

Role of strain-induced dislocations and vacancy-type defects formed during the incubation period leading to hydrogen embrittlement of iron

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Abstract. The effect of hydrogen-enhanced strain-induced lattice defects formed during the incubation period on hydrogen embrittlement fracture of iron was clarified by quantitative evaluation using low-temperature thermal desorption spectroscopy (L-TDS) from -200 °C. Tensile testing of iron specimens was conducted in solution with various concentrations of ammonium thiocyanate as a catalyst poison. Cathodic electrolysis was employed to establish conditions of low and high hydrogen content to examine the fracture characteristics of the iron specimens. The fracture elongation of the hydrogen-charged iron specimens was lower than that of the hydrogen-free specimens, although the elongation was the same regardless of the hydrogen content. In contrast, the flow stress during the deformation process increased with increasing hydrogen content. Specimens were prepared under the same hydrogen charging conditions and unloaded within a uniform elongation range. L-TDS was used to detect lattice defects with hydrogen re-charged as a probe under equilibrium conditions with dislocation cores and strain fields around the cores and vacancies in the specimens. The formation of vacancy-type defects was promoted in the presence of hydrogen during plastic deformation, and the extent of promotion was similar regardless of the hydrogen content. The concentration of hydrogen-enhanced strain-induced vacancies may thus affect the decrease in ductility due to the presence of hydrogen, and the hydrogen coordination number to its vacancies is responsible for the increase in flow stress.

1 Introduction

Hydrogen embrittlement (HE) is one issue that remains to be solved in the development of suitable materials for a sustainable society. HE has long been discussed, though in recent years, it is recognized as a challenge associated with growing demand and intensifying development of high-strength steel materials in various industries and purposes, not limited to materials used in severe environments, such as infrastructure [1] and energy fields [2]. For example, in the case of steel material components, which account for most of the weight of automobiles, an increase in the strength of these components would



improve crash safety and allow for a reduction in plate thickness, thereby contributing to weight reduction. However, when the strength of a metallic material is increased, the susceptibility to HE is generally increased. In particular, with regard to steel sheets used for automotive parts, it is necessary to consider not only the strength and other properties of the material itself, but also the influence of deformation processing on the resistance of the material to HE.

Several mechanisms [3,4] have been proposed for hydrogen in materials to cause embrittlement. Hydrogen-enhanced strain-induced vacancy (HESIV) theory [5–7] is one of the representative mechanisms of HE and proposes that the concentration of vacancies formed by plastic deformation increases in the presence of hydrogen, and that these vacancies are responsible for the brittle fracture of materials. In fractures caused by HE, including the HESIV mechanism, the interaction between lattice defects and hydrogen during the incubation period that stress or strain is applied to the material and leads to HE is strongly suspected; however, the full extent of this interaction has not yet been clarified due to analytical difficulties. We have been working on the quantitative evaluation of various lattice defects in materials through the development of low-temperature thermal desorption spectroscopy (L-TDS), in which specimens can be heated from -200 to 200 °C [8,9]. We have clarified that the formation of HESIVs is not accompanied by an increase in the dislocation density due to hydrogen [8], and that the presence of solid solution elements such as carbon and hydrogen suppresses spontaneous diffusion and annihilation during thermal activation [9]. Therefore, the HESIVs themselves and their interaction with hydrogen have been partially clarified. However, to discuss the involvement of HESIVs in HE fracture, it is necessary to investigate the influence of HESIVs on dislocation motion during plastic deformation. Vacancies trap hydrogen as a stable complex and they interact with dislocations in a similar way to a solid solution; however, this has not yet been investigated experimentally.

This work focused on the incubation period that led to HE and the relationship with dislocation mobility was investigated by quantitative evaluation of the vacancies formed.

2 Experimental

2.1 Materials

Pure iron with a purity of ≥ 99.97 mass% (6 mass ppm C) was employed. Table 1 shows the chemical composition of the iron specimen. The iron was cold-rolled to a thickness of 0.5 mm, and formed into a flat specimen with parallel sections 10 mm wide and 30 mm long, as shown in Figure 1(a). Initial specimens were annealed in Ar at 900 °C for 30 min and furnace-cooled at a sufficiently low cooling rate to reduce the formation of lattice defects as much as possible. Figure 2 shows the results of the metallographic analysis of the initial specimen by the electron backscatter diffraction (EBSD) method using field-emission scanning electron microscope (FE-SEM). Heat treatment resulted in a single-phase ferrite microstructure coarsened to a grain size of about 100 μm .

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

C	Si	Mn	P	S	Cu	Al	N	O
0.0006	< 0.003	< 0.003	< 0.002	< 0.0003	< 0.003	< 0.002	0.0009	0.0109

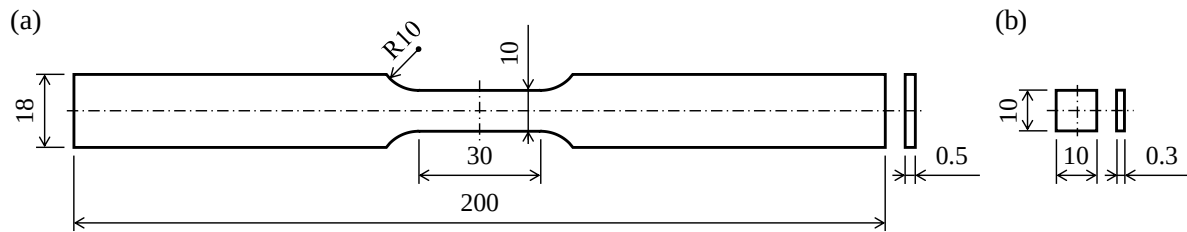


Figure 1. Geometry and dimensions of iron specimens used for (a) tensile testing and (b) L-TDS analysis.

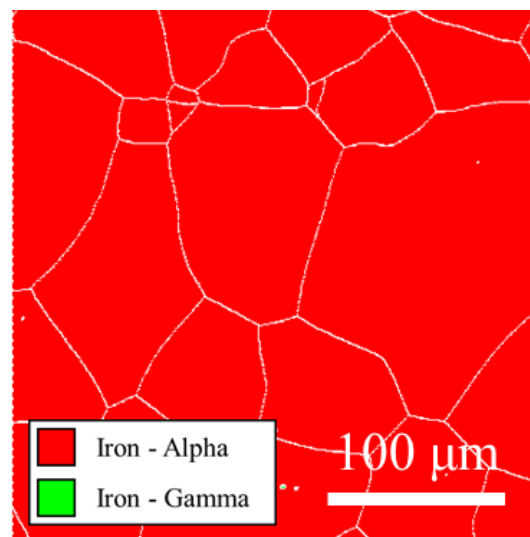


Figure 2. Phase map of initial specimen obtained by EBSD using FE-SEM.

2.2 Hydrogen charging conditions in plastic deformation with hydrogen

Figure 3 shows a schematic of the experimental procedure for the evaluation of HE fracture and the lattice defects that form during the incubation period that leads up to HE. The initial specimens prepared with and without hydrogen in Section 2.1 were subjected to a slow strain tensile test (SSRT) at a crosshead speed of $0.15 \text{ mm} \cdot \text{min}^{-1}$, which is equivalent to a strain rate of $8.3 \times 10^{-5} \text{ s}^{-1}$. The specimens were unloaded at 25% strain and used for quantitative evaluation of the lattice defects formed during the incubation period. Other specimens were tensile tested to fracture under the same conditions for evaluation of the mechanical properties, measurement of the hydrogen content at fracture, and observation of the fracture surface.

Hydrogen charging during tensile testing was performed by constant current cathodic electrolysis at 30°C using 0.1 N NaOH solution at a current density of $50 \text{ A} \cdot \text{m}^{-2}$. Various concentrations of NH_4SCN were added as a catalyst poison. Figure 4 shows the relationship between the concentration of NH_4SCN in the solution and the hydrogen content measured using thermal desorption analysis (TDA) immediately after fracture for the specimens strained with hydrogen. TDA measurements were performed from room temperature to 200°C at $100^\circ \text{C} \cdot \text{h}^{-1}$. The hydrogen content at fracture increased asymptotically with the NH_4SCN concentration. For the investigation of the effect of hydrogen content, an NH_4SCN concentration of $0.1 \text{ g} \cdot \text{L}^{-1}$ was determined as a low H condition and that at $5.0 \text{ g} \cdot \text{L}^{-1}$ as a high H condition, and the hydrogen content at fracture was 0.45 and 0.94 mass ppm under low H and high H conditions, respectively.

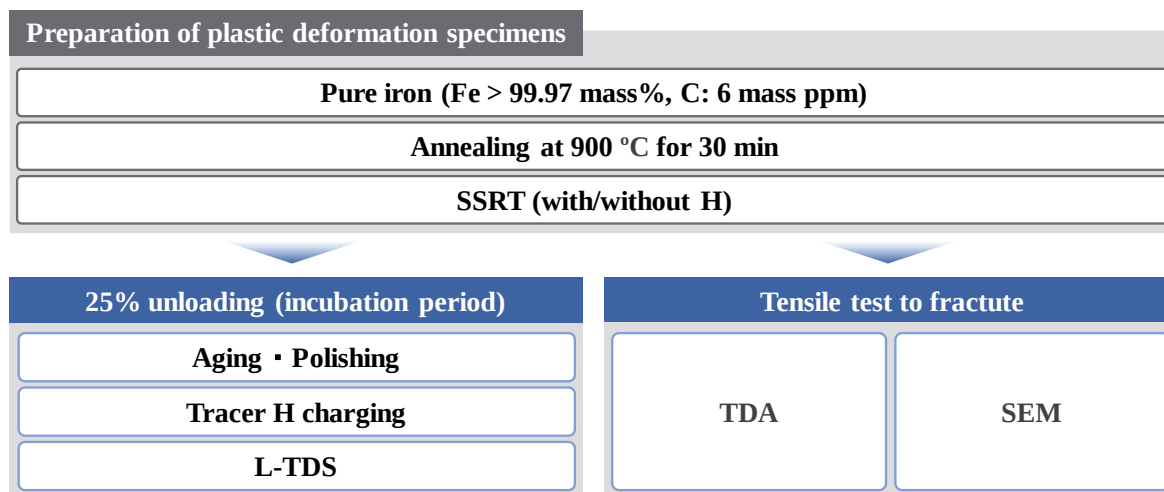


Figure 3. Experimental procedure to investigate the effect of hydrogen on the mechanical properties and strain-induced lattice defect formation during the incubation period.

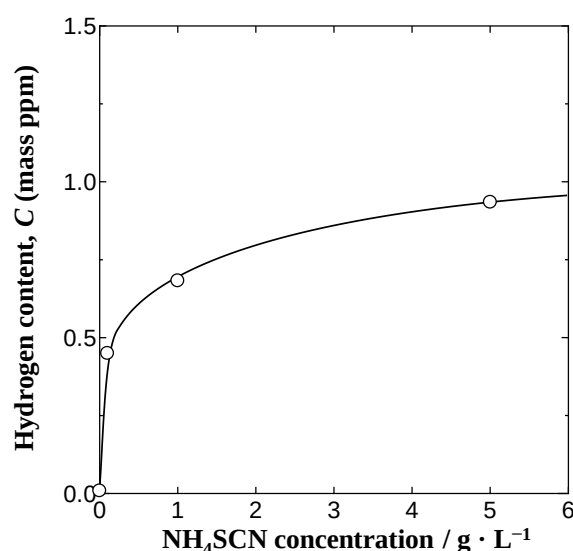


Figure 4. Relationship between NH_4SCN concentration in the NaOH solution used for hydrogen charging and the hydrogen content measured by TDA immediately after fracture. Hydrogen charging was conducted by constant current cathodic electrolysis in 0.1 N NaOH aqueous solution at a current density of $50 \text{ A} \cdot \text{m}^{-2}$ at 30°C .

2.3 Quantitative evaluation of lattice defects formed during the incubation period of HE

To quantitatively evaluate the lattice defects that form during the incubation period and lead to HE, specimens were plastically deformed by 25% strain with and without hydrogen. A 10 mm square specimen was cut from a parallel section of the tensile specimen, hydrogen was desorbed from the specimen, and mechanical and chemical polishing were performed to prepare the specimen as shown in Figure 1(b). Hydrogen was re-charged as a probe for the detection of lattice defects, and the total content of tracer hydrogen was detected by L-TDS for the quantitative evaluation of lattice defects.

Figure 5 shows an example of the quantitative evaluation of lattice defects using L-TDS [8]. Figure 5(a) shows the change in the L-TDS spectra of pure iron plastically deformed by 25% in the presence of hydrogen at different concentrations of NH_4SCN in the tracer hydrogen solution for lattice defect

detection. The spectrum is not a single peak, but represents desorption from two hydrogen trapping sites with different hydrogen activation energies. Calculation of the hydrogen activation energies confirmed that the hydrogen desorption peak on the low-temperature side is from dislocations and the shoulder peak on the high-temperature side is from vacancy-type defects. Figures 5(b) and 4(c) show examples of L-TDS spectra measured under these conditions and separated by Gaussian fitting into hydrogen desorption from dislocations and vacancies. Both spectra were separated into two hydrogen desorption peaks with good accuracy, and it was inferred that the content of tracer hydrogen corresponded to the amount of lattice defects associated with each peak. This study also involved a quantitative evaluation according to similar methods.

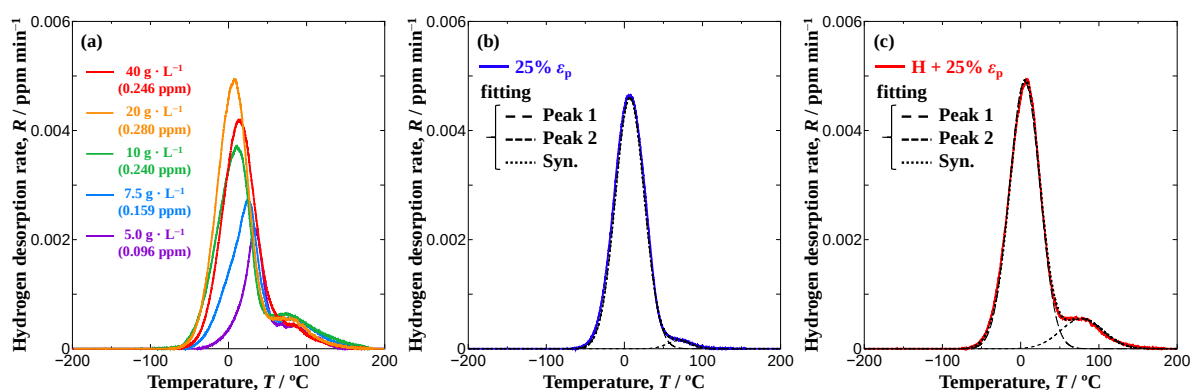


Figure 5. Tracer hydrogen desorption spectra for specimens strained by 25% with and without hydrogen, and re-charged with tracer hydrogen. (a) Change in spectra when hydrogen is re-charged at various concentrations of NH_4SCN . (b,c) Experimental spectra (b) without and (c) with hydrogen during tensile testing and results of peak separation for hydrogen desorption from dislocations and vacancies by Gaussian fitting [8].

3 Results

Figure 6 presents the results of the L-TDS analysis of pure iron subjected to 25% plastic strain with and without hydrogen, with tracer hydrogen re-charged. Tracer hydrogen desorption from dislocations and vacancy-type defects was identified in both spectra, as shown in Figure 6(a). In Figure 6(b), the spectra were separated by Gaussian fitting to show the corresponding tracer hydrogen content. In comparison to the specimen without hydrogen, the specimen with hydrogen exhibited an increase in hydrogen desorption from vacancy-type defects, with no significant difference observed between the low H and high H conditions. In contrast, no significant difference was observed in the content of hydrogen desorption at the low-temperature side corresponding to dislocations. These findings indicate that the presence of hydrogen does not influence the density of dislocations during plastic deformation. However, the formation of vacancies is enhanced, although the extent of enhancement remains small, even when the hydrogen content during plastic deformation is halved.

Figure 7 shows stress-strain curves from tensile tests with and without hydrogen, and the hydrogen content at fracture. Compared to the specimen without hydrogen, the specimen with hydrogen showed a decrease in fracture strain, and the decrease was similar for low H and high H. In contrast, the flow stress during plastic deformation increased for the specimen with hydrogen, and the extent of increase was dependent on the hydrogen content. The fracture surface was observed using scanning electron microscopy (SEM), and the fracture surface morphology under low H and high H conditions was generally the same.

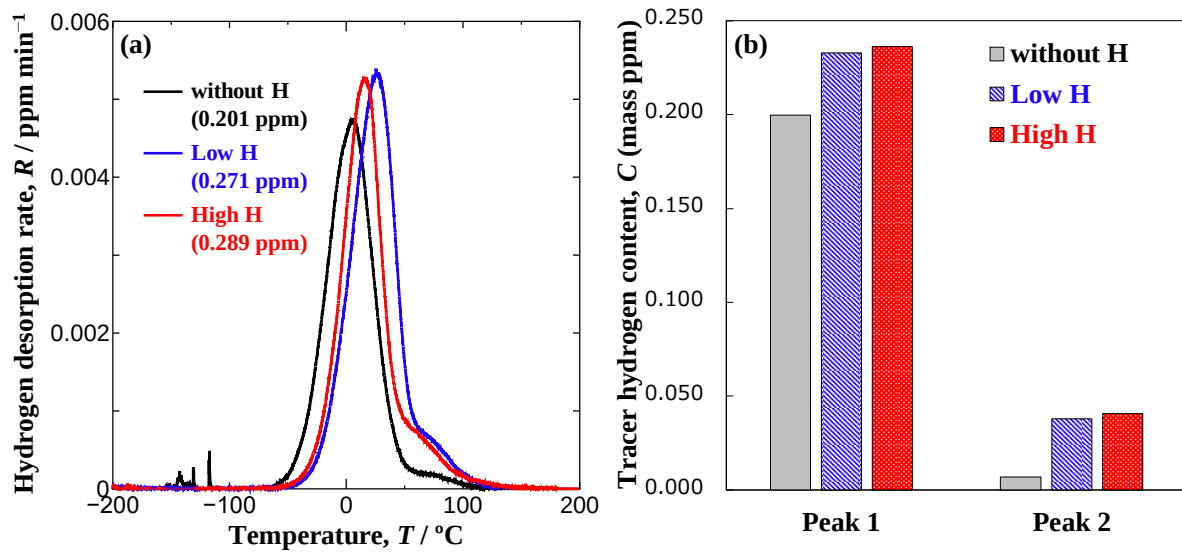


Figure 6. (a) Tracer hydrogen desorption spectra and (b) peak separation for specimen strained at 25% without and with low/high hydrogen content and re-charged with tracer hydrogen. Peak 1 and Peak 2 correspond to the content of tracer hydrogen desorbed from dislocations and vacancies separated by Gaussian fitting, respectively.

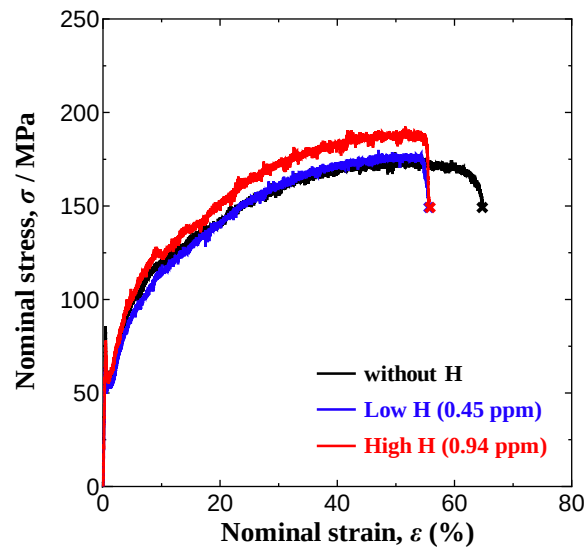


Figure 7. Nominal stress-strain curves and hydrogen content measured immediately after fracture by TDA for specimens without and with low/high hydrogen content for tensile testing at a strain rate of $8.3 \times 10^{-5} \text{ s}^{-1}$ at 30 $^{\circ}\text{C}$.

4 Discussion

The influence of lattice defects formed during the incubation period on the mechanical properties of iron is discussed. The concentration of HESIVs did not vary under the two hydrogen charging conditions. This may be attributed to the low concentration of strain-induced vacancy-type defects and the limited capacity of hydrogen to be trapped and stabilized in these defects. First-principles calculations show that two atoms are the most stable for the trapping of hydrogen in a single vacancy [10]. It is presumed that a sufficient amount of hydrogen was charged into the strain-induced vacancies that formed under

both conditions. Consequently, the concentration of HESIVs, which is considered to be the direct cause of ductility loss [7], was similar under the two conditions, and the extent of ductility loss was also considered to be the same, although the hydrogen content was different.

In contrast, trapping more than three hydrogen atoms requires more energy and molecular dynamics calculations have shown that it reduces the dislocation mobility [11]. The observed increase in flow stress with an increase in hydrogen content in the present study is consistent with this hypothesis and may be attributed to an increase in the number of hydrogen atoms trapped for a HESIV, resulting in a more stabilized complex, which act as an obstacle to dislocation motion during plastic deformation.

5 Conclusions

This study focused on the lattice defects that form during the incubation period that leads to hydrogen embrittlement. An attempt was made to quantify these lattice defects and to investigate their influence on the mechanical properties of iron by L-TDS analysis. The findings obtained from investigation of materials with different amounts of hydrogen during plastic deformation are summarized as follows:

- L-TDS detection of tracer hydrogen charged as a probe for the detection of lattice defects in pure iron that was plastically deformed with or without hydrogen did not reveal a single peak in any of the specimens, but multiple hydrogen desorption peaks due to dislocations and vacancy-type defects formed by plastic deformation. Separation of these peaks enabled the quantitative evaluation of each lattice defect based on the tracer hydrogen content.
- Among the strain-induced lattice defects, the formation of vacancy-type defects is enhanced by hydrogen. However, the extent of enhancement was independent of the hydrogen content under charging conditions of 0.46 (low H) and 0.96 (high H) mass ppm at fracture.
- Fracture elongation decreased in the specimen with hydrogen compared to the specimen without hydrogen, and the extent of the decrease was similar for the low H and high H conditions.
- Flow stress increased with increasing hydrogen content during plastic deformation.

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