Interpretation of hydrogen-induced fracture surface morphologies for lath martensitic steel

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Abstract

The mechanism by which fracture partitions between intergranular and “quasi-cleavage” in a hydrogen embrittled lath martensitic steel has been examined. Intense plasticity is found under both intergranular and “quasi-cleavage” fracture surfaces with differing slip band orientation relative to lath structures. In the intergranular fracture case, slip bands are parallel to the longitudinal direction of laths and the intersection between the slip bands and the interface is inclined to the prior austenite grain boundary, whereas in the “quasi-cleavage” fracture case, slip bands are inclined to the longitudinal direction of laths and the intersection is inclined with respect to the lath boundaries. Further, greater hydrogen accumulation is visualized in the vicinity of a grain boundary on a “quasi-cleavage” fracture surface. It is posited that local stress and hydrogen concentration provide for hydrogen-enhanced and plasticity-mediated failure by decohesion at prior austenite grain and lath boundaries.

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1. Introduction

Lath martensite is a most commonly used structure in the design of high-strength steels. The dramatic and deleterious effects of hydrogen on fracture have motivated many studies on the influence of hydrogen on the mechanical properties of lath martensitic steel (Gangloff and Somerday, 2012; Somerday and Sofronis, 2013; Takai and Akiyama, 2012). Commonly observed morphologies on hydrogen-induced fracture surfaces of lath martensitic steel are classified as either intergranular or “quasi-cleavage.” The former indicates surfaces showing “flat” features. The latter describes surfaces that exhibit cleavage-like features but do not conform to a cleavage plane and occur along a slip plane. However, the fundamental processes responsible for generating these two types of fracture surfaces and the mechanism to cause a shift between them are not well understood. Recently, through observation of the microstructure immediately beneath the fracture surfaces, Nagao et al. (2012b) showed that hydrogen-induced intergranular and “quasi-cleavage” fracture surfaces of a lath martensitic steel were created by failure along prior austenite grain and lath boundaries, respectively, and proposed a hydrogen-enhanced and plasticity-mediated decohesion mechanism along the respective boundaries to cause these failures. That is, hydrogen-enhanced mobility of dislocations causes work-hardening as well as a redistribution of hydrogen between the different traps. A consequence of the higher hydrogen concentration on the prior austenite grain and lath boundaries in addition to the raised local stress through work-hardening is that the boundary cohesive strength is reduced such that crack initiation and propagation along a boundary is favored over failure by ductile microvoid coalescence in the work-hardened matrix.

The present paper focuses on the mechanism by which fracture partitions between intergranular and “quasi-cleavage” in a hydrogen embrittled lath martensitic steel. Microstructures immediately beneath the hydrogen-induced intergranular and “quasi-cleavage” parts of the fracture surfaces are compared in detail using a combination of a focused-ion beam (FIB) lift-out technique and transmission electron microscopy (TEM). Further, a hydrogen microprint technique (HMT) (Nagao et al., 2012a; Ovejero-García, 1985) is applied to visualize hydrogen on the fracture surface to reveal the local distribution of hydrogen.

2. Experimental procedures

A middle-carbon ultra-high strength tempered lath martensitic steel was used in the present study. A slab containing 0.401C-0.26Si-1.91Mn-0.005P-0.0006S-0.23Mo-0.025Al-0.0043N (in mass%) was rolled in the recrystallization region followed by the non-recrystallization region to a plate with a thickness of 20 mm to achieve an ausforming effect (Nagao et al., 2012a). The steel plate was subsequently direct-quenched and subjected to sub-zero treatment to obtain a full lath martensite structure and tempered at 500 ºC.

Two single-notched bend specimens were machined with an electric discharge machine from the quarter thickness section parallel to the rolling direction of the plate. The dimensions of the bend specimens were 6.35 (thickness) x 12.7 x 101.6 mm, with an uncracked ligament of 8.47 mm, a notch angle of 22.5º and a notch root radius of 0.25 mm.

The bend specimens were first electroplated with an approximately 18 μm-thick zinc layer (Nagao et al., 2012a) and baked in a vacuum furnace at 150 ºC for 24 h to remove any hydrogen introduced during electroplating. One of the specimens was subsequently charged with hydrogen in a high-pressure gaseous hydrogen environment (138 MPa) at elevated temperature (250 ºC) for 21 days in an autoclave. The thermal charging introduced a peak 1 hydrogen content of 0.57 mass ppm (31.7 at. ppm), as determined by gas chromatograph hydrogen thermal desorption analysis. The peak 1 is the first peak observed in a thermal desorption analysis spectrum. In the present study, hydrogen that is desorbed from room temperature to 351 ºC during the analysis at a ramp rate of 200 ºC h⁻¹ is defined as peak 1 hydrogen. The zinc layer on the hydrogen-charged specimen provides a barrier to hydrogen egress during cooling and depressurization of the autoclave, and during the following bend test. The uncharged specimen, on the other hand, did not contain any peak 1 hydrogen.

The uncharged and hydrogen-charged specimens were subjected to four-point bend tests at a displacement rate of 0.1 μm s⁻¹ at room temperature. The outer and inner loading spans were 80.0 and 40.0 mm, respectively.

The fracture surfaces of the failed bend specimens were observed by scanning electron microscopy (SEM) with a JEOL 6060LV microscope operating at an accelerating voltage of 15 keV. A FIB instrument (FEI Dual Beam 235)
was used to extract samples normal to the fracture surface of the hydrogen-charged bend specimen from site-specific locations to enable determination of the microstructure developed immediately beneath and up to the fracture surface. These extracted samples were thinned to electron transparency in the FIB instrument and examined with a JEOL 2010 LaB6 transmission electron microscope that was operated at 200 keV. This FIB lift-out technique has been successfully used to probe the microstructure immediately beneath fracture surfaces, and it has been shown that fracture surface features remain intact during the extraction and thinning process (Martin et al., 2011a; Martin et al., 2011b; Martin et al., 2012; Nagao et al., 2012b).

The HMT is a method to replace hydrogen with silver based on a redox reaction of hydrogen with silver bromide (AgBr + H → Ag + HBr), which enables visualization of points of hydrogen emission sites as silver particles. The fracture surface was coated with liquid nuclear emulsion, Ilford L-4, using a wire-loop method (George, II, 1959) 20 min after the bend specimen was ruptured. Ilford L-4 contains silver bromide crystals (mean crystal diameter: 0.11 μm) in gelatin and it was diluted into the same volume of distilled water. The coated specimen was kept in a dark room at room temperature for 168 h to avoid reaction between silver bromide and light until most of the peak 1 hydrogen had diffused out of the specimen, it was then dipped into formalin (aqueous 36 mass% HCHO solution) for 3 s to harden gelatin (Nagao et al., 2012a), and immersed into a fixing solution (aqueous 15 mass% Na2S2O3 solution) for 10 min to eliminate any unreacted silver bromide crystals. An effective oxidizing agent, aqueous 10 mass% NaNO2 solution, was used to dilute the emulsion and prepare the fixing solution to avoid a corrosion reaction of the steel with the aqueous solutions (Nagao et al., 2012a; Ovejero-García, 1985). The specimen was observed with a JEOL 6060LV scanning electron microscope equipped with an energy dispersive X-ray (EDX) unit operating at an accelerating voltage of 15 keV.

3. Results

The microstructure of the steel used in this study is ausformed lath martensite with the substructure consisting of cementite particles and a high density of tangled dislocations. The effect of hydrogen on the bend properties is summarized in Table 1 along with the tensile properties of an uncharged round tension test specimen. The nominal bending stress, \( \sigma_{\text{nom}} \), denotes the bending stress in a straight beam of height \( a \), which is computed through \( \sigma_{\text{nom}} = \frac{6Fz}{Ba^2} \), where \( F \) is the applied force, \( z \) is the length of the moment arm, \( B \) is the thickness of the bend specimen and \( a \) is the size of the uncracked ligament. Hydrogen causes the maximum nominal bending stress to decrease from 2415 to 501 MPa for the four-point bend test.

| Test method  | Hydrogen (peak 1 content in mass ppm) | Mechanical properties |
|--------------|--------------------------------------|-----------------------|
| Uniaxial tension | Uncharged (0.00)                     | 0.2% PS* = 1290 MPa |
|               |                                      | UTS* = 1389 MPa       |
|               |                                      | TEL* = 11.0%          |
|               |                                      | RA* = 40.6%           |
| Four-point bend | Uncharged (0.00)                     | Maximum \( \sigma_{\text{nom}}^* \) = 2415 MPa |
|               | Thermally-charged (0.57)             | Maximum \( \sigma_{\text{nom}}^* \) = 501 MPa |

*Proof stress; *Ultimate tensile strength; *Total elongation; *Reduction in area; *Nominal bending stress

The fractograph acquired close to the notch root of the fractured bend specimen in the presence of hydrogen is shown in Fig. 1. The fracture surface exhibits a rough and undulating topology and shows a mixed morphology consisting of “flat” intergranular (indicated with IG) and “quasi-cleavage” (shown with “QC”) features. The projected degree of the “flat” intergranular fracture in Fig. 1 is 23%. In the absence of hydrogen, the fracture surface showed ductile microvoid coalescence.

To determine the origin of these hydrogen-induced fracture surface morphologies, samples for examination by TEM were extracted from underneath the “flat” intergranular and “quasi-cleavage” fracture surfaces using the FIB
lift-out technique. The bright-field micrographs presented in Fig. 2a and b compare the microstructure immediately beneath the “flat” intergranular, Fig. 2a; and the “quasi-cleavage” fracture surfaces, Fig. 2b.

Fig. 1. SEM image of the fracture surface of the fractured four-point bend specimen in the presence of hydrogen showing a mixed morphology consisting of “flat” intergranular (indicated with IG) and “quasi-cleavage” (shown with “QC”) features.

Beneath both the hydrogen-caused “flat” intergranular and “quasi-cleavage” fracture surfaces, intense slip bands (deformation bands) are observed and lath boundaries are disturbed to the point they are difficult to discern. Examples of the slip bands and discernible lath boundaries are indicated with arrows and arrowheads, respectively in Fig. 2a and b. Fig. 2a’ and b’ presents tracings of Fig. 2a and b, respectively. Multiple groups of parallel laths were found immediately beneath the “flat” intergranular fracture surface, which indicated that the fracture path of the “flat” part was along prior austenite grain boundaries (Nagao et al., 2012b). For the “quasi-cleavage” fracture surface, the fracture path is along lath boundaries and it is accompanied by a translath step as observed in Fig. 2b.

A distinct difference is discerned between Fig. 2a and b in the directional relationship between the activated slip systems and lath structures and also in the orientation of the activated slip systems with respect to the interfaces. Immediately beneath the intergranular fracture surface, slip bands are approximately parallel to the longitudinal direction of laths and the intersection between the slip bands and the interface is inclined to the prior austenite grain boundary, whereas beneath the “quasi-cleavage” fracture surface, slip bands are inclined to the longitudinal direction of laths and the intersection is inclined with respect to the lath boundaries.

Fig. 2. TEM micrographs and tracings showing microstructure immediately beneath the hydrogen-induced (a, a’) intergranular; and (b, b’) “quasi-cleavage” fracture surfaces. Arrows and arrowheads in (a, b) indicate slip bands and lath boundaries, respectively. Tracings in (a’, b’) include slip bands (—) and lath boundaries (—).

The local distribution of hydrogen on the fracture surface, as revealed by the HMT is presented in Fig. 3. The SEM image shown in Fig. 3a presents the fracture surface with superposed silver particles. Two grains are observed in the image. Higher magnification images shown in Fig. 3b and c are from the boxed regions presented in Fig. 3a. Fig. 3b focuses a “quasi-cleavage” fracture surface away from a grain boundary. Fig. 3c centers the “quasi-cleavage” fracture surface along with the grain boundary. The white spherical particles observed in Fig. 3a,b and c were confirmed by EDX analysis, Fig. 3d, to be silver; examples are marked with arrows in Fig. 3b and c. More silver particles are seen close to the grain boundary; the number of distinguishable silver particles in the boxed
region (18.4 μm²) presented in Fig. 3b and c is 59 and 98, respectively. The high density area of the silver particles on the “quasi-cleavage” fracture surface appears to extend as far as 7 μm from the grain boundary.

Fig. 3. HMT result showing the fracture surface with superposed silver particles. (b) and (c) are higher magnification SEM images of the boxed regions presented in (a). (d) shows an example of EDX spectrum on the white particles observed in (a), (b) and (c). “QC” and GB in (a) denote “quasi-cleavage” fracture surface and grain boundary, respectively. Examples of silver particles are marked with arrows in (b) and (c).

4. Discussion

Lath martensitic steel shows two characteristic hydrogen-induced fracture surface morphologies: intergranular and “quasi-cleavage.” To understand the origin of these fracture surface morphologies, the underlying microstructure has been examined. A notable difference is discerned in the directional relationship between the activated slip systems and lath structures and also in the orientation of the activated slip systems with respect to the interfaces: in the intergranular fracture case, slip bands are approximately parallel to the longitudinal direction of laths and the intersection between the slip bands and the interface is inclined to the prior austenite grain boundary, whereas in the “quasi-cleavage” fracture case, slip bands are inclined to the longitudinal direction of laths and the intersection is inclined with respect to the lath boundaries.

This finding suggests that macroscopic and local stresses play a role in determining the fracture path. The mechanism of hydrogen-induced failure in lath martensitic steel can be attributed to the macroscopic stresses activating different slip systems in individual grains; the enhancement of this dislocation activity by the hydrogen-enhanced localized plasticity (HELP) mechanism (Robertson, 1999; Robertson et al., 2009) will be of sufficient intensity to disrupt intersected boundaries; the corresponding hydrogen redistribution occurs amongst the traps in the plasticity processes, causing hydrogen accumulation on boundaries due to hydrogen transport by dislocations; and this enhanced plasticity further strengthens the matrix through work-hardening; then a crack initiates and propagates by interface decohesion driven by the combined action of macroscopic and local stresses as set by slip bands intersecting the boundaries that have been weakened by the locally accumulated hydrogen in the work-hardened matrix. Intergranular failure will result when slip systems intersect the prior austenite grain boundaries and “quasi-cleavage” when they intersect the lath boundaries. Which fracture mode is activated first is dictated by where the local stress accentuation along with the required hydrogen accumulation is attained first.

The HMT reveals evidence for greater hydrogen accumulation in the vicinity of a grain boundary on a “quasi-cleavage” fracture surface. This supports local hydrogen accumulation on boundaries described above. Boundaries, especially prior austenite grain, packet and block boundaries with high misorientation angle in the lath martensitic steel (Ma et al., 2011; Ueji et al., 2002) hinder the dislocation movement, leading to a dislocation pile-up at the boundaries. This causes greater hydrogen accumulation near the boundaries with hydrogen transported by mobile dislocations. In addition, mobile dislocations would dump hydrogen on the boundaries when they are annihilated at the boundaries or intersect the boundaries. Lath boundaries with low misorientation angle (Morito et al., 2006) would also be included in addition to the high misorientation angle boundaries in this case.
The mechanistic steps in the generation of intergranular and “quasi-cleavage” fractures of hydrogen embrittled lath martensitic steel are summarized as follows: decohesion of prior austenite grain or lath boundaries leading respectively to intergranular or “quasi-cleavage” fracture depends on local stress and local hydrogen concentration associated with dislocation slip. The activated slip systems, the amount of slip and the degree of stress imposed on the boundaries will reflect the grain orientation relative to the externally imposed macroscopic stress as well as the local stress state and will be accelerated by the presence of hydrogen. This hydrogen-enhanced and plasticity-mediated decohesion mechanism is proposed to explain the interplay between intergranular and “quasi-cleavage” fractures in hydrogen embrittled lath martensitic steel.

5. Conclusions

The mechanism by which the fracture surface morphology changes between intergranular and “quasi-cleavage” in a hydrogen embrittled lath martensitic steel has been examined. A combination of a FIB lift-out technique and TEM was used to observe the microstructure immediately beneath the fracture surface. Further, the local distribution of hydrogen on the fracture surface was revealed by a HMT.

The experimental observations acquired by these methods lead to the conclusion that the condition to cause either hydrogen-induced intergranular or “quasi-cleavage” fracture depends on local stress and local hydrogen concentration set by activated slip systems impacting prior austenite grain or lath boundaries.

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References

Gangloff, R., Somerday, B. (Eds.), 2012. Gaseous Hydrogen Embrittlement of Materials in Energy Technologies, Vols. 1,2, Woodhead Publishing Ltd., Sawston, Cambridge.

George, II, L., Vogt, G., 1959. Electron Microscopy of Autoradiographed Radioactive Particles. Nature 184, 1474-1475.

Ma, X., Wang, L., Liu, C., Subramanian, S., 2011. Role of Nb in Low Interstitial 13Cr Super Martensitic Stainless Steel. Materials Science and Engineering A 528, 6812-6818.

Martin, M., Fenske, J., Liu, G., Sofronis, P., Robertson, I., 2011a. On the Formation and Nature of Quasi-Cleavage Fracture Surfaces in Hydrogen Embrittled Steels. Acta Materialia 59, 1601-1606.

Martin, M., Robertson, I., Sofronis, P., 2011b. Interpreting Hydrogen-Induced Fracture Surfaces in Terms of Deformation Processes: A New Approach. Acta Materialia 59, 3680-3687.

Martin, M., Somerday, B., Ritchie, R., Sofronis, P., Robertson, I., 2012. Hydrogen-Induced Intergranular Failure in Nickel Revisited. Acta Materialia 2012, 2739-2745.

Morito, S., Huang, X., Furuhara, T., Maki, T., Hansen, N., 2006, The Morphology and Crystallography of Lath Martensite in Alloy Steels. Acta Materialia 54, 5323-5331.

Nagao, A., Hayashi, K., Oi, K., Mitao, S., 2012a. Effect of Uniform Distribution of Fine Cementite on Hydrogen Embrittlement of Low Carbon Martensitic Steel Plates. ISIJ International 52, 5182-5189.

Nagao, A., Smith, C., Dadfarnia, M., Sofronis, P., Robertson, I., 2012b. The Role of Hydrogen in Hydrogen Embrittlement Fracture of Lath Martensitic Steel. Acta Materialia 60, 5182-5189.

Ovejero-Garcia, J., 1985. Hydrogen Microprint Technique in the Study of Hydrogen in Steels. Journal of Materials Science 20, 2623-2629.

Robertson, I., 1999. The Effect of Hydrogen on Dislocation Dynamics. Engineering Fracture Mechanics 64, 649-657.

Robertson, I., Birnbaum, H., Sofronis, P., 2009. Hydrogen Effects on Plasticity in “Dislocations in Solids, Vol. 15”. In: Hirth, J., Kubin, L. (Eds.). Elsevier, New York, NY, pp. 249.

Smith, D., 1996, On the General Grain Boundary. Interface Science 4, 11-27.

Somerday, B., Sofronis, P. (Eds), 2013. Hydrogen-Materials Interactions, ASM International, Materials Park, OH.

Takai, K., Akiyama, E. (Eds.), 2012. Special Issue on Common Bases for Hydrogen Embrittlement Studies, ISIJ International 52.

Ueji, R., Tsuji, N., Minamino, Y., Koizumi, Y., 2002. Ultragrain refinement of plain low carbon steel by cold-rolling and annealing of martensite. Acta Materialia 50, 4177-4189.