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Weldability of Direct Quenched, Low-Carbon, Ti-B-Containing Steels

Boron additions prove beneficial to HAZ toughness

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ABSTRACT. On the basis of the thermodynamic equilibrium between nitrides of titanium, aluminum and boron in austenite, the soluble boron that influences the hardenability of direct quenched steels was calculated. The variation in tensile strength and impact toughness of steels has a good correlation with the calculated value at the start cooling temperature, 920°C. Impact toughness of the heat-affected zone (HAZ), however, was not influenced by the soluble boron alone but by the soluble boron to soluble nitrogen ratio at the welding peak temperature, 1350°C. Only when the ratio was kept below 0.2 did the HAZ show a ferrite dominant microstructure and higher than 100 J of absorbed energy at -20°C. During the welding cooling cycle, soluble boron combines with soluble nitrogen to form boron nitrides, consequently reducing the soluble boron and hardenability. Unlike conventional high-carbon steel, a low-carbon steel containing a controlled amount of boron showed no cold cracking, without preheating, and a high HAZ toughness, with an energy transition temperature of -37°C.

KEY WORDS

HAZ Toughness
Hardenability
Weld Toughness
Cold Cracking
Hydrogen Cracking
Boron Additions
DQ Steel
Low-Carbon Steel

Introduction

Cold cracking, which is often associated with stress intensification near discontinuities in a steel weldment, is one of the serious weldability problems of structural steels. Preheating and/or postheating is usually practiced to prevent it. Weld heat-affected zone (HAZ) toughness is, on the other hand, an important property for welded joints if they are to perform their intended function in service. In general, as HAZ toughness decreases with the increase of heat input, the maximum heat input is strictly controlled to obtain the desired toughness. Therefore, using a steel with low cold cracking susceptibility and high HAZ toughness, even when fabricated with high heat input welding processes, increases welding productivity markedly by the elimination of preheating and/or postheating and the application of high heat input welding. To meet the demand for steel with these characteristics, modified steel manufacturing processes and microalloying are both being considered by steel makers. As direct quenched (DQ) steel is known to have higher hardenability than reheat and quenched (RQ) steel, direct quenched steel is being widely investigated to replace reheat and quenched steel (Ref. 1). Because of its higher hardenability, DQ steel could be manufactured with a low carbon equivalent number and thus be expected to give good weldability (Ref. 2). In terms of microalloying adjustments, low-carbon steel is the most promising as it shows both a low cold cracking susceptibility and high HAZ toughness with high heat input welding (Ref. 3). The loss of strength due to the low carbon content is compensated for by the appropriate addition of strengthening elements such as nickel, molybdenum and vanadium. Titanium is also often added for the refinement of HAZ microstructure (Ref. 4).

It is well-known that a small addition of boron in steel increases hardenability through its segregation at the austenite grain boundaries during the quenching process. Segregation of boron, moreover, was reported to suppress the cold cracking susceptibility of a weldment through the retardation of hydrogen diffusion (Ref. 5). All these results suggest that the carbon content of steel could be reduced

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markedly without losing its strength through the utilization of the DQ process and a small addition of boron. As boron, however, is a strong nitride forming element, it is difficult to predict the effect on hardenability during the quenching process. The situation becomes more complicated when aluminum and titanium are present together because those are strong nitride forming elements as well.

In this study, the effect of boron on the hardenability of DQ steel containing aluminum, titanium and boron is studied first. Then HAZ toughness and cold cracking susceptibility of low-carbon DQ steel with a controlled amount of boron are investigated and compared with a conventional high-carbon RQ steel.

Experimental Procedures

To study the effect of boron on the hardenability of DQ steel, ten steels with different aluminum, titanium and boron contents were prepared. All other elements of the steels, except for aluminum, titanium and boron, are almost the same as 0.06%C-0.3%Mn-0.3%Si-1.4%Mn and boron are present together because those are strong nitride forming elements as well.

The microstructural characterization of plates and simulated HAZs was performed using optical and thin foil transmission electron microscopy. The amount of boron combined in boron nitrides that precipitated during the welding cooling cycle was analyzed by inductively coupled plasma atomic emission spectrometry using precipitate residue obtained by the selective potentiostatic etching by electrolytic dissolution method (SPEED). The electrolyte for SPEED was 10% MA-MeOH (10% maleic anhydride, 2% tetramethylammonium chloride, methanol), and K$_2$S$_2$O$_7$ and HCl were used for the solution of the precipitate residue.

Results and Discussion

Hardenability and Toughness of Direct Quenched Steels

Boron in steel is either free (soluble) boron or combined boron, which, for example, forms nitrides. As it is only free boron that influences the hardenability of steel during the quenching process, it is a prerequisite to estimate the soluble boron at the quenching temperature to predict the hardenability of steel. Following R. Habu, et al.’s methodology (Ref. 7) in which the soluble boron of RQ steels at the reaustenitizing temperature was estimated using thermodynamic analysis in the Al-B-N system, the soluble boron at the start cooling temperature (SCT), 920°C, of direct quenched steel in the Al-Ti-B-N system was estimated. The assumptions in this analysis are as follows:

1) The effective boron influencing the hardenability of direct quenched steel is the soluble boron in austenite at the SCT.
2) Before quenching, Ti-N, Al-N and B-N are in an equilibrium state and each nitride’s solubility product is shown in Equations 1–3 below.
3) Solubility product in Ti-N, Al-N and B-N systems is also applicable to the Ti-Al-B-N system.
4) Titanium, aluminum and boron form only nitrides, Ti-N, Al-N, B-N, in...
austenite. As the analyzed aluminum combined in aluminum oxide was too small to determine, the possibility of any oxide formation was excluded.

With these assumptions, the soluble boron at the SCT, 920°C, of each steel was calculated by solving the following seven equations simultaneously. As a result of calculation, if one nitride could not be formed, the corresponding equation was excluded in a calculation.

\[
\log[\text{Ti}][\text{N}] = -16192/T + 4.72 \quad (\text{Ref. 8})
\]
\[
\log[\text{Al}][\text{N}] = -7400/T + 1.95 \quad (\text{Ref. 9})
\]
\[
\log[\text{B}][\text{N}] = -13970/T + 5.24 \quad (\text{Ref. 10})
\]

\[
\text{Ti} = [\text{Ti}] + [\text{Ti}]_{\text{TiN}}
\]
\[
\text{Al} = [\text{Al}] + [\text{Al}]_{\text{AlN}}
\]
\[
\text{B} = [\text{B}] + [\text{B}]_{\text{BN}}
\]
\[
\text{N} = [\text{N}] + [\text{N}]_{\text{T-N}} + [\text{N}]_{\text{AlN}} + [\text{N}]_{\text{BN}}
\]

where \( T \) is the absolute temperature, \( \text{Ti} \), \( \text{Al} \), \( \text{B} \), and \( \text{N} \) are the content of each element in the steel, respectively. \( [X] \) is the soluble content of element \( X \), \([X]_{\text{XN}}\) the amount of \( X \) combined in nitride \( X-N \) and \([N]_{\text{XN}}\) the amount of nitrogen combined in nitride \( X-N \) in austenite, respectively. As an example, Fig. 1 shows the result of a calculation of soluble boron and boron nitride for Steel 5. It shows that the content of boron in steel, 0.0006%, remains as soluble boron down to 1025°C and then decreases continuously along with the precipitation of boron nitrides until it becomes only 0.0001% at the SCT. The calculated content of soluble boron at the SCT for other steels is given in Table 1. It is evident that the soluble boron at the SCT is different from the boron content of steel depending on the aluminum, titanium and nitrogen in the steel. Figure 2 shows the variation of tensile strength of steels that were quenched at approximately the same cooling rate 12-15°C/s with the calculated content of soluble boron at the SCT. It shows a good correlation \((R^2 = 0.851)\), indicating that the hardenability of direct quenched steel containing titanium, aluminum and boron could be determined by the content of soluble boron at the SCT, and it can be estimated by thermodynamic analysis. Y. Kamada, et al. (Ref. 11), have reported that the hardenability of direct quenched steel is influenced by the soluble boron at the FRT. It is believed, however, that the effective boron that could be used for determining the hardenability of direct quenched steel is the soluble boron at the SCT rather than at the FRT.

The variation of the impact absorbed energy of steels at -40°C is shown in Fig.

Table 1 — Titanium, Aluminum, Boron and Nitrogen Content of Steels and the Calculated Soluble Boron and Soluble Nitrogen Content at 920°C and 1350°C, Respectively.

<table>
<thead>
<tr>
<th>Steel</th>
<th>Ti (wt-%)</th>
<th>Al (wt-%)</th>
<th>B (wt-%)</th>
<th>N (wt-%)</th>
<th>Sol. B (ppm)</th>
<th>Sol. N (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.013</td>
<td>0.023</td>
<td>0.0015</td>
<td>0.0020</td>
<td>15</td>
<td>6.55</td>
</tr>
<tr>
<td>2</td>
<td>0.012</td>
<td>0.028</td>
<td>0.0013</td>
<td>0.0034</td>
<td>13</td>
<td>12.16</td>
</tr>
<tr>
<td>3</td>
<td>0.013</td>
<td>0.023</td>
<td>0.0016</td>
<td>0.0062</td>
<td>4.86</td>
<td>29.49</td>
</tr>
<tr>
<td>4</td>
<td>0.012</td>
<td>0.023</td>
<td>0.0013</td>
<td>0.0054</td>
<td>4.85</td>
<td>25.31</td>
</tr>
<tr>
<td>5</td>
<td>0.013</td>
<td>0.023</td>
<td>0.0006</td>
<td>0.0080</td>
<td>1.2</td>
<td>53.07</td>
</tr>
<tr>
<td>6</td>
<td>0.012</td>
<td>0.033</td>
<td>0.0018</td>
<td>0.0140</td>
<td>1.32</td>
<td>106.47</td>
</tr>
<tr>
<td>7</td>
<td>0.014</td>
<td>0.027</td>
<td>0.0014</td>
<td>0.0062</td>
<td>4.71</td>
<td>27.06</td>
</tr>
<tr>
<td>8</td>
<td>0.014</td>
<td>0.030</td>
<td>0.0005</td>
<td>0.0092</td>
<td>1.52</td>
<td>54.09</td>
</tr>
<tr>
<td>9</td>
<td>0.014</td>
<td>0.025</td>
<td>0.0020</td>
<td>0.0064</td>
<td>7.4</td>
<td>28.72</td>
</tr>
<tr>
<td>10</td>
<td>0.015</td>
<td>0.039</td>
<td>0.0005</td>
<td>0.0027</td>
<td>5</td>
<td>6.8</td>
</tr>
</tbody>
</table>
3, and it can be divided into three regions depending on both the soluble boron at the SCT and the quenching rate. Optical microscopy showed that Region 1, with about 100-200 J of absorbed energy, has ferrite with a small amount of bainite; Region 2, with about 20-40 J, has bainite with a small amount of ferrite; while Region 3, with about 200-250 J, has a mixed microstructure of martensite and bainite. The details of these microstructures are best seen by electron microscopy. Figure 4 shows the typical microstructure of Region 3. Martensite with lath width of about 0.2 μm (A) and bainite with cementites within them inclined at about 50-60 deg to the growth direction of the ferrite laths (B) are shown. Figure 5, Region 2 microstructure, shows ferrite laths with the second phases along the boundaries (A). According to the selected area diffraction pattern (SADP) of the second phase (B), it is retained austenite. It is believed that as ferrite laths grow, carbon diffuses into the austenite ahead of the austenite/ferrite interface, resulting in a layer of carbon-rich austenite. Entrapped carbon-rich austenite transforms to martensite in part and eventually forms a martensite/austenite (M-A) constituent. Therefore, the high toughness of Region 3 is attributed to the mixed microstructure of low-carbon martensite and lower bainite, while the low toughness of Region 2 is due to the bainite with a brittle M-A constituent. The above results indicate that the calculated amount of soluble boron at the SCT determines the impact toughness as well as the tensile strength.

Hardenability and Toughness of the HAZ

Figure 6 shows the variation of the impact absorbed energy in the HAZ at -20°C with the tensile strength of steel. Within the tensile strength range investigated (603-811 MPa), all HAZs having ferrite with a small amount of bainite (open marks) have higher than 100 J of absorbed energy, while HAZs having bainite with a small amount of ferrite (solid marks) have lower than 100 J. Therefore, the hardenability of the HAZ during the welding cooling cycle should be controlled to produce a ferrite dominant microstructure for high toughness.

Assuming that the hardenability of the HAZ is influenced by the soluble boron at the start cooling temperature, i.e., the welding peak temperature in this case, the content of soluble boron at 1350°C was calculated to see the correlation between them. Figure 7 shows the variation of the impact absorbed energy in the HAZ at -20°C with the calculated content of soluble boron at 1350°C. All boron in each steel is soluble boron at the temperature regardless of the steel composition. It shows that the impact toughness of the HAZ has no correlation with the soluble boron at the welding peak temperature. Except for one steel, all steels that have more than 13 ppm of the soluble boron have below 100 J of absorbed energy with a bainite dominant microstructure. However, Steel 6 has about 130 J of absorbed energy with a ferrite dominant microstructure even though it has 18 ppm of soluble boron. This anomaly can be explained by considering the effect of nitrogen in steel. Unlike other steels, Steel 6 has a lot of soluble nitrogen, 106.47 ppm, at 1350°C (see Table 1 for the other steels). It is believed that soluble nitrogen combines with soluble boron to form boron nitrides during the welding cooling cycle, consequently reducing the soluble boron, which influences the hardenability of the HAZ. Boron nitride precipitates in the HAZ of Steel 6 confirm this fact — Fig. 8. Figure 9 shows the variation of analyzed boron that combined in boron nitrides at the HAZ of Steels 1-4 and 7 after the welding cooling cycle with the content of soluble nitrogen at the welding peak temperature. Steels 1-4 and 7 have approximately the same soluble boron content of 13-16 ppm at the welding peak temperature. It shows that the greater the content of soluble nitrogen the HAZ has at the welding peak temperature, the more boron nitrides precipitate in the HAZ. According to the stability of the nitrides, titanium nitride is expected to precipitate before boron nitride during the welding cooling cycle. However, the diffusivity of boron is much higher than that of titanium (about 10^5 times as high at
900°C for example), it is believed that the soluble nitrogen combines with the soluble boron first (Ref. 12).

Following the above discussions, if the thermodynamic analysis is applied for the prediction of HAZ hardenability, the effect of soluble nitrogen should be incorporated. In this study, the soluble boron to soluble nitrogen ratio at the welding peak temperature is proposed as the parameter that includes the effect of soluble nitrogen. Figure 9 shows the variation of the impact absorbed energy in the HAZ with the parameter. Compared to Fig. 7, it has a good relationship and shows that this parameter should be kept below 0.2 for the HAZ to have a ferrite dominant microstructure and impact absorbed energy above 100 J at -20°C.

Weldability of Low-Carbon Ti-B Containing Steel

For the verification of the improvement of HAZ toughness and weldability of low-carbon steel, the HAZ impact absorbed energy and cold cracking susceptibility of Steel 5 were characterized and compared with those of a conventional high-carbon steel. As the soluble boron to soluble nitrogen ratio at 1350°C of Steel 5 is 0.11, it satisfies the requirement of the high HAZ toughness as described above. The conventional steel has a chemical composition of 0.12%C-0.3%Si-1.4%Mn-0.1%Ni-0.2%Mo-0.04%V and was manufactured by the RQ process. The thickness of both steels is 30 mm, and the tensile strength of Steel 5 and conventional steel is 612 and 657 MPa, respectively. Figure 11 shows the variation of impact absorbed energy in the HAZ of both steels with temperature. The applied thermal cycle for HAZ simulation was described in the experimental procedures. It shows that the HAZ toughness of Steel 5 is improved markedly. The energy transition temperature (Tr E) of Steel 5 is -37°C, whereas that of the conventional steel is about 7°C. The microstructures of both steels before the welding thermal cycle show little difference, having a mixed microstructure of ferrite and bainite. However, the microstructure of the HAZ after the welding thermal cycle is quite different — Fig. 12. Steel 5 has a mixed microstructure of ferrite and bainite, while the conventional steel has a bainite dominant microstructure. Therefore, it is clear that the high HAZ toughness of Steel 5 is due to the morphology and distribution of ferrite.

The cold cracking susceptibility of each steel was characterized by the y-groove cracking test. A detailed method of the testing is regulated in the JIS Z3158. If a specimen shows no cracking in the test, no cracking is expected in the real structures because the restraint of the test is much more severe than in most real structures (Ref. 13). Welding was performed at 190 A, 22 V and 15 cm/min with a low-hydrogen electrode (AWS E9016G, 1.4 mm). The specimen was left for two days after welding and then sliced into five pieces. A crack ratio (crack length/bead height) of each cross section was measured and averaged. When welded without preheating, the conventional steel shows a 40% crack ratio while Steel 5 shows no cracking, implying that Steel 5 could be welded without cold cracking in the real structures. Figure 13 shows the results of Vickers hardness measurement across the HAZ and weld metal at 0.5-mm intervals. It shows that the maximum hardness of the HAZ of Steel 5, 309 HV, is much lower than that of the conventional steel, 380 HV. Therefore, the absence of cold cracking in Steel 5 even without preheating is attributed to the low hardness in the HAZ.

Conclusions

The effect of boron on the hardenability during quenching and on the welding cooling cycle of direct
Fig. 13 — Variation of the Vickers hardness for Steel 5 and conventional high-carbon steel as a function of the distance from the center of the weld metal.

The hardenability of the HAZ, however, was also influenced by the soluble nitrogen at the welding peak temperature. Only when the soluble boron to soluble nitrogen ratio at the welding peak temperature was kept below 0.2 did the HAZ show a ferrite dominant microstructure and higher than 100 J of absorbed energy at -20°C.

3) Soluble boron combines with soluble nitrogen to form boron nitrides during the welding cooling cycle, resulting in the reduction of soluble boron, which influences the hardenability of the HAZ.

4) Unlike a conventional high-carbon steel, a low-carbon steel containing a controlled amount of boron showed no cold cracking, even without preheating, and a high HAZ toughness with an energy transition temperature of -37°C.

References