# DISLOCATION MOBILITY AND HYDROGEN – A BRIEF REVIEW

#### I. M. Robertson and H. K. Birnbaum

Department of Materials Science and Engineering, University of Illinois, Urbana, IL 61801 USA

## ABSTRACT

The effect of hydrogen on dislocation dynamics has been studied by applying the *in situ* deformation technique in a controlled environment transmission electron microscope. This approach allows the observations of the influence of hydrogen on the dislocation behavior to be observed in real time and at high spatial resolution. These dynamic experiments show that hydrogen enhances the mobility of dislocations in FCC, BCC and HCP ordered and disordered materials. The enhancement occurs for all dislocation types including partial and perfect lattice dislocations and grain boundary dislocations. These observations are attributed to the hydrogen atmosphere formed on the dislocation elastically shielding it form interactions with elastic stress centers. The connection between these microscopic observations and the macroscopic enhanced failure due to hydrogen will be made.

### 1. INTRODUCTION

The deleterious effects of hydrogen on the mechanical properties of iron and steels were first reported in 1875 as a reduction in the ductility and fracture stress due to the presence of hydrogen [1]. Since then hydrogen embrittlement of metals has been the subject of extensive study. The conclusions reached are that hydrogen embrittlement is fairly ubiquitous, occurring in most metals, with the exceptions of Cu, Au, Ag and W although they too may be susceptible under appropriate conditions, and that hydrogen embrittlement can be accompanied by a change in the fracture mode from ductile transgranular to either transgranular cleavage or "brittle" intergranular fracture, can increase the slip localization and planarity, and can in some metals, Nb, V, Zr, Ti and alloys based on them, result in the formation of a brittle hydride phase. Some of the many proposed mechanisms to explain the observed effects of hydrogen on deformation and fracture include the internal pressure mechanism, in which the pressure of hydrogen in voids generates sufficient stress to nucleate and propagate a crack [2, [3, [4]; hydrogen adsorption at crack tips and surface imperfections, which results in a reduction in the surface energy [5]; hydrogen reduction of the cohesive strength of the lattice - the decohesion model [6, [7]; film-induced cleavage [8, [9] hydrogen accumulation at precipitates and second phases, which results in dislocation generation or crack nucleation and propagation [10]; stress-induced nucleation, growth and cleavage of a brittle hydride [11, [12, [13]; hydrogen reduction in the stacking-fault energy [14, [15], which increases slip planarity [16, [17, [18]; hydrogen stabilization and increase in the density of strain-induced vacancies, which leads to the formation of microcracks or microvoids [19]; hydrogen adsorption induced dislocation injection from surfaces [20]; and hydrogen-enhanced localized plasticity - the HELP mechanism [21, [22]. In situations impractical for establishing high internal hydrogen pressures in voids, only three mechanisms are considered viable: the stress-induced formation of hydrides and their subsequent cleavage, the HELP, and the decohesion mechanism. Based on the evidence available it appears that it is highly unlikely that any one of these mechanisms is capable of explaining all the observations and it is most likely that more than one operates. It is also possible that one mechanism will dominate initially but as conditions change this may change too.

In this paper a brief review of the experimental evidence for hydrogen enhancing dislocation motion is presented; detailed reviews of this [22] and the other mechanisms can be found elsewhere [6].

In most investigations of hydrogen embrittlement there is generally evidence of plasticity in the form of tear ridges and dimples on fracture surfaces [23, [24], and indirectly through the influence of hydrogen on the macroscopic stress-strain response [25, [26, [27, [28]. The debate is over when the dislocation activity occurs and its correlation with hydrogen embrittlement. Advocates of the decohesion mechanism postulate that any signs of plasticity are an after effect of the embrittlement process and are not intrinsic to the failure process [29]. Oriani and Josephic attributed their observed hydrogen-enhanced relaxation rate to a decrease in the internal stress caused by hydrogen assisted decohesive nucleation and growth of microvoids, which caused the generation of dislocations. Beachem [23] was the first to offer an alternate explanation in that hydrogen enhanced rather than retarded the motion of dislocations. Since then there has been a significant amount of evidence supporting the claim that hydrogen enhances the mobility of dislocations with the most direct experimental evidence coming from active in situ deformation experiments in a controlled environment transmission electron microscope; the details of these experiments can be found in ref. [22] Over a period of some twenty years Birnbaum, Robertson and coworkers studied the influence of hydrogen on the deformation response in a wide range of fcc, bcc, and hcp disordered and ordered metallic systems dynamically in the TEM. A common feature in all materials investigated was that hydrogen enhanced the mobility of the dislocations even in systems in which hydride formation was anticipated and observed [13]. Enhanced dislocation velocities were observed for perfect screw and edge dislocations, partial dislocations and grain boundary dislocations. The images shown in figure 1 show the change in position of dislocations that are mobile in the grain boundary plane as a function of increasing hydrogen content. Prior to the introduction of hydrogen to the controlled environment transmission electron microscope, and hence the specimen, these dislocations were at rest but under stress [30]. Although all dislocations moved, the distance they moved and the hydrogen pressure at which this occurred varied for each

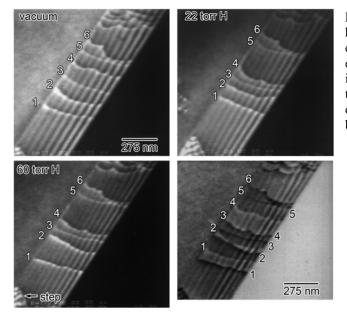


Figure 1. Effect of introducing hydrogen into the controlled environment transmission electron microscope and hence into the 310S stainless steel on the motion of extrinsic dislocations in a grain boundary.

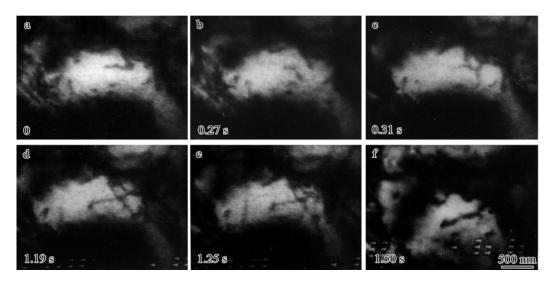


Figure 2. Effect of hydrogen on dislocations contained with a cell structure.

dislocation; this is the same as for lattice dislocations. The external hydrogen pressure is indicated although it should be appreciated that the input fugacity is several orders of magnitude greater because of dissociation and ionization of the gas molecule by the electron beam [31]. Introducing hydrogen to a series of moving dislocations causes an increase in the velocity by as much as a factor of two [13].

In the dynamic TEM experiments, the enhancement of the dislocation velocity occurred away from the crack and even when no crack was present. In addition, the presence of hydrogen was observed to facilitate dislocation emission from dislocation cell wells away from any active crack, see Fig. 2 [32].

The enhancement of the dislocation velocity by hydrogen is attributed to the hydrogen atmosphere associated with the dislocation effectively shielding its interaction with elastic stress centers [21]. An expression of this effect is that the separation distance between dislocations in a pile-up should decrease and collectively they should move closer to the obstacle in the presence of hydrogen. This is shown in Fig. 3, in which a comparison image has been created by superimposing a negative image of the final configuration of the dislocations in 90 torr of hydrogen gas on the initial configuration (vacuum) [30]. All dislocations move closer together and closer to the obstacle.

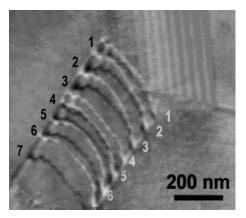


Figure 3. Impact of 90 torr of hydrogen gas on the dislocation configuration in a pile-up at a grain boundary in 310S stainless steel. White dislocations show position in hydrogen and black dislocations shown initial positions.

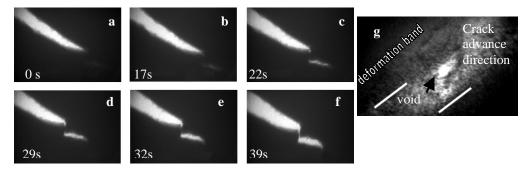


Figure 4. Crack advance in IN903 due to the introduction of hydrogen (a-f). The crack was initially under load but stationary prior to introduction of hydrogen. (g) Void formation in a deformation band ahead of the advancing crack.

Birnbaum, Robertson and coworkers also studied the effect of hydrogen on the propagation of cracks in the thicker non-transparent regions of the specimens. Introduction of hydrogen to a stressed but stationary crack caused thinning ahead of the crack, formation of a void or microcrack, and crack extension through linkage of these microcracks. Removing the atmosphere from the cell and from the specimen caused crack propagation to stop. Reintroducing the gas caused the crack advance to restart. An example of this is shown for IN903 in Figure 4. As can be seen in the figure, thinning occurs ahead of the crack, then a microcrack opens, and crack advance occurs through linkage of the microcrack and the main crack. Examination of the deformation region ahead of the active crack shows an intense deformation band in which a void has formed and grown, Fig. 4e.

A criticism of the HELP mechanism is the link between enhanced plasticity and hydrogen-enhanced failure. Recently, Sofronis and coworkers [33] have investigated the effect of hydrogen on the bifurcation of a homogeneous deformation in a plane-strain tension specimen to either shear band localization or necking bifurcation. It is important to appreciate that shear band bifurcation is a precursor to materials failure. This theoretical study showed that hydrogen-induced softening and lattice dilatation can cause shear localization in a material that exhibits a positive work hardening coefficient. Such a bifurcation cannot occur in a work-hardened material subjected to plane strain uni-axial tension in the absence of hydrogen. They also demonstrated that hydrogen reduces the macroscopic strain at which necking bifurcation takes places. These observations provide the link between the microscopic observation of enhanced localized dislocation activity and the macroscopic material response.

## Acknowledgements

We would like to acknowledge the work of the graduate and postdoctoral students who made this paper possible. The microscopy presented in this work was performed in the Center for Microanalysis of Materials at the University of Illinois which is partially supported by the U.S. Department of Energy under grant DEFG02-91-ER45439. This material is based upon work supported by the U.S. Department of Energy, Division of Materials Sciences under Award No. DEFG02-91ER45439, through the Frederick Seitz Materials Research Laboratory at the University of Illinois at Urbana-Champaign.

- Johnson, W.H., On some remarkable changes produced in iron and steel by the action of hydrogen and acids. Proc. Roy. Soc. London, 23: p. reproduced in "Hydrogen damage": Ed. Cedric D. Beachem, American Society for Metals, Ohio, 1977. 1875.
- 2. Zapffe, C., Discussion of Metal Arc Welding of Steels by S. A Herres. Transactions, American Society for Metals, **39**: p. 191- 192 1947.
- 3. Bernstein, I.M., The role of hydrogen in the embrittlement of iron and steel. Materials Sci. Engng., **6**(1): p. 1-19 1970.
- 4. Tien, J.K., et al., Hydrogen transport by dislocations. Metall. Trans A, **7A**(6): p. 821-829 1976.
- 5. Petch, N.J., Lowering of the fracture stress due to surface adsorption. Philosophical Magazine, 1(8): p. 331 335 1956.
- 6. Oriani, R.A., Hydrogen-the versatile embrittler. Corrosion, **43**(7): p. 390-7 1987.
- 7. Chen, X.G.W.W., The kinetics and micromechanics of hydrogen-assisted cracking in Fe-3 pct Si single crystals. Metall. Trans. A, Phys. Metall. Mater. Sci., (1): p. 59-70 1991.
- 8. Pasco, R.W., K. Sieradzki, and P.J. Ficalora, A surface chemistry kinetic model of gaseous hydrogen embrittlement. Scripta Metallurgica, **16**(7): p. 881-3 1982.
- 9. Sieradzki, K., Kinetic aspects of slow crack growth in the gaseous hydrogen embrittlement of steels. J. Mater. Sci., **14**(11): p. 2703-8 1979.
- 10. Pressouyre, G.M., Trap theory of hydrogen embrittlement. Acta Metall., **28**(7): p. 895-911 1980.
- 11. Westlake, D.G., Habit planes of zirconium hydride in zirconium and zircaloy. J.Nucl. Mater., **26**(2): p. 208-216 1968.
- 12. Birnbaum, H.K., Mechanical properties of metal hydrides. J. Less-Common Met., **104**(3): p. 31 41 1984.
- 13. Shih, D.S., I.M. Robertson, and H.K. Birnbaum, Hydrogen embrittlement of alpha titanium: in situ TEM studies. Acta Metall., **36**(1): p. 111-24 1988.
- 14. Windle, R.H. and G.C. Smith, The effect of hydrogen on the plastic deformation of nickel single crystals. Mater. Sci. J., **2**: p. 187-191 1968.
- 15. Cornet, M., M.F. Trichet, and S. Talbot-Bernard, Influence of hydrogen on plastic deformation and fracture of iron, studied by electron microscopy and Auger spectrography. *Memoires Scientifiques de la Revue de Metallurgie*, **74**: p. 307 -316 1977.
- 16. Tang, X. and A. Thompson, Hydrogen effects on slip character and ductility in Ni-Co alloys. Mater. Sci. Engng. A, A186(1-2): p. 113-119 1994.
- 17. Bernstein, I.M. Role of microstructure and the environment on dislocation behavior. in *Micromechanics of Advanced Materials. Symposium in Honor of Professors James C.M.Li`s 70th Birthday. Proceedings.* 1995.
- Ulmer, D.G. and C.J. Altstetter, Hydrogen-induced strain localization and failure of austenitic stainless steels at high hydrogen concentrations. Acta Metall. Mater., 39(6): p. 1237-48 1991.
- Nagumo, M. and H. Matsuda, Function of hydrogen in intergranular fracture of martensitic steels. Phil. Mag. A, 82(17-18): p. 3415-3425 2002.
- 20. Lynch, S.P., Mechanisms of hydrogen-assisted cracking. Met. Forum, **2**(3): p. 189-200 1979.
- Birnbaum, H.K. and P. Sofronis, Hydrogen-enhanced localized plasticity-a mechanism for hydrogen-related fracture. Mater. Sci. Eng. A, Struct. Mater., Prop. Microstruct. Process., A176(1-2): p. 191-202 1993.

- 22. Robertson, I.M., The effect of hydrogen on dislocation dynamics. Eng. Fracture Mech., **68**(6): p. 671-92 2001.
- 23. Beachem, C.D., A new model for hydrogen -assisted cracking (hydrogen embrittlement). Metallurgical Transactions A, **3**: p. 437 451 1972.
- 24. Yeh, M.S. and J.H. Huang, Internal hydrogen-induced subcritical crack growth in Ti-6Al-4V. Scr. Mater., **36**(12): p. 1415-21 1997.
- 25. Oriani, R.A. and P.H. Josephic, Hydrogen-enhanced load relaxation in a deformed medium carbon steel. Acta Metallurgica, **27**: p. 997 1005 1979.
- 26. Abraham, D.P. and C.J. Altstetter, Hydrogen-enhanced localization of plasticity in an austenitic stainless steel. Metall. Mater. Trans. A, Phys. Metall. Mater. Sci., **26A**(11): p. 2859-71 1995.
- 27. Sirois, E. and H.K. Birnbaum, Effects of hydrogen and carbon on thermally activated deformation of nickel. Acta Metal. et Mater., **40**(6): p. 1377-1385 1992.
- 28. Lunarska, E., Effect of hydrogen on relaxation phenomena in pure iron. Scripta Metallurgica, **11**: p. 283-287 1977.
- 29. Oriani, R.A. and P.H. Josephic, Hydrogen-enhanced load relaxation in a deformed medium-carbon steel. Acta Metal. et Mater., **27**: p. 997-1005 1979.
- 30. Ferreira, P.J., I.M. Robertson, and H.K. Birnbaum, Hydrogen effects on the interaction between dislocations. Acta Mater., **46**(5): p. 1749-57 1998.
- 31. Bond, G.M., I.M. Robertson, and H.K. Birnbaum, On the determination of the hydrogen fugacity in an environmental cell TEM Facility. Scripta Metallurgica, **20**(5): p. 653-658 1986.
- 32. Robertson, I.M. and H.K. Birnbaum, HVEM study of hydrogen effects on the deformation of nickel. Acta Metallurgica, **34**(3): p. 353-366 1986.
- 33. Liang, Y., P. Sofronis, and N. Aravas, On the effect of hydrogen on plastic instabilities in metals. Acta Mater., **51**: p. 2717 2730 2003.