Influence of boron and nitrogen on tempered martensite embrittlement

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Abstract. The propensity of boron-containing and molybdenum-containing steels to tempered martensite embrittlement was carried out. Investigation conducted by serial curves of impact strength and fractographical studying of samples fracture obtained with a scanning electron microscope (SEM). Fracture of samples depending on conditions of their tempering (temperature and cooling rate) is determined. The study has shown that commercial boron-containing steel does not show a tendency to tempered martensite embrittlement. It was found that addition of boron into steel with a low concentration of nitrogen (0.004 mass\%) leads to a decrease of impact strength, but does not embrittle steel. An increase of the nitrogen concentration to 0.016 wt. \% leads to embrittlement, regardless of the boron concentration introduced up to 0.025\% by weight.

1. Introduction

The phenomenon of tempered martensite embrittlement is known since middle of the last century. A considerable number of papers have been devoted to this problem [1-6]. At the same time, influence on tempered martensite embrittlement of such a microimpurity as boron introduced into steel in an amount of 0.0001 to 0.005 wt. \%, i.e. much lower than phosphorus in the technical literature is mentioned little, and data given often contradict each other. For example, it is noted [7, 8] that boron promotes the development of tempered martensite embrittlement, and in [4, 9], on the contrary, boron suppresses it. The aim of this study is to clarify the effect of boron on the propensity of boron-containing steels to cold shortness and tempered martensite embrittlement. This investigation is carried out in comparison with molybdenum-containing steels (molybdenum suppresses tempered martensite embrittlement).

2. Materials and methods

A series of commercial (30Mn1B, 35MnTiB, 38CrVB, 40CrVTiB, 30CrMo, 40CrMo, 38CrMnMo, 40CrMnNiMo) and laboratory (40MnV-VI) meltings was investigated.

Commercial steel (one heat of each grade) was obtained in electric arc-furnace. Laboratory heats were obtained in a vacuum induction furnace VSG-30A with a crucible of 25 kg capacity. The melt was cast into a conical ingot with a diameter of 113 (upper) / 110 (bottom) × 220 mm and a mass of 20 kg. A total of 6 heats of 40MnV-VI steel with different microalloying were melted and investigated.

The ingots were rolled into square-section bars with a square side of 40 mm.

As a method of estimating propensity of steel to tempered martensite embrittlement, serial curves of impact strength tests carrying out at different temperatures was used. In our opinion and the authors'
opinion [10], this method is more accurate than the method of evaluation of impact strength after tempering at different temperatures with subsequent tests only at room temperature.

Thermal treatment of the samples consisted of quenching in water at a temperature of 880 °C and tempering at temperature of the greatest propensity to embrittlement (cooling after tempering in water and with furnace).

Microfractograms were carried out on a scanning electron microscope JEOL JSM-6460 LV (South Ural State University). Impact strength were controlled in according to GOST 9454-78 on samples tempering at temperature of the greatest propensity to embrittlement (cooling after tempering in water and with furnace).

Steel 30CrMo was prone to cold shortness. Nevertheless, retaining a high proportion of the ductile component in all fractures of 35MnTiB steel samples fractures, which in all cases remain shear (figure 2c). However, impact strength of samples were cooled with a furnace and tested at minus 20 °C, a lowered toughness was recorded (figure 1b), which is due to a sharp increase in the brittle component in fracture. Nevertheless, retaining a high proportion of the ductile component in all fractures of 35MnTiB steel

| Grade / Heat | C    | Si   | Mn   | S    | P    | Cr   | Ni   | Mo   | Cu   | V    | Ti   | Al   | B    | N    |
|--------------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|
| Commercial boron-containing steel |      |      |      |      |      |      |      |      |      |      |      |      |      |      |
| 30Mn1B       | 0.31 | 0.14 | 1.20 | 0.009| 0.015| 0.27 | 0.06 | 0.01 | 0.06 | 0.006| 0.017| 0.026| 0.005| 0.006|
| 35MnTiB      | 0.33 | 0.23 | 1.10 | 0.027| 0.014| 0.09 | 0.09 | 0.02 | 0.13 | 0.005| 0.044| 0.040| 0.003| 0.007|
| 38CrVB       | 0.38 | 0.28 | 0.68 | 0.026| 0.007| 0.88 | 0.07 | 0.04 | 0.10 | 0.081| 0.042| 0.036| 0.002| 0.010|
| 40CrVTiB     | 0.43 | 0.25 | 0.66 | 0.028| 0.008| 0.85 | 0.05 | 0.05 | 0.08 | 0.080| 0.042| 0.032| 0.003| 0.010|
| Commercial molybdenum-containing steel |      |      |      |      |      |      |      |      |      |      |      |      |      |      |
| 30Cr2Mo      | 0.34 | 0.27 | 0.76 | 0.031| 0.017| 0.99 | 0.18 | 0.15 | 0.18 | 0.005| 0.007| 0.030| 0.030| 0.008|
| 40CrMo       | 0.42 | 0.31 | 0.79 | 0.031| 0.020| 0.97 | 0.24 | 0.16 | 0.14 | 0.006| 0.001| 0.010| 0.010| 0.010|
| 38CrMnMo     | 0.37 | 0.27 | 0.77 | 0.031| 0.017| 0.99 | 0.17 | 0.15 | 0.18 | 0.005| 0.007| 0.032| 0.032| 0.010|
| 40CrMnNiMo   | 0.42 | 0.32 | 0.56 | 0.027| 0.027| 0.69 | 0.84 | 0.18 | 0.15 | 0.004| 0.001| 0.004| 0.026| 0.010|
| Laboratory boron-containing steel (40MnV-VI) |      |      |      |      |      |      |      |      |      |      |      |      |      |      |
| 43-1         | 0.36 | 0.18 | 0.96 | 0.015| 0.014| 0.28 | 0.02 | 0.02 | 0.05 | 0.07 | tr.  | 0.018| 0.001| 0.004|
| 43-2         | 0.35 | "   | "   | "   | "   | "   | "   | "   | "   | "   | "   | "   | "   | "   |
| 43-3         | 0.35 | "   | "   | "   | "   | "   | "   | "   | "   | "   | "   | "   | "   | "   | 0.027| "   | "   | "   | "   | "   | "   | "   |
| 44-1         | 0.35 | 0.19 | 0.99 | 0.015| 0.014| 0.36 | 0.02 | 0.02 | 0.08 | 0.07 | tr.  | 0.013| 0.001| 0.016|
| 44-2         | 0.36 | "   | "   | "   | "   | "   | "   | "   | "   | "   | "   | "   | "   | "   | 0.027| "   | "   | "   | "   | "   | "   | "   |
| 44-3         | 0.36 | "   | "   | "   | "   | "   | "   | "   | "   | "   | "   | "   | "   | "   | 0.028| "   | "   | "   | "   | "   | "   | "   |

\( ^* \text{tr.} \) – the same concentration of chemical element in heat.

\( ^* \text{tr.} \) – traces of element

3. Results and discussion

A comparative analysis propensity of boron-containing and molybdenum-containing steels to tempered martensite embrittlement was carried out in the following pairs: 30Mn1B - 30CrMo; 35MnTiB - 40CrMo; 38CrVB - 38CrMnMo; 40CrVTiB - 40CrMnNiMo. The results of impact strength tests are shown in figure 1.

After the tests, fractures of the samples were subjected to microfractographical studies. According to data obtained, 30Mn1B steel samples exhibited a fiber fracture at all test temperatures (figure 2a). At the same time, samples of steel 30CrMo (after cooling in water) observed a quasi-cleavage fracture (~ 15% of cleavage fracture) after testing at minus 20 °C, and in the samples cooled with a furnace, at the same test temperature already 85-90% of cleavage fracture. The data obtained show that 30Mn1B and 30CrMo steels are not prone to tempered martensite embrittlement. However, along with this, steel 30CrMo was prone to cold shortness.

Cooling after tempering (in air or with furnace) does not have a significant effect on the appearance of 35MnTiB steel samples fractures, which in all cases remain shear (figure 2c). However, impact strength of samples were cooled with a furnace and tested at minus 75 °C, a lowered toughness was recorded (figure 1b), which is due to a sharp increase in the brittle component in fracture. Nevertheless, retaining a high proportion of the ductile component in all fractures of 35MnTiB steel
samples. A significant deformation of specimens and shear fractures allows steel 35MnTiB that are not prone to tempered martensite embrittlement.

![Serial curves of impact strength.](image)

The serial curves of change impact strength for steel 40CrMo practically merge (see figure 1b). Magnitude of toughness decreases very insignificantly with decreasing temperature and without any sharp changes in test curves. Consequently, cooling rate after a two hour tempering at 600 °C does not affect on cold shortness or embrittlement of this steel. Despite alloying with molybdenum and a high tempering temperature, fractures of this steel had quasi-cleavage fracture after testing at negative temperatures (cleavage component predominates).

Microfractographical studies of steels 38CrVB, 38CrMnMo, 40CrVTiB and 40CrMnNiMo make it possible to draw similar conclusions about samples fracture at low temperatures occurred crystalline, mainly along the grain boundaries. However, it is important to note that boron-containing steels are not inferior to high cost nickel- and molybdenum-containing steels by impact strength. This circumstance makes it possible to consider boron-containing steels as an alternative to their replacement.

Combined effect analysis of boron, titanium and nitrogen on the tendency to tempered martensite embrittlement was carried out on laboratory fractional smelting (heat 43 and heat 44). Introduction of boron into steel without titanium (heat 43-2) and with titanium (heat 43-3) at a low concentration of nitrogen (0.004 wh. %) leads to a decrease of toughness (figure 4). Microfractographical study of samples fractures showed a large part of surface fracture has a shear component (table 2). Steel
microalloyed with boron and with nitrogen of 0.014-0.020 wt. % (heat 44-2), characteristic for the metal of arc melting, retention of toughness value at the same level was observed (see figure 4).

Figure 2. Microfractograms of samples fracture at +20 °C (left) and -75 °C (right).
Figure 3. Microfractograms of samples fracture at +20 °C (left) and -75 °C (right).
Table 2. Influence of microalloying on samples fracture.

| Heat  | Chemical composition, wt. % | shear component, % | cleavage component, % |
|-------|-----------------------------|-------------------|-----------------------|
|       | N  | Al | B      | Ti  |                |                  |
|       |    |    |        |     | Laboratory boron-containing steel (40MnV-VI) |                  |
| 43-1  | 0.004 | 0.018 | < 0.0005 | tr. | 73 | 27 |
| 43-2  | 0.004 | 0.018 | 0.0016 | tr. | 70 | 30 |
| 43-3  | 0.004 | 0.018 | 0.0013 | 0.027 | 75 | 25 |
| 44-1  | 0.016 | 0.013 | < 0.0005 | tr. | 25 | 75 |
| 44-2  | 0.016 | 0.013 | 0.0017 | tr. | 25 | 75 |
| 44-3  | 0.016 | 0.013 | 0.0021 | 0.028 | 25 | 75 |

tr. – traces of element

Figure 4. Microalloying influence on impact strength of 40MnV-VI.

Complex microalloying with boron and titanium (heat 44-3) showed a decrease value of impact strength by 15-20%. It is important to note that all three fractions (heat 44) have, in the main, a brittle fracture and only small areas of shear fracture (table 2).

4. Conclusion

The data given on the cold-shortness and sensitivity of steels to tempered martensite embrittlement indicate a significant superiority of steels microalloyed with boron over molybdenum-containing steels.

Boron-containing steels are not inclined to tempered martensite embrittlement and are not inferior to alloyed nickel- and molybdenum-containing steels under equal test conditions.

Introduction of boron into steel with a low concentration of nitrogen leads to a decrease of toughness without embrittlement of steel. Additional microalloying with titanium at a greater extent lowers the toughness, which is most likely due to formation of special titanium carbides along the grain boundaries.

It is noted that steel with a normal (for arc melting) nitrogen concentration (0.014-0.016 wt. %) without microalloying with boron and titanium has a significant effect on samples fracture (the
samples have a predominantly brittle fracture) with a sufficiently high toughness. This circumstance indicates the embrittlement of nitrogen, which, when combined with nitride-forming elements (for example, chromium, vanadium or aluminium), is released along the grain boundaries. The introduction of boron into such a steel without microalloying with titanium does not lead to a change in the toughness or the type of fracture. And the introduction of boron into steel in the presence of titanium reduces the impact strength by 15-20% without changing the appearance of the fracture.

**Acknowledgements**

The work was supported by Act 211 Government of the Russian Federation, contract № 02.A03.21.0011.

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