atoms in grain boundaries and forms hard phase of boride. Because of the formation of boride, the relative content of carbon in the residual liquid phase increases. Most eutectic g phases change to α-Fe at room temperature, and untransformed g phases exist in the matrix by the form of retained austenite. XRD analysis of alloys #1 and #2 was carried out to further determine the phase of as-cast unmodified roll material, as shown in Fig. 3. It can be seen that the matrix structure of roll material is composed of α-Fe and austenite (g-Fe), and the strength of α-Fe diffraction peak is higher than that of austenite, which indicates that the number of α-Fe matrix is more, while the number of austenite is less. The α-Fe is martensite, this is helpful to enhance the hardness of the material and improve the wear resistance of the material. As shown in Figs. 1 and 2, borocarbides are distributed along the grain boundaries in the network and there are broken network and necking locally. XRD patterns analysis shows that borocarbides are made up of M23(B,C)6, M3(B0.7C0.3) and (W,Mo)2(B,C). In alloys #1 and #2, the volume fractions of borocarbides are 21.26 vol. % and 23.81 vol. % respectively. The borocarbide content on the boundary slightly increased with increasing carbon content.

TABLE 2 shows the hardness test results of as-cast alloys #1 and #2. It is obvious that alloy#2 has a higher hardness than alloy#1. This is mainly because that the carbon content of alloy #2 is two times that of 1 alloy #1. Most of carbon forms high-hardness borocarbides with alloy elements, increasing the hardness obviously.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>C</th>
<th>B</th>
<th>Cr</th>
<th>W</th>
<th>V</th>
<th>Mo</th>
<th>Mn</th>
<th>Si</th>
<th>S</th>
<th>P</th>
<th>Ti</th>
<th>Mg</th>
<th>Re</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>1#</td>
<td>0.42-0.48</td>
<td>1.0-1.5</td>
<td>&lt;5.0</td>
<td>&lt;2.0</td>
<td>&lt;2.0</td>
<td>&lt;0.5</td>
<td>&lt;1.2</td>
<td>&lt;0.04</td>
<td>&lt;0.05</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>Bal</td>
<td></td>
</tr>
<tr>
<td>2#</td>
<td>0.90-1.00</td>
<td>1.0-1.5</td>
<td>&lt;5.0</td>
<td>&lt;2.0</td>
<td>&lt;2.0</td>
<td>&lt;0.5</td>
<td>&lt;1.2</td>
<td>&lt;0.04</td>
<td>&lt;0.05</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>Bal</td>
<td></td>
</tr>
<tr>
<td>3#</td>
<td>0.90-1.00</td>
<td>1.0-1.5</td>
<td>&lt;5.0</td>
<td>&lt;2.0</td>
<td>&lt;2.0</td>
<td>&lt;0.5</td>
<td>&lt;1.2</td>
<td>&lt;0.04</td>
<td>&lt;0.05</td>
<td>&lt;0.2</td>
<td>—</td>
<td>—</td>
<td>Bal</td>
<td></td>
</tr>
<tr>
<td>4#</td>
<td>0.90-1.00</td>
<td>1.0-1.5</td>
<td>&lt;5.0</td>
<td>&lt;2.0</td>
<td>&lt;2.0</td>
<td>&lt;0.5</td>
<td>&lt;1.2</td>
<td>&lt;0.04</td>
<td>&lt;0.05</td>
<td>&lt;0.3</td>
<td>&lt;0.15</td>
<td>&lt;0.2</td>
<td>Bal</td>
<td></td>
</tr>
<tr>
<td>5#</td>
<td>0.90-1.00</td>
<td>1.0-1.5</td>
<td>&lt;5.0</td>
<td>&lt;2.0</td>
<td>&lt;2.0</td>
<td>&lt;0.5</td>
<td>&lt;1.2</td>
<td>&lt;0.04</td>
<td>&lt;0.05</td>
<td>&lt;0.4</td>
<td>&lt;0.25</td>
<td>&lt;0.4</td>
<td>Bal</td>
<td></td>
</tr>
</tbody>
</table>
To improve the microstructure and mechanical properties, the as-cast alloys were modified by rareearth, magnesium and titanium (RE-Mg-Ti) compounds. Figs. 4-6 are metallographic and scanning electron microscope graphs after modification. Fig. 4 shows the solidification microstructure of boron-bearing high speed steel roll after Ti modification. Compared with Fig. 2,

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Macro hardness / HRC</th>
<th>Matrix microhardness / HV</th>
</tr>
</thead>
<tbody>
<tr>
<td>1#</td>
<td>64.84</td>
<td>820–950</td>
</tr>
<tr>
<td>2#</td>
<td>67.02</td>
<td>950–1000</td>
</tr>
</tbody>
</table>
it is found that the eutectic borocarbides present necking and broken network whereas large network borocarbides exist on grain boundaries of unmodified boron-bearing high speed steel rolls. The austenite grain and eutectic structure of high speed steel roll are refined by adding Ti element. The eutectic borocarbides show obvious necking and net broken network and this is mainly due to the fact that Ti is a strong carbide forming element. When Ti is added to high speed steel solution, it combines with carbon to form titanium carbides, which become the first precipitates during solidification. TiC and austenite are both face centered cubic lattice, and the lattice constants of TiC and austenite are very similar, which are 0.433 nm and 0.357 nm respectively.

Fig. 4. OM (a) and SEM (b) of #3 as-cast boron-bearing high speed steel roll

Fig. 5. OM (a) and SEM (b) of #4 as-cast boron-bearing high speed steel roll

Fig. 6. OM (a) and SEM (b) of #5 as-cast boron-bearing high speed steel roll
The complex formability of crystal lattice is very low, so the \(\gamma\)-Fe can grow with TiC as heterogeneous core, refine primary austenite and further refine borocarbides.

Figs. 5 and 6 show solidification microstructures of boron-bearing high speed steel rolls after Re-Mg-Ti compound modification treatment. From the comparison of Figs. 4 and 5, it can be seen that the solidification structure of the rolls modified with Re-Mg-Ti is more refined as compared to the single modification with Ti, and the necking and broken network of borocarbides at grain boundary are more obvious. A large number of necking and broken network are beneficial to the further improvement of the morphology of borocarbides by subsequent high-heat treatment. At the same time, some granular structures appear after modification.

This is because Re has a quite low melting point (798°C to 1016°C) and large atomic radius. It is a strong supercooled element in the solidification process of high speed steel and the equilibrium constant \(K_0\) is much less than 1, which leads to severe segregation during solidification. Re is enriched in molten steel at the front of primary austenite dendrite growth by solute redistribution, which results in large constitutional supercooling, prevents austenite growth and refines austenite dendrites. The refinement of primary austenite leads to the enhancement of the separation of residual liquid steel during eutectic reaction. In the process of eutectic growth, eutectic austenite is preferentially crystallized in primary austenite on both sides of narrow channel by the way of “dissociation”, which promotes further separation of residual molten steel. Finally, the eutectic borocarbides are refined and the network structure shrinks or breaks. At the same time, Re reduces the content of S and O in molten steel, purifying grain boundary. Mg has low melting point and large atomic radius. It is a surface active and strong component undercooled element. Mg tends to concentrate in molten steel around austenite when molten steel solidifies. In eutectic crystallization, Mg is adsorbed selectively on the surface of preferred growth direction of eutectic borocarbides and the adsorbent film is formed, which inhibits the growth of W, Mo, Cr atoms in molten steel on eutectic borocarbides and makes eutectic borocarbides round.

Although borocarbides are necked and broken, as can be seen in Fig. 6, there remain a large number of Mg-RE compounds around the borocarbides at grain boundaries, making the bonding between borocarbides and matrix not very strong, and may affect the mechanical properties of materials.

### 3.2. Mechanical property of Boron-bearing high speed steel roll material

For all alloys under study, we observed the macro hardness of alloy #2, #3 and #4 except for #5 are all higher than that of alloy #1 which contains roughly about half of the carbon content of the others. Carbon can form carbides with W, Mo, Cr, V and other alloy elements in molten steel. As the number of carbides increases, the hardness of the materials increase. For the alloys with the same carbon content, their hardness values differ slightly excluding alloy #5. Because hardness is mainly determined by the amount of carboborides in the microstructure and the matrix hardness. Based on Figs. 4 and 5, modification has no obvious influence on the the amount of carbides. Moreover, the effect of modification on the matrix hardness is also less, thus alloys #2-#4 exhibit similar hardness values. After modification, the hardness of 5# material is 61.8 HRC. It may be due to the addition of excess RE-Mg-Ti complex modifier. The binding of Ti to C in the matrix is suspected of causing insufficient carbon content in the same matrix, and therefore the hardness of the alloy reduces. In addition, the deterioration of Mg results in a substantial reduction of carbides in the solidified structure and a decrease in hardness. Excessive RE leads to the formation of rare earth oxides and sulphides, they cannot float up and accumulate at the grain boundary of molten steel. Because of these reasons, the hardness of the material decreases.

The effect of tempering temperature on Rockwell hardness of different high-speed steel materials is shown in Fig. 8a. Low alloy boron-bearing high speed steel roll material is different from ordinary high-carbon high-vanadium high speed steel roll and the hardness tends to decrease with the increase of tempering.
temperature. The hardness of the material decreases, especially when the tempering temperatures are above 500°C. Since there is not much alloying elements (such as tungsten, molybdenum, vanadium, etc.) added to the alloys, also the alloys have not been quenched, so dispersion hardening is expected to have a weak effect in that a large number of dispersive precipitates cannot be formed during tempering. It was also observed that alloy #5 gives the lowest hardness value, this is because the addition amount of modifier is too much, resulting in the formation of more rare earth magnesium compounds and the aggregation around the grain boundary, so hardness of the material is lower. The effect of modification on the hardness of low alloy boron-bearing high speed steel rolls has no obvious regularity. When tempering temperature exceeds 400°C, the hardness of alloy #4 is slightly higher than that of other materials. The reason for this may be that the eutectic borocarbides are finer and more evenly distributed by modification, and there is a decrease in the segregation of alloying elements. Tempering hardness in the range of 400~500°C can still be kept at a high level, and satisfies the requirements of rolling production. In addition, the hardness of #4 alloy is higher than that of other alloys. It has a hardness of HRC 61‐62 after tempering at 500°C.

The effect of tempering temperature on impact toughness of high speed steel is shown in Fig. 8b. The tempering temperature has no obvious effect on impact toughness of materials. The impact toughness of alloy #1 is higher compared with other materials. Again, this is because alloy #1 contains half of the carbon content of the others. High carbon content makes carbides segregate, increasing the heterogeneity of carbides. Meanwhile the carbon content in the matrix increases, which increases the brittleness of materials and leads to the decrease of impact toughness of materials. The impact toughness of the modified alloys is slightly higher than that of the unmodified alloys when the tempering temperature is over 400°C. This is due to the eutectic network borocarbides exist in grain boundaries of unmodified alloys, which severs the connection among grains and reduces greatly the bonding strength.

The effect of tempering temperature on impact toughness of high speed steel is shown in Fig. 8b. The tempering temperature has no obvious effect on impact toughness of materials. The impact toughness of alloy #1 is higher compared with other materials. Again, this is because alloy #1 contains half of the carbon content of the others. High carbon content makes carbides segregate, increasing the heterogeneity of carbides. Meanwhile the carbon content in the matrix increases, which increases the brittleness of materials and leads to the decrease of impact toughness of materials. The impact toughness of the modified alloys is slightly higher than that of the unmodified alloys when the tempering temperature is over 400°C. This is due to the eutectic network borocarbides exist in grain boundaries of unmodified alloys, which severs the connection among grains and reduces greatly the bonding strength.

When the material is impacted by external forces, owing to the serious deformation at the interface between eutectic borocarbides and grains, cracks can occur easily along this interface. And the cracks continue to propagate in the grain and cleavage fracture happens. When the cracks encounter network borocarbides the cracks will pass through the grain and propagate along the boundary, increasing the speed of the crack propagation. Therefore, the impact toughness of the unmodified alloys is slightly lower. The morphology of the eutectic borocarbides in the modified cast high speed steel is changed from continuous network to broken network and nodular-like. Borocarbides are distributed evenly and their sizes are small. Meanwhile, RE element in modifier has the function of purifying molten steel and removing impurity and degassing. This reduces the content of harmful impurities such as sulphur and phosphorus on grain boundary, and greatly reduces the intergranular embrittlement. It is not easy for cracks to propagate along grain boundaries but mainly through cleavage of grains. In addition, the modifier can play the role of non-spontaneous nucleation and refinement of crystalline structure. Some modifier atoms can enter the matrix of the alloys and have a solution strengthening effect on the matrix, and also improve the hardenability of the alloys. Therefore, the toughness of the modified alloy is slightly higher compared with unmodified alloys. Alloy #4 was tempered at 500°C, and has the highest impact toughness of 6.8 J/cm².

3.3. Wear resistance of boron-bearing high speed steel roll

Wear resistance of the alloys tempered at different temperatures was studied by measuring the wear loss of the specimens before and after wear testing. The reciprocal of the wear loss is considered as the abrasion resistance. The effect of tempering temperature on wear loss of boron-bearing high speed steel roll is shown in Fig. 9. Tempering temperature has little effect on the wear loss of alloys #1, #2, #3 and #5. The more amount of wear loss, the less wear resistant the material is. The wear loss of all alloys is greater than or close to that of the high-carbon high-vanadium high speed steel. When tempering temperature varies from 300°C to 500°C, alloy #4 shows least wear loss,
hence it offers the greatest wear resistance. The main reason is that the matrix precipitates diffusely a large amount of phases with the increase of tempering temperature, and these precipitate phases become effective particles to improve the wear resistance of the alloy. When the tempering temperature exceeds 500°C, the precipitated particles aggregate together and grow up, which greatly reduces the alloying elements in the matrix, and cause the hardness of the matrix to decrease. When tempering temperature passes 530°C, the precipitates in the matrix reintegrate into the matrix with the increase of tempering temperature. The low-alloy boron-bearing high speed steel showed a somehow greater wear loss than other high-carbon high speed steel alloys. Accordingly, it is more wear resistant.

Fig. 9. Effect of tempering temperature on wear loss of boron-bearing high speed steel roll

All of modified alloys exhibited greater wear resistance than the unmodified alloys when tempering temperature is in the range of 300–500°C. For one thing, modification refines the matrix structure and eutectic borocarbides of high speed steel roll material, which improve the toughness and reduce the formation and diffusion of alloy cracks. On the other hand, with the increase of tempering temperature, the matrix precipitates gradually diffuse phase. Such precipitate phase grows during tempering. The precipitation hardening leads to a reduction of wear loss and consequently improves the wear resistance. As the tempering temperature exceeds 500°C, there is no obvious change in wear resistance.

4. Conclusions

(1) The as-cast microstructure of low-alloy boron-bearing high speed steel rolls includes lath martensite matrix, a small amount of retained austenite and various types of borocarbides. The as-cast alloy has a hardness above 64 HRC.

(2) With the increase of tempering temperature, the hardness of the alloy decreases. The hardness of the alloy tempered in the range of 400-500°C can be kept above 61 HRC. The impact toughness of modified high speed steel is slightly higher compared with unmodified high speed steel with the same carbon content.

(3) Alloy #4 has a hardness of HRC 61-62 and impact toughness of 6.8 J/cm² after tempering at 500°C. It has strong resistance to cutting wear and fatigue wear, and the alloy has excellent wear resistance.

Acknowledgement

The authors would like to thank the financial support for this work from Natural Science Foundation of Shaanxi Province under grant (2018JM5096).

REFERENCE