

Identification of lattice defects beneath fracture surfaces of cold-drawn pearlitic steel fractured in elastic/plastic regions in the presence of hydrogen

K Nishiyama¹, T Manabe², D Hirakami² and K Takai³

¹ Graduate Student, Sophia University, 7-1 Kioi-cho Chiyoda-ku Tokyo 102-8554, Japan

² Nippon Steel & Sumitomo Metal, 20-1 Shintomi, Futtsu, Chiba Prefecture 293-8511, Japan

³ Faculty of Science and Technology, Department of Engineering and Applied Science, Sophia University, Tokyo, Japan

Corresponding author's e-mail address: kei175348@yahoo.co.jp

Abstract The kinds of lattice defects formed beneath fracture surfaces were analyzed using thermal desorption analysis (TDA) for cold-drawn pearlitic steel that was fractured in the elastic/plastic regions in the presence of hydrogen. A sample thickness of 0.3 mm made it possible to obtain two separate peaks: a low temperature peak and a high temperature peak. Tensile tests and constant load tests were conducted under various hydrogen charging conditions to prepare samples with different elongations and fracture times. Samples of 0.3 mm in thickness beneath fracture surfaces were charged with hydrogen to determine the kinds of lattice defects and hydrogen desorption profiles were obtained using TDA. For samples that were fractured in the plastic region, a broad hydrogen desorption profile continuing to around 180 °C was obtained compared to samples without hydrogen charging and straining. Since this broad desorption profile was disappeared by aging at 200 °C, it probably corresponded to desorption from vacancies. In contrast, for samples that were fractured in the elastic region, this broad desorption profile was not obtained. These findings indicate that one of the factors causing hydrogen embrittlement in the plastic region is probably vacancies, whereas other factors cause it in the elastic region.

1 Introduction

Quasi-cleavage fracture modes are reported as representative hydrogen embrittlement fracture modes in cold-drawn pearlitic steel. Hydrogen-enhanced lattice defects (HELDS) are considered to be one of the mechanisms causing quasi-cleavage fracture. As a result, various approaches are taken to clarify the mechanism of hydrogen embrittlement with respect to lattice defects. In a previous study, the formation of hydrogen-enhanced strain-induced lattice defects was not observed when cold-drawn pearlitic steel with hydrogen was fractured in the elastic region, whereas when it was fractured in the plastic region, the formation of such defects was observed [1]. However, since that analysis of the states of hydrogen present was conducted under a diffusion-limited condition of hydrogen, only a single peak was obtained by TDA. Furthermore, it made it impossible to separate hydrogen-enhanced strain-induced lattice defects. In this study, we aimed to separate lattice defects formed in the elastic plastic regions by bringing the analysis conditions close to the thermal desorption rate-limiting condition of hydrogen and setting the TDA measurement position just below the fracture surface of specimens.



2 Experimental

2.1 Materials

Specimens were prepared of cold-drawn pearlitic steel corresponding to JIS SWRS82B. Specimens were cold-drawn from 13 to 6 mm in diameter, after austenitization at a temperature of 880 °C for 600 s and isothermal transformation at a temperature of 530 °C for 120 s. Then, specimens were aged at a temperature of 300 °C for 600 s. The chemical composition of the specimens is shown in Table 1.

The microstructure was pearlite, consisting of the ferrite (α) phase and cementite (θ) elongated in the drawing direction.

2.2 Specimen preparation

Obtaining multiple peaks of the hydrogen desorption profile was conducted by thinning specimens and bringing them close to the thermal desorption rate-limiting condition of hydrogen. First, specimens were cut to thicknesses of 0.3, 0.5, 1, 3 and 5 mm, respectively. Then they were polished using emery papers (# 800 to 2000 grit) and charged with hydrogen by immersion in a 5 mass % NH_4SCN solution kept at a temperature of 30 °C until they were saturated. After hydrogen charging, hydrogen desorption profiles were obtained by TDA.

2.3 Evaluation of relationship between the amount of lattice defects and distance from fracture surface

In order to evaluate the amount of lattice defects in fractured specimens, the relationship between the amount of lattice defects and the distance from the fracture surface was examined in specimens fractured in the plastic region with hydrogen in tensile testing. The surfaces of the specimens were polished using emery papers (# 800 to 2000 grit). Specimens were electrochemically charged with hydrogen in a 0.1 N solution of $\text{NaOH} + 5 \text{ g}\cdot\text{L}^{-1} \text{NH}_4\text{SCN}$ at a current density of $30 \text{ A}\cdot\text{m}^{-2}$ and a temperature of 30 °C. Charging was performed for 144 h. This was the time required for the hydrogen concentration at the center of the specimens to reach the equilibrium. After hydrogen charging, tensile testing was conducted at a crosshead speed of $0.055 \text{ mm}\cdot\text{min}^{-1}$. Figure 1 shows the results of tensile testing and Fig. 2 is a schema showing how samples were cut out from the fracture surface. The samples were cut to 0.5 mm in thickness were numbered from (1) to (4) in order from the fracture surface and these samples were aged at 30 °C for 7 days to degas the contained hydrogen. These samples were then polished to 0.3 mm and tracer hydrogen was charged in a 5 mass % NH_4SCN solution at 30 °C for 1 day. Hydrogen is trapped in lattice defects in the material. As a result, it is possible to evaluate the amount of lattice defects in the material by charging hydrogen after degassing the contained hydrogen. The hydrogen that is charged to investigate the amount of lattice defects is called “Tracer Hydrogen.” Tracer hydrogen content of each sample was measured by TDA. This content corresponds to the amount of lattice defects.

Table 1. Chemical composition of specimen material (mass %)

C	Si	Mn	P	S
0.84	0.25	0.73	0.017	0.005

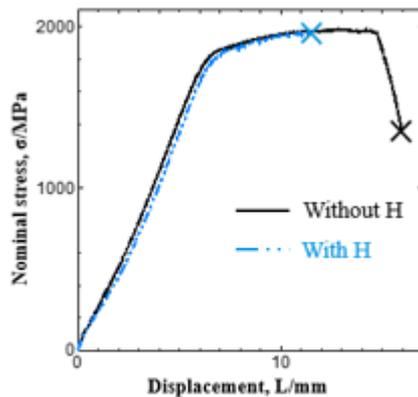


Fig. 1. Nominal stress–displacement curves of specimens with/without hydrogen

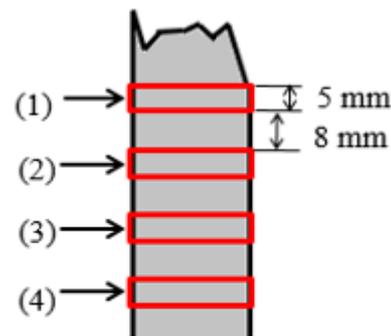


Fig. 2. Schema showing how specimens were cut out from the fracture surface

2.4 Comparison of tracer hydrogen desorption profiles of specimens showing different fracture strain by tensile tests with hydrogen

In the same experimental procedure as in section 2.3, only the hydrogen charging conditions were changed to obtain specimens with different fracture strain. The specimens were electrochemically charged with hydrogen in a 0.1 N solution of NaOH + 3.5, 4.0 and 5.0 g·L⁻¹ NH₄SCN at a current density of 30 and 50 A·m⁻² and a temperature of 30 °C. Fig. 3 shows the nominal stress-displacement curves obtained by tensile testing. These specimens were cut to a thickness of 0.5 mm just below the fracture surface and aged at 30 °C for 7 days to degas the contained hydrogen. The samples were then polished to 0.3 mm and tracer hydrogen was charged in a 5 mass % NH₄SCN solution at 30 °C for 1 day. The tracer hydrogen content of each sample was measured by TDA.

2.5 Comparison of tracer hydrogen desorption profiles of specimens showing different fracture times by constant load tests with hydrogen

Constant load tests were carried out at $0.4\sigma_B$ (stress lower than the proportional limit) and $0.9\sigma_B$ (stress higher than the proportional limit) corresponding to 0.2% proof stress in the presence of hydrogen, and the hydrogen desorption profiles just beneath the fracture surfaces were compared. Here, σ_B represents the tensile strength. First, the surfaces of the specimens were mechanically polished using emery papers (# 800 to 2000 grit). For constant load tests at a stress level lower than the proportional limit, tests were conducted at a load stress of $0.4\sigma_B$ in a 20 mass% NH₄SCN solution at a temperature of 50 °C without pre-charging hydrogen. After dividing the fracture time of this experiment (immersion) by the same fracture time, the fracture time ratio is obtained as unity. For constant load tests at a stress level higher than the proportional limit, hydrogen pre-charging was conducted in a 0.1 N NaOH solution with 1.5 to 3 g·L⁻¹ NH₄SCN at a current density of 30 A·m⁻² and a temperature of 30 °C until the specimens were saturated with hydrogen. Then constant load tests were carried out at a load stress of $0.9\sigma_B$. After dividing two fracture times of this experiment (electrolysis) by the fracture time of the previous experiment (immersion), the fracture time ratios are obtained as 0.7 and 7.5. These specimens were cut to a thickness of 0.5 mm just beneath the fracture surface and degassed at 30 °C for 7 days to remove the contained hydrogen. They were mechanically polished to 0.3 mm and tracer hydrogen was then charged in a 5 mass % NH₄SCN solution at 30 °C for 1 day. The tracer hydrogen content of each sample was measured by TDA.

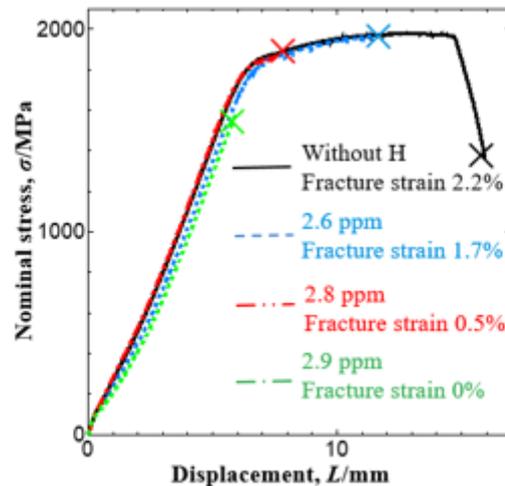


Fig. 3. Nominal stress–displacement curves for various strain amounts

2.6 Identification of lattice defect corresponding to high temperature shoulder

Obtaining multiple peaks in the TDA profile was performed on specimens to which strain was applied in the presence of hydrogen. Polishing, hydrogen charging and tensile tests were carried out under the same conditions as in section 2.3, and specimens having the same fracture strain as in section 2.3 were obtained. Two samples were cut out to 0.5 mm from just below the fracture surfaces and aged at 30 °C for 7 days to degas the contained hydrogen. One sample was subjected to aging at 200 °C for 2 h, whereas the other one was not. It was reported that vacancies are disappeared by aging treatment at 200 °C. As a result, it is possible to identify vacancy peak by comparing those with and without aging. Then these two samples were polished to 0.3 mm and tracer hydrogen was charged in a 5 mass % NH_4SCN solution at 30 °C for 1 day. Tracer hydrogen content of each sample was measured by TDA.

3 Results and Discussion

3.1 Hydrogen desorption profiles of samples with different thickness

Fig. 4 shows the TDA profiles of each sample with a different thickness charged with hydrogen under the conditions in section 2.2. The peak temperature and desorption end temperature decreased as the sample thickness was reduced. The sample thickness of 0.3 mm in particular made it possible to obtain two separate peaks: a low temperature peak and a high temperature peak. This result indicates that the condition of the sample approached the thermal desorption rate-limiting and it was determined to use the thickness of 0.3mm for obtaining multiple peaks in this study.

3.2 Relationship between tracer hydrogen content and distance from fracture surface

Fig. 5 shows the relationship between the tracer hydrogen content and the distance from the fracture surface. Numbers (1) -(4) correspond to those in the schema in Fig. 2. The closer the samples were to the fracture surface, the more tracer hydrogen content was obtained by TDA. This result suggests that the amount of lattice defects increased as the measurement position was moved closer to the fracture surface. Based on this result, samples just below the fracture surfaces were used in the sections 2.4, 2.5, and 2.6 since these samples contained a sufficient amount of lattice defects at the time of fracture.

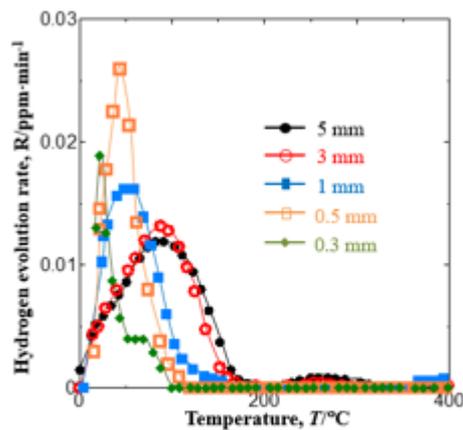


Fig. 4. TDA profiles of samples with a thickness of 0.3 mm to 5 mm

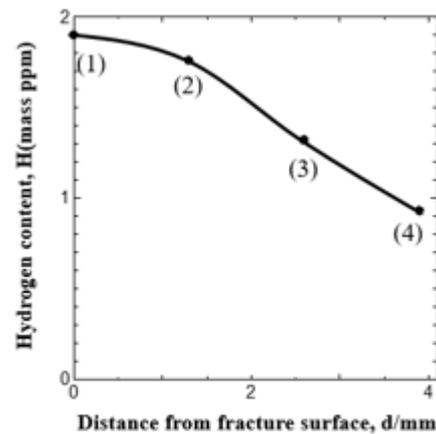


Fig. 5. Tracer hydrogen content at each distance from fracture surface

3.3 Comparison of tracer hydrogen desorption profiles of samples cut out from just below fracture surface with different fracture strain

Fig. 6 shows the tracer hydrogen desorption profiles of samples cut out from just below the fracture surface with different fracture strain with hydrogen. For the specimens that fractured in the elastic region, no increase in tracer hydrogen content was observed when compared with a specimen without hydrogen and straining. In contrast, for the specimens that fractured in the plastic region, the tracer hydrogen content increased and a broad hydrogen desorption profile appeared that continued to around 180 °C.

3.4 Comparison of tracer hydrogen desorption profiles of samples cut out from just below fracture surface with different fracture time

Fig. 7 shows the hydrogen desorption profiles of unstrained samples that were fractured in the plastic region in tensile testing and in the elastic region in constant load test. In constant load test, there was little change in the profile and hydrogen content when compared with the hydrogen desorption profile of the unstrained sample. In addition, compared to the sample that was fractured in the plastic region in tensile testing, there was no broad shoulder on the high temperature side, as shown in section 3.3. The hydrogen desorption profiles of the unstrained samples that were fractured at different time are shown in Fig. 8. Loading in the plastic region increased the hydrogen content more than for the unstrained sample. Furthermore, the shoulder on the high temperature side became broader as the time to be fractured was increased.

3.5 Obtaining multiple peaks in TDA profile of samples fractured in the plastic region with hydrogen

Fig. 9 shows the tracer hydrogen desorption profiles of “unstrained”, “H + strain” and “H + strain (200 °C aging)” samples. Here, H + strain is a sample that the strain was applied in the presence of hydrogen, H+strain (200 °C aging) is the one that strain was applied in the presence of hydrogen then aged at 200 °C. Compared to the unstrained sample, the tracer hydrogen content increased for the “H + strain” and “H + strain (200 °C aging)” samples. In addition, the shoulder on the high temperature side, which was generated by applying plastic strain in the presence of hydrogen, decreased as a result of aging at 200 °C and the desorption end temperature was the same as that of the “Non-strain” sample. These results suggested that the amount of lattice defects increased by applying the strain in the presence of hydrogen and defects corresponding to the shoulder at the high temperature that disappeared upon aging at 200 °C was the vacancy peak. This implies that vacancies are involved in the fracture in the plastic region in the presence of hydrogen.

4 Conclusion

The kinds of lattice defects formed beneath fracture surfaces were analyzed using TDA for cold-drawn pearlitic steel specimens that were fractured in the elastic/plastic regions in the presence of hydrogen.

(1) At a thickness of 0.3 mm, the condition of the samples approached the thermal desorption rate-limiting of hydrogen. As a result, two separate peaks could be obtained from TDA profiles: the low temperature peak and the high temperature peak.

(2) It was found that the amount of lattice defects was higher as the measurement position of the specimens was closer to the fracture surface. Hence, for the measurement of the amount of lattice defects of fractured specimens, the measurement position was set just below the fracture surface.

(3) After comparing TDA profiles samples with different fracture strain and time, following observations were made: (i) In tensile testing, amount of lattice defects was not increased in elastic region and shoulder appeared on high temperature side in plastic region. (ii) In constant load tests, amount of lattice defects was not increased in elastic region, however, it was increased slightly in plastic region. There is tendency for defects to increase with the increased time to be fractured.

(4) The sample that was fractured in the plastic region in tensile testing with hydrogen displayed the broad shoulder on the high temperature side in the tracer hydrogen desorption profile, which disappeared upon aging at 200 °C. As a result, the types of defect, which corresponded to the shoulder, was presumably the vacancies.

References

[1] R. Konno, T. Manabe, D. Hirakami and K. Takai : *Tetsu-to-Hagané*, **104** (2018) 36.

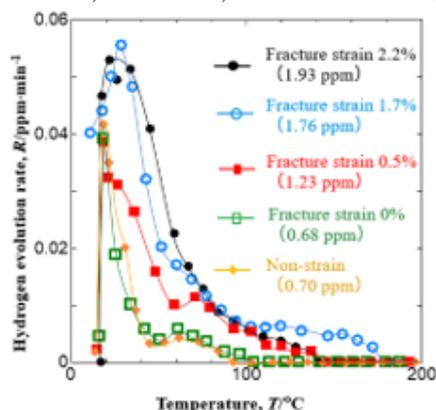


Fig. 6. TDA profiles of unstrained samples fractured at various strain levels by SSRT

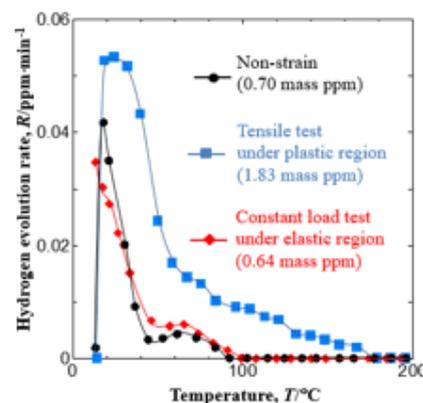


Fig. 7. TDA profiles of unstrained samples fractured by tensile testing and constant load testing

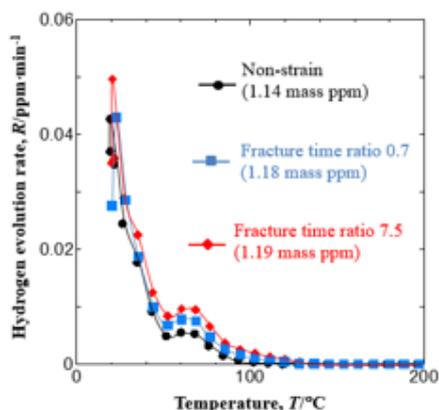


Fig. 8. TDA profiles of unstrained samples fractured in fracture time ratio of 0.7 and 7.5

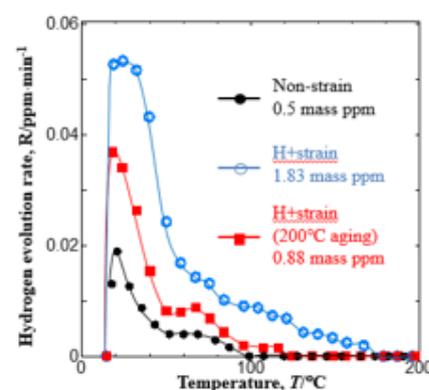


Fig. 9. TDA profiles of unstrained samples fractured at 1.7% strain by SSRT with/without aging at 200 °C