

## THE ROLE OF PLASTIC FRACTURE PROCESSES IN HYDROGEN EMBRITTLEMENT

Anthony W. Thompson<sup>1</sup> and I. M. Bernstein<sup>2</sup>

## INTRODUCTION

As the name implies, "hydrogen embrittlement" usually refers to a brittle fracture induced by hydrogen, where "brittle" refers in turn to the relative magnitude of the macroscopic ductility parameters, such as elongation or reduction of area (RA). Such terminology is generally reasonable but has the disadvantages that (i) not all losses in ductility lead to genuinely brittle behaviour, e.g., a loss in RA from 60% to 30%; and (ii) macroscopic brittleness need not, and often does not correspond to a brittle fracture surface appearance.

Indeed, the inference often drawn, that hydrogen generally causes *microscopically* brittle fracture, is quite incorrect. One purpose of this paper is to illustrate that most types of hydrogen fracture modes which do occur are microscopically ductile. We then discuss the implications of this circumstance for mechanisms of hydrogen-assisted fracture.

## OBSERVATIONS

It is now known that hydrogen can cause losses in RA of over 50%, with the microscopic fracture mode being microvoid coalescence with or without hydrogen; this is true in plain carbon steels, austenitic stainless steels, nickel-base alloys, and others [1, 2, 3]. This fracture mode, of course, is quite ductile microscopically, as Figure 1 illustrates. Microvoid coalescence can also be observed in combination with smooth, stretched areas separated by tear ridges, Figure 2; this is still a ductile type of fracture, although less easy to describe than the mode of Figure 1.

When the smoother areas of a surface like Figure 2 become flatter and exhibit tear ridges and small "tongues", the mode is called "quasi-cleavage" [4], as in Figure 3. This term historically was coined to describe fractures which strongly or weakly *resemble* cleavage, but which contain tear ridges (as Figure 3 does) and have facets which have not been shown to correspond to cleavage planes [4]. Many of the best-defined examples of this mode have been found in tempered high-chromium steels [4, 5], as in the 13% Cr martensitic steel of Figure 3, although the literature now contains so many cases of poorly-defined fractures which were *called* quasi-cleavage that the term is on the verge of becoming meaningless. In any case, substantial local plasticity is needed for the development of this fracture mode [4, 5, 6].

<sup>1</sup> Science Center, Rockwell International, Thousand Oaks, California 91360, U. S. A.

<sup>2</sup> Department of Metallurgy and Materials Science, Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213, U. S. A.

It is also observed that classical cleavage can be induced by hydrogen, as shown in Figure 4; note that even in this highly brittle (macroscopic) mode, local intense shearing to form the cleavage steps occurs, and that the fracture is preceded and accompanied by highly-localized plastic deformation along the fracture plane [4, 7].

Fracture of hydrogen-charged material also occurs by an intergranular mode in many cases. This may involve microvoid coalescence, tear ridges, and extensive slip line markings, as in Figure 5 [6]. It is common in steels to see tear ridges on intergranular surfaces caused by hydrogen, except at K levels very near the threshold value [6]. Thus, in many cases, even intergranular fractures reveal considerable local plasticity.

There are three conclusions to be drawn from these observations. (i) None of these fracture modes are peculiar to hydrogen, but are typical of generally-observed types of fracture [4]. (ii) Each of these fracture modes may comprise substantial local plasticity on the scale of fractographic observation. It is often stated or implied that cleavage and intergranular fractures are brittle on a still finer scale, nearing atomic dimensions. Our point, however, is that on an "intermediate" scale comparable to microstructural sizes, local plasticity can occur in all modes. (iii) The question which therefore has to be answered about hydrogen-assisted fracture is, "How does hydrogen cause deformation and fracture to become localized and thus macroscopically less ductile?" The important question clearly is *not*, "How does hydrogen cause fracture to be microscopically brittle", because in general that is not what hydrogen does.

#### DISCUSSION

The available fractographic evidence, then, suggests that while on a local scale (on the order: to atomic dimensions) the fracture could be highly brittle (either cleavage, or intergranular or interfacial fracture), the more dominant fracture features are plastic in character. The plasticity tends to be more highly localized as macroscopic ductility decreases.

A reasonable working hypothesis is that hydrogen can affect fracture on both scales, with the relative importance and proportions of each being controlled by those metallurgical features which determine the sensitivity of a given alloy (or alloy class) to hydrogen-assisted fracture. The plastic localization aspect, however, deserves special emphasis because macroscopic ductility appears strongly related to it. Current evidence suggests the following sequence of events:

1) Hydrogen is transported to a potential crack centre or to the stress field of a growing or stopped (plastically blunted) crack. Transport can either be through the lattice or by dislocation atmospheres [9]. If we assume that this dynamic cracking process can be modelled to be quasi-static, then at any time, the hydrogen concentration profile surrounding a crack centre can be derived.

2) At regions of very high hydrogen concentrations, or where a void volume exists, there will be a high driving force for molecular hydrogen formation to take place. The resulting pressure will not only provide a localized high stress to promote local plasticity and fracture (whose mode will depend on the intrinsic plasticity of the alloy), but it will also modify the hydrogen distribution in the surrounding volume [10].

3) At other regions of high hydrogen potential, fracture can occur by a reduction of the cohesive strength of an interface or of the lattice itself. Rice [11] has considered this possibility, and in a semi-quantitative model has related the ease of separation to the ability of hydrogen to reduce either the interfacial or lattice surface energy. The factors relating the ease with which this can happen are those which determine the intrinsic plasticity of a given material or crystal class (e.g., it is easier to cleave bcc iron than fcc nickel); the same factors may have a bearing on the tendency of a given material to exhibit strain localization and shear instability [2, 12].

4) When locally brittle fracture does occur, its role in the overall fracture process (and associated fracture mode) will depend on both kinetic considerations and metallurgical variables. The former will be dependent on hydrogen entry and transport, with transport probably more critical in terms of cracking rates. To obtain an estimate of a necessary transport rate to sustain "continuous" brittle crack growth, we take an upper limit of the crack rate,  $V$ , of  $\sim 10^{-3}$  cm/sec [13]; this in turn implies an apparent diffusivity  $D^*$ , defined as

$$V = \sqrt{D^* \Delta t} / \Delta t, \text{ or } D^* = V^2 \Delta t, \text{ or } D^* = 10^{-6} \Delta t \text{ cm}^2/\text{sec}.$$

For time scales to fracture of minutes, i.e.,  $\Delta t \geq 100$  sec, this value will generally not correspond to lattice diffusivity of hydrogen. (For the steel case just cited [13], this diffusivity is of order  $10^{-6}$  cm<sup>2</sup>/sec). Thus intermittent crack growth (with associated plasticity), or enhanced transport (e.g., by dislocations [9]), or both, must be occurring. Either process involves dislocation interaction with the crack centre and therefore a mixed fracture mode in many cases. Obviously, the relative amounts of ductile and brittle fracture will depend on the specific transport parameters.

An equally critical factor is the continuity of the embrittled phase or interface. For lattice cleavage this will be related to the mean spacing of second phase particles which can act as crack blunters. For grain boundary fracture, this will depend on a similar parameter, as well as the specific trapping ability of a given unit of boundary length. For other interfaces, particle size and shape will be the major controlling factors. What we have just described are metallurgical variables amenable to control. If, for example, we desire a fracture that is predominantly ductile, then fine, closely spaced lattice or grain boundary precipitates are preferred, as are spherical, fine precipitates for those second phase particles that exhibit interface fracture.

5) Can hydrogen affect the fracture mode at regions more distant from high local hydrogen potentials? There is not evidence yet that this can happen but one possibility is that hydrogen affects local plasticity processes, intensifying the appearance of macroscopic brittleness [12]. Possible evidence that this may happen includes Beachem's results on microvoid coalescence [6], and Erwin et al's results on hydrogen directly affecting slip planarity [14].

There are a number of poorly-understood aspects of this problem. The evidence of local plasticity which we have presented for most cases of hydrogen-assisted fracture suggests that the pivotal one of these is the strain localization process, whether it takes the form of macroscopic "superbands" [12] or of microscopic shear instability [15]. The role hydrogen plays in such localization seems to be a critical area for further work.

## SUMMARY

We have described the many ways hydrogen can affect fracture mode. Highly brittle fracture can be accounted for by cohesive energy changes at interfaces, grain boundaries and in the lattice; the extent to which this dominates the final fracture appearance is dependent on both the change in operative surface energy as well as kinetic competition between a growing crack and hydrogen transport. For most alloy systems and strength levels, this mode does not appear to dominate.

Local pressure build-up at trapping centres promotes localized plastic tearing processes which, if sufficiently constrained, can produce a macroscopically brittle, yet locally ductile, fracture appearance.

Either the brittle or ductile processes can serve to generate the nuclei for final fracture. Failure of the ligaments between these nuclei will be important in many cases, and can result either from hydrogen-free fracture processes, or perhaps from hydrogen enhancement of the plasticity of these processes. We expect many mixed-mode hydrogen fractures to arise from behaviour of this type.

## ACKNOWLEDGEMENTS

This work was supported by the National Science Foundation, Grant DRM 75-10741 (A.W.T.) and by the Office of Naval Research, Contract N00014-75-C-0265 (I.M.B.).

## REFERENCES

1. THOMPSON, A. W. and BERNSTEIN, I. M., "Advances in Corrosion Science and Technology", Vol. 7, Plenum, New York, in press.
2. THOMPSON, A. W., "Effect of Hydrogen on Behavior of Materials", TMS-AIME, New York, 1976, 467.
3. GARBER, R., BERNSTEIN, I. M. and THOMPSON, A. W., Scripta Met., 10, 1976, 341.
4. BEACHEM, C. D. and PELLOUX, R. M. N., "Fracture Toughness Testing and Its Applications", (STP 381), ASTM, Philadelphia, 1965, 210.
5. BEACHEM, C. D., J. Basic Eng., 87, 1965, 299.
6. BEACHEM, C. D., Met. Trans., 3, 1972, 437.
7. KITAJIMA, K. and FUTAGAMI, K., "Electron Microfractography", (STP 453), ASTM, Philadelphia, 1969, 33.
8. THOMPSON, A. W., "Hydrogen in Metals", ASM, Metals Park, 1974, 91.
9. TIEN, J. K., THOMPSON, A. W., BERNSTEIN, I. M. and RICHARDS, R. J., Met. Trans., 7A, 1976, 821.
10. LI, J. C. M., ORIANI, R. A. and DARKEN, L. S., Zeits. für Phys. Chem., 49, 1966, 271.
11. RICE, J. R., "Effect of Hydrogen on Behavior of Materials", TMS-AIME, New York, 1976, 455.

12. HAHN, G. T., BARNES, C. R. and ROSENFELD, A. R., "Influence of Microstructure and Second Phases on Fracture Toughness", Report ARL TR 75-0194, Aerospace Research Laboratories, USAF, Wright-Patterson AFB, Ohio, June, 1975.
13. GERBERICH, W. W., "Hydrogen in Metals", ASM, Metals Park, Ohio, 1974, 115.
14. ERWIN, W. E., BERNSTEIN, I. M. and THOMPSON, A. W., unpublished research, 1976.
15. THOMPSON, A. W. and WEIHRAUCH, P. F., Scripta. Met., 10, 1976, 205.

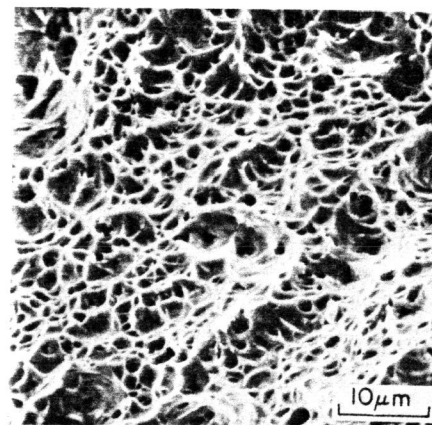


Figure 1 Scanning Electron Microscope (SEM) View of Microvoid Coalescence in Hydrogen-Charged 304L Austenitic Stainless Steel, with about 50% Loss in RA

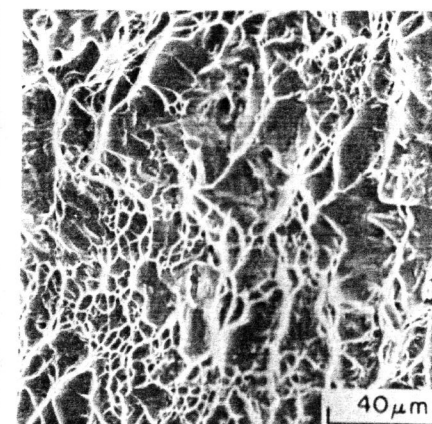


Figure 2 SEM Fractograph of Mixed Microvoid Coalescence and Tear Ridge Structures, in Hydrogen-Charged 21% Cr-6% Ni-9% Mn Stainless Steel, with about 40% Loss in RA

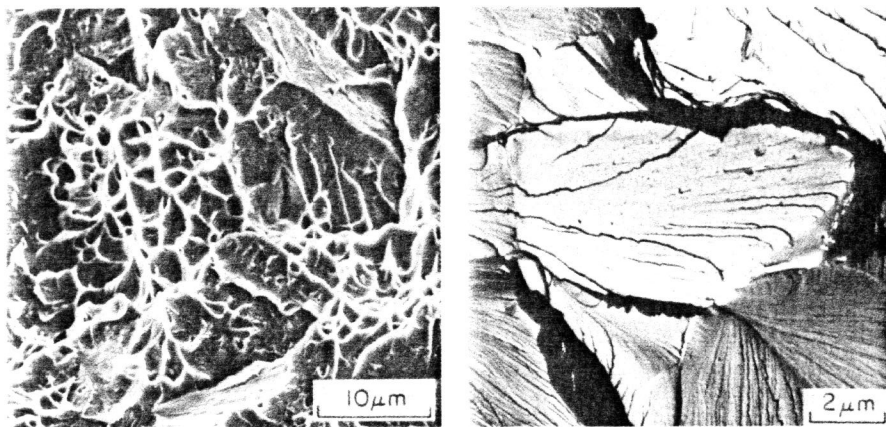


Figure 3 SEM Fractograph of Mixed Microvoid Coalescence and Cleavage-Like (Quasi-Cleavage) Fracture in Hydrogen-Charged PH 13-8 Mo, a Martensitic 13% Cr-8% Ni Steel, with a Loss of 60% of the Notch Strength

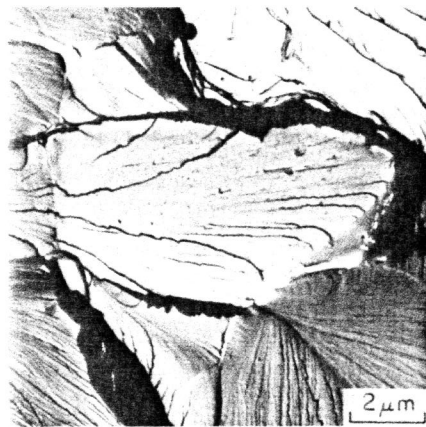


Figure 4 Replica Electron Micrograph of Cleavage Fracture in Hydrogen-Charged Cb-752 (Nb-10% W-2.5% Zr) with 75% Loss in Elongation. (Photograph Courtesy M. W. Mahoney)

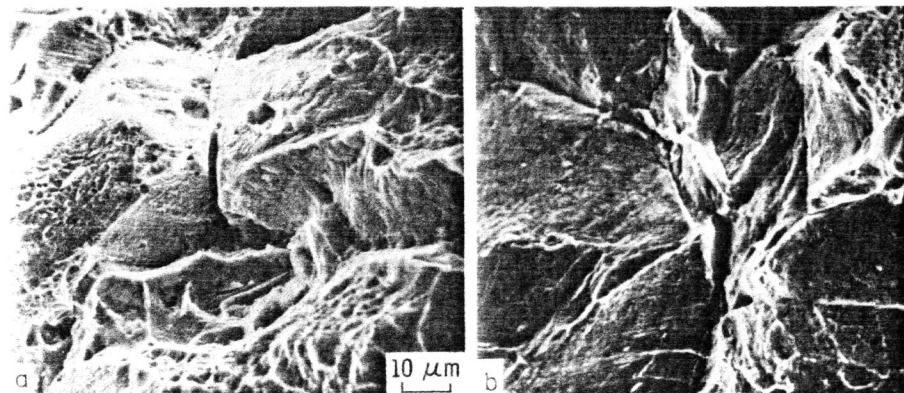


Figure 5 SEM Fractographs of Mixed Microvoid Coalescence and Intergranular Fracture in A-286 Precipitation-Strengthened Stainless Steel. (a) Without Hydrogen, (b) Hydrogen-Charged, about 50% Loss in RA, same Magnification as (a). From Thompson [8]