The effect of high boron additions on the microstructure of cast steel

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ABSTRACT

This study summarizes research into the effect of high boron additions on the microstructure of cast steel under the certain carbon (0.42 C wt.%) and chromium (11.65 Cr wt.%) content. Varying amounts of boron between 0.48 - 4.75 wt.% was added into steel melt. The boron analysis of the alloys was conducted by wet chemical analysis. The microstructure of the specimens was characterized with optical microscopy, Scanning Electron Microscope with Energy Dispersive X-Ray Analysis (SEM/EDX) and X-Ray Diffraction (X-RD). The experimental results showed that high boron steel was successfully produced by sand casting with high casting yield. The microstructure of boron alloyed high chromium cast steel consists of three dimensional networks of M2B borides surrounding the martensitic matrix in as cast condition. Under the certain carbon and chromium content, boron carbide volume fraction is directly depended on the boron additions. Due to the high amount of chromium and boron, carbides and borides were embedded in each other in all additions. In the specimens having less than 2.44 B wt.%, carbide/boride structure was fishbone type with dendritic distribution over the matrix whereas rod/needle like structure with randomly distribute was observed in specimens having 2.44 - 4.75 B wt.%. In all specimens containing boron, M2B and M2(C, B)6 type carbides/boride peaks were detected by X-RD analysis.

1. Introduction

High strength, hardness and wear resistant steels are studied and used since their invention. During their service life, they are used to process materials and withstand harsh tribological loads without compromising their performance. In order to achieve this, steels are improved by the dispersed carbides on the tempered martensitic matrix. However due to their advanced manufacturing technology and the necessity for alloying elements make them expensive [1,2].

Because of the shortage of alloying elements in World War II, scientists used boron in order to achieve desired mechanical properties in steels [3]. It has been found that with the little additions of boron between 0.001 - 0.003 wt.%, the hardenability of the steel increased which was having the same effect of 0.6 Mn wt.%, 0.7 Cr wt.% or 0.5 Mo wt.% or 1.5 Ni wt.% added steels [3-5]. The hardenability mechanism can be explained by the slowing down the nucleation of proeutectoid ferrite on the austenite grain boundaries by reducing the energy of the interface between adjacent austenite grains [3,4,6].

In addition to hardenability, boron is strong carbide former. With its good combination of properties, such as; high hardness (29.1 GPa), low density (2.52 g.cm-3), high melting point (2450 ºC) and high elastic modulus (448 GPa) makes boron carbide suitable for high temperature and high wear resistant applications [7].

Scientists mostly studied on the addition of the low boron wt.%, mostly parts per million (ppm) levels in steels. There are a few researches that studied high boron steels. Egorov and Sapozhnikov investigated the effect of high boron additions (4.9-5.1 wt.%) on the microstructure of cast steel having 0.15-1.2 wt.% carbon contents [8]. They have reported that by increasing the carbon content in cast steel; chromium containing boride and carbon-boride phases formed, small microhardness change is also mentioned due to structural change. The wear resistance of high boron (1.18 - 3.0 wt.%) steels was examined by Hanguang et al. [9-11]. According to their findings; boride networks were found out on top of metallic matrix of the cast steel. By increasing the quenching temperature, mechanical properties such as hardness, tensile strength

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is enhanced which was provided by the microstructural change. Lentz and Röttger carried out the solidification and phase formation of high boron (0.23-2.02 wt.%) steels [12,13]. They have provided that by increasing the boron content, solidification sequence is also changed. In these scientific papers, valuable information about mostly wear properties and the matrix microstructures are discussed. However the morphology of carbides and borides need to be studied further.

The aim of this study is to investigate the microstructure of high boron alloyed of cast steel under the certain carbon (0.42 C wt.%) and chromium (11.65 Cr wt.%) content.

2. Materials and methods

The cast steel manufactured by melting of AISI 430 type of steel scraps in a 500 kg induction furnace with charge materials of ferrosilicon, ferromanganese, ferromolybdenum, graphite etc. In order to achieve desired chemical composition, deoxidation of melt was performed by using aluminum wire. Different amounts of calculated ferro-boron (0.5 - 5.0 wt.%) was added into melt at 1550 ºC superheat and then poured into sand moulds of Y blocks (DIN 1683 - GTB 18/5). Chemical composition of alloy was determined by spectrometer (Bruker Q4-Tasman) which is given in Table 1.

Y blocks were prepared for electrical discharge machining (EDM) by milling. All sides of Y blocks were cleaned (2 mm depth). The metallographic samples were cut from bottom parts of the Y blocks by EDM and labeled (Figure 1). Specimens having 10x10x10 mm dimensions were prepared by grinding and polished up to 1 µm diamond paste.

The boron analysis of the alloys was conducted by wet chemical analysis; Inductively Coupled Plasma - Optical Emission Spectrometry (Perkin Elmer Optima 4300DV). Powder - chip mixture was liquefied in acid solution and analyzed by ICP-OES.

The microstructure of the specimens were analyzed by using Optical Microscope (Leica DM 4000 M) and Scanning Electron Microscope with Energy Dispersive X-Ray Analysis (Jeol JEM 6060 LV - SEM/EDX) after etching with Ralph solution [14].

Carbide/Boride distribution was determined by Leica DM 4000 M phase analyst. Specimen preparations and carbide/boride volume fraction calculations were conducted according to ASTM E1245 – 03 [15]. X-ray diffraction (XRD) analysis was performed on D8 DISCOVER µMR diffractometer with Copper Kα radiation coupling continuous scanning at 40 kV and 40 mA as an X-Ray source in order to determine type of carbides/borides in microstructure. Specimens were scanned in the 2θº ranging from 20º to 80º with scanning speed of 2º/min and step space of 0.02º.

### Table 1. Chemical composition of cast steel alloy.

| Alloying Elements (wt. %) | C   | Si  | Mn  | Cr  | Cu  | Ti  | Ni  | S   | P   | Fe   |
|--------------------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|------|
| Cast Steel Alloy Without Boron | 0.428 | 1.496 | 0.766 | 11.65 | 0.969 | 0.018 | 0.211 | <0.015 | 0.022 | Remain |

![Figure 1. Sampling and labeling sequence of Y block.](image-url)
3. Results and discussion

3.1. Boron analysis of alloys

The results of wet chemical boron analysis are given in Table 2. When considered the high affinity of boron on oxygen and nitrogen [3], non laboratory casting conditions and finally human factors, the casting yield was higher than expected (Table 2).

3.2. Microstructure of alloys

The microstructures of high boron alloyed steel alloy under the certain carbon (0.42 C wt.%) and chromium (11.65 Cr wt.%) content are given in Figure 2 and Figure 3 in as cast condition. The microstructure of steel alloy without boron addition consists of a martensitic matrix and interdendritic eutectic chromium carbides, (Figure 2 a, highlighted green). Due to the high amount of alloying elements (11.65 Cr wt.%, 1.496 Si wt.%, etc.) martensitic matrix is expected upon cooling to the room temperature. The experimental results indicate that boron between 0.48 - 2.05 wt.% alloyed cast steel comprises eutectic borides and carbides having a dendritic network shape on the grain boundaries, (Figure 2 b-e, highlighted red). In addition, fishbone shaped carbide/borides are also formed (Figure 3 b-e, red areas). However, when the boron weight percentage increases more than 2.05 wt.%, rod/needle like carbide/borides are formed and randomly distributed over the matrix (Figure 2 f-h, highlighted blue, Figure 3 f-h highlighted yellow). The thickness and volume fraction of carbide/borides also increases with increasing boron concentration (Figure 2 g-h and Figure 3 g-h). The transition between specimens having 2.05 B wt.% to 2.44 B wt.% is obvious,

![Figure 2](image_url) Microstructures of boron alloyed high chromium steel, a) Without B, b) 0.48 B wt.%, c) 1.12 B wt.%, d) 1.18 B wt.%, e) 2.05 B wt.%, f) 2.44 B wt.%, g) 3.10 B wt.%, h) 4.75 B wt.%, M: Martensite, Etchant: Ralph, specimens cut from E-2 Y block sections.

| Specimen # | Calculated Boron (wt.%) | Boron Analysis (wt.%) | Casting Yield (%) |
|------------|-------------------------|-----------------------|------------------|
| I          |                        |                       | -                |
| II         | 0.5                    | 0.48 ± 0.01           | 96               |
| III        | 1.0                    | 1.12 ± 0.01           | 112              |
| IV         | 1.5                    | 1.18 ± 0.01           | 78.7             |
| V          | 2.0                    | 2.05 ± 0.02           | 102.5            |
| VI         | 3.0                    | 2.44 ± 0.03           | 81.3             |
| VII        | 4.0                    | 3.10 ± 0.03           | 77.5             |
| VIII       | 5.0                    | 4.75 ± 0.10           | 95               |

Table 2. Boron analysis of the specimens.
however according to findings there is not an obvious change after 3.10 B wt.% addition. The only change was the boride/carbide thickening that was mentioned above. In addition, boron additions did not alter the matrix; it remained same as seen in boron free sample which is martensitic.

Many researchers were also observed martensitic matrix and interdendritic eutectic carbides which constitute a three-dimensional networks surrounding the matrix in the microstructure of high boron cast alloys [8,9,16 - 18]. Zhang et. al. pointed out that the matrix is mainly martensite and with small amount of austenite in the microstructure of boron free cast steel alloy [17]. The concentration of 0.4 wt.% boron in the Fe-Cr-B alloy resulted in eutectic phase of network structure at the grain boundary, and when compared with boron free sample, matrix is not changed. As boron concentration increases, the amount of the eutectic phase increases with distribution along the grain boundary. They also reported that the formation of Fe₂B and (Cr, Fe)₆(C, B)₃ phase increases with increasing boron concentration [17].

Egorov and Sapozhnikov were obtained randomly distributed, thick rod/needle type carbides/borides in the alloy having 0.39 C wt., 5.0 B wt.% [8]. Sude Ma

Figure 3. Carbide/Boride shapes of boron alloyed high chromium steel, a) Without B, b) 0.48 B wt.%, c) 1.12 B wt.%, d) 1.18 B wt.%, e) 2.05 B wt.%, f) 2.44 B wt.%, g) 3.10 B wt.%, h) 4.75 B wt.%, M: Martensite, Etchant: Ralph, specimens cut from E-2 Y block sections.

Figure 4. The relation between carbide/boride distributions with respect to boron content.

and Jianjun Zhang explained that the solidification of Fe-Cr-B alloy produced a dendritic matrix and interdendritic M,B borides, which constitute a three-dimensional networks surrounding the dendritic matrix [18]. Zhuang et. al. illustrated four different carbide/boride shapes on their samples [19]. The result of obtained carbide/boride shapes in the microstructure of high boron steel alloy is in good agreement in the studies by Egorov and Sapozhnikov [8] and Zhuang et. al [18].
In the high boron alloyed of cast steel under the certain carbon (0.42 C wt.%) and chromium (11.65 Cr wt.%) content boron carbide volume fraction is given in Figure 4. It is shown that boron carbide volume fraction increases with increasing the boron content expected. The carbides and borides embedded in each other; hence it was not possible to differentiate by X-RD.

Figure 5. X-RD analysis of the cast steel with different boron content.

Figure 6. EDS analysis of boron alloyed high chromium steel having 1.12 B wt.%. 

In the high boron alloyed of cast steel under the certain carbon (0.42 C wt.%) and chromium (11.65 Cr wt.%) content boron carbide volume fraction is given in Figure 4. It is shown that boron carbide volume fraction increases with increasing the boron content expected. The carbides and borides embedded in each other; hence it was not possible to differentiate by X-RD.
X-RD analysis result of the specimens is given in Figure 5. In free boron sample, $M_7(C, B)_5$ type chrome carbides were identified (M: Fe, Cr). In all specimens containing boron, $M_B$ and $M_{(C, B)}$ type carbides/boride peaks were detected. Some researchers detected similar carbide/boride types on the specimens having identical chemical composition under the equivalent X-RD parameters ($2\theta$º, Copper Kα radiation). It is known that EDX analysis is not recommended in detecting boron [22]. In order to differentiate carbides from borides, EDX analysis performed nonetheless. However, carbides and borides could not be separated due to chrome carbides and borides that were embedded in each other. This is confirmed by SEM/EDX analysis on as cast specimen having 1.12 B wt.%, (Figure 6, point 1). Table 3 identifies the points from Figure 6.

| Point | Structure                      |
|-------|--------------------------------|
| 1     | Fe:B + Chrome Carbide Mixture  |
| 2     | Fe:B + Chrome Carbide Mixture  |
| 3     | Martensitic Matrix             |
| 4     | Carbide/Boride Mixture         |

4. Conclusions

The main conclusion deduced from this work on the investigation of the microstructure of high boron alloyed cast steel under the certain carbon (0.42 C wt.%) and chromium (11.65 Cr wt.%) content may be summarized as follows:

- Knowing the strong affinity of boron on oxygen and nitrogen, high boron (0.48-4.75 wt.%) alloyed cast steel under the certain carbon (0.42 C wt.%) and chromium (11.65 Cr wt.%) content was successfully manufactured with high casting yield.

- Specimen without boron consists of martensitic matrix with chromium carbides network. Small amounts of boron additions (up to 2.05 B wt.%) created borides combined with existed carbides. The boron additions formed fishbone carbide/borides and changed their distribution to dendritic network.

- On alloys having higher boron percentages (2.44 - 4.75 wt.%) fishbone shape and dendritic network distribution were modified to new form of rod/need like carbide/borides that are randomly distributed over the matrix.

- By increasing the boron content (2.44 - 4.75 wt.%), carbide/boride volume fraction increased. There is almost no visible change other than carbide/boride coarsening between the boron content of 3.10 - 4.75 wt.%. Boron additions did not modify the martensitic matrix, it remained unchanged.

- Carbides and borides were embedded in each other. In all specimens containing boron, $M_B$ and $M_{(C, B)}$ type carbides/boride peaks were detected.

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