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Detection of hydrogen trap distribution in steel using a microprint technique

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Abstract

The distribution of hydrogen trapped at defects has been visualized by means of a hydrogen microprint technique (HMT). A low carbon steel having a ferrite/pearlite structure with second phases along grain boundaries was subjected to notch-tensile and three-point bending tests with/without hydrogen pre-charging. HMT was applied to tested specimens re-charged with hydrogen. Accumulation of hydrogen was confirmed in strain-concentrated areas as well as along grain boundaries and in pearlite. A noteworthy finding was a substantial increase in defects acting as traps of diffusive hydrogen when specimens were deformed in the presence of hydrogen. The increased defects were annealed out at temperatures as low as 150 °C, indicating their point defect nature. Another finding was the appearance of a zone denuded of silver precipitation in highly strained areas such as near grain boundaries and the fracture surface, where tritium autoradiography revealed the evolution of defects having high binding energy with hydrogen.
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1. Introduction

The mechanism of hydrogen-related failure of materials has been discussed mostly with regard to hydrogen concentration, but the solid solubility of hydrogen in iron is extremely small in normal environments according to Sievert's law [1]. Most hydrogen is in trapped states at various defects. A key issue is the state of hydrogen that affects the failure, i.e. whether it is in solution or in trapped states. Detection of hydrogen states is a difficult task because of hydrogen's low sensitivity to external stimulations, high mobility and small quantity. Hydrogen thermal desorption analysis (TDA) is a useful means for analyzing hydrogen states [2,3], but TDA presents average values over an entire specimen, lacking information about local distributions of hydrogen. Visualization of hydrogen distribution is then useful and several techniques have been developed [4–9]. Hydrogen microprint technique (HMT), originally devised in 1985 [4], utilizes the reduction of silver ions by hydrogen to metallic silver, and is useful for detecting mobile hydrogen besides of its handiness operative under ambient atmosphere. Recently, improvements of the technique in the spacious resolution and detection efficiency have been conducted [10,11]. It is also noted that hydrogen can be used as a probe of defects [12], apart from its role as an embrittling agent. The distribution as well as the thermal desorption behavior of hydrogen introduced into defected materials could be utilized as a tool for investigating issues concerning defects in the mechanical behavior of materials.

In a previous study [13], a substantial increase in the defect density acting as traps of diffusive hydrogen was observed on straining ferritic steels using tritium as a probe of defects. The increase was dependent on the slip constraint along grain boundaries and was correlated with the ductile crack growth resistance associated with microvoid nucleation. It has been also revealed that the presence of hydrogen enhanced the increase in the strain-induced defects [14] with strong correlations with the susceptibility to hydrogen-related failure [14–16].

The above findings suggest an essential role of strain-induced defects on mechanical behaviors of materials, including hydrogen-related failure, but available information about the defects has been limited to TDA results. In the present study, HMT has been applied to detect strain-

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induced defects in areas with different strain concentrations. The aim was to investigate the increase in the density of the defects having different binding energies with hydrogen, when specimens were deformed in the presence of hydrogen, as well as the accumulation of hydrogen at strain concentration sites.

2. Experimental procedures

The steel used in the present study was a low carbon steel, 0.06C–0.49Si–0.07Mn–2.01Ni (mass %) having a ferrite/pearlite structure with carbides present along grain boundaries that act as barriers for slip extension [13]. The fracture behavior of the steel has been examined precisely in previous studies [13,17]. Notched tensile and three-point bending tests were conducted using specimens with/without hydrogen pre-charging. The tensile specimen was 2 mm thick and 6 mm wide with a double machined notch of 1.5 mm in depth and 0.3 mm in width. The three-point bending test specimen was 10 mm thick and 20 mm wide with a machined notch of 10 mm in depth and 0.1 mm in width. For hydrogen pre-charging, cathodic electrolysis was conducted in a 3% NaCl+3 g/l NH_4SCN aqueous solution at a current density of 0.5 mA/cm^2 for 20 and 24 h for the tensile and bending test specimens, respectively. When hydrogen pre-charging was applied, strained specimens were kept at room temperature for 24 h for degassing, and hydrogen was re-charged for HMT. In a previous study [13], it was observed that about 90% of tritium charged to a specimen given tensile strain of 20% was degassed in 24 h at room temperature.

The present study involved three procedures. The first one was to detect the defects associated with strain concentration. Notched tensile specimens were strained to a nominal strain of 3% at an elongation rate of 1 mm/min, and areas in the front and central parts of the notches were examined with HMT. Some of the specimens were subsequently annealed at 150 °C for 1 h. In the specimens subjected to the three-point bending test, a longitudinal cross section of the fractured specimen was examined with HMT in areas at 200 μm and 1 mm from the fracture surface. The second procedure was to examine the effect of hydrogen on the creation of defects by straining. Tensile specimens with/without hydrogen pre-charging were compared. The third procedure was to examine the binding strength of hydrogen with defects based on the diffusivity of hydrogen. The release of the trapped hydrogen may take place earlier from weaker traps. A standard time interval of 15 min between the finish of hydrogen recharging and the emulsion coating in HMT was shortened to 8 min, and the results were compared with those for the 15-min interval. The specimens were those used in the three-point bending test in the presence of hydrogen.

The procedure of HMT is as follows. Prior to hydrogen charging for HMT, one side of the surface to be observed was polished for metallographic observation and coated with a plastic film. Hydrogen charging was conducted from the opposite surface for 2 or 20 h under the same conditions as those for pre-charging. After hydrogen charging, the specimen was cleaned by acetone and the surface was etched with 3% nital for metallographic observation after removal of the coating film. A monogranular film of a nuclear emulsion, Konica NR-H2 diluted into a fourfold volume of a 5% $NaNO_2$ aqueous solution to avoid spurious corrosion [4], was placed on the surface using a wire-loop method [18]. After exposure for 30 min at room temperature, the sample was placed in a fixer at 20 °C for 5 min, followed by immersion in a 0.01 M NaOH aqueous solution to harden the film [10]. Finally, the specimens were rinsed with a 5% $NaNO_2$ aqueous solution and ethanol.

An additional observation was conducted by means of tritium autoradiography (TAR). Since TAR utilizes Ag precipitation induced by β-ray emitted from tritium, TAR can detect strongly trapped tritium that does not diffuse out to the surface, while HMT detects diffusive hydrogen. In the present study, tritium-charged specimens were kept at room temperature for 72 h for degassing before the emulsion coating so as to detect the distribution of non-diffusive tritium. The nuclear emulsion used for TAR was Ilford L4 diluted to a twofold volume of pure water and the exposure time was 97 days at −20 °C under a nitrogen atmosphere. Details of the procedure was similar to the one described previously [18].

3. Experimental results

Straining substantially increased the hydrogen absorption capacity under the given charging conditions. Fig. 1a is a HMT micrograph of a non-deformed specimen. The hydrogen charging time for HMT was 20 h. The small white spots observed are Ag particles, confirmed by electron probe microanalysis (EPMA). Accumulation of hydrogen along ferrite boundaries and in pearlite was evident. Fig. 1b shows the notch front area of a notched tensile specimen given 3% strain, indicating a substantial formation of strain-induced defects within grains. Slip bands were a preferred site of Ag precipitation. Fig. 1c is an area similar to that of Fig. 1b after annealing at 150 °C. The high density of Ag particles no longer appeared, indicating the annealing out of the defects that acted as traps of hydrogen. The increase in strain-induced trap sites was significant in the front area of the notch compared with the central part of the specimen. An increase in strain-induced traps and dependence on strain concentration were also observed in areas 200 μm and 1 mm from the fracture surface in a specimen subjected to the three-point bending test.

Increased creation of defects was expected from the

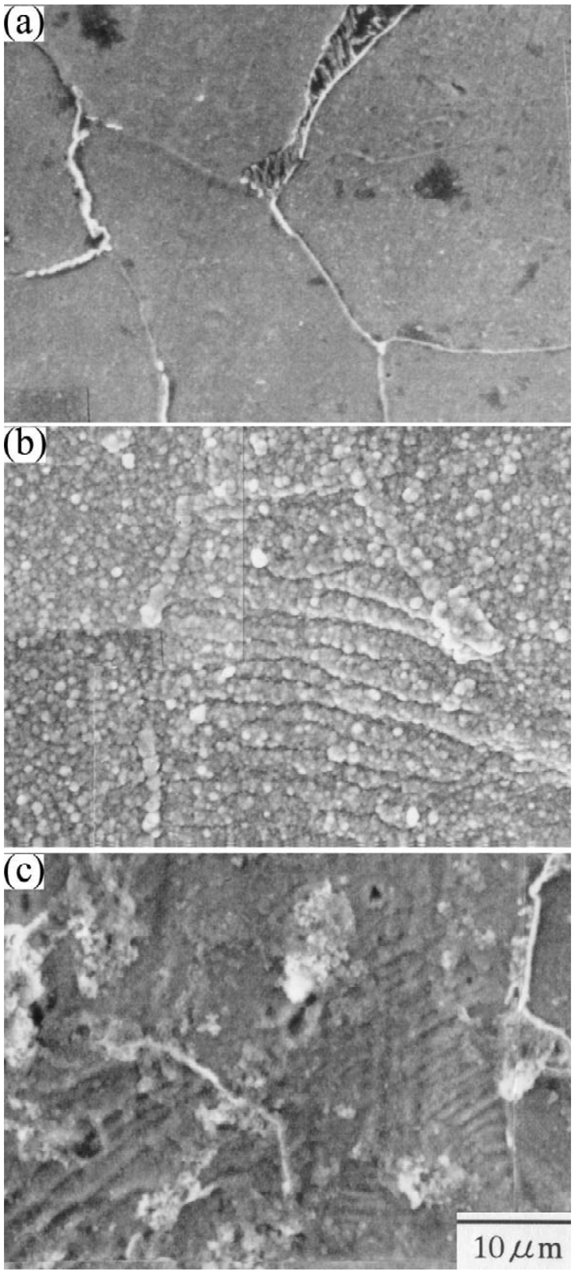

Fig. 1. HMT micrographs of the notch front area of notched-tensile specimens, (a) without straining, (b) given 3% strain and (c) annealed at 150 °C after straining. The hydrogen charging time for HMT was 20 h.

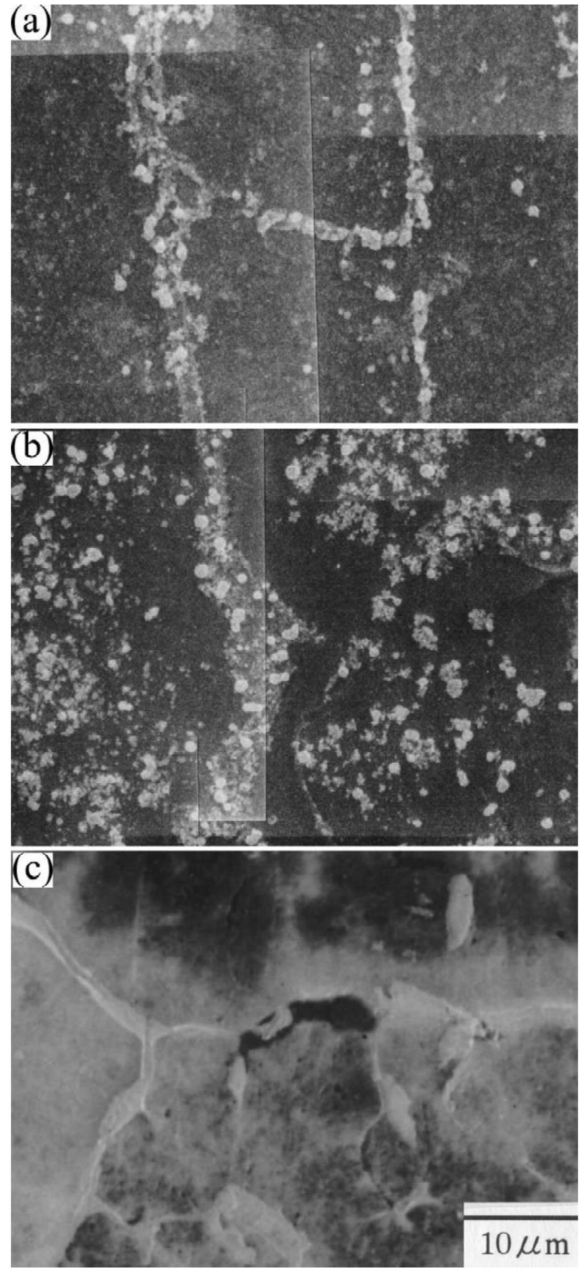

Fig. 2. HMT micrographs of the central area of notched tensile specimens given 3% strain, (a) without and (b) with hydrogen pre-charging. (c) Tritium autoradiograph of the same specimen as that in (b). The hydrogen charging time for HMT was 2 h.

TDA results [14] when specimens were strained in the presence of hydrogen. Specimens with/without hydrogen pre-charging for 20 h were subjected to tensile straining and examined by HMT. The hydrogen charging time for HMT was 2 h. Fig. 2a and b compare HMT micrographs of the central area of a notched tensile specimen given 3% plastic strain without/with hydrogen pre-charging, respectively. In Fig. 2b, pre-charged hydrogen had been degassed at room temperature for 5 days before HMT. The density of Ag particles in Fig. 2a was much less than that in Fig. 1b because of the shorter hydrogen-charging time for HMT and lower strain concentration of the observed area, but precipitation of Ag particles along grain boundaries and in pearlite was more distinct than in Fig. 1a. In Fig. 2b, many Ag particles appeared within grains, and a zone denuded of Ag particles was noticed near grain boundaries. A zone denuded of Ag was also observed near grain boundaries in a hydrogen-pre-charged specimen subjected to the three-point bending test, which coincided with that in the case of tensile straining.

The origin of the denuded zone was then examined by means of TAR. While HMT utilizes hydrogen diffusing out to the surface, TAR reveals irreversibly trapped tritium that remains in the material. Fig. 2c is an autoradiograph of a specimen similarly treated as in Fig. 2b. When compared with Fig. 2b, the precipitation of Ag particles was very fine with different distributions among grains. A probable reason of fine Ag appearance in Fig. 2c might be that Fig. 2c is an enlarged micrograph of a low magnification one with a low resolution of Ag particles. A dark area in the central part of the micrograph is likely an artifact due to the breakage of the emulsion film. Nevertheless, the difference of the images along grain boundaries is noted between Fig. 2b and c. In HMT (Fig. 2b), denuded zone of silver particles along grain boundaries indicates the absence of diffusive hydrogen, while TAR (Fig. 2c) shows there a substantial presence of strongly trapped, i.e. irreversibly trapped tritium.

Since the binding energy of hydrogen with defects affects hydrogen diffusivity [19], the change in the HMT results stemmed from the difference in time intervals between the finish of hydrogen charging and HMT, and this indicates that HMT can be utilized to discern different types of defects. In specimens subjected to the three-point bending test in the presence of hydrogen, fine Ag particles were densely precipitated within grains when the time interval was shortened to 8 min. On the other hand, with a time interval of 15 min the precipitation of Ag particles was more distinct along grain boundaries and in pearlite, which are sites of higher binding energies than strain-induced defects.

4. Discussion

The principle of HMT is to visualize ‘‘diffusive’’ hydrogen including that reversibly trapped in a solid solution. In the present study, hydrogen accumulation at strain-concentrated areas was observed as predicted [20]. Strain-induced creation of trapping sites for diffusive hydrogen (Fig. 1a) and its enhancement when deformed in the presence of hydrogen (Fig. 2a and b) are consistent with a previous study using TDA [14]. A noteworthy finding was the disappearance of the trap sites by annealing at 150 °C the deformed specimen, again corresponding to a TDA result [12]. The defects acting as the trap sites have been assigned to point defects [12,14–16], presumably vacancies, but freshly created dislocations are another possible traps since the stress field of which is to be reduced on annealing due to segregation of C atoms. However, a similar increase in the hydrogen absorption capacity and its reduction on annealing was also observed with an interstitial-free (IF) steel, i.e. a very low carbon steel added titanium and aluminum as fixers of interstitial C and N atoms [21]. Further, the dependence of the increase in hydrogen absorption capacity on the amount of strain is concave (a positive curvature) [12,21], while a linear dependence is expected if freshly created dislocations are the trap sites of hydrogen. The enhanced creation of defects when strained in the presence of hydrogen is in accord with experimental and theoretical results [22,23] that showed the increase in vacancy density by combining with hydrogen. Such considerations lead to the conclusion that vacancies are probable trap sites of the increased diffusive hydrogen in strained specimens.

Another problem in assigning the trap site of diffusive hydrogen to vacancies is that the reported binding energy of hydrogen with vacancy is as high as 44 kJ/mol in iron [23], questioning a reversible nature of the trap. A formula of the diffusion constant of hydrogen under local equilibrium with reversible traps was derived by Oriani [19]. Using his formula, observed thermal desorption curves from a steel given various amount of strain could be reproduced with 44 k/mol and 1×10^{-5} for the binding energy and trap density, respectively [24]. Together with the analyses by Oriani of experimental data [19], hydrogen trapped at vacancies may be assumed to be diffusive.

A noteworthy finding in Fig. 2b was the appearance of a zone denuded of Ag particles near grain boundaries. The TAR in Fig. 2c revealed that the origin of the denuded zone is the presence of strong traps of hydrogen. The fracture behavior of the steel used in the present study showed [13] that second phases along grain boundaries that act as barriers against slip extension reduced ductile crack growth resistance and were associated with the creation of defects acting as reversible traps of hydrogen. It was further shown [17] that the presence of hydrogen enhanced the decrease in ductile crack growth resistance. The present findings are consistent with previous TDA results, and support the proposed mechanism of decreased ductile crack growth resistance that is related to hydrogen through the increase in vacancy density.

5. Conclusions

HMT has been successfully applied to visualize the accumulation of diffusive hydrogen in strain-concentrated areas. The accumulation was much reduced in samples annealed at 150 °C after plastic deformation, suggesting point-like defects acting as the trap of hydrogen. The density of strain-induced defects increased when specimens were strained in the presence of hydrogen. A zone denuded of silver particles appeared in highly strained areas such as near grain boundaries and the fracture surface, but TAR showed evolution of strong hydrogen traps therein. The present findings are consistent with previous TDA results concerning the fracture behavior of the present steel.

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