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Interpreting hydrogen-induced fracture surfaces in terms of deformation processes: A new approach

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Observations of fracture surfaces and deformation beneath fracture surfaces produced by hydrogen-assisted cracking in pipelines steels, which were published in a recent paper (M.L. Martin, I.M. Robertson, and P. Sofronis, Acta Materialia, 59 (2011) 3680–3687), are discussed, and it is argued that the conclusions made regarding mechanisms of fracture are not justified.

Keywords: Ferritic steels; Hydrogen embrittlement; Scanning electron microscopy (SEM); Dislocations; Fracture mechanisms

In a recent study concerning gaseous hydrogen-assisted cracking (HAC) of API grade X60 and X80 pipelines steels, Martin et al. [1] examined fracture surfaces by scanning-electron microscopy (SEM) and atomic force microscopy. They also characterized the dislocation distribution beneath fracture surfaces using transmission electron microscopy (TEM) of thin foils prepared by focused-ion-beam (FIB) and ion-milling techniques. The information obtained from these studies was discussed in terms of various proposed mechanisms of HAC, and they concluded that the observations were best explained in the framework of the (solute) hydrogen-enhanced localized plasticity (HELP) mechanism, and that the adsorption-induced dislocation-emission (AIDE) mechanism and the "classical" hydrogen-enhanced decohesion (HEDE) mechanisms could be discounted. The purpose of the present note is to question the interpretation of the observations, indicate why such conclusions are not warranted, and make some general comments and suggestions.

Martin et al. [1] showed that the fracture surfaces produced by HAC exhibited transgranular "quasi-cleavage" facets (with river lines and tear ridges) plus some relatively featureless, undulating facets: At high magnifications, the relatively featureless facets exhibited fine details, which were described as "mounds" ~50 nm diameter and ~5 nm height (Fig. 1) [1]. Whether similar fine-scale details were present on other facets (in regions between the tear ridges/river lines) was not clear, but images in a previous paper by Martin et al. [5] suggest that fine details (not clearly resolved at the magnifications shown) were probably present. Underneath the relatively featureless facets, TEM showed that there was a high density of dislocation lines/loops, with no gradient in dislocation density over the region examined – up to 1.5 μm beneath fracture surfaces (see Figs. 5–7 in Ref. [1]). The authors suggested that the "mounds" were a likely consequence of either near-surface relaxations associated with formation of new surfaces or fracture through weak regions associated with the dislocation structure and local high hydrogen concentration.

The preceding interpretations of the experimental observations and the overall conclusions regarding mechanisms of HAC are questionable for a number of reasons. Most importantly, Martin et al. [1] indicated that the samples were obtained from Dr. Brian Somerday and, according to Somerday [6] (and noted in Ref. [2]), the specimens were heat-treated for 20–30 min in air at ~275 °C after HAC prior to final fracture. This heat-treatment was carried out in order to heat-tint the fracture surfaces produced by HAC, and thereby facilitate measurements of crack lengths. Martin et al. [1,5] did not disclose this critically important information, which has a direct bearing on the interpretation of both fine-scale fracture-surface features and the dislocation arrangements beneath fracture surfaces.

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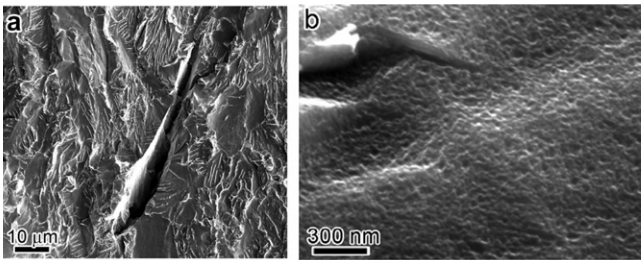

Figure 1. Examples of SEM images of fracture surface of a pipeline steel tested in hydrogen gas: (a) at low magnification, showing facets exhibiting river lines/tear ridges and relatively flat facets, plus a secondary crack; and (b) at high magnification, showing fine-scale details on a relatively flat facet [1]. Information in the literature [2,3] (referenced in Ref. [1]) indicates that tests were carried out under slowly rising load conditions at ~20 °C in high-pressure hydrogen gas (5.5–21 MPa). Comparisons with tests in air showed that the hydrogen environment resulted in a decrease in fracture toughness [2,3]. Crack growth in air would result in large, deep dimples on fracture surfaces [4]. Images are reproduced on a smaller scale than in Ref. [1].

There was also no information in the paper [1] regarding how mating areas of opposite fracture surfaces corresponded to each other, e.g. whether fine-scale features matched peak-to-peak or peak-to-trough, which would have been helpful in identifying how the features were formed. It would also have been useful to know more about the relationship between the overall fracture topography (different types of facets) and the underlying microstructure, besides the information that the facet size generally corresponded to the grain size (~5 μm). According to Ref. [3], the X60 steel had a polygonal-ferrite microstructure, and the X80 steel exhibited ferrite and acicular ferrite structures, sometimes with a small amount of upper bainite. However, Martin et al. [1] neglected to state whether the images in their paper corresponded to the X60 steel or the X80 steel.

The fracture-surface details (Fig. 1(b)) described by Martin et al. [1] as "mounds" appear to me to be shallow depressions (delineated by cusps around them), since more secondary-electron emission would be expected from cusps than from depressions, so that cusps are bright and depressions are relatively dark. Whether these features were produced by the fracture process or by oxidation during heat-treatment (or both) is, of course, a pertinent question [6]. To answer this question, it would obviously be sensible to examine carefully preserved fracture surfaces produced by HAC without a subsequent heat-treatment. However, such fracture surfaces were not available, and so I cleaved a ferritic steel at −196 °C, and examined the same cleavage facets by high-resolution SEM before and after heat-tinting for 30 min at ~275 °C in air in order to get an idea of the effects of such a heat-treatment on fine-scale fracture topography.

The heat-treatment produced a brown interference colour on the fracture surfaces, indicating the presence of an oxide film ~60 nm thick [7]. SEM fractography showed that nanoscale details, such as steps, tear ridges and cusps around isolated dimples, were still apparent after heat-tinting but were not as sharp, with some of the finest details being obscured by the oxide film. Some features not present prior to heat-tinting, e.g. fine cracks in the oxide film, were apparent – but nothing resembling the details shown in Figure 1b. Thus, assuming no other corrosion occurred on the fracture surfaces examined by Martin et al. [1], the fine-scale features they observed are probably produced by the fracture process, although they would have been altered somewhat by oxidation. If this is the case, then the features are possibly small, shallow dimples resulting from a nanovoid coalescence process. This explanation seems more likely than the two suggestions by Martin et al. [1], which are vague and unconvincing – with the atomistic processes involved in cleavage-like crack growth not clearly described in either case.

Previous studies of HAC of steels and other materials (e.g. [8–10]) have shown that fracture surfaces are sometimes dimpled on a microscopic to nanoscopic scale – features that led Beachem [8] to first propose a localized-plasticity mechanism for HAC based on solute hydrogen facilitating dislocation activity. In-situ TEM studies of crack growth in a ("thick") thin-foil specimen of a steel in hydrogen gas have also shown that crack growth can occur by the nucleation, growth, and coalescence of ~50 nm-sized voids ahead of cracks [11]. Such voids could be nucleated at slip-band intersections (or other dislocations structures) or by vacancy clusters stabilized by the presence of hydrogen. Some voids could also be nucleated at small carbides, and isolated large dimples on some facets are probably associated with carbides. The high density of dislocations beneath fracture surfaces, indicative of high local strains, is consistent with void nucleation (at the sites mentioned) and their coalescence by dislocation activity.

The AIDE mechanism proposed by Lynch, which involves adsorbed hydrogen promoting dislocation nucleation from crack tips, thereby facilitating the link up of cracks with voids ahead of cracks, can account for observations of nanoscale dimples on cleavage-like facets, as discussed in detail elsewhere [9,10,12–15]. Martin et al. [1], on the other hand, argue that the fairly uniform dislocation density beneath the fracture surfaces does not support the AIDE mechanism, on the basis that dislocations emitted from a crack tip should be distinguishable from other dislocations, and should locally increase the dislocation density adjacent to the fracture surface. However, for the pipeline steels fractured in gaseous hydrogen, embrittlement is not that severe [2,3], and dislocations nucleated at the crack tip would be emitted into a highly strained plastic zone containing a high density of dislocations. Thus, dislocations emitted from the crack tip would probably be incorporated into the existing dislocation network and become indistinguishable from dislocations generated by sources ahead of cracks – a possibility that was acknowledged by Martin et al. [1].

The dislocation structures beneath fracture surfaces observed by Martin et al. [1] would, in any case, not be representative of those that existed after HAC because the heat-treatment after cracking would cause some thermally activated dislocation rearrangement/annihilation. (Reductions in residual stress are observed for steels even when stress-relieved at only 200 °C for 1 h [16].) Oxide-induced stresses may also cause some local