Effect of Accelerated Cooling after Controlled Rolling on the Hydrogen Induced Cracking Resistance of Line Pipe Steel

By Hiroshi TAMEHIRO,** Tetsuo TAKEDA,** Shoichi MATSUDA,*** Koichi YAMAMOTO*** and Naoki OKUMURA****

Synopsis

The effect of accelerated cooling after controlled rolling on the hydrogen induced cracking (HIC) resistance of line pipe steels produced from continuously cast slabs was examined, and the relation between HIC resistance and the microstructure in the segregated zone at the mid-thickness of plate was clarified.

The optimization of accelerated cooling conditions reduced the volume fraction of high carbon martensite or upper bainite formed in the segregated zone, and this resulted in significant improvement of HIC resistance.

The above result can be explained by the model that the high cooling rate as well as the optimized start and stop temperatures in accelerated cooling suppress the rejection of carbon from the non-segregated area to segregated zone during the austenite to ferrite transformation causing the more uniform profile of carbon distribution in the through-thickness direction of plate.

I. Introduction

Hydrogen induced cracking (HIC) of steel occurs in a corrosive environment containing wet hydrogen sulphide (H$_2$S). In the case of line pipe steel produced from continuously cast (CC) slab, HIC parallel to the plate surface occurs in the segregated zone at the mid-thickness of plate.$^{1-5}$ In a high pH environment, the reduction of non-metallic inclusions, the sulphide shape control$^{6-8}$ or the addition of alloying elements such as nickel and copper$^{9,10}$ is very effective for improving HIC resistance. In a low pH environment (for example, pH 3.5), however, it is impossible to suppress HIC completely by the addition of alloying elements which are so far considered effective for the improvement of hydrogen embrittlement in a high pH environment or by the high purity steel production technique industrially available at present. This may be caused by the facts that there exists no element able to prevent the invasion of hydrogen in a low pH environment by forming a protective film on the steel surface, and that there exists low temperature transformation product (hereafter designated as hard phase) containing inclusions such as manganese sulphide (MnS) and calcium oxide (CaO) in the segregated zone.$^{1-5}$

Therefore, it is very important to thoroughly investigate all metallurgical factors that control the initiation, propagation and arrest of HIC, and to propose a new method for improving HIC resistance in a low pH environment.

It is known that the microstructure obtained by such heat treatment as quenching and tempering is favorable for the prevention of HIC.$^{6,9,10}$ However, the relation between HIC resistance and the microstructure in the segregated zone has not been clarified. On the other hand, accelerated cooling after controlled rolling is currently drawing attention as a new technique for manufacturing line pipe steel.$^{11,12}$ Although this process is able to control the microstructure of plate relatively easily, the relation between the conditions such as start and stop temperatures of accelerated cooling and HIC resistance or the microstructure in the segregated zone has not been investigated.$^{13-16}$

In this paper, the effect of the accelerated cooling conditions after controlled rolling on HIC resistance, mechanical properties, and the microstructural change in the segregated zone is investigated. The mechanism of improvement of HIC resistance obtained by this process is also discussed.

II. Experimental Procedures

All test steels were commercially produced CC slabs of 210 mm in thickness. These slabs were cut to a suitable size for laboratory rolling which was 210 mm thick × 350 mm wide × 400 mm long. Their chemical compositions are shown in Table 1, where ESSP is the index to indicate the degree of shape controlling of sulphide by calcium. Elongated MnS disappears at ESSP of more than 1.0. These slabs were hot rolled after reheating at 1 150 °C or 1 200 °C for 1 hr. The finish rolling temperature was in the range from $A_{3}$ temperature to 50 °C above the $A_{3}$ temperature, and total rolling reduction below 950 °C was 75 to 80 %. Accelerated cooling after controlled rolling was conducted at a cooling rate of about 30 to 35 °C/s, changing start and stop temperatures on the surface of plate. Further, air cooling was also conducted after rolling for comparison with accelerated cooling. The plate thickness was 16 mm for every test steel.

With all test steels, mechanical properties were examined in the transverse direction. Full thickness tensile tests, full size 2 mm V-notch Charpy tests and Battelle type DWT tests (DWTT) were conducted. HIC tests were performed using test solution of a H$_2$S-saturated solution containing 5 % NaCl plus 0.5 % acetic acid (NACE solution of pH 3.0 to 3.5)$^{17}$ HIC resistance was evaluated in terms of HIC crack area ratio (CAR) of the test specimen using ultrasonic testing. In addition, microstructural observa-

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tion by optical microscope and scanning electron microscope (SEM), micro Vickers hardness (Hv 25 g) test in the segregated zone, and measurement of the carbon distribution in the segregated zone by ion microanalyzer (IMA) were carried out.

### III. Experimental Results

Figures 1 to 4 show the effect of the stop temperature of accelerated cooling on HIC resistance and mechanical properties of plates. The optimum temperature range is 350 to 550 °C for improving HIC resistance. CAR increases above and below this range. HIC resistance of the accelerated cooled (ACC) plate, compared with the air cooled (CR) plate, is improved unless the stop temperature decreases too low. In the CR plate, CAR is 20 to 70 %, while that of the ACC plate decreases to 0 to 10 %. However, the suppression of HIC is usually influenced not only by the accelerated cooling conditions but also by other metallurgical factors such as chemical composition, inclusions, etc. The temperature range in which CAR becomes 0 % varies with the test steel. In steel N-2, CAR does not become 0 % because of high manganese content which easily forms the hard phase in the segregated zone. In steel B, the temperature range in which CAR becomes 0 % is very narrow, only in the vicinity of about 490 °C, because sulphide shape control by calcium is insufficient compared with in other steels and that hydrogen cracking susceptibility is high due to high strength.

On the other hand, as for changes in mechanical properties accompanying accelerated cooling, though the tensile strength of the ACC plate increases by 2 to 5 kgf/mm², the low temperature toughness is almost the same as that of the CR plate in the stop temperature range in which HIC resistance is improved. This is due to the fine-grained duplex microstructure consisting of ferrite and bainite without ferrite-pearlite banded structure. The separation observed on the fracture surface in Charpy and DWTT specimens is reduced by the disappearance of banded structure, which is considered to be caused by the improved toughness in the through-thickness direction.

The change of the microstructure at the mid-thickness of steel N-2 plates with the stop temperature of accelerated cooling is shown in Photo. 1. In the CR plate, a continuous banded microstructure which

<table>
<thead>
<tr>
<th>Steel</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Nb</th>
<th>V</th>
<th>Mo</th>
<th>B</th>
<th>Other elements</th>
<th>ESSP*</th>
<th>C_{np}**</th>
<th>A_{90}*** temp. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-1</td>
<td>0.104</td>
<td>0.30</td>
<td>1.05</td>
<td>0.004</td>
<td>0.0010</td>
<td>0.04</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>Ni, Cu, Ti, Ca</td>
<td>2.44</td>
<td>0.31</td>
<td>752</td>
</tr>
<tr>
<td>N-2</td>
<td>0.082</td>
<td>0.28</td>
<td>1.33</td>
<td>0.007</td>
<td>0.0009</td>
<td>0.04</td>
<td>0.09</td>
<td>—</td>
<td>—</td>
<td>Ni, Ti, Ca</td>
<td>1.15</td>
<td>0.34</td>
<td>740</td>
</tr>
<tr>
<td>M</td>
<td>0.057</td>
<td>0.17</td>
<td>1.08</td>
<td>0.005</td>
<td>0.0013</td>
<td>0.04</td>
<td>—</td>
<td>0.25</td>
<td>—</td>
<td>Ni, Ti, Ca</td>
<td>1.53</td>
<td>0.31</td>
<td>766</td>
</tr>
<tr>
<td>B</td>
<td>0.024</td>
<td>0.19</td>
<td>1.17</td>
<td>0.009</td>
<td>0.0017</td>
<td>0.04</td>
<td>—</td>
<td>—</td>
<td>0.001</td>
<td>Ni, Cu, Ti, Ca</td>
<td>0.74</td>
<td>0.25</td>
<td>771</td>
</tr>
</tbody>
</table>

* ESSP=[Ca] (1-124[O])1.25[S] (Effective sulphide shape controlling parameter)
** C_{np}=C+Mn/6+(Ni+Cu)/15+(Cr+Mo+V)/5 (%) 
*** A_{90} temp.=869-C+24.6-Si-66.1-Mn-36.1-Ni-20.1-Cu-24.8-Cr (°C)
mainly consists of hard phases such as high carbon martensite (M*) and upper bainite (Bu) is observed with a width of about 25 µm and the pearlite free zone (PFZ) with a width of about 40 µm exists at both sides of the banded microstructure. While in the ACC plate the banded microstructure disappears and a more homogeneous microstructure is formed. Namely, the fraction of such hard phases as M* and Bu is markedly reduced and these hard phases are finely dispersed. But in the case of higher stop temperature, the dispersion of the continuous banded microstructure is insufficient and in the case of lower stop temperature, Bu increases in addition to the finely dispersed M*.

Figure 5 shows the effect of the start temperature of accelerated cooling, relative to the calculated Ar3 temperature, on CAR of steel M plates. The start of accelerated cooling from higher than the Ar3 temperature completely suppresses the initiation of HIC. When accelerated cooling starts below this temperature, the banded hard microstructure at the mid-thickness of plate does not disappear.

Figure 6 shows the effect of the cooling rate after rolling on CAR and maximum hardness at the mid-thickness of steel N-1 plates. Although CAR is 0 % except at the cooling rate of 0.5 °C/s (air cooling),
the maximum hardness increases by about $30 \text{ Hv}$ at the cooling rate of $9 \, ^\circ\text{C/s}$. According to microscopic observation, the banded hard microstructure at the mid-thickness of plate does not disappear completely. Therefore, it is necessary to cool after rolling at a cooling rate of more than $15 \, ^\circ\text{C/s}$ for improving HIC resistance.

In order to clarify the mechanism for the improvement of HIC resistance by accelerated cooling, the initiation and propagation characteristics of HIC were examined. Photograph 2 shows the initiation sites of HIC in steel N-2 CR plate observed on the test specimen which was taken out of NACE solution during the test and had only small cracked area (CAR=0.2%) detected by ultrasonic testing. At the initiation site, there existed small niobium carbonitrides ($\text{NbCN}$) and oxide particles ($\text{CaAl}_2\text{O}_3$) of about $5 \, \mu\text{m}$ in size, in addition to MnS. However, the composition and distribution of these inclusions and precipitates are almost the same for both CR and ACC plates.

Photograph 3 shows HIC propagation paths in the CR plates. In order to examine the correspondence between HIC paths in the segregated zone and austenite ($\gamma$) grain boundaries, the microstructure was revealed by using an etchant which preferentially attacks $\gamma$ grain boundaries. Although the microscopic HIC propagation paths in the segregated zone are considerably complicated, these can be divided roughly into two types: path along the hard phases in the segregated zone (Photos. 3(a) and (b)), and path along the interface between PFZ and hard phases (Photo. 3(c)). In the former case, the boundary of the hard phase frequently coincides with the prior non-recrystallized $\gamma$ grain boundary (Photo. 3(d)). In such case, it seems that HIC is very easy to propagate.

From the above result, it is supposed that for the improvement of HIC resistance it is important to decrease the propagation paths, that is, it is necessary

![FIG. 6. Effect of cooling rate of accelerated cooling on CAR and maximum hardness at mid-thickness of steel N-1 plates.](image1)

![PHOTO. 2. Initiation sites of HIC in steel N-2 CR plate.](image2)

(a), (b), (c): Steel N-1
(d): Steel B
Photo. 3: Typical HIC propagation paths in CR plates.
to reduce the absolute amount of hard phases, to make hard phases finely distributed or not to allow their coincidence with the prior \( \gamma \) grain boundary. Accelerated cooling after rolling can be considered as providing a good effect in these respects. Further, even when HIC has initiated at an inclusion or precipitate such as MnS or Nb(CN) in the segregated zone, it is possible to suppress its propagation through the decrease of the fraction of the hard phases.

Figure 7 shows the relation between the maximum hardness in the segregated zone at the mid-thickness and CAR of steels N-1 and B plates processed by different stop temperatures. HIC does not occur in the test specimen whose maximum hardness is less than about Hv 250. This hardness level is almost the same for both steels. Hv 250 fortuitously is the value very close to the critical hardness of Re 22 (Hv 248)\(^{18}\) at which sulphide stress corrosion cracking (SSC) takes place. It is generally known that the susceptibility of steel to hydrogen embrittlement becomes greater with increasing strength or hardness. Therefore, the hardness in the segregated zone may be considered as a macroscopic parameter of HIC susceptibility.

IV. Discussion

In the preceding section, it was found that by accelerated cooling after rolling the banded hard microstructure in the segregated zone of plate disappears and HIC is suppressed. In order to examine this mechanism, the microstructure in the segregated zone was quantitatively analyzed by SEM observation of steel B. An example of SEM observation is given in Photo. 4. In the CR plate, thinly elongated M* exists continuously on the elongated prior \( \gamma \) grain boundary, while in the ACC plate with a stop temperature of 490 °C, which is free from HIC, M* on the \( \gamma \) grain boundary is finely dispersed and its percentage of occupation on the prior \( \gamma \) grain boundary is much smaller than that in the CR plate. As the stop temperature decreases below 490 °C, Bu increases and the elongated \( \gamma \) grain boundary is almost entirely occupied by the hard phases. Based on the above result, the fraction of microstructure occupying the \( \gamma \) grain boundary per unit length was determined, the result of which is given in Fig. 8. The fraction of hard phases becomes a minimum value at the stop temperature of about 490 °C. The fraction of M* and Bu is well related to CAR; with increasing M* and Bu, CAR increases linearly as shown in Fig. 9. Therefore, the improvement of HIC resistance by interruption of accelerated cooling at 490 °C can be considered to have resulted from the fraction of M* and Bu on the elongated \( \gamma \) grain boundary being controlled at a low level.

Next, let us consider the reason why the hard phases such as M* and Bu decrease by accelerated cooling starting at higher than the \( A_{13} \) temperature. Figure 10 shows the distribution of carbon concentration in the through-thickness direction in the segregated zone at the mid-thickness of steel N-2 plates whose microstructures are shown in Photo. 1. In the ACC plate, carbon is uniformly distributed irrespective of the non-segregated area or segregated zone. While in the CR plate, a carbon concentrated region exists at both sides of the segregated zone. These results suggest that at the latter stage of the austenite to ferrite (\( \gamma \)-\( \alpha \)) transformation, the carbon concentration in the untransformed \( \gamma \) becomes high compared with the ACC plate and it transforms to the thinly elongated M*.

The rejection of carbon to the segregated zone in the CR plate is considered to occur for the following
reasons (Fig. 11).

1. Manganese concentration in the segregated zone is assumed to be 1.7 times higher than that in the non-segregated area.

2. Therefore, \(\gamma\)-\(\alpha\) transformation in the segregated zone is retarded compared with that of the non-segregated area.

3. As a result, the diffusion of carbon is restricted to one direction in a certain region between the non-segregated area and the segregated zone.

In the above model, it is assumed that carbon distributes uniformly in \(\gamma\) because the carbon concentration seems to be homogenized during slab-heating.

The \(\gamma\)-\(\alpha\) transformation temperature in the non-segregated area and segregated zone of plate calculated by taking into consideration the segregation of manganese only, and the difference in \(\gamma\)-\(\alpha\) transformation time calculated by supposing the cooling rate of plate by air as 30 °C/min are given in Table 2.

Assuming \(\gamma\)-\(\alpha\) transformation is governed by the diffusion of carbon in \(\gamma\), the width of PFZ, \(X\), is given by\(^{10}\): 

\[
X = \left[ Dr(C) \right]^{1/2} \frac{(C_{\gamma} - C_{\alpha})}{(C_{\gamma}^{\alpha} - C_{\gamma}^{\alpha})^{1/2}(C_{\alpha} - C_{\gamma})^{1/2}}
\]

where, 

- \(Dr(C)\): diffusion coefficient of carbon in \(\gamma\)
- \(C_{\gamma}\): bulk concentration of carbon
- \(C_{\gamma}^{\alpha}\): carbon concentration of \(\gamma\) at \(\gamma\)-\(\alpha\) interface
- \(C_{\alpha}\): carbon concentration of \(\alpha\) at \(\gamma\)-\(\alpha\) interface.

According to Table 2, PFZ width calculated by the above equation (\(X_{\text{calc}}\)), PFZ width observed (\(X_{\text{obs}}\)) and other data in case \(\gamma\)-\(\alpha\) transformation progressed with the unidirectional diffusion of carbon at a temperature of 700 °C for 127 sec are given in Table 3, where the temperature of 700 °C is the average value of \(A_{3}\) for the non-segregated area and \(A_{3}\) for the segregated zone. The observed width is a little smaller than the calculated width, but both agree fairly well. Following the above model, it is clearly seen that carbon rejected from PFZ concentrates at both sides of the segregated zone in a certain width.

As is apparent from the above discussion, even if the carbon concentration is uniform through the non-segregated area and segregated zone, the enrichment of carbon at both sides of the segregated zone occurs in such case that the difference in \(\gamma\)-\(\alpha\) transformation time between the non-segregated area and segregated zone becomes large due to the low cooling rate. In the case of accelerated cooling with higher cooling rate, however, the distribution of carbon concentration is uniform due to the very small amount of carbon diffusing to the segregated zone.

As a result, the hard phases such as M* and Bu
decrease and are finely distributed in the segregated zone.

However, when the start temperature of accelerated cooling decreases below the $A_{\gamma}$ temperature, HIC resistance cannot be improved. This is because as is the case of the CR plate, the thinly elongated M* and Bu appear due to the increased amount of carbon rejected to the segregated zone by the enlargement of the difference in $\gamma\rightarrow\alpha$ transformation time between the non-segregated area and the segregated zone (Fig. 12).

V. Conclusions

The effect of accelerated cooling after controlled rolling on HIC resistance of line pipe steels produced from CC slabs was examined, and the relation between HIC resistance and the microstructure in the segregated zone at the mid-thickness of plate was discussed, as a result of which the following conclusions were obtained.

1) HIC resistance is remarkably improved by accelerated cooling in which the cooling rate as well as the start and stop temperatures are specified. The optimum accelerated cooling conditions are as follows: start temperature above the $A_{\gamma}$ temperature; cooling rate more than 15 °C/s; stop temperature between 400 °C and 550 °C.

2) The micro-hardness in the segregated zone is considered as a macroscopic parameter of HIC susceptibility. The critical hardness at which HIC initiates is about Hv 250.

3) HIC propagation paths can be divided roughly into two types: path along the interface between PFZ and hard phases such as M* and Bu, and path along the hard phase in the segregated zone.

4) CAR is controlled by the volume fraction of hard phases such as M* and Bu formed in the segregated zone and their distribution. CAR increases linearly with increasing M* and Bu occupying the elongated prior $\gamma$ grain boundary.

5) The reason why the hard phases such as M* and Bu decrease by accelerated cooling is that the optimized accelerated cooling suppresses the rejection of carbon from the non-segregated area to segregated zone, causing the more uniform profile of carbon distribution in the through-thickness direction of plate.

REFERENCES


Table 3. Comparison of PFZ between calculated value ($X_{\text{cal}}$) and observed value ($X_{\text{obs}}$).

<table>
<thead>
<tr>
<th>Temperature, cooling condition</th>
<th>Time difference</th>
<th>$\left(D(t)\right)^{0.2}$</th>
<th>$C_{\gamma}^{*}$</th>
<th>$C_{\alpha}$</th>
<th>$C_{0}$</th>
<th>$X_{\text{cal}}$</th>
<th>$X_{\text{obs}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>700 °C, CR (30 °C/min)</td>
<td>127 sec</td>
<td>11.7 μm</td>
<td>0.90 %</td>
<td>0.02 %</td>
<td>0.082 %</td>
<td>41.3 μm</td>
<td>40 μm</td>
</tr>
</tbody>
</table>

![Fig. 12. Difference in $\gamma\rightarrow\alpha$ transformation time between non-segregated area and segregated zone due to start temperature of accelerated cooling.](image-url)