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Investigation of relationship between microstructure and tensile properties in hydrogen environment using Cr-Mo steels

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Abstract: It is well known that the elongation of smooth tensile specimens of Cr-Mo steel, which is used in hydrogen vessels, decreases in the presence of hydrogen. This deterioration is ascribable to cracking at the steel surface during the necking process [1-2]. However, the relationship between the microstructure and crack initiation at the surface has not been clarified sufficiently. Thus, the purpose of this study is to identify the mechanism of hydrogen-induced crack initiation by using smooth tensile specimens of Cr-Mo steel.The steel examined in this study was quenched and tempered JIS-SCM435, a Cr-Mo low alloy steel.The slow strain rate technique (SSRT) was used with the smooth tensile specimens in air and during cathodic hydrogen charging. After rupture, the specimens were cut along the tensile direction for SEM observation of the surface cracks on the cross section.As a result, both elongation and reduction in area decreased in the presence of hydrogen. The reduction in area was 69.3% in air and 59.6% in the hydrogen charging environment. Numerous surface cracks were observed at the specimen surface in the test with hydrogen charging, while surface cracks were not found on the specimen tested in air. Additionally, it was found that a high density of microvoids formed in the vicinity of the hydrogen-induced surface cracks. The average density of the microvoids on the specimen tested in the presence of hydrogen was clearly higher than that of the specimen tested in air when compared at the same level of reduction in area.

1. INTRODUCTION

To commercialize hydrogen-energy systems, use of higher strength, more economical conventional steels will be necessary. Therefore, many experiments on the tensile, fatigue, and hydrogen-diffusion properties of such materials have been conducted in high pressure hydrogen gas [1-5]. It is well known that elongation of smooth tensile specimens of Cr-Mo steel, which is used in hydrogen vessels, decreases in the presence of hydrogen. This deterioration is ascribable to cracking at the surface during the necking process [2]. However, the relationship between the steel microstructure and surface crack initiation has not been clarified sufficiently. Thus, the purpose of this study is to identify the mechanism of hydrogen-induced crack initiation in a smooth tensile specimen of Cr-Mo steel.

2. EXPERIMENTAL PROCEDURE

Quenched and tempered JIS-SCM435, a Cr-Mo low alloy steel, was used in this study. Table 1 shows chemical composition of specimen. The steel was heated at 900℃ for 30 min followed by quenching in oil, then tempered at 665℃ for 60 min followed by quenching in water. After that, mechanical properties were measured in the atmospheric environment. At this time, it was confirmed that hydrogen was not exist in the material by Thermal Desorption Analysis method. The tensile strength and 0.2% yield strength of the steel were 887 MPa and 756 MPa, respectively, and total elongation was 24% with a JIS 14B specimen. The steel showed a lath martensitic microstructure with cementite particles.

Hydrogen was charged to the specimen by cathodic hydrogen charging. The solution was 0.1N NaOH, and the current density in cathodic hydrogen charging was 100 A/m^2. The amount of hydrogen charged under this condition is equivalent to that in 115 MPa high pressure hydrogen gas [6].

The slow strain rate technique (SSRT) using smooth tensile specimens was applied in air and simultaneously with cathodic hydrogen charging. The constant crosshead speed was 0.001 mm/sec, and the length of the parallel part was 30 mm. After rupture, the specimens were cut along the tensile

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direction for SEM observation of surface cracks on the cross section. The acceleration voltage in SEM observation was 5 kV.

Table 1. Chemical composition of specimen (mass%)

C	Si	Mn	P	S	Ni	Cr	Mo
0.34	0.21	0.74	0.023	0.006	0.01	1.06	0.17

3. RESULTS AND DISCUSSION

The SSRT results show that both total elongation and reduction in area decreased in the presence of hydrogen. The reduction in area was 69.3% in the atmospheric environment and 59.6% with hydrogen charging. Fig. 1 shows the fracture surfaces obtained by SSRT in air and with hydrogen charging. In air, a dimple fracture surface was observed overall. With hydrogen charging, a fragile fracture surface (quasi-cleavage) was observed around the side surface of the specimen. Numerous surface cracks were observed on the specimen surface in the SSRT test conducted simultaneously with hydrogen charging, while such surface cracks were not found on the specimen tested in air. Fig. 2 shows the results of SEM and EBSD analysis at the depth of 8 μm from the side surface around a surface crack. Propagation of the surface crack propagated into the specimen center was confirmed. An orientation analysis revealed that the surface crack path consisted of {011} facets. These results are agreement with the results of previous studies [7-8].

Fig. 3 shows cross-sectional images of specimens tested in air and with hydrogen charging, compared at the same reduction in area before crack initiation at the surface, where true strain was 0.35. Microvoids formed both in air and with hydrogen charging. The positions of the formed microvoids, especially at the interface between cementite particles and the matrix, are agreement in the two environments. However, the density of the microvoids was different in the two environments. The average density of the microvoids found in the hydrogen-induced specimen was clearly higher than that in the specimen tested in air when observed at the same reduction in area.

Fig. 4 shows the microvoid area density with respect to distance from the specimen surface. In air, the microvoid area density at the specimen surface was almost the same as that in the central part. In contrast, with hydrogen charging, a larger number of microvoids were found around the surface than in the central part. These results indicated that hydrogen enhanced the formation

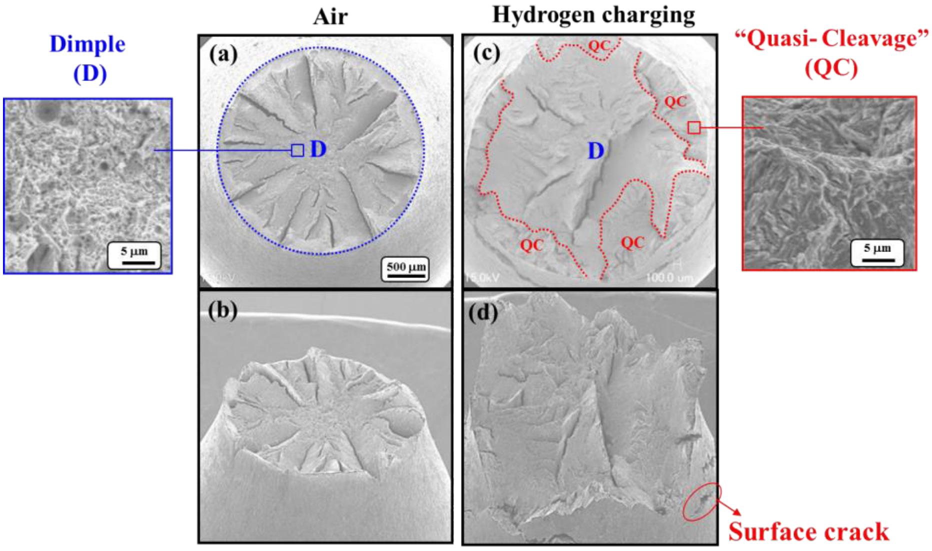

Fig. 1 Fracture surfaces of ruptured tensile specimens.
(a) Top view (air), (b) Side view (air),
(c) Top view (hydrogen charging), (d) Side view (hydrogen charging).

of microvoids. Thus, it is suggested that the presence of hydrogen promotes the generation of microvoids, especially at the interface between cementite particles and the matrix, and consequently deteriorates ductility. Also, it is considered that surface cracks were initiated by microvoids near the specimen surface. The reason for the high density of microvoids around the specimen surface is thought to be that hydrogen was always induced from outside the specimen under cathodic hydrogen charging.From these results, the process of fracture under hydrogen charging is considered to comprise the following phases 1-4:

1. Microvoids, which exist with a high density around the specimen surface, are presumed to be the origin of crack initiation with hydrogen charging.
2. Surface cracks propagate by the connection of microvoids and hydrogen assisted cracking. The fractured surface formed by cracking at the surface is influenced by hydrogen and becomes a quasi-cleavage fracture.
3. The surface cracking leads to the reduction of sectional area observed in the tensile test. Therefore, the triaxial stress on the residual part of the specimen increases.
4. Generation and connection of microvoids are promoted by the increase of triaxial stress. Eventually, the specimen reaches dimple fracture regardless of the presence of hydrogen.

According to this series of steps, it is considered that the specimen surface side undergoes quasi-cleavage fracture, whereas dimple fracture occurs in the central portion of the specimen.

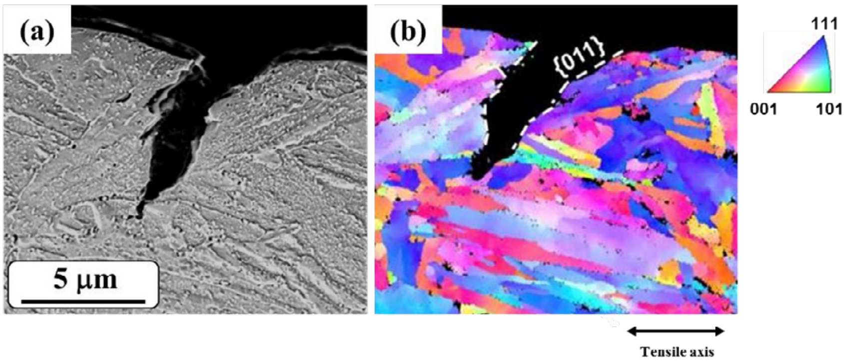

Fig.2 (a) SEM image and (b) corresponding EBSD orientation map of an area in the vicinity of a surface crack generated in the presence of hydrogen in a hydrogen charging specimen.

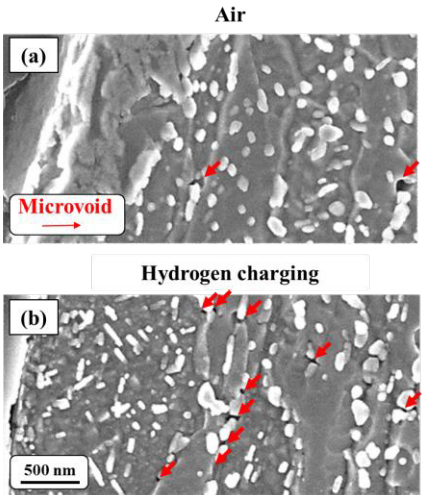

Fig. 3 Cross-sectional SEM images at ε_t=0.35 of ruptured tensile specimens. (a) Air, (b) Hydrogen charging.

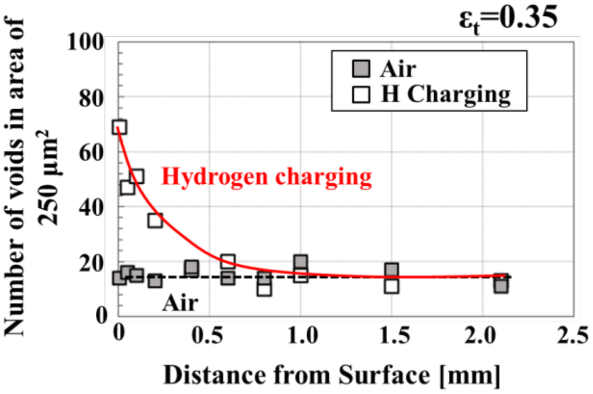

Fig. 4 Relationship between area density of microvoids and distance from specimen surface at ε_t=0.35 of the tensile specimens.

4. CONCLUSION

A SSRT test of JIS-SCM 435 steel was conducted in air and with concurrent cathodic hydrogen charging to observe the fracture surface and surface cracks in detail. The following results were obtained.

(1) Both total elongation and reduction in area decreased with hydrogen charging. Numerous surface cracks were observed on the surface of the specimen tested with hydrogen charging, while such surface cracks were not found on the specimen tested in air.

(2) An orientation analysis revealed that the surface crack path consisted of {011} facets.

(3) Numerous microvoids formed around the surface crack.

(4) The positions of microvoid formation observed at the interface between cementite particles and the matrix were in agreement in the two environments.

(5) In air, the microvoid area density in the vicinity of the specimen surface was almost the same as that in the central part of the specimen. On the other hand, with hydrogen charging, a larger number of microvoids were found around the surface than in the central part.

(6) It is considered that the dense microvoids in the vicinity of the specimen surface generate a surface crack.

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