



LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

LLNL-JRNL-856660

Hydrogen embrittlement. One dislocation at a time.

V. V. Bulatov, W. Cai

October 31, 2023

Nature Materials

Disclaimer

This document was prepared as an account of work sponsored by an agency of the United States government. Neither the United States government nor Lawrence Livermore National Security, LLC, nor any of their employees makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States government or Lawrence Livermore National Security, LLC. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States government or Lawrence Livermore National Security, LLC, and shall not be used for advertising or product endorsement purposes.

Untangling hydrogen embrittlement, one dislocation at a time

Tiniest atom in Nature, hydrogen is pervasive and sneaky. When they come in contact with a metal, hydrogen atoms, either from gas or liquid sources, rush into the solid and squeeze through the narrow spaces between the host metal atoms. Being chemically active, atomic hydrogen can potentially bind to either host or impurity atoms, forming hydrides and hence changing material properties. Metals, well known and widely used in industry for their strength and ductility, can become dangerously brittle when exposed to hydrogen. Hydrogen embrittlement – loss of ductility leading to catastrophic failure of a load-bearing part – is a serious problem for a wide range of industries. For example, hydrogen produced when water molecules break down in coolants used in a nuclear reactor can result in sudden failure of its pressure vessel. In another example, while blending hydrogen gas in natural gas pipelines provides a promising pathway for transitioning into the hydrogen economy, it could also lower fatigue resistance of the pipeline steel, making it more susceptible to crack growth due to cyclic loading resulting from pressure fluctuations in the pipeline. Hydrogen embrittlement can be similarly important in other industrial applications [1].

Remarkably, it still remains unknown exactly why hydrogen makes a metal brittle. This is not for lack of trying as many theories and models, often conflicting and highly debated, have developed over many decades of hydrogen research [2]. Perhaps the only statement that most practitioners could agree on is that loss of ductility in many metals has something to do with how hydrogen interacts with dislocations – ubiquitous line-shaped crystal defects responsible for the ductility of a metal. It is the motion of dislocations that causes a crystal to slide along its atomic planes resulting in an irreversible change of the material's shape, i.e. crystal plasticity. Generally, dislocations are highly mobile in ductile/plastic crystals and less mobile or even immobile in brittle crystals. Yet, controversially, a well-known model of hydrogen-assisted local plasticity (HELP) relates loss of ductility precisely to an enhancement in dislocation mobility due to hydrogen [3]. The key idea of HELP is that, by making dislocation motion easier, hydrogen promotes slip localization resulting in accumulation of local atomic misfit and potentially dangerous stress concentrations. Such local stress accumulation can at times lead to initiation of a crack threatening material's integrity. Governed by weak link statistics, development of an initial stress concentrator into a catastrophic failure is notoriously difficult to predict and control. In addition to HELP model not being universally accepted, debates continue as to the nature of atomic scale mechanisms by which hydrogen assists dislocation motion. Or even if any such assistance is real [ref]. Indeed, theoretical arguments and, indirectly, experimental observations have been presented both for an enhancing and inhibiting role of hydrogen in dislocation motion.

In [4] the authors present perhaps the first ever unambiguous experimental observations of hydrogen enhanced dislocation mobility in iron. Being the majority element in industrial steels, iron in its elemental form arranges its atoms in a body-centered cubic (BCC) lattice. In BCC metals, the screw dislocations (with line direction parallel to the Burgers vector) are known to control the plastic deformation behavior of the material, and are the focus of the authors' attention. Taking abundant precaution, the authors painstakingly harvest screw dislocations in

configurations most conducive for direct *in situ* observations in an electron microscope. Magnified millionfold, they measure, observe and photograph – in real time – how much mechanical force it takes to start a dislocation moving and how far it moves when the metal is charged (supplied) with atomic hydrogen and when it is hydrogen-free. In their experiments the authors establish an unprecedented level of control over the motion of individual dislocations. Perhaps the most interesting and convincing is their observation that hydrogen enhanced dislocation mobility is reversible: high mobility in the presence of hydrogen recovers back to the reference state of low dislocation mobility once all hydrogen is removed. The recovery is not immediate and is facilitated by forcing a dislocation to move back and forth under oscillating loads, thus suggesting that hydrogen binds to the dislocation and is reluctant to let it go. Consistent with previous suggestions [5], the authors present a theoretical model for the mechanism by which hydrogen interacts with a screw dislocation and makes its motion easier by lowering the energy barrier for kink-pair nucleation,. Further theoretical studies are clearly needed to fully explain the observed phenomenon, e.g. going beyond the empirical potential model employed in this study and possibly using more accurate quantum mechanical methods [6]. The question of whether the HELP mechanism is responsible for hydrogen embrittlement remains open. Nevertheless the authors make an important and definitive step towards solving the overall puzzle: from here on it would be harder to speculate against the possibility that hydrogen can and does indeed enhance dislocation mobility in BCC metals such as iron.

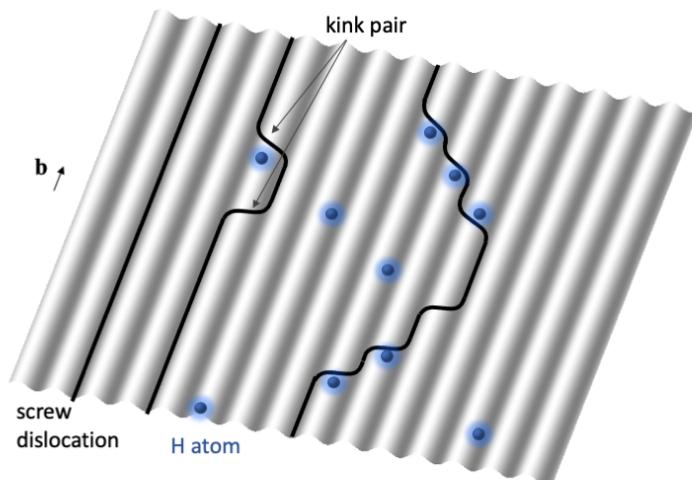


Figure 1. Schematic of dislocation motion in a crystal. The washboard surface represents energy barriers resisting dislocation motion through a crystal lattice. A screw dislocation (thick black line) is initially parallel to the Burgers vector \mathbf{b} . Presence of hydrogen atoms can facilitate nucleation of kink pairs by which the dislocation can begin to move forward.

References

1. Hydrogen embrittlement – effects on industry

2. O. Barrera, D. Bombac, Y. Chen, T. D. Daff, E. Galindo-Nava, P. Gong, D. Haley, R. Horton, I. Katzarov, J. R. Kermode, C. Liverani, M. Stopher, and F. Sweeney, Understanding and mitigating hydrogen embrittlement of steels: a review of experimental, modelling and design progress from atomistic to continuum, *J. Mater. Sci.* 53, 6251 (2018).
3. H.K. Birnbaum, P. Sofronis, Hydrogen-enhanced localized plasticity—a mechanism for hydrogen-related fracture, *Mater. Sci. Eng. A* 176, 191 (1994).

[ref] J. Song and W. A. Curtin, Atomic mechanism and prediction of hydrogen embrittlement in iron, *Nature Materials* 12, 145 – 151 (2012).

4. L. Huang, D. Chen, D. Xie, S. Li, Y. Zhang, T. Zhu, D. Raabe, E. Ma, J. Li, Z. Shan, Quantitative tests revealing hydrogen enhanced dislocation motion in α -iron, *Nat. Mater.* ##, ### (2023).
5. M. Itakura, H. Kaburaki, M. Yamaguchi, T. Okita, The effect of hydrogen atoms on the screw dislocation mobility in bcc iron: A first-principles study, *Acta Materialia*, 61, 6857 (2013).
6. P. P.P.O. Borges, E. Clouet, L. Ventelon, *Ab initio* investigation of the screw dislocation-hydrogen interaction in bcc tungsten and iron, *Acta Materialia*, 234, 118048 (2022).