Hydrogen Microprint Analysis on the Effect of Dislocations on Grain Boundary Hydrogen Distribution in Steels

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Hydrogen related intergranular fracture in high strength steels and steel welds are often explained by the hydrogen segregation at grain boundary that induces decohesion of the boundary. In this study, distribution of hydrogen in the grain boundary was visualized by a hydrogen microprint technique (HMT), and the effect of dislocations on hydrogen distribution in steel was analyzed. 0.02%C steel with ferrite microstructure was subjected to a plastic deformation up to 20% and HMT analysis, and then quantitative analysis of hydrogen concentration was conducted by measuring the area of silver particles formed by the reductive reaction between AgBr and hydrogen. The grain boundary hydrogen density was defined by an area of silver particle at the grain boundary per unit grain boundary length and diffusible hydrogen charged. And, it was found that the grain boundary hydrogen density decreases with increasing prestrain since hydrogen is trapped by dislocations inside the grain. The effect of dislocations introduced by martensitic transformation was also investigated using 0.1%C steels in as-quenched and quenched and tempered conditions. Silver particles were mainly observed on lath boundary in the as-quenched condition, while hydrogen density at the prior austenite boundary increased after tempering. It can be said that hydrogen segregation at the prior austenite grain boundary is affected by dislocations and lath boundary in martensite microstructure. Effect of dislocations on hydrogen distribution was also discussed based on dislocation densities and hydrogen contents.

KEY WORDS: hydrogen microprint technique; thermal desorption analysis; ferrite; martensite; dislocation; grain boundary.

1. Introduction

Prevention of hydrogen related brittle fracture such as delayed fracture and weld cold cracking is one of the most important issues for ensuring the safety and integrity of recent steel structures using high strength steels. Intergranular fracture is a typical fracture appearance seen in the cracking of high strength steels caused by hydrogen embrittlement.^{1–5)} According to the decohesion mechanism,⁶⁾ these intergranular crackings are explained by the hydrogen behavior in steel as the following; i) hydrogen intrusion into steel by corrosion reaction or welding process, ii) hydrogen diffusion in steel with the interaction between lattice defects, iii) hydrogen segregation at grain boundary, and iv) reduction of the cohesive energy of grain boundary. Thermal desorption analysis has successfully revealed hydrogen trapping behavior by various kinds of defects, such as dislocation, grain boundary and precipitates,^{7–9)} and trapping energy for each defect has been quantified experimentally.^{7–11)} Hydrogen trapping energies with defects in steel were used in the numerical study for explaining the

thermal desorption behavior of hydrogen.^{12,13)} First principle study clarified that significant reduction occurs in the cohesive energy by the segregation of hydrogen atoms in the grain boundary.¹⁴⁾

On the other hand, hydrogen microprint technique (HMT) is a powerful tool for directly detecting the presence of hydrogen in steel microscopically.^{15–22)} Hydrogen emission from a specimen surface is visualized as Ag particle by the reductive reaction between hydrogen and AgBr.^{15,16)} Many kinds of steels were subjected to the analysis by HMT to investigate hydrogen distribution in the steel. It was seen that hydrogen is trapped at grain boundary,^{15–18)} inclusions,^{19,20)} slip bands²¹⁾ and cementite.²²⁾ Accumulation of hydrogen by stress field was also clarified using HMT.¹⁹⁾ These results gave important understandings for hydrogen behavior in steel. However quantitative analysis of hydrogen concentration should be necessary for discussing the critical condition for intergranular fracture. In this study, we tried to conduct a quantitative analysis of hydrogen concentration at grain boundary in order to obtain clear understanding of the effect of hydrogen trap site, mainly dislocation, on grain boundary segregation of hydrogen.

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2. Experimental Procedures

2.1. Materials

Carbon steels containing 0.02% and 0.1% carbon were used for the test. Chemical compositions of the steels are shown in **Table 1**. Using laboratory ingots of 50 kg, hot rolling was applied to obtain plates with 15 mm thickness. Both steel plates were first annealed by heating at 950°C and cooled in air to obtain homogeneous microstructure. Then, tensile specimens was machined from the 0.02%C steel and tensile strain of 10% or 20% was applied to introduce dislocations into the ferrite matrix. On the other hand, the 0.1% carbon steel was then heated at 1 200°C and quenched in water to obtain martensitic microstructure that contains high density of dislocations by martensitic transformation. Quenched and 500°C tempered sample of 0.1% steel was also prepared to change dislocation density. Examples of microstructure are shown in **Fig. 1**. 0.02%C steel shows ferritic microstructure with vary little amount of cementite on the grain boundary. Deformation bands are seen inside the ferrite grain in 20% strained sample. On the other hand, 0.1%C shows lath martensitic microstructure.

Dislocation density of the specimen was measured by X-ray diffraction with the Williamson-Hall method,²³⁾ and measured dislocation densities for each sample are shown in **Table 2**. Dislocation density of Sample-A, 0.02%C in annealed condition, was relatively low, and dislocation density increased with increasing applied prestrain, Samples-B and -C. Sample-D, 0.1%C in as-quenched condition, has the highest dislocation density among the steels used in this study, while it decreased with applying tempering. Detailed observation of dislocation structure of the samples was conducted by TEM, and microphotographs are shown in **Fig. 2**. It is clearly seen that dislocation density is

Fig. 1. Examples of microstructure of the steels used; (A) 0.02%C annealed, (C) 0.02%C 20% prestrained, and (D) 0.1%C Quenched.

enhanced by applying plastic straining. In the 0.02%C with 20% prestrain, dislocations form cell structures. Sample-D, 0.1%C steel in as-quenched condition, shows very fine lath structure with higher dislocation density. But, dislocations were recovered and width of lath increased by applying tempering.

2.2. Cathodic Charging and Hydrogen Thermal Desorption Analysis

Cuboids specimens with the size of 10 mm in thickness and 10 mm × 20 mm in width and length were machined from the steel plates and electrochemical polishing was

Fig. 2. TEM microphotographs of the steel used; (A) 0.02%C, annealed, (B) 0.02%C, 10% prestrained, (C) 0.02%C, 20% prestrained, (D) 0.1%C, quenched, and (E) 0.1%C, quenched and tempered.

Table 2. Specimen preparation conditions and dislocation density.

Sample	Steel	Conditions	Microstructure	Dislocation density (m^{-2})
A	0.02%C	Annealed	Ferrite	1.52E+15
B		10% prestrained		9.44E+15
C		20% prestrained		1.07E+16
D	0.1%C	Quenched	Martensite	1.48E+16
E		Quenched and Tempered		8.01E+15

Table 1. Chemical compositions of the steels used.

Steel	C	Si	Mn	P	S	Al	N	O
0.02%C	0.02	0.01	<0.01	<0.001	0.0007	0.002	0.0015	0.0028
0.1%C	0.10	0.01	<0.01	<0.001	0.0006	0.006	0.0014	0.0041

applied to remove surface strained layer. Then, the specimen was cathodically charged with hydrogen in a 3%NaCl+0.3 g/L NH₄SCN aqueous solution at 1.0 mA/cm² for 240 min. Two specimens were cathodically charged under the same condition. One sample was subjected to thermal desorption analysis (TDA) to determine a content of diffusible hydrogen that was charged into the specimen. The other sample was used for the HMT analysis. Gas chromatography was used for measuring hydrogen concentration and heating rate in the TDA analysis was 200°C/h. TDA profiles of the samples are shown in Fig. 3. All the TDA profiles showed the peak desorption rate at around 100°C, and small amount of hydrogen desorption is seen at 400°C and over. In the 0.02%C steel, the peak height of the desorption rate increased with straining because of the increase in the number of hydrogen trapping site such as dislocation. On the other hand, peak height decreased by tempering in the 0.1%C steel since dislocation density decreased as shown in Table 2. Diffusible hydrogen is defined as the hydrogen desorbed below 350°C in the TDA profile, and the contents are presented in Fig. 3.

2.3. Hydrogen Microprint Conditions

Hydrogen microprint technique was applied to visualize hydrogen locally distributed corresponding to microstructure. HMT is a method to replace hydrogen with silver so

that hydrogen location can be visualized by silver particles formed by the following reductive reaction between hydrogen and silver bromide:

After the cathodic hydrogen charging, an observation side was coated with a liquid nuclear emulsion using a wire-loop method.²³⁾ The specimens were coated with the emulsion 6 min after the hydrogen charging. The coated specimens were then kept in a dark room for 24 hr to avoid a possible reaction between silver bromide and light, then dipped into formalin (aqueous 36 mass% HCHO solution) for 3 sec to harden gelatin,²⁴⁾ and then immersed into a fixing solution (aqueous 15 mass% Na₂S₂O₃ solution) for 10 min to eliminate any remaining AgBr crystals that had not reacted with hydrogen. All the tests were performed at room temperature and an aqueous solution of 10%NaNO₂ was used to dilute the emulsion and to make the fixing solution in order to avoid a corrosion reaction of the steels with the aqueous solutions.^{11,12)} Then, silver particles on the specimen surface were observed with SEM.

3. Results and Discussion

3.1. Hydrogen Microprint Results

Figure 4 shows SEM microphotographs of Sample-A (0.02%C, annealed). Many silver particles are observed at the grain boundary and inside the grain. Silver particles are clearly observed by the backscattered electron image (Fig. 4(c)). SEM images of Sample-C (0.02%C, 20% prestrained) are shown in Fig. 5. Many silver particles were observed inside the grain, while number of grain boundary particle was very small comparing to that of inside the grain.

Figure 6 shows SEM microphotographs of Samples-D (0.1%C, as-quenched) and -E (0.1%C, quenched and tempered). Both samples show martensitic microstructure containing prior austenite grain boundary and lath structure. Many small silver particles are observed on the lath boundary and accumulation of hydrogen at prior austenite grain boundary seems to be small. As presented in Figs. 4–6, qualitative behavior of hydrogen distribution in steels with

Fig. 3. Thermal desorption profiles of the steels after cathodic charged at 1.0 mA/cm² for 240 min.

Fig. 4. SEM microphotographs of Sample-A (0.02%C, annealed); (a), (b) secondary electron images, (c) backscattered electron image.

different hydrogen trapping sites can be visualized by the HMT. However, it is difficult to estimate the grain boundary hydrogen concentration by just comparing the SEM microphotographs since charged hydrogen content of the samples was different as shown in Fig. 3. Accordingly, we will try to analyze the grain boundary hydrogen quantitatively in the next section.

3.2. Evaluation of Grain Boundary Hydrogen Concentration

As shown in Figs. 4–6, silver particles were clearly recognized by the backscattering electron images. Hence, area of silver particles was measured using the backscattered electron images and grain boundary hydrogen density was

Fig. 5. SEM micrographs of Sample-C (0.02%C, 20% pre-strained); (a) secondary electron image, (b) backscattered electron image.

Fig. 6. SEM micrographs of Sample-D (0.1%C, as-quenched) (a), (b) and Sample-E (0.1%C, quenched and tempered) (c), (d); (b) and (d) are backscattered electron image.

analyzed. **Figure 7** shows traced images of silver particles observed at the grain boundary and inside the grain of Sample-A. It is seen that silver particles are unevenly distributed in the grain boundary and inside the grain. In Fig. 7, many grains include silver particles, but several grains show no particle inside. This may reflect the lattice orientation in a relationship with the slip direction. Therefore, statistically enough grains need to be examined for the quantitative analysis of hydrogen concentration. In the current study, observation area of more than 0.24 mm² for 0.02%C steel and 0.1 mm² for 0.1%C steel were selected and area of silver particles on the grain boundary and inside the grain boundary were measured separately by image analysis.

Table 3 shows the measurement results of silver particles on the grain boundary and inside the grain for all the samples. In order to derive the grain boundary hydrogen density from the measurement of silver particle area, the area of silver particles on grain boundary was normalized by the grain boundary length and diffusible hydrogen content, as shown in Table 3. So, the grain boundary hydrogen density was given as an area of silver particle at the grain boundary per unit grain boundary length and diffusible hydrogen. It is interesting to note that area of silver particles at grain boundary increased with prestrain while there is not so large difference in the total grain boundary length. Grain boundary region itself might be affected by prestrain, resulting in increased capacity for hydrogen trap. However, normalized hydrogen content was used since hydrogen distribution behavior among different hydrogen trap sites is of main interest in this paper.

Figure 8 shows the grain boundary hydrogen density for all the specimens. Grain boundary hydrogen density of Sample A, 0.02%C in annealed condition, is relatively high, but decreases with prestrain. It is considered that the dislocations induced by prestrain trapped hydrogen atoms and reduced the ratio of hydrogen distributed at the grain boundary. On the other hand, Sample-D, 0.1%C in as-quenched condition, shows quite low hydrogen density. Presumably this is because high amounts of dislocation and lath boundary introduced by martensitic transformation became strong trap sites for diffusible hydrogen. Grain boundary hydrogen density increased by applying tempering because of the reduction in dislocation density. Further data such as hydrogen trap energy and hydrogen trap site density should be necessary to obtain more concrete understanding of the relation among hydrogen diffusion, trap behavior and

Fig. 7. Traced images of silver particles observed in Sample-A (0.02%C, annealed); (a) grain boundary, (b) inside the grain.

Table 3. Measurement of silver particle area and grain boundary density.

Steel	0.02%C (ferrite)			0.1%C (martensite)	
	A annealed	B 10% prestrain	C 20% prestrain	D as quenched	E quenched & tempered
Area of silver particles at G.B.*1, $[A_{GB}]$ (μm^2)	1 325	1 630	4 107	10	117
Total grain boundary length, $[L]$ (μm)	11 117	8 143	10 485	467	1 054
Diffusible hydrogen content, $[C]$ (ppm)	0.057	0.228	0.559	0.155	0.114
Grain boundary hydrogen density $[A_{GB}/(L \cdot C)]$ ($\mu\text{m}^2/\mu\text{m}/\text{ppm}$)	2.10	0.88	0.70	0.14	0.97

*1 G.B.: “grain boundary” means “prior austenite grain boundary” in the case of Steels D and E.

Fig. 8. Grain boundary hydrogen density analyzed by measurement of area of grain boundary silver particles.

lattice defects. However, it became clear that grain boundary hydrogen concentration is strongly affected by the lattice defects such as dislocation, and the hydrogen microprint technique can be quite useful tool for visualizing and quantifying hydrogen distribution and concentration in steel.

4. Conclusions

Distribution of hydrogen in the steels with different lattice defects was analyzed by a hydrogen microprint technique (HMT) using 0.02%C and 0.1%C steels and the effect of dislocations on hydrogen distribution in steel was analyzed. Results are summarized as follows:

(1) In the 0.02%C steel with ferrite microstructure, silver particles formed by the reductive reaction between hydrogen and silver bromide were seen both on the grain boundary and inside the grain. However, many silver particles were observed inside the grain when applied with prestrain up to 20%.

(2) Silver particles were mainly observed on lath boundary and accumulation of hydrogen at the prior austenite grain boundary was small both in as-quenched and tempered martensite of 0.1%C steel. But, it was difficult to find the effect of tempering on the hydrogen distribution by merely comparing SEM microphotographs obtained by HMT.

(3) Quantitative analysis on the hydrogen concentration was conducted by measuring area of silver particles using the backscattering electron images, and the grain boundary hydrogen density was defined by an area of silver particle at the grain boundary per unit grain boundary length and dif-

fusible hydrogen charged. It was found that grain boundary hydrogen density decreased with increasing prestrain since hydrogen was trapped by the dislocations inside the grain.

(4) As-quenched martensite showed very low hydrogen density at prior austenite grain boundary due to the effect of high dislocation density and lath boundary structure, whereas prior austenite grain boundary hydrogen density increased by applying tempering because of the reduction in dislocation density.

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