1. Introduction

The delayed fracture properties of high strength steels with tensile strength exceeding 1 200 MPa are usually lower, which is unfavourable for their wide applications, and the delayed fracture properties of high strength steels are related to hydrogen behavior in the materials. The study of hydrogen behavior in the materials becomes one of main contents improving delayed fracture properties of materials. The electrochemical permeation technique with simplicity, high sensitivity and flexibility, developed by Devanathan and Stachurski, has proved to be very important to the studies of hydrogen behavior in materials. In general, some crystal defects such as dislocations, grain boundaries, inclusion interfaces, carbide interfaces, exist in metals and alloys, which as hydrogen traps may reduce diffusion coefficient of hydrogen. Therefore, controlling the hydrogen traps in high strength steels could improve their delayed fracture properties. In the paper, the effect of fined microstructure and retained austenite on the delayed fracture properties of 1 500 MPa bainite–martensite dual-phase high strength steels and hydrogen traps in them have been investigated.

2. Experimental Procedure

The materials investigated were vacuum-induction melting bainitic steels (U20Si, XBU25A, U25A, U20DSi), and 30CrMnSiA high strength steel was selected to compare with them, their compositions were given in Table 1. The details of the heat treatment were shown in Table 2.

The experiments of stress corrosion cracking (SCC) were carried out in 3.5% NaCl solution at 298 K, using modified wedge-opening-loading (WOL) specimens. The experimental results show that for novel 1 500 MPa bainite/martensite dual-phase high strength steel is larger than 50 MPa·m²/², exceeding conventional high strength steel. Its crack growth rate \( \frac{da}{dt} \) is about \( 1 \times 10^{-5} \text{ mm/s} \), which is less than that of conventional high strength steel. Hydrogen trapping phenomena in the steel were investigated by electrochemical permeation technique. The lath boundaries and stable retained austenite are beneficial hydrogen trap, slowing down the segregation of hydrogen on the crack tip, hence \( K_{\text{ISCC}} \) increases and crack growth rate decreases.

KEY WORDS: delayed fracture; hydrogen embrittlement; bainite/martensite dual-phase high strength steel; stress corrosion cracking; electrochemical permeation technique.

Delayed Fracture Properties of 1 500 MPa Bainite/Martensite Dual-phase High Strength Steel and Its Hydrogen Traps

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where \( l \): specimen thickness, \( t_l \): time lag, which was the time taken for the permeation to reach 0.63 of its steady-state value. All tests were done at 298 K, 323 K, 353 K, respectively. The apparent trap parameter (\( \alpha \)), the difference of trap parameter (\( \Delta \alpha \)) and the trap binding energy (\( E_B \)) were calculated according to McNabb and Foster\(^7\) model.

3. Experimental Results

3.1. Microstructure of Materials

U20Si, XBU25A, U25A and U20DSi are bainite/martensite dual-phase high strength steels. Their austenite grain sizes and microstructures are similar and the microstructures are shown in Fig. 2. From Fig. 2 it can be seen that the microstructure of bainite/martensite dual-phase high strength steels (XBU25A) for thermomechanical treatment is markedly fined. Bainite/martensite lath sizes change from 10 to 5 \( \mu \)m in length and 0.7 to 0.6 \( \mu \)m in width in the specimens of conventional heat-treatment and thermomechanical heat-treatment. The 30CrMnSiA is tempered troostite.

The retained austenite exists as films by transmission electron microscope (TEM) (Fig. 3). The volume percentage of retained austenite is shown in Table 2. It is seen that addition of more Si can make retained austenite increase.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Cr</th>
<th>Mo</th>
<th>Ni</th>
<th>W</th>
<th>V</th>
<th>Ti</th>
<th>S</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>U20Si</td>
<td>0.27</td>
<td>1.8</td>
<td>1.8</td>
<td>0.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.009</td>
<td>0.007</td>
</tr>
<tr>
<td>XBU25A</td>
<td>0.27</td>
<td>1.3</td>
<td>1.8</td>
<td>0.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.009</td>
<td>0.007</td>
</tr>
<tr>
<td>U25A</td>
<td>0.27</td>
<td>1.3</td>
<td>1.8</td>
<td>0.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.009</td>
<td>0.007</td>
</tr>
<tr>
<td>U20DSi</td>
<td>0.27</td>
<td>0.3</td>
<td>1.8</td>
<td>0.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.009</td>
<td>0.007</td>
</tr>
<tr>
<td>30CrMnSiA</td>
<td>0.33</td>
<td>0.97</td>
<td>0.88</td>
<td>0.90</td>
<td>0.02</td>
<td>0.08</td>
<td>0.02</td>
<td>0.01</td>
<td>0.01</td>
<td>0.003</td>
<td>0.012</td>
</tr>
</tbody>
</table>

Table 1. Chemical compositions of specimens.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Austenitizing Temperature (K)</th>
<th>Holding Time (min)</th>
<th>Cooling Mode</th>
<th>Tempering Temperature (K)</th>
<th>Yield Strength (MPa)</th>
<th>Tensile Strength (MPa)</th>
<th>Retained Austenite (vol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>U20Si</td>
<td>1173</td>
<td>18</td>
<td>Air cooling</td>
<td>553</td>
<td>1220</td>
<td>1520</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>18 (1133K, Hot-deformation)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>XBU25A</td>
<td>1133</td>
<td>true strain 36%,</td>
<td>Air cooling</td>
<td>553</td>
<td>1260</td>
<td>1520</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>rate of strain 6x10^{-3}s^{-1}</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>U25A</td>
<td>1173</td>
<td>18</td>
<td>Air cooling</td>
<td>553</td>
<td>1210</td>
<td>1510</td>
<td>6</td>
</tr>
<tr>
<td>U20DSi</td>
<td>1173</td>
<td>18</td>
<td>Air cooling</td>
<td>553</td>
<td>1230</td>
<td>1530</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Oil quenching</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30CrMnSiA</td>
<td>1153</td>
<td>18</td>
<td></td>
<td>713</td>
<td>1360</td>
<td>1510</td>
<td></td>
</tr>
</tbody>
</table>

Table 2. Processing parameters.

Fig. 1. The scheme of hydrogen permeation curves.

\[ D_A = l^{1/6} t_l \]
The Fig. 4 shows X-ray diffraction spectrums before and after charging hydrogen of U20Si, it can be calculated that the contents of retained austenite in two specimens are 9%, which shows that the film retained austenite exhibits better chemical stability.

3.2. Delayed Fracture Properties

Table 3 gives the delayed fracture properties of materials, which indicates that \( K_{\text{ISC}} \) increases, \( (\text{da}/\text{dt})_i \) decreases as the microstructure is fined and retained austenite increases in the bainite/martensite dual-phase high strength steels.

The fractographic analysis suggests that the fracture mode of SCC for the four bainite/martensite dual-phase high strength steels is quasicleavage; by contrast, the fracture mode of SCC for 30CrMnSiA is intergranular, as shown in Table 3.

Fig. 2. SEM micrographs for materials. (a) U25A; (b) XBU25A; (c) 30CrMnSiA. M: martensite; B: bainite.

Fig. 3. TEM Images for U20Si. (a) Retained austenite bright field imaging; (b) retained austenite dark field imaging.

Fig. 4. X-ray diffraction energy spectrum for U20Si before and after charging hydrogen. (a) U20Si, (b) U20Si charging hydrogen with cathodic current density \( i = 10 \text{ mA/cm}^2 \) for 4 h.

Table 3. Delayed fracture properties of steels.

<table>
<thead>
<tr>
<th>Steels</th>
<th>( K_{\text{ISC}} ) (MPa ( \cdot ) m(^{1/2} ))</th>
<th>((\text{da}/\text{dt})_i ) ((\times 10^{-5}))</th>
<th>mm/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>U20Si</td>
<td>51.5</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td>XBU25A</td>
<td>53.8</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>U25A</td>
<td>44.6</td>
<td>1.8</td>
<td></td>
</tr>
<tr>
<td>U20DSi</td>
<td>40.5</td>
<td>2.7</td>
<td></td>
</tr>
<tr>
<td>30CrMnSiA</td>
<td>36.2</td>
<td>3.2</td>
<td></td>
</tr>
</tbody>
</table>
shown in Fig. 5.

3.3. Hydrogen Traps in Materials

McNabb and Foster\(^7\) have derived an equation which represents the relationship between the apparent diffusion coefficient \(D_A\) and lattice diffusion coefficient \(D_L\).

\[
D_L = D_A(1 + \alpha) = D_A \left(1 + N \frac{k}{p}\right) \quad \text{(2)}
\]

The apparent trap parameter \(\alpha\) can thus be calculated from Eq. (2), where \(k\) and \(p\) is trapping and escaping rate, respectively, \(N\) is trap density.

If energy levels around the trap site are assumed to be those shown in Fig. 6,\(^1\) then \(k\) and \(p\) can be written:

\[
k = v_0 \exp(E_D/RT) \quad \text{(3)}
\]

\[
p = v_1 \exp(-(E_S + E_D)/RT) \quad \text{(4)}
\]

Choo assumed that the vibration frequencies \(v_0\) and \(v_1\) are the same,\(^9\) and the Eq. (5) could be derived, therefore the trap binding energy \(E_B\) could be obtained.

\[
\alpha = Nk/p = N \exp(E_B/RT) \quad \text{(5)}
\]

However, since various types of hydrogen traps exist in materials, it is not possible to measure the effect of a single type of trap from one kind of specimen. The effect of one type of trap can be obtained from the difference of apparent trap parameter \(\alpha\) of two specimens, which differ only in the amount of single trap. If the amount of one type trap is different in two specimens, the difference of trap parameter \(\alpha\) of the two specimens can be obtained from Eq. (6).

\[
\frac{D_L}{D_{A1}} - \frac{D_L}{D_{A2}} = \Delta \alpha = \Delta N \frac{k_i}{p_i} \quad \text{(6)}
\]

where \(D_{A1}\) is apparent diffusion coefficient in specimen 1, \(D_{A2}\) is apparent diffusion coefficient in specimen 2, in which the amount of trap site \(i\) is varied from specimens 1, \(\Delta N_i\) is the difference in the number of trap site \(i\) between specimen 1 and 2. Assuming that the trap density does not vary with temperature, the difference of trap parameter \(\Delta \alpha\) obtained at different temperatures for the same specimens can be expressed as Eq. (7) by combining Eqs. (5) and (6). Thus, the binding energy between trap site \(i\) and hydrogen can be obtained.

\[
\frac{\Delta \alpha_{i2}}{\Delta \alpha_{i1}} = \exp(E_B/R(T_2^{-1} - T_1^{-1})) \quad \text{(7)}
\]

In order to obtain \(\alpha\), it is necessary to know \(D_L\). In this work, \(D_L\) value used to calculate \(\alpha\) is:

\[
D_L = 7.23 \times 10^{-4} \exp(-5.69 \text{ kJ mol}^{-1}/RT) \quad \text{(8)}
\]

Calculated values of \(D_A\) and \(\alpha\) are shown in Table 4.

The difference of trap parameters \(\Delta \alpha\) obtained from the apparent trap parameters \(\alpha\) comparing U25A and XBU25A, U20DSi and U20Si, respectively, describes the effect of bainite or martensite lath boundaries and retained austenite, it is presented in Table 5.

The trap binding energy \(E_B\) of retained austenite and bainite or martensite lath boundaries was calculated from Eq. (7), which is 40.4 kJ/mol and 28.1 kJ/mol, respectively. It is also apparent that the trapping effect of retained austenite is stronger than that of dislocations, microvoids and grain boundaries because the trap binding energy is larger than the values of dislocations (19.2 kJ mol\(^{-1}\)), microvoids (27.6 kJ mol\(^{-1}\)) obtained by Choo and Lee, and the trapping effect of the lath boundaries is similar to them.

4. Discussion

The improving of delayed fracture properties for bainite/martensite dual-phase high strength steels is due to different microstructure from 30CrMnSiA. Addition of certain amount Si in bainite/martensite dual-phase high strength steel assured that carbide-free precipitates and that there was more filmy retained austenite exhibiting a better mechanical-stability, thermal-stability and chemical-stability.
in it. The transformation of martensite did not create under charging hydrogen and stress, which avoided factors of microstructure generating hydrogen induced cracking. Since the retained austenite has good ductility, it may inhibit crack propagation; by the way, retained austenite acts as a hydrogen trap too, which may reduce local hydrogen segregation rate, and weak accumulation of hydrogen on crack tip. Therefore, retained austenite improves the resistance to delayed fracture.

In addition, the bainite/martensite dual-phase microstructure obtained by thermomechanical heat-treatment is markedly finer than that of conventional treatment. This is because austenitizing temperature of thermomechanical treatment is lower, recrystallization-free austenite was found. The defects such as dislocation in intragranular provide subsequent transformation with more nucleation location. The finer the bainite/martensite dual-phase microstructure, the more the lath boundaries are. Since the lath boundary is a hydrogen trap, which increase of lath boundary also leads to increase of hydrogen traps, which makes hydrogen distribute homogeneously. It is difficult for hydrogen concentration on crack tip to arrive to critical value of crack propagation. Thus, the resistance to delayed fracture is also improved.

### Table 4

The diffusion coefficients ($D_A$) and trap parameters ($\alpha$) at different temperature.

<table>
<thead>
<tr>
<th>Steels</th>
<th>Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>298</td>
</tr>
<tr>
<td></td>
<td>$D_A$ ($\times 10^{12}$ cm$^2$·s$^{-1}$)</td>
</tr>
<tr>
<td>U20DSi</td>
<td>0.613</td>
</tr>
<tr>
<td>U20Si</td>
<td>0.348</td>
</tr>
<tr>
<td>U25A</td>
<td>0.423</td>
</tr>
<tr>
<td>XBU25A</td>
<td>0.335</td>
</tr>
<tr>
<td>30CrMnSiA</td>
<td>0.710</td>
</tr>
</tbody>
</table>

### Table 5

The difference in trap parameters ($\Delta \alpha$) between U25A and XBU25A, U20DSi and U20Si.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>U25A and XBU25A</th>
<th>U20DSi and U20Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>45.1</td>
<td>90.3</td>
</tr>
<tr>
<td>323</td>
<td>15.0</td>
<td>31.5</td>
</tr>
<tr>
<td>353</td>
<td>7.7</td>
<td>7.1</td>
</tr>
</tbody>
</table>

5. Conclusions

1. $K_{SCC}$ for novel 1500 MPa bainite/martensite dual-phase high strength steel is larger than 50 MPa·m$^{1/2}$, exceeding conventional high strength steel. Its crack growth rate ($d a/d t_{II}$) is about $1 \times 10^{-5}$ mm/s, which is less than that of conventional high strength steel.

2. The fracture mode of SCC for bainite/martensite dual-phase high strength steels is quasicleavage; by contrast, the fracture mode of SCC for 30CrMnSiA is intergranular.

3. The trap binding energy ($E_B$) of retained austenite and bainite or martensite lath boundaries is 40.4 kJ/mol and 28.1 kJ/mol, respectively.

4. The reason of improvement in delayed fracture properties for bainite/martensite dual-phase high strength steels is related to stable filmy retained austenite and bainite or martensite lath boundaries acting as hydrogen traps.

REFERENCES