Hydrogen Delayed Fracture Properties and Internal Hydrogen Behavior of a Fe–18Mn–1.5Al–0.6C TWIP Steel

Kyoung Ho SO,1) Ji Soo KIM,1) Young Soo CHUN,1) Kyung-Tae PARK,2) Young-Kook LEE3) and Chong Soo LEE1)

1) Department of Materials Science and Engineering, Pohang University of Science and Technology, Pohang 790-784, Korea. E-mail: cslee@postech.ac.kr 2) Division of Advanced Materials Science and Engineering, Hanbat National University, Daejeon 305-719, Korea. 3) Department of Metallurgical Engineering, Yonsei University, Seoul 120-749, Korea.

(Received on June 15, 2009; accepted on September 1, 2009)

The hydrogen delayed fracture (HDF) properties and internal hydrogen behavior were investigated in a Fe–18Mn–1.5Al–0.6C steel, a representative twinning induced plasticity (TWIP) aided steel. Slow strain rate tests (SSRT) were employed on both smooth and notched specimens to evaluate the effects of diffusible hydrogen on the HDF properties of the steel. Results showed that the fracture stress, fracture strain and time to fracture of the hydrogen pre-charged specimens were relatively insensitive to the amount of diffusible hydrogen. Fracture surface exhibited a ductile dimple fracture mode regardless of the diffusible hydrogen concentration. It was found that most hydrogen became non-diffusible after SSRT. The major trapping sites of hydrogen were dislocations, grain boundaries and twins. The activation energies for detrapping of hydrogen were estimated 35 kJ/mol for dislocations or grain boundaries, and 62 kJ/mol for twins. A comparison of the HDF properties of the present steel with those of other high strength steels revealed that the TWIP steel appeared to be relatively immune to hydrogen delayed fracture. This was due to the combined effects of (a) higher hydrogen solubility of austenite matrix (b) negligible portion of diffusible hydrogen to the total hydrogen, (c) decrease of diffusible hydrogen content during the deformation, and (d) no transformation of austenite to either ε or α’ martensite.

KEY WORDS: hydrogen delayed fracture; twin induced plasticity; hydrogen trapping site; thermal desorption analysis.

1. Introduction

During the last several decades, immense efforts have been made to develop high strength steels to meet the needs for weight savings and to cope with environmental regulations in the automotive industry. As a result, various kinds of high strength steels have been developed by controlling alloy compositions, refining microstructures, utilizing phase transformation and so on. Recently, an increasing interest has been focused on the austenitic steel containing 15–25 wt% manganese so called twinning induced plasticity (TWIP) aided steels,1–5) which show not only high tensile strength (>1 200 MPa) but also large elongation to fracture (~70%). Such large elongation is attributed to the consecutive formation of twins during deformation. Correspondingly, the tensile toughness (tensile strength multiplied by elongation to fracture) of TWIP steels is much higher than that of advanced high strength steels such as dual phase (DP) steels and transformation induced plasticity (TRIP) aided steels.

Hydrogen delayed fracture (HDF), a kind of hydrogen embrittlement, is one of the important issues in the development of high strength steels, because the susceptibility of hydrogen embrittlement increases with the increase of strength of steels. Hydrogen embrittlement is known to occur due to excessive accumulation of hydrogen at the preferential sites as well-summarized in the earlier literatures.6–11) It was also reported that diffusible hydrogen which desorbs at low temperatures is mainly responsible for HDF of steels.12) Although several studies have been carried out on HDF of high manganese steels,13–17) the effects of the diffusible hydrogen content on the mechanical properties of the TWIP steel have not been investigated in a quantitative manner. Also, the main trapping sites of diffusible hydrogen and activation energies for its desorption at those sites in the TWIP steel have not been clarified yet.

Therefore, the purposes of this study are to investigate the hydrogen susceptibility of a Fe–18Mn–1.5Al–0.6C TWIP steel, to find the quantitative relationship between the HDF properties and diffusible hydrogen content, to identify the major trapping sites of diffusible hydrogen and to determine the activation energies for hydrogen desorption at the trapping sites. For these purposes, a series of slow strain rate tests (SSRT) and thermal desorption analysis (TDA) were conducted.

2. Experimental Procedures

The material used in this work was a Fe–18Mn–1.5Al–0.6C TWIP steel with a chemical composition of 17.9 Mn,
1.4 Al, 0.58 C, and balance Fe (in wt%). The cold-rolled plates (2.5 mm thick) were annealed at 1 173 K for 15 min followed by air cooling, resulting in fully recrystallized microstructure. A schematic diagram for thermomechanical history of the steel is shown in Fig. 1(a). After annealing, both smooth and notched specimens for SSRT were machined as depicted in Fig. 1(b).

Hydrogen was introduced into the specimens by electrochemical pre-charging in a 3% NaCl aqueous solution containing 3 g/L of NH₄SCN with the current density of 1–51 A/m² for 48 h, and then specimens were ground with SiC paper up to 1 500-grit. Prior to SSRT, the specimens were plated with cadmium in a fluoroborate bath containing 460 g distilled water, 427 g liquid Cd(BF₄)₂, 48 g NH₄BF₄ and 21.6 g H₃BO₄ to prevent the evolution of hydrogen before and during SSRT. SSRT was carried out using an Instron machine (model 5582) with a constant stroke rate of 0.1 mm/min, equivalent to an initial strain rate of $4.8 \times 10^{-5}$/s, at room temperature. After SSRT, the fractured specimens were immediately put into liquid nitrogen to prevent hydrogen release and kept until removal of cadmium coating for hydrogen analysis.

The hydrogen content was measured by means of TDA using a gas chromatograph with a linear heating rate of 100 K/h. The sample gas was analyzed with a 5 min interval using helium as a carrier gas. To determine the activation energy for hydrogen desorption of each trapping site, other heating rates of 200 K/h and 300 K/h were also applied and the model proposed by Kissinger¹⁸ was employed. In the present analysis, the hydrogen content detected below 673 K and above 673 K was defined as the diffusible and non-diffusible hydrogen content, respectively.

3. Results

3.1. Effects of Diffusible Hydrogen on Fracture

Figure 2 shows the optical microstructures after (a) hot rolling, (b) hot rolling and cold rolling and (c) hot and cold rolling with subsequent annealing at 1 173 K. It is noted that a large amount of deformation twins was produced in the austenite grains after cold rolling, and the prior austenite grain boundaries were not clearly seen in the microstructure (Fig. 2(b)). In order to investigate any new phases which might form during the rolling or annealing processes, the XRD patterns of three specimens corresponding to the Figs. 2(a), 2(b) and 2(c) were taken. All the specimens revealed only the FCC austenite ($\gamma$) phase peaks indicating that no new phases were formed by cold rolling and annealing. The grain sizes of austenite shown in Figs. 2(a) and 2(c) were approximately $9.8 \mu m$ and $10.0 \mu m$, respectively. Table 1 shows tensile properties of specimens annealed at 1 173 K for 15 min.

Prior to SSRT, the diffusible hydrogen contents of the specimens charged with the current density of 1–51 A/m² for 48 h were obtained by measuring the area of the TDA curves below 673 K. As shown in Fig. 3, the diffusible hydrogen content increased with increasing the charging current density. However, after SSRT, it decreased significantly, for example from 0.82 to 0.03 mass ppm for a current density of 41 A/m²: the diffusible hydrogen contents after SSRT are listed in Table 2. It is noticed from Table 2 that, after SSRT, the remaining diffusible hydrogen contents of the specimens charged with the current density of 1–51 A/m² for 48 h were obtained by measuring the area of the TDA curves below 673 K. As shown in Fig. 3, the diffusible hydrogen content increased with increasing the charging current density. However, after SSRT, it decreased significantly, for example from 0.82 to 0.03 mass ppm for a current density of 41 A/m²; the diffusible hydrogen contents after SSRT are listed in Table 2. It is noticed from Table 2 that, after SSRT, the remaining diffusible hydrogen contents

<p>| Table 1. Tensile properties of cold rolled 18Mn–1.5Al–0.6C sheet which was annealed at 1 173 K for 15 min. |
|---------------------------------|----------------|---------------|----------------|</p>
<table>
<thead>
<tr>
<th>Y.S. (MPa)</th>
<th>U.T.S. (MPa)</th>
<th>Uniform El. (%)</th>
<th>Total El. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>318</td>
<td>891</td>
<td>65</td>
<td>69</td>
</tr>
</tbody>
</table>

Fig. 2. Optical micrographs showing microstructures taken after (a) hot rolling, (b) hot rolling and cold rolling, and (c) hot rolling, cold rolling and annealing at 1 173 K.
of both smooth and notched specimens were not affected by the charging current density: they were in the range of 0.03–0.05 mass ppm. The dramatic decrease of diffusible hydrogen after SSRT (as compared to that of before SSRT) is attributed partly to the emission of diffusible hydrogen from the specimen during or after the fracture, and partly to the movement of diffusible hydrogen to the non-diffusible trap sites during deformation. It is considered that the amount of emitted hydrogen during or after the fracture is small since the specimen is directly immersed into liquid nitrogen after the fracture. We believe that the most of diffusible hydrogen moved to the non-diffusible trap sites during the deformation.

The SSRT results for both smooth and notched specimens are listed in Tables 3 and 4, respectively: true fracture stress and strain for the former, and notch fracture stress and time to fracture for the latter with the corresponding charging current density. Similar to the remaining diffusible hydrogen content after SSRT, the mechanical properties of the specimens charged at different current density were not much different both in the smooth specimens and notched specimens.

Fracture surfaces of the smooth and notched specimens after SSRT are shown in Fig. 4. The uncharged specimens (Diff. [H]=0 mass ppm) showed the fully ductile fracture mode with dimples in both smooth and notched specimens. The ductile fracture mode was not changed with the increase of the diffusible hydrogen content, being consistent with the HDF properties aforementioned. However, the smooth specimens revealed much smaller dimple size than the notched specimens, which was presumably due to the different degree of stress concentration.19) Once a microvoid is formed near the notch tip, it would grow much faster than the one in the smooth specimen, resulting in the larger dimples on the fractured surface.

### 3.2. Hydrogen Trapping Sites and Activation Energies

It is well known that most of the internal hydrogen are trapped at various defects such as dislocation, grain boundary, and microvoid than normal lattice sites.9,20,21) These trapping sites are classified into the reversible (weak) ones and irreversible (strong) ones depending on the magnitude of their activation energy.22) Since diffusible hydrogen trapped at the reversible trapping sites is known to be mainly responsible for HDF, it is important to investigate the reversible trapping sites of the present TWIP steel and to estimate the activation energies for hydrogen desorption at those sites. The present steel charged with the current density of 1 A/m² for 48 h showed two peaks below 673 K as shown in Fig. 5, i.e. ~350 K and ~500 K. The following experiments were conducted to identify the trapping sites corresponding to each peak.

#### 3.2.1. 350 K Peak

Three specimens were used; the first one is unstrained, the second is 30% pre-strained, and the third is 30% pre-strained and annealed at 843 K for 30 min. After that all three specimens were charged with the current density of 21 A/m² for 48 h, and then the optical microstructure observation and TDA were carried out. The resultant hydrogen desorption rate curves and microstructures are shown in Figs. 6 and 7, respectively. As seen in Fig. 6, the hydrogen
content increased significantly by straining from 0.38 ppm in the unstrained specimen to 1.02 ppm in the 30% pre-strained specimens containing high densities of dislocations and deformation twins. By contrast, it decreased again by annealing to the value comparable to that in the unstrained specimen. It should be mentioned that, after annealing, the dislocation density decreased whereas mechanical twins remained as seen in Fig. 7. Accordingly, the decrease of the hydrogen content was associated with the decrease of the dislocation density and therefore it could be concluded that the peak at ~350 K was resulted from desorption of hydrogen mostly trapped by dislocations.

Another effort was made to isolate the effect of grain boundaries since the activation energies for hydrogen desorption from dislocations and grain boundaries are reported to be similar each other.11) Three cold rolled samples were annealed at different temperatures of 1 073 K, 1 173 K, and 1 273 K for 15 min, and were charged with the current density of 21 A/m² for 48 h. Then, TDA and microstructural
observation for these specimens were made. The hydrogen content decreased with increasing annealing temperature (Fig. 8), and the mean grain size increased with the annealing temperature: 5.0, 9.9, and 19.9 μm for 1073 K, 1173 K and 1273 K, respectively (Fig. 9). The larger the grain size is, the smaller the grain boundary area becomes. In addition, the dislocation density of three specimens is to be almost same by full annealing. In this case, the decrement of the diffusible hydrogen content is obvious to be attributed to the decrease of the grain boundary area. Therefore, the peak observed at /H11011 350 K in Fig. 5 is considered to be originated from detrapping of hydrogen from both grain boundaries and dislocations.

3.2.2. Internal Hydrogen Behavior and 500 K Peak

In order to understand internal hydrogen behavior in more detail, TDA and microstructural observation was made on the following three smooth specimens pre-charged with the current density of 51 A/m² for 48 h: (a) unstrained, (b) strained to 20%, and (c) fractured. Here, after fracture, a half of broken specimen was annealed at 1273 K for 30 min and charged again at the same charging condition (51 A/m² for 48 h). As seen in Fig. 10, two peaks were observed on the hydrogen desorption curves. The height of the first peak appeared at ~350 K decreased with increasing strain. This reduction of the peak height was attributed to the hydrogen transportation from the reversible trapping sites to the irreversible trapping sites during deformation. Johnson and Hirth,23) suggested that hydrogen can be transported by the dislocations generated during straining. The height of the second peak appeared at /H11011 500 K increased with increasing strain but decreased after annealing. In addition, as shown in Fig. 11, the mechanical twins formed extensively in the fractured specimen, and it disappeared after annealing. Considering the variation of the second peak height along with the disappearance of mechanical twins by post annealing of the fractured specimen, it could be concluded that the second peak appeared at ~500 K was due to the detrapping of hydrogen from twin boundaries.

3.2.3. Activation Energies

The activation energies of three trapping sites described above, i.e. dislocations, grain boundaries and twin boundaries, were estimated by employing the model proposed by Kissinger18):

\[ \frac{\partial \ln(\phi / T_c^2)}{\partial (1/T_c)} = - \frac{E_a}{R} \] ...........................(1)

where \( T_c \) is the peak temperature in the hydrogen desorption rate curve, \( \phi \) is the heating rate, \( E_a \) is the trap activation energy and \( R \) is the gas constant. For this, three specimens charged at the current density of 21 A/m² for 48 h were fractured and then TDA was done with the linear heating rates of 100 K/h, 200 K/h and 300 K/h. The resultant Arrhenius plots of \( \ln(\phi / T_c^2) \) vs. \( (1/T_c) \) for two peaks are shown in Fig. 12, and the activation energy was inferred from the slope of the plot. The activation energy for the first
peak associated with hydrogen desorption from dislocations and/or grain boundaries was \(\approx 35 \text{ kJ/mol}\). This value is in good agreement with that reported by Choo and Lee\(^{11}\) and Ono and Meshii,\(^{24}\) ensuring the reliability of the present analysis. The activation energy for the second peak associated with hydrogen desorption from twin boundaries was \(\approx 62 \text{ kJ/mol}\).

4. Discussion

It is generally known that the HDF resistance of steels is greatly affected by several factors: crystal structure, tensile strength, and so on.\(^{25}\) Considering that the austenitic TWIP steel is the newly developed high strength steel, it is essential to examine its relative immunity to HDF by comparing its HDF characteristics with those of either high strength steels having a different crystal structure or other austenitic steels. For this purpose, the HDF properties of the present TWIP steel are compared with those of the martensitic steel containing boron, TRIP steels and other austenitic stainless steels.

4.1. Comparison with Boron Bearing Martensitic Steel

Wang\(^{26}\) et al. investigated the HDF behavior of the boron-bearing steel (JIS F10T). They used a boron-bearing steel with tempered martensitic matrix showing ultimate tensile strength (UTS) of 1050 MPa and the prior austenite grain size of \(\approx 13 \mu\text{m}\), which were comparable to those of the present steel (900 MPa, \(\approx 9.9 \mu\text{m}\)).

The variations of the fracture stress with the diffusible hydrogen content for the present steel and the boron-bearing steel are plotted in Fig. 13: the data of boron-bearing steel were inferred from Wang\(^{26}\) et al.\(^{26}\) The fracture stress of the boron-bearing steel decreased sharply with increasing the diffusible hydrogen content, whereas the fracture stresses of both smooth and notched specimens of the present TWIP steel decreased very slowly. It should be noted that only \(\approx 2\) mass ppm of the diffusible hydrogen content caused hydrogen degradation in the boron-bearing steel. However, in the present TWIP steel, no remarkable degradation occurred both in the smooth and notched specimens. The fracture surface morphology of the present TWIP steel also evidenced the excellent HDF resistance, i.e., ductile fracture regardless of the amount of diffusible hydrogen (Fig. 4). For boron-bearing steel, Wang\(^{26}\) et al.\(^{26}\) reported that the area ratio of intergranular fracture increased with increasing the diffusible hydrogen content.

In general, FCC steels have a much better resistance to
hydrogen degradation than BCC (or martensitic) steels with comparable strength.\textsuperscript{10} The better HDF resistance of FCC austenite can be explained by considering the hydrogen desorption rates of two different structured steels. Figure 14 compares the hydrogen desorption rate curves of the present TWIP steel and boron-bearing steel. As seen in Fig. 14, the hydrogen desorption rate of the present TWIP steel was almost 0 mass ppm/s and then increased rapidly above 750 K, but that of the boron-bearing steel remained 0 mass ppm/s until 1100 K. It is clear that the total hydrogen content (the sum of the diffusible hydrogen content desorbed below 673 K and non-diffusible hydrogen content desorbed above 673 K) of the present steel was considerably higher than that of the boron-bearing steel. It coincides with the well-known fact that FCC steels have higher hydrogen solubilities than BCC steels.\textsuperscript{10} In addition, it is of interest to note that the portion of diffusible hydrogen to the total hydrogen is almost negligible in the present TWIP steel while that of the boron bearing steel is considerable.

From the above observation, it can be concluded that the excellent immunity to HDF of the present steel comes from the two main reasons: (a) higher hydrogen solubility of austenite matrix and (b) negligible portion of diffusible hydrogen to the total hydrogen. Besides, as aforementioned, there is an additional effect of hydrogen transport from the weak trapping sites to the strong trapping sites during deformation, causing the decrease of the diffusible hydrogen content.

4.2. Comparison with TRIP Steel and Other Austenitic Steels

It is known that some austenitic steels suffer from hydrogen degradation.\textsuperscript{13,27–30} During the tensile test of TRIP steels in gaseous hydrogen, McCoy \textit{et al.}\textsuperscript{28} observed that $\alpha'$ martensite formed prior to or during the test causes a ductility loss, and that the alloys strengthened by $\varepsilon$ martensite and mechanical twins without $\alpha'$ martensite are resistant to hydrogen embrittlement. It was also reported that austenitic stainless steels are susceptible to hydrogen embrittlement. Yang \textit{et al.}\textsuperscript{29} showed that the hydrogen induced martensite transformation and surface cracking occurred in the 304 stainless steel. Zhang \textit{et al.}\textsuperscript{30} reported that the hydrogen induced fracture occurred mainly along strain induced $\alpha'$ martensite and twin boundaries. Accordingly, hydrogen degradation is likely to be closely associated with strain or hydrogen induced martensite.

Because the present steel shows excellent resistance to hydrogen degradation, it is expected that no martensite transformation occurs by straining or hydrogen charging. The XRD results of the uncharged and charged smooth specimens before and after SSRT are shown in Fig. 15. No
other phases except FCC austenite were present in the four specimens, indicating that any martensite transformation did not occur by straining or hydrogen charging. Only mechanical twins appeared massively after SSRT regardless of hydrogen charging as shown in Fig. 16. The above XRD analysis and microstructure observation inform that the better immunity to hydrogen degradation of the present steel compared with other austenitic steels was in part due to the absence of strain and/or hydrogen induced martensite transformation.

5. Summary

Hydrogen delayed fracture (HDF) properties and internal hydrogen behavior of a Fe–18Mn–1.5Al–0.6C TWIP steel were investigated by means of the slow strain rate test and thermal desorption analysis. The following conclusions are made.

(1) The fracture stress, fracture strain and ‘time to fracture’ of pre-charged specimens were relatively insensitive to the diffusible hydrogen content. The microstructure was maintained fully austenitic without forming any martensite phase either by hydrogen charging or deformation. The fracture surface revealed the ductile dimple fracture mode in spite of hydrogen charging.

(2) The main trapping sites of the diffusible hydrogen were identified as dislocations, grain boundaries, and twins. The estimated activation energies for desorption of hydrogen were 35 kJ/mol for dislocations (or grain boundaries), 5.8 kJ/mol for twin boundaries, and 62 kJ/mol for twin boundaries.

(3) The excellent immunity to HDF of the present austenitic Fe–18Mn–1.5Al–0.6C TWIP steel was attributed to the following several reasons: (a) higher hydrogen solubility of austenite matrix, (b) negligible portion of diffusible hydrogen to the total hydrogen, (c) decrease of diffusible hydrogen content during the deformation, and (d) no transformation of austenite to either ε or α′ martensite.

Acknowledgements

This study was supported by a grant from the Fundamental R&D Program for Core Technology of Materials funded by the Ministry of Knowledge and Economy, Republic of Korea. The authors thank to Dr. K. Tsuzaki and Dr. E. Akiyama of NIMS, Japan for their help on hydrogen charging and analysis.

REFERENCES