# Relationship between hydrogen states present in the vicinity of the fracture surface and hydrogen embrittlement susceptibility for ferrite-martensitic dual-phase steels

**D Asari[1], S Mizokami[2], M Fukahori[2] and K Takai[3]**

[1]Graduate School of Science and Technology, Sophia University, 7-1 Kioi-cho, Chiyoda-ku, Tokyo 102-8554, Japan
[2]Mazda Motor Corporation, 3-1 Aki-gun, Hiroshima 730-8670, Japan
[3]Faculty of Science and Technology, Department of Engineering and Applied Sciences, Sophia University, Tokyo, Japan

Corresponding author's e-mail address: asari1228@eagle.sophia.ac.jp

**Abstract**.  The relationship between hydrogen states present in the vicinity of the fracture surface and hydrogen embrittlement susceptibility was investigated for ferrite-martensitic dual-phase steels. Hydrogen embrittlement susceptibility was evaluated in tensile tests based on the ratio of the fracture strength of hydrogen charged and not-charged specimens. Tensile tests at strain rates of $8.33 \times 10^{-6}$ s$^{-1}$ and $1.67 \times 10^{-6}$ s$^{-1}$ were conducted on specimens containing different amounts of hydrogen. The hydrogen states present near the fracture surface were analyzed by thermal desorption analysis just after the specimens fractured. The results indicated that hydrogen embrittlement susceptibility markedly increased as the amount of hydrogen increased. Additionally, only the specimen that fractured at the highest amount of hydrogen showed not only a lower temperature peak but also a higher temperature peak. Hydrogen embrittlement susceptibility also increased at slower strain rates, and also showed the higher temperature peak. The relationship between hydrogen states present in the vicinity of the fracture surface and mechanical properties indicated that the defects corresponding to higher temperature peaks probably increased hydrogen embrittlement susceptibility. Since microvoids at the crack tips were observed by SEM only in specimens that fractured at lower strain rates, the defects corresponding to higher temperature peaks were probably voids.

## 1    Introduction

In recent years, automobile manufacturers have been required to reduce carbon dioxide emissions while ensuring collision safety, resulting in greater demand for high-strength thin steels that satisfy both light weight and safety requirements. If hydrogen embrittlement is hindering the further strengthening of the vehicle body frame, understanding this phenomenon is an important issue in satisfying social demands. Dual-phase (DP) steel, which has the two-phase structure of ferrite-martensite, is widely used for the body frame of vehicles because it satisfies the requirements for both strength and ductility.

However, it is reported that the strength difference between martensite and ferrite promotes hydrogen concentration at ferrite/martensite interfaces and that this concentration accelerates crack propagation [1]. Furthermore, as a promoting factor of crack propagation, it is also reported that cracking along ferrite/martensite interfaces is attributed to the decohesion and boundary sliding

associated with enhanced dislocation mobility [2]. For these reasons, it is clear that investigating the relationship between hydrogen and lattice defects is one approach to clarifying the hydrogen embrittlement mechanism of DP steels. Therefore, in this study, we investigated the lattice defects involved in hydrogen embrittlement from the perspective of the relationship between the hydrogen states present in the vicinity of the fracture surface and hydrogen embrittlement susceptibility.

## 2    Experimental

### 2.1    Materials

DP steels with a ferrite-martensite microstructure were used in the present study. Table 1 gives the chemical composition of the specimens used. Fig. 2 shows the shape of the specimens with a thickness of 1 mm and a gauge length of 20 mm.

### 2.2    Examination of hydrogen charging condition

The time taken to reach an equilibrium hydrogen condition at both the surface and center of the specimens was measured. The specimens were charged electrochemically with hydrogen at a current density of 100 $A \cdot m^{-2}$ in a 0.1 N NaOH aqueous solution containing a $NH_4SCN$ additive of 5 $g \cdot L^{-1}$ kept at a temperature of 30 □. The charging time was 24, 48, 72 and 96 h. Immediately after hydrogen charging until the specified time, the amounts and states of hydrogen present in the samples were analyzed by thermal desorption analysis (TDA) using a gas chromatograph at a heating rate of 100 □ · $h^{-1}$ in the temperature range from room temperature to 300 □. TDA profiles at different charging times are shown in Fig. 2 (a). The relationship between the charging time and amount of hydrogen present is shown in Fig. 2 (b). From the results in Fig. 2 (a) and (b), the hydrogen charging time for reaching an equilibrium condition was determined to be 72 h.

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

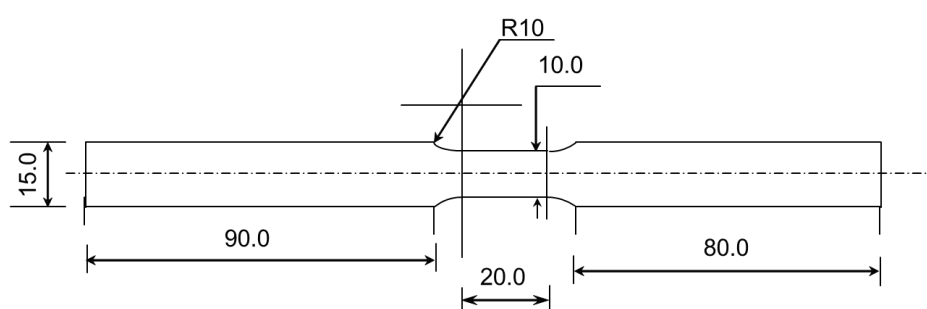| C | Si | Mn | P | S |
|------|------|-----|-------|-------|
| 0.14 | 0.51 | 2.5 | 0.008 | 0.003 |


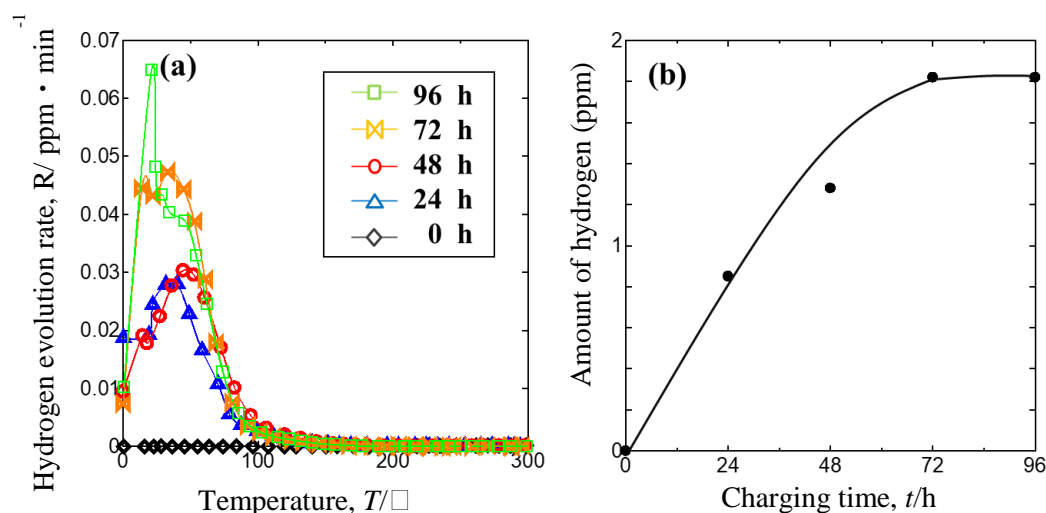
**Fig 1.** Specimen for tensile and constant load tests

**Fig 2.** Effect of hydrogen charging time: (a) thermal desorption profiles and (b) amount of hydrogen present based on thermal desorption profiles

### 2.3    *Evaluation of hydrogen embrittlement susceptibility*

Hydrogen embrittlement susceptibility was determined as the ratio of the fracture strength of hydrogen charged and not-charged specimens obtained in tensile tests. Specimens were precharged electrochemically with hydrogen at current densities of 30 and 100 $A \cdot m^{-2}$ in a 0.1 N NaOH aqueous solution containing a $NH_4SCN$ additive of 0, 0.2, 2, and 5 $g \cdot L^{-1}$ kept at a temperature of 30 □. After precharging, tensile tests were conducted at strain rates of $8.33 \times 10^{-6}$ $s^{-1}$ and $1.67 \times 10^{-6}$ $s^{-1}$. Hydrogen charging was conducted concurrently during the tensile tests at 30 □ under the same charging conditions to keep the hydrogen content of the specimens constant.

### 2.4    *Clarifications of the vicinity of fracture surface*

Hydrogen states present near the fracture surface were analyzed by TDA just after the specimens fractured in the tensile tests under the conditions mentioned above. Before conducting tensile tests, a mark was placed at a 20-mm distance between the gauge marks, and after fracturing, the part inside the mark was cut out using a fine cutter. It was immediately cooled with liquid nitrogen and analyzed by TDA at a heating rate of 100 $□ \cdot h^{-1}$ in the temperature range from room temperature to 300 □. Fracture surfaces were observed using a scanning electron microscope (FE-SEM).

## 3    **Results and discussion**

### 3.1    *Effect of the amounts of hydrogen*

Figure 3 (a) shows the stress-strain curves obtained in the tensile tests at a strain rate of $8.33 \times 10^{-6}$ $s^{-1}$ for different amounts of hydrogen and also shows the amount of hydrogen obtained by TDA just after fracturing. The results indicate that hydrogen embrittlement susceptibility noticeably increased as the amount of hydrogen increased. Fig. 3 (b) shows the TDA profiles of the specimens which fractured at different amounts of hydrogen. Only the specimen that fractured at the highest amount of hydrogen (4.5 mass ppm) showed not only a lower temperature peak but also a higher temperature peak. This suggests that defects corresponding to the higher temperature peak probably increased hydrogen embrittlement susceptibility.

### 3.2    Effect of strain rates

Figure 4 (a) shows the stress-strain curves obtained by the tensile tests at different strain rates. Hydrogen embrittlement susceptibility increased at slower strain rates. Fig. 4 (b) shows the TDA profiles of the specimens which fractured at different strain rates. At slower strain rates, a higher temperature peak around 150 □ newly appeared in the TDA profiles. Previous studies have reported that the higher temperature peaks of DP steels were presumed to be the desorption peaks of vacancy clusters introduced by deformation [3]. Therefore, the results of the present study suggest that the formation of vacancy clusters is promoted by the incursion of a certain amount of hydrogen because the higher temperature peaks appeared only for high amounts of hydrogen or at lower strain rates, which allowed sufficient time for hydrogen to diffuse. It is also inferred that susceptibility to hydrogen embrittlement increases due to the formation of vacancy clusters.
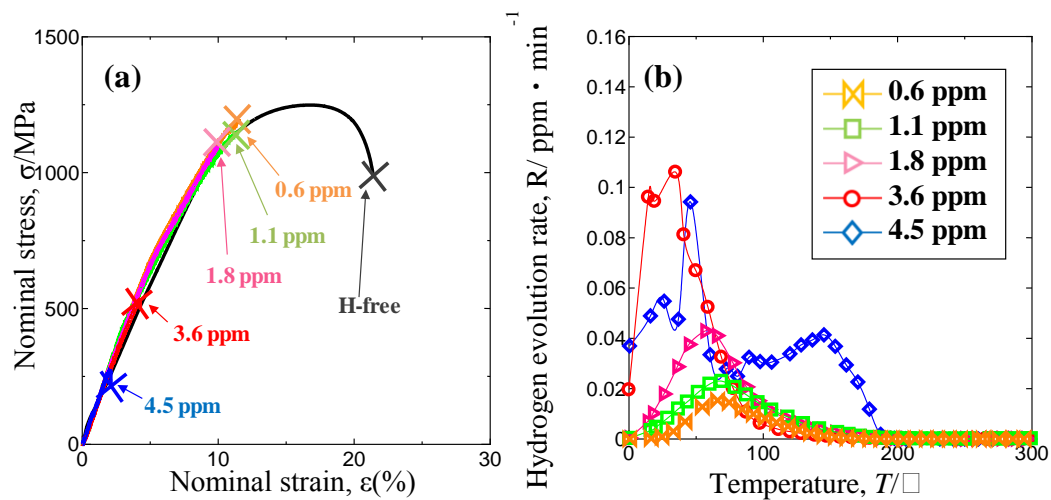


**Fig 3.** (a) Stress-strain curves for specimens at different amounts of hydrogen and (b) thermal desorption profiles at different amounts of hydrogen
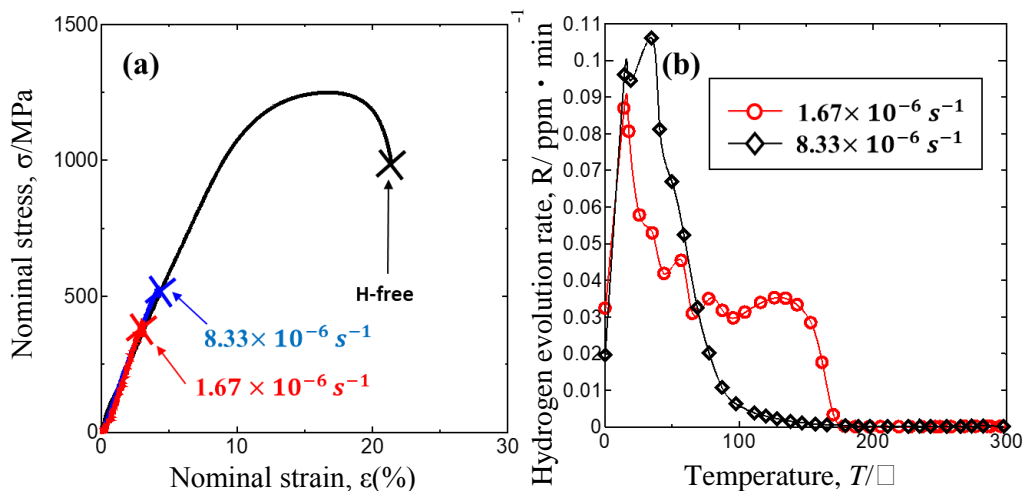


**Fig 4.** (a) Stress-strain curves for specimens at different strain rates and (b) thermal desorption profiles at different strain rates
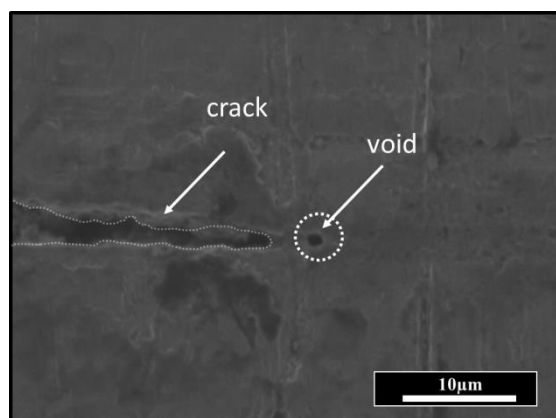
**Fig 5.** Microvoids at the crack tips in H-charged specimen fractured by lower strain rate SSRT

Figure 5 shows the vicinity of the fracture surface obtained in a tensile test at a strain rate of $1.67{\times}10^{-6}$ s$^{-1}$. Microvoids with a diameter of approximately 0.5 μm are observed at the crack tips. Since microvoids were not observed at a higher strain rate of $8.33{\times}10^{-6}$ s$^{-1}$, this is also evidence that defects corresponding to higher temperature peaks were probably microvoids.

## 4    Conclusions

The relationship between hydrogen states present in the vicinity of the fracture surface and hydrogen embrittlement susceptibility was examined for ferrite-martensitic dual-phase steels in relation to different amounts of hydrogen and strain rates. The results obtained in the present study can be summarized as follows.

(1) Only the specimen that fractured at the highest amount of hydrogen (4.5 mass ppm) showed not only a lower temperature peak, but also a higher temperature peak; the other specimens that fractured at lower amounts of hydrogen (3.5 ppm or less) showed only lower temperature peaks.
(2) When the strain rates were lowered, hydrogen embrittlement susceptibility increased even under the same hydrogen charging condition. The higher temperature peak appeared only in specimens that fractured at lower strain rates in the tensile tests.
(3) Microvoids with a diameter of approximately 0.5 μm at the crack tips were observed in the vicinity of the fracture surface in specimens that fractured only at lower strain rates in tensile tests.
(4) Defects corresponding to higher temperature peaks were probably microvoids. In addition, the formation of microvoids is probably a factor that increases hydrogen embrittlement susceptibility.

## References
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