Hydrogen-Enhanced Local Plasticity in Aluminum: An *Ab Initio* Study

Gang Lu,[1,2,*] Qing Zhang,[1] Nicholas Kioussis,[1] and Efthimios Kaxiras[2]
[1]*Department of Physics, California State University Northridge, Northridge, California 91330*
[2]*Department of Physics, Harvard University, Cambridge, Massachusetts 02138*
(Received 13 April 2001; published 8 August 2001)

Dislocation core properties of Al with and without H impurities are studied using the Peierls-Nabarro model with parameters determined by *ab initio* calculations. We find that H not only facilitates dislocation emission from the crack tip but also enhances dislocation mobility dramatically, leading to macroscopically softening and thinning of the material ahead of the crack tip. We observe strong binding between H and dislocation cores, with the binding energy depending on dislocation character. This dependence can directly affect the mechanical properties of Al by inhibiting dislocation cross-slip and developing slip planarity.

DOI: 10.1103/PhysRevLett.87.095501 PACS numbers: 62.20.Fe, 62.20.Mk

The mechanical properties of solids are not only a function of their intrinsic atomic structure, but also of the environment in which they exist. Small amounts of impurity atoms in the environment can drastically change the response of a solid to external loading. Hydrogen embrittlement is one of the most important and well-studied processes of environmental degradation of materials. After over a century of studies, the definitive mechanism of H embrittlement still remains unknown although significant progress has been made toward developing a detailed understanding of the problem. Three general mechanisms for H embrittement have been proposed: (1) formation of a hydride phase; (2) H-enhanced local plasticity; and (3) H-induced grain boundary weakening [1]. The underlying atomic processes and the relative importance of the three mechanisms, however, remain uncertain and controversial. In this paper, we study a key aspect of H embrittlement, referred to as H-enhanced local plasticity (HELP) [2], which has attracted much attention recently. There seems to be overwhelming evidence that plasticity is a fundamental contributor to H embrittlement of virtually all susceptible metals and alloys, including Al, the model material we consider in this paper [1,3,4]. The most dramatic experimental observation is that H increases dislocation mobility significantly under constant stress. This H-enhanced mobility is observed for screw, edge, and mixed dislocations as well as for isolated dislocations and dislocation tangles [1,5]. Other important experimental results include the observations of slip planarity [4,6] and strong binding between H and dislocation cores [1].

In contrast to the vast body of experimental evidence, theoretical studies of the HELP mechanism are scarce. To our knowledge, the only theoretical investigation of the HELP mechanism is based on finite-element modeling of elastic interactions among dislocations in the presence of H [7]. Although this approach was able to explain the H-enhanced dislocation mobility through the H-induced "elastic shield" effect, it completely ignores the effects of H on dislocation core structure and contains no information for the relevant atomic processes, which are critical for a complete understanding of the phenomenon. The purpose of our work is to provide a comprehensive understanding of the aforementioned experimental results based on an *ab initio* theoretical framework, which hopefully can set the stage for an atomistic theory of H embrittlement.

In this paper, we have used the recently developed semidiscrete variational Peierls-Nabarro (SVPN) model [8–10] with *ab initio* determined γ surfaces [11] and elastic constants. This approach has been shown to predict reliable dislocation core properties by comparing its predictions to direct atomistic simulations based on the same force law as that used for the γ-surface calculations [8,9]. The uniqueness of the approach when combined with *ab initio* calculations for the energetics is that it produces essentially an atomistic simulation for dislocation core properties without suffering from the uncertainties associated with empirical potentials. For example, atomistic simulations based on embedded atom method (EAM) potentials predict that dislocations in Al will dissociate into partials [12,13], while experimentally no such dissociation is observed [14], a discrepancy which can be traced to the fact the EAM potentials underestimate the intrinsic stacking fault energy [9].

In the SVPN approach, the equilibrium structure of a dislocation is obtained by minimizing the dislocation energy functional

$$U_{\mathrm{disl}} = U_{\mathrm{elastic}} + U_{\mathrm{misfit}} + U_{\mathrm{stress}} + Kb^2 \ln L\,, \quad (1)$$

with respect to the dislocation displacement density [8–10]. The γ surface determined from *ab initio* calculations enters the equation through the U_{misfit} term. We identify the dislocation configuration-dependent part of the elastic energy and the misfit energy as the core energy, $U_{\mathrm{core}} = U_{\mathrm{elastic}} + U_{\mathrm{misfit}}$, while the configuration-independent part of the elastic energy $Kb^2 \ln L$ is excluded because it is irrelevant in the variational procedure and it has no contribution to the dislocation core structure. The response of a dislocation to an applied stress is achieved by the minimization of the energy functional at the given value of the applied stress. An instability is reached when an optimal solution for the density distribution no longer exists, which is manifested numerically by the failure of the minimization procedure to convergence. The Peierls stress is then defined as the critical value of the applied stress giving rise to this instability.

In order to study the interaction between H and dislocations, we have carried out *ab initio* calculations of the γ surface with H placed at interstitial sites of the Al lattice. Specifically, we have used a large supercell containing six Al layers in the [111] direction with four atoms per layer to simulate a low concentration of H impurity ($\sim$4 at. %). Two sets of calculations were performed with H placed at the octahedral and the tetrahedral sites in Al. The *ab initio* calculations are based on the pseudopotential [15] plane-wave method with the generalized gradient approximation to the exchange-correlation functional [16]. A kinetic energy cutoff of 12 Ry for the plane-wave basis is used and a k-point grid consisting of $(8, 8, 4)$ divisions along the reciprocal lattice vectors is sampled for the Brillouin zone integration. In our calculations, the H atom is allowed to relax freely according to the Hellmann-Feynman force acting on it while Al atoms are restrained to move only along the [111] direction. Volume relaxation is performed for each sliding distance to minimize the tensile stress on the supercell. Table I lists the various stacking fault energies obtained for the pure Al and the Al + H systems. Although the octahedral site is more stable for H without sliding, the energy for the tetrahedral site can be lower for certain sliding vectors. Therefore the energies in Table I and Fig. 1 are given with respect to the lowest values of the two sites for each sliding. From Table I we find that H decreases the energy of the various stacking faults by up to 50%, which could change dislocation properties significantly. For example, one can predict that dislocations would be emitted more easily from a crack tip when H is present based on the lowering of the unstable stacking fault energy along the $[1\bar{2}1]$ direction [17]. In fact, this prediction is in accordance with atomistic simulations for Ni, where dislocations are found to be emitted more rapidly from a crack tip in the presence of H [18].

The γ surface for both the pure Al and the Al + H systems is shown in Figs. 1(a) and 1(b), respectively. The energy along various high symmetry directions is determined from *ab initio* calculations while the rest of the γ surface is obtained by fitting a symmetrized polynomial basis, which guarantees the correct rotational symmetry of the γ surface on the (111) plane. Comparing the two γ surfaces, we find an overall reduction in energy in the presence of H. In order to understand how H affects the elastic properties of Al, we also calculate the various elastic constants for both the pure Al and the Al + H systems using *ab initio* approaches. We used a smaller unit cell with only four Al atoms and one H impurity to facilitate these calculations, and find that, even at such a high concentration of H, the prelogarithmic elastic energy factors entering the model [9] change only by a few percent at most [19].

Having determined all the necessary parameters that enter the model, we can start to investigate the core properties for various dislocations in Al. We have studied screw (0°), 30°, 60°, and edge (90°) dislocations. The Peierls stress for these dislocations is shown in Table II. We find that the Peierls stress, which is the minimum stress to move a stationary dislocation, is reduced by more than an order of magnitude in the presence of H. Moreover this H-enhanced mobility is observed for screw, edge, and mixed

TABLE I. Fault vectors and energies (J/m^2) for four important stacking faults of the pure Al and the Al + H systems.

	Vector	Al	Al + H
Intrinsic stacking	$1/6[12\bar{1}]$	0.164	0.103
Unstable stacking	$1/10[12\bar{1}]$	0.224	0.126
Unstable stacking	$1/4[101]$	0.250	0.132
Run-on stacking	$1/3[12\bar{1}]$	0.400	0.310

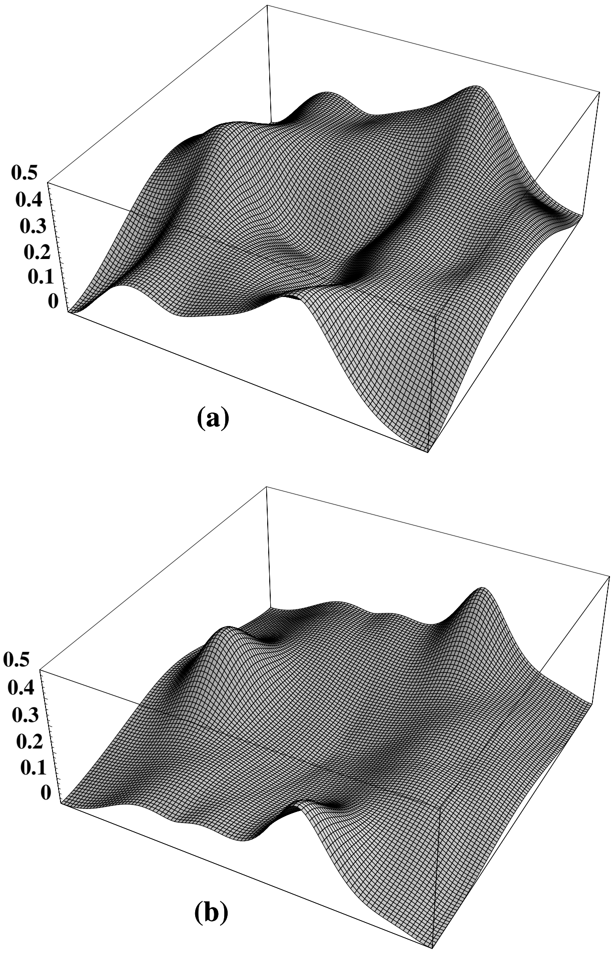

FIG. 1. The γ surfaces (J/m^2) for displacements along a (111) plane for (a) pure Al and (b) Al + H systems. The corners of the plane and its center correspond to identical equilibrium configurations, i.e., the ideal lattice. The two energy surfaces are displayed in exactly the same perspective and on the same energy scale to facilitate comparison of important features.

TABLE II. Peierls stress (σ_p, MPa), core energies (E_{core}, eV/Å) for the four dislocations in the pure Al and the Al + H systems and binding energy (E_b, eV/atom) for the four dislocations.

		Screw	30°	60°	Edge
σ_p	Al	254	51	97	3
	Al + H	1.7	1.2	1.4	0.3
E_{core}	Al	−0.08	−0.11	−0.17	−0.20
	Al + H	−0.14	−0.18	−0.27	−0.32
E_b		0.06	0.07	0.10	0.12

dislocations, which is compatible with the experimental results. Not only is our calculation the first successful attempt to explain HELP associated with individual dislocation behavior, it also invalidates the perception that the only plausible explanation of HELP must be based on elastic interactions among dislocations and that dislocation-lattice interaction is not important [1]. On the contrary, we find the dislocation-lattice interaction to be very important and that the dislocation core structure is responsible for the observed H-enhanced dislocation mobility. Our result, however, does not exclude the possibility that dislocation-dislocation interactions do play a role in HELP [7].

Other important experimental results that any theory of H embrittlement must explain are the observed H trapping in dislocation cores and the H-induced slip planarity. To this end, we have calculated the energetics of dislocations for the pure Al and the Al + H systems. The results are shown in Table II. We remind the reader that E_{core} listed here is only the displacement density dependent part of the total energy, excluding the large positive elastic term $Kb^2 \ln L$ which renders the total energy positive [9]. The binding energy of H is defined as the difference between dislocation core energies with and without the presence of H. From these results we find that there is strong binding between H and dislocation cores and that H is attracted (trapped) to dislocation cores to lower the core energies. More importantly, we find that the binding energy is a function of dislocation character, with edge dislocations having the greatest and screw dislocations having the lowest binding energy, respectively. For a mixed dislocation, we find that the binding energy increases with the amount of edge component. These results have significant consequences for the experimentally observed inhibition of cross-slip and slip planarity in the presence of H. Experiments show that in the presence of H slip is confined to the primary slip plane and dislocation cross-slip is restricted, which leads to the observed slip planarity. On the other hand, removal of H from the sample allows a dislocation segment on the primary plane to reorient towards the screw orientation and to complete the cross-slip process [20]. It was believed from the experimental evidence that any process, such as cross-slip, that increases the screw component length at the expense of the edge component will be made more difficult by the presence of H [20]. Our results for the binding energy of H in dislocation cores are the key for understanding these experimental observations: Since the edge dislocation has twice the binding energy as the screw, it will cost much more energy for an edge dislocation in the presence of H to transform to a screw dislocation in order to cross-slip. In the same vein, it costs more energy for a mixed dislocation to transfer its edge component to a screw dislocation for cross-slip. In other words, H can stabilize the edge component of a mixed dislocation and inhibit the dislocation cross-slip process, leading to the observed slip planarity. It is also interesting to point out that our results for the binding energy of H are in qualitative agreement with those from atomistic simulations of H in Ni, where the binding energies of H to edge dislocations and screw dislocations are found to be 0.12 and 0.09 eV per H atom, respectively [21].

To further understand these results, we calculate the displacement density for the various dislocations which is presented in Fig. 2. We find that although the intrinsic stacking fault energy is reduced by almost 40% in the presence of H, dislocations are not dissociated into partials [22]. This result is important because it discredits the argument that the observed restriction of cross-slip may result from the increased separation of partials due to the reduction of the stacking fault energy [23]. In fact, our result is consistent with the experimental findings that no widely spaced dislocation partials were ever observed in transmission electron microscopic studies of Al containing large concentrations of H [20]. Therefore, we believe that the observed slip planarity and restriction of cross-slip is due to the strong binding between H and the edge component of dislocations, not only for Al, but possibly also for other metals [4,20,24].

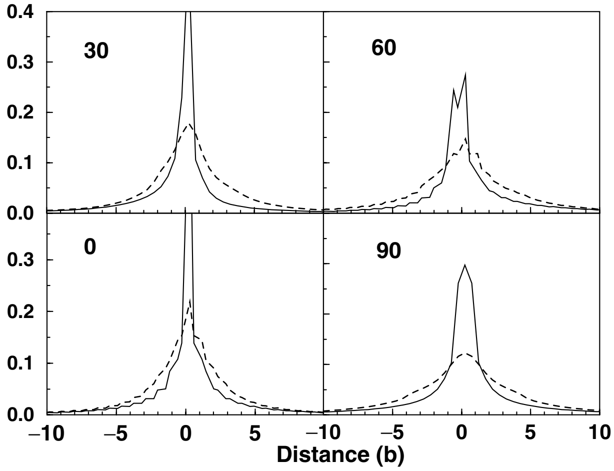

FIG. 2. Dislocation displacement density for four dislocations (clockwise): screw (0°), 30°, 60°, and edge (90°) for the pure Al (solid lines) and the Al + H (dashed lines) systems.

Based on the experimental observations and the results we obtained in this study, we identify the following processes which we believe could lead to the H-induced fracture. (a) H is attracted to crack tips: Application of external stress produces local concentration of tensile stress in the vicinity of cracks, which attracts H since H prefers to stay in slightly enlarged interstitial sites. (b) Thinning and softening: These segregated H impurities at the crack tip can facilitate dislocation generation and enhance dislocation mobility, which will lead to extensive plastic deformation in front of the crack, causing thinning and softening of the material ahead of the crack. (c) Lowering fracture stress: The thinning and softening processes, along with the localization of slip due to the inhibition of cross-slip, allow the crack to propagate at lower stress levels, prior to general yielding away from the crack tip. Although our calculations concern Al, we believe that the results are also applicable to other metals. Furthermore we should point out that the above processes are not likely to be the only mechanism operating in H embrittlement [5], but are the most relevant processes in line with the HELP theory.

In summary, we have studied the interaction of interstitial H with dislocations in Al using the SVPN model with *ab initio* determined parameters. We find that H can lower the Peierls stress of dislocations by more than an order of magnitude, strongly supporting the HELP model. We also find there is a strong binding of H to dislocation cores and that the binding energy is a function of dislocation character. Our findings explain the experimentally observed restriction of the cross-slip process and slip planarity in the presence of H. The dislocations do not dissociate into partials even though the intrinsic stacking fault energy is reduced by 40% in the presence of H. Finally, based on the results of our calculations, we identify the processes which could lead to H embrittlement.

The work at California State University Northridge was supported by Grant No. DAAG55-97-1-0093 from the U.S. Army Research Office. The work at Harvard University was supported by Grant No. F49620-99-1-0272 from the U.S. Air Force Office for Scientific Research. We would like to thank Petros Sofronis and Daniel Orlikowski for useful discussions.

---

*Email address: glu@cmt.harvard.edu

[1] S. M. Myers *et al.,* Rev. Mod. Phys. **64**, 559 (1992), and references therein.
[2] C. D. Beachem, Metall. Trans. **3**, 437 (1972).
[3] S. P. Lynch, J. Mater. Sci. **21**, 692 (1986); T. Matsumoto and H. K. Birnbaum, Trans. Jpn. Inst. Met. **21**, 493 (1980).
[4] F. Zeides, Ph.D. thesis, University of Illinois, 1986.
[5] H. K. Birnbaum and P. Sofronis, Mater. Sci. Eng. A **176**, 191 (1994).
[6] D. G. Ulmer and C. J. Altstetter, Acta Metall. Mater. **39**, 1237 (1991).
[7] P. Sofronis and H. K. Birnbaum, J. Mech. Phys. Solids **43**, 49 (1995).
[8] V. V. Bulatov and E. Kaxiras, Phys. Rev. Lett. **78**, 4221 (1997).
[9] G. Lu, N. Kioussis, V. V. Bulatov, and E. Kaxiras, Phys. Rev. B **62**, 3099 (2000).
[10] G. Lu, N. Kioussis, V. V. Bulatov, and E. Kaxiras, Philos. Mag. Lett. **80**, 675 (2000).
[11] When a crystal is cut along its slip plane and the upper half is displaced relative to the lower by a vector $\vec{f}$, the energy increase per unit area is defined as γ and the energy surface $\gamma(\vec{f})$, with $\vec{f}$ spanning the entire slip plane, is called the γ surface.
[12] V. V. Bulatov, O. Richmond, and M. V. Glazov, Acta Mater. **47**, 3507 (1999).
[13] M. J. Mills, M. S. Daw, and S. M. Foiles, Ultramicroscopy **56**, 79 (1994).
[14] M. S. Duesbery, *Dislocations in Solids,* edited by F. R. N. Nabarro (North-Holland, Amsterdam, 1989), Vol. 8, p. 67.
[15] D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).
[16] J. P. Perdew, Phys. Rev. B **33**, 8822 (1986).
[17] J. R. Rice, J. Mech. Phys. Solids **40**, 239 (1992).
[18] M. S. Daw and M. I. Baskes, in *Chemistry and Physics of Fracture,* edited by R. M. Latanision and R. Jones (Martinus Nijhoff Publishers, Dordrecht, The Netherlands, 1987), p. 196.
[19] The prelogarithmic elastic energy factors K_e and K_s for Al (Al + H) are 7.00 (7.13) GPa and 4.59 (4.68) GPa, respectively.
[20] P. J. Ferreira, I. M. Robertson, and H. K. Birnbaum, Acta Mater. **47**, 2991 (1999).
[21] J. E. Angelo, N. R. Moody, and M. I. Baskes in *Hydrogen Effects in Materials,* edited by A. W. Thompson and N. R. Moody (TMS, Warrendale, PA, 1996), p. 161.
[22] The small double peak in the 60° dislocation does not suggest dissociation. It actually comes from the nonequivalent atomic spacing of the lattice (see Ref. [9]).
[23] D. P. Abraham and C. J. Altstetter, Metall. Mater. Trans. A **26**, 2859 (1995).
[24] P. J. Ferreira, I. M. Robertson, and H. K. Birnbaum, Mater. Sci. Forum **207**, 93 (1996).