Enhanced Lattice Defect Formation Associated with Hydrogen and Hydrogen Embrittlement under Elastic Stress of a Tempered Martensitic Steel

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(Received on July 26, 2011; accepted on November 15, 2011)

Hydrogen behavior and hydrogen-enhanced lattice defect formation under elastic stress of tempered martensitic steel were clarified with respect to dislocations and vacancies by thermal desorption analysis (TDA) using hydrogen as a probe of defects and a positron probe microanalyzer (PPMA). The relationship between hydrogen embrittlement and lattice defects associated with hydrogen was also investigated. The amount of lattice defects increased gradually with increasing time of applied stress during hydrogen charging. The specimen fractured under elastic stress in the presence of hydrogen macroscopically showed brittle fracture without necking. Whereas fracture surface was attributed to localized plastic deformation, since the morphology of the microscopic fracture surface was mostly quasi-cleavage fracture. The increased lattice defects in the near-fracture area were subsequently removed by annealing at 200°C. The mean positron annihilation lifetime measured with the PPMA for a fractured specimen was longer in the near-fracture area than in other areas. Thus, the most probable reason for the increase in the amount of lattice defects can be ascribed to an increase in the amount of vacancies or vacancy clusters. Regarding hydrogen embrittlement involving microscopic plastic deformation, the localized enhanced vacancies due to interactions between dislocations and hydrogen under elastic stress directly caused ductility loss, because ductility loss occurred even though hydrogen was completely removed by degassing before the tensile test. Besides hydrogen content and applied stress, the time of formation and accumulation of vacancies are also concluded to be important factors causing hydrogen embrittlement.

KEY WORDS: hydrogen embrittlement; lattice defect; vacancy; dislocation; elastic stress; thermal desorption analysis; martensitic steel.

1. Introduction

One of the authors has previously investigated the interactions between dislocations and hydrogen during plastic deformation of pure iron with a bcc lattice and Inconel 625 with an fcc lattice.1) Under a condition of a low strain rate, a large amount of hydrogen was transported by moving dislocations in both metals. The changes in the amount of lattice defect formation that took place in the metals were also examined under conditions where hydrogen interacted with moving dislocations.2) The results revealed that plastic straining in the presence of hydrogen markedly enhanced the formation of lattice defects compared with plastic straining without hydrogen, even though the strain level was the same. The accumulation of lattice defects associated with hydrogen was involved in ductility loss in both steels.

It has been reported that elastic stress does not significantly affect the apparent diffusion coefficient of hydrogen in pure iron,3,4) ARMCO steel and AISI 4340 steel.5) An investigation showed that the hydrogen permeation rate was increased by the application of elastic stress and that the steady-state permeation rate in pure iron also increased with increasing applied stress.3) Similarly, an increase in the hydrogen permeation rate under applied elastic stress was also reported for ARMCO steel and AISI 4340 steel.5)

In general, it is essential to examine the influence of elastic stress and the duration of applied stress on hydrogen behavior, since hydrogen embrittlement occurs after the passage of time under elastic stress. However, the effects of elastic stress and the duration of applied elastic stress on hydrogen trapped weakly at a high density of various lattice defects in high-strength steel have not been clarified. Furthermore, there have been few reports regarding the role of lattice defects in the process of hydrogen embrittlement under elastic stress.6)

In this context, the time dependence of hydrogen content
and the amount of lattice defects occurring in a tempered martensitic steel under elastic tensile stress was examined in the present study. The relationship between hydrogen embrittlement and enhanced lattice defects associated with hydrogen under elastic tensile stress was also investigated.

2. Experimental

2.1. Material

The material examined in the present study was induction-heating quenched and tempered martensitic steel. The specimens were round bars of 5 mm in diameter and induction heat-treated at 1010°C and 525°C. The grain size of prior austenite was 12 μm. The tensile strength (σb) and proof stress of 0.2% were 1433 MPa and 1340 MPa, respectively. The fracture elongation, uniform elongation and reduction in area were 9.7%, 6.1% and 66.4%, respectively. The chemical compositions were 0.32 mass% C, 1.75 mass% Si, 0.72 mass% Mn, 0.015 mass% P and 0.007 mass% S. Since the martensitic steel examined in the present study contains high silicon content of 1.75 mass%, carbides precipitated in this steel were finer than those in steels with low silicon content of 0.22 mass%[7] and the carbide precipitation along the prior austenite grain boundary tended to be suppressed.[8] Thus, this martensitic steel prevents intergranular fracture and shows higher resistance to hydrogen embrittlement.[9]

2.2. Hydrogen Charging and Hydrogen Analysis

Prior to hydrogen charging, the specimen surface was polished with #1000 emery paper so that the surface was uniform. Hydrogen charging of specimens was conducted by two methods. One was by immersion in a 20 mass% NH4SCN solution kept at a temperature of 50°C according to the FIP (Fédération International de la Précontrainte) test procedure.[10] The other was by cathodic electrolysis using a constant electric current at a current density of 30 A/m² in an aqueous solution of H2SO4 at pH 2.0 kept at a temperature of 50°C.[11]

Hydrogen analysis was carried out by TDA using a gas chromatograph at a heating rate of 100°C h⁻¹ in the temperature range of room temperature to 250°C. A standard gas mixture of Ar +50 vol. ppm of H2 was used for calibration of the hydrogen content.

2.3. Time Dependence of Absorbed Hydrogen Content under Elastic Stress

In order to clarify whether any effect can be attributed to the existing states of hydrogen in steel under stress regardless of the hydrogen charging method, hydrogen analysis was carried out immediately after the two types of hydrogen charging under non-stress (0σb) and elastic stress (0.6σb or 0.8σb) for various hydrogen charging times. Prior to hydrogen analysis, the specimens were removed from the solution and cut to the center of the hydrogen charging length of 30 mm.

2.4. Time Dependence of Enhanced Lattice Defects under Elastic Stress

The procedure used for estimating the amount of lattice defects associated with hydrogen under elastic stress is shown schematically in Fig. 1. Hydrogen charging was carried out in a 20 mass% NH4SCN solution under constant elastic stress (0.6σb or 0.8σb) for various times until fracture. Specimens were hydrogen-charged and stressed or fractured, removed from the solution, cut to the center of the hydrogen charging length of 30 mm or the near-fracture area (approximately 1 mm from the fracture surface), held at 30°C for 168 h without stress to remove hydrogen, and then surface-polished with #1000 emery paper so that the surface was uniform. Since most of the hydrogen in steel is trapped at various lattice defects[12–14] and the absorbed hydrogen content increases with an increasing amount of lattice defects under identical hydrogen charging conditions,[13] hydrogen was used as a probe for lattice defect detection. Accordingly, the increase/decrease in the amount of lattice defects associated with hydrogen under elastic stress was evaluated in relation to the increase/decrease in the hydrogen content of the specimens hydrogen recharged under the conditions above in a new solution without stress for 48 h, i.e., the time for the hydrogen concentration to reach equilibrium at the center of the specimens.

Three types of specimens machined to 1 mm in thickness and 20 mm in gage length were prepared to measure the positron annihilation lifetime showing the information of defect structure under elastic stress using the positron probe microanalyzer. The first type (i), denoted here as [non-stressed], was not stressed. The second type (ii), denoted as [0.7σb, 75 h], was stressed at 0.7σb for 75 h in water. The third type (iii), denoted as [H+0.7σb, 75 h (fractured)], was stressed at 0.7σb for 75 h until fracture in a 20 mass% NH4SCN solution at 50°C. The surfaces of all three types of specimens were polished with #1000 emery paper so that they were uniform. Chemical polishing with a mixture of phosphoric acid and hydrogen peroxide solution was then carried out to remove the surface layer resulting from mechanical polishing. The PPMA is a positron annihilation lifetime measurement system using an intense positron microbeam with a typical beam diameter of about 30–100 μm.[15] A one-dimensional scanning measurement was carried out using the positron probe microanalyzer at beam energy of 30 keV that provides information at depths to

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~1 μm, a step scan of 0.2 mm and a beam diameter of 100 μm.

### 2.5. Relationship between Lattice Defects Enhanced under Elastic Stress and Hydrogen Embrittlement

The procedure used for evaluating the effects on hydrogen embrittlement of enhanced lattice defects associated with hydrogen under elastic tensile stress is shown schematically in Fig. 2. Five types of specimens were prepared for different durations of applied elastic stress during hydrogen charging. The first specimen, denoted here as [non-stressed], was used as the reference without stress. The other specimens, denoted as [H+stress (24 h)], [H+stress (48 h)], [H+stress (72 h)], and [H+stress (96 h)], were hydrogen charged in a 20 mass% NH4SCN solution under elastic stress of 0.8σB for 24, 48, 72 or 96 h, held at 30°C for 168 h without stress to remove hydrogen, and then surface polished with #1000 emery paper so that their surface was uniform. A tensile test was carried out at a tensile rate of 1 mm/min in the air for the five specimens having different amounts of initial lattice defects without hydrogen. The effects of the enhanced lattice defects during applied elastic stress on hydrogen embrittlement were examined in terms of the ratio of reduction in fracture strain.

### 3. Results and Discussion

#### 3.1. Time Dependence of Absorbed Hydrogen Content under Elastic Stress

Figure 3 shows the stress-strain curve of the tempered martensitic steel together with constant applied stress levels (0, 0.2, 0.4, 0.6 and 0.8σB) indicated by the arrows.

Figure 4 shows the TDA profiles and hydrogen contents of specimens hydrogen-charged under the different hydrogen charging conditions at a temperature of 50°C for 48 h under non-stress (0σB) and elastic stress (0.6σB or 0.8σB) that was shown in Fig. 3. Since the absorbed hydrogen desorbed at room temperature and disappeared at approximately 200°C in both TDA profiles, it was presumably weakly trapped. In addition, the absorbed hydrogen content under stress (0.6σB and 0.8σB) was larger than that under non-stress (0σB) after hydrogen charging for 48 h.

The applied stress time dependence of the absorbed hydrogen content under non-stress (0σB) and elastic stress (0.6σB or 0.8σB) is summarized in Fig. 5. It is noteworthy that the hydrogen content and the rate of hydrogen absorption under applied stress were larger than that under non-stress for both hydrogen charging methods.

In order to clarify the relationship between applied stress and the absorbed hydrogen content, hydrogen analysis was carried out immediately after hydrogen charging under various stress levels for 24 h. Figures 6(a) and 6(b) show the amounts of hydrogen charged by immersion in a NH4SCN solution and by cathodic electrolysis, respectively. Although the hydrogen content increased linearly with increasing stress in the range from non-stress to 0.6σB, an increase in hydrogen content was not observed under the application of stress of 0.8σB for either hydrogen charging method.

The following two factors are presumed to increase hydrogen content under elastic tensile stress.

(A) An increase in the reaction of hydrogen entry because of the fracture of the oxide films on the specimen surface associated with applied tensile stress.

(B) An increase in the solute hydrogen concentration resulting from a reduction in the chemical potential.

With regard to factor (A), it is assumed that there were no oxide films on the specimen surface at the start of hydrogen charging because the specimens were polished with...
1000 emery paper prior to hydrogen charging. In addition, as seen in Fig. 5(b), the hydrogen content did not decrease with hydrogen charging, since cathodic electrolysis was performed in the immune zone; as a result, oxide films were not formed on the specimen surface. For these reasons, it is unlikely that the hydrogen content increased due to factor (A).

Regarding factor (B), on the other hand, an increase in solute hydrogen associated with applied tensile stress has been reported. An increase in solute hydrogen resulting...
from a reduction in the chemical potential associated with applied tensile stress has also been reported for ARMCO steel, AISI 4340 steel,\(^{31}\) 75%Pd–25%Ag alloy,\(^{16}\) martensitic steel\(^{17}\) and nickel.\(^{18}\) The solute hydrogen concentration under stress \((C_o)\) can be obtained with the following equation:

\[
C_o = C_0 \exp \left( \frac{\sigma_B V_H}{3RT} \right)
\]

where \(C_0\) is the concentration of solute hydrogen under no stress, \(\sigma_B\) is applied stress, \(V_H\) is the molar volume of hydrogen \((2 \times 10^{-6} \text{ m}^3/\text{mol})\), \(R\) is the gas constant and \(T\) is the test temperature. Equation (1) clearly indicates that the concentration of solute hydrogen increases linearly with increasing applied stress compared with a non-stress condition. Since the specimens used in the present study were smooth and had a thin diameter, uniaxial stress can be assumed. The increase in hydrogen content by the application of stress to 0.6\(\sigma_B\) as shown in Figs. 6(a) and 6(b) is consistent with Eq. (1). Nevertheless, the hydrogen content decreased under applied stress of 0.8\(\sigma_B\). This implies that the increase in the hydrogen content by applied stress was not influenced solely by the increase in solute hydrogen \((\text{factor } (B))\). The most probable reason for this is that the concentration of solute hydrogen as shown in Eq. (1) results in fewer lattice defects in pure metals. In contrast, the specimens used in this study were tempered martensitic steel of which has a high density of various lattice defects that act as traps of hydrogen. In addition, it has been reported that mobile dislocations can slip microscopically at one-third of the tensile strength regardless of the level of applied elastic stress.\(^{19}\) Our concern here is the influence of lattice defects at a high stress level of 0.8\(\sigma_B\). Therefore, we will describe the effects of lattice defects in the next section.

### 3.2. Time Dependence of Enhanced Lattice Defects under Elastic Stress

It was shown in the preceding section that the change in the hydrogen content in tempered martensitic steel under elastic stress could not be explained only by the increase in solute hydrogen \((\text{factor } (B))\). The following factor is also presumed to increase hydrogen content under elastic tensile stress.

\((\text{C})\) A change in the amount of lattice defects acting as hydrogen trapping sites.

We will consider the possibility of factor \((\text{C})\). In order to clarify lattice defects in the tempered martensitic steel in detail, the change in the amount of lattice defects under elastic tensile stress was evaluated according to the procedure shown schematically in Fig. 1. Figure 7 shows the relationship between the tracer hydrogen content \((\text{amount of lattice defects})\) of specimens, using hydrogen as a probe, and the time of applied stress \((0.6\sigma_B\) or \(0.8\sigma_B\)) during hydrogen charging by immersion in a 20 mass\% NH\(_4\)SCN solution at 50°C for various times until fracture. For both stress levels, the tracer hydrogen content \((\text{amount of lattice defects})\) of non-fractured specimens \((\text{cut into } 30 \text{ mm in length})\) decreased in the early stage \((i.e., 0-24 \text{ h})\), and then increased gradually with increasing time of applied stress. Fracture occurred at 158 h under stress of 0.6\(\sigma_B\) and at 101 h under stress of 0.8\(\sigma_B\). Hydrogen analysis was carried out for the fractured specimens in the near-fracture area \((\text{approximately } 1 \text{ mm from fracture surface})\). Note that the tracer hydrogen content \((\text{amount of lattice defects})\) in the near-fracture area \((\text{plots: } \bigtriangleup, \bigtriangleup)\) markedly increased compared with other areas \((\text{plots: } \bigcirc, \bigcirc)\). Consequently, it is clear that the amount of lattice defects changed with the time of applied stress under hydrogen charging.

### 3.3. Decrease in Enhanced Lattice Defects under Elastic Stress

The tracer hydrogen content \((\text{amount of lattice defects})\) decreased in the early stage of applying elastic stress as shown in Fig. 7. This reduction in the amount of lattice defects under elastic stress is quite similar to previous results reported for rotational bending tests of martensitic steels under elastic stress.\(^{19}\) Stress relaxation tests were carried out at applied stress levels of 0.2\(\sigma_B\) to 0.8\(\sigma_B\) to investigate the stability of mobile dislocations under elastic stress. The results clearly showed that the amount of stress relaxation from the initial applied stress increased with increasing applied elastic stress for the tempered martensitic steel used in this study. This implies that the stability of mobile dislocations decreased with increasing applied elastic stress and that mobile dislocations may have been reconfigured, \(i.e.,\) transformed to stable configurations, by the application of greater stress. It has been reported that the dislocation density estimated from the local strain obtained by Hall’s method was reduced by applied elastic tensile strain for high-strength nickel–chromium–molybdenum steel of various strength levels and at different heat treatment temperatures.\(^{20}\) The change in the dislocation density in the early stage of tensile deformation was investigated for as-quenched martensitic steel and the results revealed that the dislocation density decreased due to annihilation of dislocation dipoles by pre-straining of 0.15%.\(^{21}\) The formation of a dislocation cell structure and pile-ups at grain boundaries also take place because of the reconfiguration of dislocations. The movement of mobile dislocations in the early
stage of elastic tensile deformation has also been reported for tempered martensitic steel\textsuperscript{22} and 1 700 MPa grade 18Ni maraging steel\textsuperscript{23}. Based on the literature noted here, the reduction in the tracer hydrogen content (amount of lattice defects) in the early stage most likely resulted from the reconfiguration of dislocations to stable configurations and the annihilation of dislocations.

3.4. Increase in Enhanced Lattice Defects under Elastic Stress

In Fig. 7, the tracer hydrogen content (amount of lattice defects) increased gradually with increasing time of applied stress and then fracture ultimately occurred. The rate of increase in lattice defects under applied stress of 0.8\(\sigma_B\) was larger than that seen for 0.6\(\sigma_B\). Moreover, the tracer hydrogen content in the near-fracture area (plots: \(\blacktriangleleft, \triangle\)) markedly increased and was almost equal under elastic stress of 0.6\(\sigma_B\) and 0.8\(\sigma_B\). The incremental tracer hydrogen content (amount of lattice defects) in the near-fracture area (plots: \(\blacktriangleleft, \triangle\)) in Fig. 7, indicating incremental in the amount of lattice defects localized there, is compared with the mean tracer hydrogen content (amount of lattice defects) in the center part of the hydrogen charged length of 30 mm (plots: ●, ○). The results suggest some lattice defects formed and accumulated locally in the near-fracture area.

Figure 8 shows scanning electron micrographs of fracture surfaces of specimens immersed in a 20 mass\% NH\textsubscript{4}SCN solution at 50\(^\circ\)C under applied elastic stress of 0.8\(\sigma_B\). The macroscopic fracture shows no necking, \textit{i.e.}, flat brittle fracture surface and shear lip as shown in Fig. 8(a). This fracture morphology is typical in the hydrogen embrittlement for smooth round bar of tempered martensitic steels under the constant elastic stress. The microscopic fracture surface in Fig. 8(b) shows quasi-cleavage fracture observed in a major part of the flat fracture surface, indicating the fracture morphology involved localized ductile fracture. This suggests that localized plastic deformation took place under elastic stress in the near-fracture area.

We will verify these results by means of another method. We used a conventional positron annihilation lifetime apparatus to investigate if any change occurred in the deeper regions (~100 \(\mu\)m) of the specimens, though the measured region was several mm in diameter, and found the same results as mentioned above. Figure 9 shows a photograph of three specimens measured using the positron probe microanalyzer (PPMA). Specimen (i) was not stressed. Specimen (ii) was stressed at 0.7\(\sigma_B\) for 75 h in water. Specimen (iii) was stressed at 0.7\(\sigma_B\) for 75 h until fracture in a 20 mass\% NH\textsubscript{4}SCN solution at 50\(^\circ\)C. Figure 10 shows the mean positron annihilation lifetimes of these three specimens measured in the gauge part parallel to the tensile direction. The mean positron annihilation lifetimes of specimens (i) and (ii) was approximately 160 ps and did not change under applied stress without hydrogen for either specimen. In contrast, the mean positron annihilation lifetimes of specimen (iii) increased to between 170 and 180 ps in the area away from fracture surface. It was notably longer, \textit{i.e.}, more than approximately 200 ps, in the near-fracture area (approximately 1 mm from fracture). These data are consistent with the results shown in Fig. 7 for the lattice defect evaluation using hydrogen as a probe.

For the reasons noted above, hydrogen-related failure under elastic stress can be reasonably ascribed to localized plastic deformation in the near-fracture area, even though the involvement of plastic deformation may appear less at

**Fig. 8.** Scanning electron micrographs of fracture surfaces of specimens hydrogen charged in a 20 mass\% NH\textsubscript{4}SCN solution at 50\(^\circ\)C under applied elastic stress of 0.8\(\sigma_B\).

**Fig. 9.** Photograph of specimens measured with the positron probe microanalyzer. (i) Non-stressed, (ii) stressed at 0.7\(\sigma_B\) for 75 h in water and (iii) stressed at 0.7\(\sigma_B\) for 75 h until fracture in a 20 mass\% NH\textsubscript{4}SCN solution at 50\(^\circ\)C.
the macroscopic level.

3.5. Kind of Enhanced Lattice Defects under Elastic Stress

Lattice defects formed with the passage of time under applied elastic stress in the presence of hydrogen as shown in Figs. 7 and 10. Therefore, we will discuss the kind of enhanced lattice defects with respect to the difference in the lattice defect annihilation temperature and the mean positron annihilation lifetimes. Figure 11 shows TDA profiles in the near-fracture area of specimens before and after annealing at 200°C for 2 h. These specimens fractured at stress of 0.8σB and were hydrogen charged until saturation under the above-mentioned conditions in a new NH4SCN solution without stress. The tracer hydrogen content (amount of lattice defects) in the near-fracture area of the fractured specimens (4.5 mass ppm) was reduced by annealing to the level of the non-stressed specimen (3.1 mass ppm) that was shown in Fig. 7. The decrease in the TDA profiles due to annealing was mostly in the high-temperature range and the termination of desorption shifted to the low-temperature range.

The hydrogen desorption peak obtained from the TDA profiles correlated with the binding energies of hydrogen desorbed from lattice defects. Since trapped hydrogen increases with an increasing amount of lattice defects, the hydrogen content is an important quantity relevant to defect density. This annealing result indicates that the disappearance of lattice defects formed microscopically in the near-fracture area corresponds to the disappearance of trapping sites of higher binding energy with hydrogen. This decrease in hydrogen desorption in the high-temperature range of the TDA profiles due to low-temperature annealing is quite similar to previous findings reported for tensile plastic straining in the presence of hydrogen for pure iron and medium-carbon steels.

In the preceding section, the mean positron annihilation lifetimes of the fractured specimen (iii) in the near-fracture area (approximately 1 mm from fracture), which was stressed at 0.7σB during hydrogen charging, was more than approximately 200 ps. The longer positron annihilation lifetimes correspond to larger size of vacancies or vacancy clusters. All things considered, since the enhanced lattice defects under elastic stress were annihilated by annealing at 200°C and the mean positron annihilation lifetimes increased due to applied stress in the presence of hydrogen, the lattice defects that formed in the near-fracture area were not dislocations but rather vacancies or vacancy clusters.

3.6. Formation Process of Lattice Defects under Elastic Stress

We will consider the reason why the amount of lattice defects, i.e., vacancies or vacancy clusters, increased with increasing time of applied elastic stress with hydrogen charging.

Hydrogen transportation by moving dislocations because of localized plastic deformation in the elastic deformation area was reported for nickel-chromium-molybdenum steel. When cyclic elastic stress was applied to a hydrogen-charged pure iron specimen in a vacuum chamber, hydrogen desorption increased gradually during elastic deformation, indicating hydrogen transportation by moving dislocations. These results imply that plastic deformation is caused by moving dislocations under elastic stress.

Next, the reason why the amount of vacancies increases
due to dislocation motion is considered. Vacancy formation during plastic deformation without hydrogen is known to be caused by dislocation dynamics such as the combination of edge dislocations with opposite characteristics located on slip planes an atomic plane distance apart \(^{29}\) or the intersection and cutting of screw dislocations. \(^{33,34}\) It has been reported that vacancies were formed non-uniformly in pure iron given strain of 23\% without hydrogen, based on a positron annihilation lifetime measurement. \(^{35}\) The results showed that vacancies were heterogeneously introduced by plastic deformation and that the concentration of vacancies was high in a necking region. This is because of an increase in the amount of macroscopic deformation and dislocations cut by a number of slips in a necking region. Accordingly, vacancies were formed during plastic deformation as a consequence of dislocation dynamics.

In the present study, the morphology responsible for fracture was localized plastic deformation, while fracture occurred macroscopically under elastic tensile stress. Together with the marked increase in the tracer hydrogen content (amount of lattice defects) in the near-fracture area as shown in Fig. 7, the mean positron annihilation lifetimes measured with the positron probe microanalyzer (PPMA) increased at the near-fracture surface as shown in Fig. 10, signifying the involvement of localized plastic deformation in the near-fracture area. The three results presented above are consistent with this conclusion.

These results revealed that localized plastic deformation occurs in the hydrogen-related fracture site and the formation of vacancies is then enhanced due to the dynamic interaction of dislocations, even though brittle fracture occurs macroscopically under elastic stress.

3.7. Relationship between Lattice Defects Enhanced under Elastic Stress and Hydrogen Embrittlement

In order to clarify the relationship between vacancies or vacancy clusters formed under elastic stress and hydrogen embrittlement, tensile tests were conducted according to the procedure shown schematically in Fig. 2. **Figure 12** shows the stress-strain curves of five specimens: the [non-stressed] specimen used as the reference without stress and the [H+stress (24 h)] specimen, [H+stress (48 h)] specimen, [H+stress (72 h)] specimen, and [H+stress (96 h)] specimen, hydrogen charged in a 20 mass\% NH\(_4\)SCN solution at 50\(^\circ\)C under elastic stress of 0.8\(\sigma_r\) for 24, 48, 72 or 96 h, held at 30\(^\circ\)C for 168 h without stress to release all the hydrogen and then subjected to tensile stress until failure. These stress-strain curves indicate that ductility loss increased with increasing time of applied stress, even though hydrogen was completely removed by degassing before the tensile test. In other words, ductility loss increased with an increasing amount of initial vacancies at the beginning of the test.

The increased lattice defects formed by the application of stress with hydrogen charging were annihilated by low-temperature annealing at 200\(^\circ\)C as shown in Fig. 11. Accordingly, in order to clarify the direct effects of vacancies on hydrogen embrittlement, the vacancies causing ductility loss were removed by low-temperature annealing at 200\(^\circ\)C and then a tensile test was conducted on the specimens to see whether ductility loss was recovered. Two types of specimens were prepared. The first specimen, denoted as [H+stress (96 h)+200\(^\circ\)C], was successively annealed at 200\(^\circ\)C for 2 h as the [H+stress (96 h)] specimen that experienced the ductility loss shown in Fig. 12. The second type, denoted as [non-stressed+200\(^\circ\)C], was successively annealed at 200\(^\circ\)C for 2 h as the [non-stressed] specimen to match the heat treatment history and used as the reference without stress. A tensile test was conducted on the two specimens under the conditions shown in Fig. 2, and hydrogen embrittlement was examined in terms of the ratio of reduction in fracture strain. **Figure 13** shows the stress-strain curves of three specimens: the [H+stress (96 h)+200\(^\circ\)C] specimen, [non-stressed+200\(^\circ\)C] specimen and [H+stress (96 h)] specimen. Low-temperature annealing at 200\(^\circ\)C, i.e., annihilation of vacancies, recovered nearly all of the decrease in fracture strain.

Consequently, tempered martensitic steel specimens having vacancies formed under continued application of elastic stress in the presence of hydrogen experienced ductility loss, even though hydrogen was completely removed by degassing before the tensile test. This result implies that hydrogen
embrittlement was caused by an increase in vacancy density, even though hydrogen was not present.

In the present study, localized plastic deformation occurred in the tempered martensitic steel specimens owing to the localized stress concentration such as inclusions, precipitates, pittings, etc. although brittle fracture took place macroscopically under elastic stress. The dynamic interaction of dislocations in that process resulted in the formation of vacancies and then the vacancies were stabilized by trapped hydrogen. Presumably, solute hydrogen increased associated with the application of stress, or hydrogen was in a weakly trapping state. At that time, vacancy formation caused by the dynamic interaction of dislocations was probably active in the areas of high dislocation density and slip bands. When the amount of vacancies in steel increases, vacancy diffusion, agglomeration and then vacancy clustering occur. Subsequently, vacancies become microvoids and crack-growth resistance decreases, leading to final fracture. The role of hydrogen is to promote these behavior. From the result in Fig. 7 that the tracer hydrogen content (amount of lattice defects) in the near-fracture area at 0.8σB equaled that at 0.6σB, it is inferred that hydrogen embrittlement takes place when a certain amount of vacancy clusters accumulates.

It is noteworthy in Fig. 5(a) that hydrogen embrittlement under elastic stress during immersion in a 20 mass% NH4SCN solution at 50°C did not occur for 24–48 h. It did not occur at the time of the maximum hydrogen content but rather during the decrease in hydrogen content after about 100 h had elapsed. This result indicates that the hydrogen content in steel is not the dominant factor in hydrogen-related failure under elastic stress. Vacancies caused ductility loss in the steel specimens, even though hydrogen was completely removed by degassing before the tensile test and low-temperature annealing at 200°C annihilated the vacancies, recovering nearly all of the decrease in fracture strain as shown in Figs. 12 and 13. These results indicate that, in addition to the direct involvement of hydrogen, the formation and accumulation of localized vacancies due to the dynamic interaction of dislocations under elastic stress are also important factors causing hydrogen embrittlement. In the present study, besides hydrogen content, high strength and applied stress, time was also closely involved in hydrogen embrittlement with respect to the formation and accumulation of vacancies and necessary factors for the occurrence of hydrogen embrittlement.

4. Conclusions

Changes in hydrogen content and lattice defect formation associated with hydrogen under elastic tensile stress of tempered martensitic steel were examined. The relationship between hydrogen embrittlement and lattice defects associated with hydrogen was also investigated. The results obtained in this study can be summarized as follows.

1. The maximum absorbed hydrogen content and the rate of hydrogen absorption under applied stress were larger than that under non-stress. Hydrogen content increased linearly with increasing stress, although an increase in hydrogen content was not observed under applied stress of 0.8σB.

2. Hydrogen embrittlement under elastic stress during immersion in a 20 mass% NH4SCN solution at 50°C did not occur for 24–48 h. It did not occur at the time of the maximum hydrogen content but rather during the decrease in hydrogen content after about 100 h had elapsed. This result indicates that hydrogen-related failure involves not only applied stress and hydrogen content, but also time of applied stress with hydrogen charging.

3. The macroscopic fracture showed no necking, i.e., typical brittle fracture surface. The microscopic fracture surface showed mostly quasi-cleavage fracture, indicating that the fracture morphology involved localized ductile fracture. This suggests that localized plastic deformation took place under elastic stress in the near-fracture area.

4. Using hydrogen as a probe of lattice defects, it was found that the amount of lattice defects decreased in the early stage of applying elastic stress and then increased gradually with increasing time of applied stress. It markedly increased in the near-fracture area compared with other areas. The mean positron annihilation lifetimes of fractured specimens was measured with a positron probe microanalyzer to clarify the distribution of lattice defects and was found to be longer than that of other specimens. It was especially longer in the near-fracture area, indicating the formation of a high density of vacancies or vacancy clusters. The results obtained using hydrogen as a probe of lattice defects were consistent with the results measured with the positron probe microanalyzer.

5. Lattice defects increased with increasing time of applied stress in the presence of hydrogen and were annihilated by annealing at 200°C. This result and the longer positron annihilation lifetimes suggest that the hydrogen-enhanced lattice defects were vacancies or vacancy clusters.

6. Tempered martensitic steel specimens showed an increasing amount of vacancies with increasing time of applied stress and suffered ductility loss in tensile tests after hydrogen degassing. Annealing at 200°C to annihilate vacancies recovered almost all of the decrease in fracture strain. This implies that ductility loss was caused only by the accumulation of vacancies, even though hydrogen was completely removed by degassing specimens before the tensile test.

7. The amount of lattice defects in the near-fracture area at applied stress of 0.8σB almost equaled that at 0.6σB. It is inferred that hydrogen embrittlement occurs when a critical amount of vacancy clusters accumulates.

8. For hydrogen embrittlement involving microscopic plastic deformation, in addition to the presence of hydrogen, localized hydrogen-enhanced vacancies formed by the interaction between dislocations and hydrogen under elastic stress also directly cause ductility loss. Besides hydrogen content and applied stress, time of the formation and accumulation of vacancies was also closely involved in hydrogen embrittlement and is concluded to be an important factor causing hydrogen embrittlement.

Acknowledgement

This study was supported by a Grant-in-Aid for Science Research B (No. 22360293) from the Japan Society for the Promotion of Science (JSPS). In addition, the positron annihilation lifetime measurements with a positron probe microanalyzer in this work were supported by "Nanotechnology
Network Japan” at the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.

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