

Hydrogen Embrittlement of Aluminum: The Crucial Role of Vacancies

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(Received 22 November 2004; published 18 April 2005)

We report first-principles calculations which demonstrate that vacancies can combine with hydrogen impurities in bulk aluminum and play a crucial role in the embrittlement of this prototypical ductile solid. Our studies of hydrogen-induced vacancy superabundant formation and vacancy clusterization in aluminum lead to the conclusion that a large number of H atoms (up to 12) can be trapped at a single vacancy, which overcompensates the energy cost to form the defect. In the presence of trapped H atoms, three nearest-neighbor single vacancies which normally would repel each other, aggregate to form a trivacancy on the slip plane of Al, acting as embryos for microvoids and cracks and resulting in ductile rupture along these planes.

DOI: 10.1103/PhysRevLett.94.155501

PACS numbers: 62.20.Fe, 62.20.Mk

Hydrogen degradation of the structural properties of solids, referred to as embrittlement, is a fundamental problem in materials physics. Despite intense studies, the definitive mechanism of H embrittlement in metals remains poorly understood. Four general mechanisms have been proposed: (i) formation of a hydride phase; (ii) enhanced local plasticity; (iii) grain boundary weakening and (iv) blister and bubble formation [1]. The underlying atomic processes and relative importance of the four mechanisms remain uncertain, and it is likely that a combination of these processes may contribute to embrittlement simultaneously. For these mechanisms to be operational, however, a critical local concentration of H is required, either to form a hydride phase or to initiate cracking at microvoids and grain boundaries. One of the outstanding problems in the current theories of hydrogen embrittlement is the lack of a comprehensive and coherent atomistic mechanism to account for the critical H concentrations at crack tips. Moreover, it is widely observed that H-enhanced dislocation mobility is a prelude to the embrittlement and that the fracture planes coincide with the slip plane of the material, which is not the typical situation [1]; how all these phenomena come about still remains a mystery. It is generally believed that dislocations are central to H embrittlement phenomena, and a large body of work has been dedicated to elucidate hydrogen-dislocation interaction and its consequences on embrittlement [1,2]. Vacancies, being ubiquitously present in solids and having the ability to act as impurity traps, could play a central role in the embrittlement process, but detailed arguments about this role or estimates of its relative importance are totally lacking.

Recent experiments on H-metal systems offer clues on the role that vacancies may play in H embrittlement. One set of experiments has established that H could induce superabundant vacancy formation in a number of metals, such as Pd, Ni, Cr, etc.[3,4]. The estimated vacancy concentration, C_V , in these systems can reach a value as high

as at 23% [3]. A conclusion drawn from these experiments is that H atoms, originally at interstitial positions in the bulk, are trapped at vacancies in multiple numbers with rather high binding energies. It was speculated that several (three to six) H atoms can be trapped by a single vacancy, with the highest number (six) corresponding to the number of octahedral sites around a vacancy in either the fcc or the bcc lattice [3]. Actually, we shall show below based on first-principles theoretical calculations that in Al, the prototypical simple metal and ductile solid, up to *twelve* H atoms can be trapped at a single vacancy site. The consequence of H trapping is that the formation energy of a vacancy defect is lowered by a significant amount, an energy that we define as the H-trapping energy. Such reduction in the vacancy formation energy could result in a drastic increase (10^7 fold for Fe) of equilibrium vacancy concentrations [5]. The superabundant vacancy formation in turn provides more trapping sites for H impurities, effectively increasing the apparent H solubility in metals by many orders of magnitude. For example, it was observed experimentally that about 1000 at. ppm of H atoms can enter Al accompanied by vacancy formation at the surface under aggressive H charging conditions, which should be contrasted with the equilibrium solubility of H in Al of about 10^{-5} at. ppm at room temperature where the experiments were carried out [6]; this is a staggering change of *eight* orders of magnitude in concentration. It was further observed that the H-vacancy defects clustered and formed platelets lying on the {111} planes, which directly lead to void formation or crack nucleation on the {111} cleavage planes [6].

In order to elucidate the complex nature of H-vacancy interaction and to shed light on experimental results, we have performed first-principles calculations to examine the energetics and electronic structure for the relevant H-vacancy complexes in Al. Because of the extremely low solubility of H in bulk Al, experiments are usually difficult and results are dependent on H charging condi-

tions; for such systems, first-principles calculations are particularly useful to complement experimental approaches. Our first-principles calculations are based on density functional theory with the VASP implementation [7] and ultrasoft pseudopotentials [8]. The local-density approximation (LDA) is used in all of our calculations, with checks based on the generalized gradient approximation (GGA) for selected cases. For Al, we find that LDA results are consistently closer to experimental values than GGA results, so here we will rely mainly on LDA numbers to draw physical conclusions. We employ a supercell containing 108 atomic sites in a simple cubic lattice to model bulk Al, with a $4 \times 4 \times 4$ reciprocal space grid in the supercell Brillouin zone and a plane-wave kinetic energy cutoff of 220 eV for the Al-H system. With these parameters, we obtain the formation energy of a single vacancy (0.66 eV) and the binding energy for the nearest-neighbor (NN) divacancy in pure Al (-0.06 eV) in excellent agreement with other theoretical [9] and experimental results [10] (Table I). We note that the NN divacancy formation energy is negative, implying that it is unstable compared to two isolated single vacancies. This counterintuitive result is due to charge redistribution in the neighborhood of the vacancy, which has been interpreted as formation of directional covalent or metallic bonds that stabilizes the single vacancy configuration against the formation of the divacancy [9,12].

Our main objective is to understand the atomistic mechanisms of H-vacancy interaction in Al. First we address the relative site preference of H in bulk Al. To this end, we have calculated the total energy of a single H atom situated near the vacancy site, or at interstitial tetrahedral and octahedral bulk sites which are as far as possible from the vacancy within the supercell. For H atoms, the tetrahedral interstitial site in bulk Al is slightly more favorable than the octahedral interstitial site by 0.07 eV. We find that the H atom prefers to occupy the vacancy site over the interstitial tetrahedral site in bulk by 0.40 eV. The corre-

TABLE I. The vacancy formation energy, ΔH_V^F ; the binding energy for the divacancy, $\Delta H_{2V}^b = 2\Delta H_V^F - \Delta H_{2V}^F$, where the last term is the formation energy of the divacancy. The total energy with a H atom occupying the octahedral interstitial site is set to zero, relative to which the total energy of a H atom occupying the tetrahedral interstitial site, E_T , and the total energy of a H atom trapped at a single vacancy, E_V are defined. The last two columns are LDA and GGA results from other theoretical calculations. All energies are given in eV. The experimental values marked by an asterisk have been called into question due to incorrect interpretations on the experimental part, see Ref. [9] for details.

	LDA	GGA	Exp.[10]	LDA	GGA
ΔH_V^F	0.66	0.54	0.67 ± 0.03	0.70 [9]	0.54 [9]
ΔH_{2V}^b	-0.06	-0.07	$0.2^*, 0.3^*$	-0.07 [9]	-0.08 [9]
E_T	-0.07			-0.05 [11]	-0.13 [11]
E_V	-0.47				-0.46 [11]

sponding experimental value is 0.52 eV [1], and theoretical results range from 0.33 eV to about 1 eV [11,13]. The lowest-energy position for the H atom in the presence of a vacancy is *not* at the geometric center of the vacancy site, but rather at an off-center position close to a tetrahedral site adjacent to the vacancy site [see Fig. 1(a)]. We also find that the H atom is negatively charged, consistent with the view that the H impurity can be regarded as a screened H^- ion in free-electron-like metals [14]. Previous studies based on the jellium model of Al have shown that as the jellium conduction electron density decreases, the excess charge buildup at the H atom is also reduced and the electrons of the H^- ion are less localized [14,15]. Therefore, the kinetic energy of the H^- electrons is lowered at the vacancy site where the conduction electron density is lower. At the same time, it is energetically favorable for the H^- ion to sit off center of the vacancy, to minimize the Coulomb interaction energy with the nearby Al ions.

Having established the stability of a single H atom at a single vacancy in Al, the ensuing question is whether multiple H atoms, in particular, H_2 molecules would be stable at this defect. This is an interesting problem on its own right, but it is also relevant to H_2 bubble formation that gives rise to H embrittlement. To examine the stability of an H_2 molecule at a vacancy site, we compare the binding energy of the H_2 unit at the vacancy and in vacuum. The binding energy E_b of the H_2 unit at a vacancy site is calculated as

$$E_b = E_c(V_{Al} + H_2) + E_c(V_{Al}) - 2E_c(V_{Al}H), \quad (1)$$

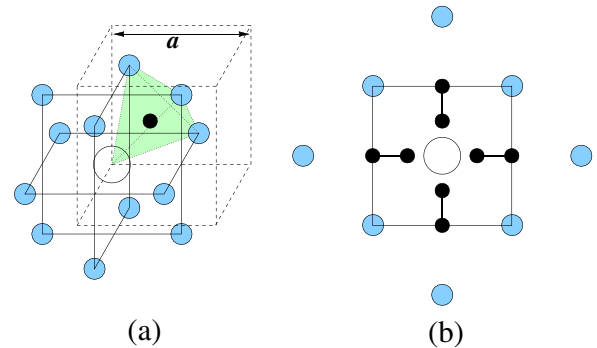


FIG. 1 (color online). Schematic representation of the environment of a vacancy in Al. (a) The vacancy as a large open circle and its 12 nearest neighbors as smaller gray (blue) circles, which lie on highlighted [100] planes. The cube in dashed lines represents the conventional cell of the fcc lattice of side a . A shaded tetrahedron with one corner at the vacancy site is also shown, and the geometric center of which corresponds to the lowest-energy site for a H interstitial atom (shown as black circle) in bulk Al. (b) The arrangement of four of the six H_2 molecules surrounding the vacancy, on a [100] plane, with the first- and second-nearest-neighbor Al atoms indicated. The other two molecules lie directly above and below the plane of the figure, along an axis perpendicular to this plane passing through the vacancy site. In both (a) and (b) the ions are placed at the ideal lattice sites, with the atomic relaxations not shown explicitly.

where $E_c(V_{\text{Al}} + \text{H}_2)$ is the cohesive energy of a system with an H_2 unit at the center of the vacancy, $E_c(V_{\text{Al}})$ is the cohesive energy of a system with a single vacancy in the absence of the H_2 unit, and $E_c(V_{\text{Al}}\text{H})$ is the cohesive energy of a system with a single H atom at the vacancy (in the off-center tetrahedral site). Interestingly, we find the this binding energy to be $+0.06$ eV, indicating a weak repulsion between the 2 H atoms in the H_2 unit at the vacancy site. This is to be compared to the binding energy of an H_2 molecule in vacuum, which is -6.67 eV. The positive binding energy of H_2 at the vacancy site does not imply that there is no bonding between the 2 H atoms; it simply states that these 2 H atoms would prefer to be trapped at two single vacancy sites *individually* rather than in the same vacancy site *as a pair*. The weakening of the H-H bond at the vacancy site is remarkable given the fact that each H atom in the H_2 unit in this situation is quite far away (2.6 Å) from the nearest Al ions.

We find that the equilibrium interatomic distance between the H atoms at the vacancy is 0.83 Å, 12% longer than the H_2 bond length (0.74 Å) of the molecule in vacuum; this is due to the partial occupation of antibonding states between the H atoms. This can be understood as follows: each H atom is associated with a doubly occupied bound state in the presence of conduction electrons, and hence is negatively charged. When the 2 H atoms approach each other, the two bound states split up into a bonding and an antibonding level. In contrast to what happens in vacuum, the screening of the conduction electrons reduces the bonding-antibonding energy splitting, and the antibonding level may be occupied by conduction electrons if the Fermi energy of the metal is high enough [15]. The occupation of antibonding states weakens the H_2 bond and increases the bond length. Our results agree qualitatively with the jellium model calculations which also found the H_2 binding energy to be positive and the bond length increased, ranging from 0.81 to 0.86 Å depending on the jellium density. In particular, for low jellium electron density (corresponding to the center of a vacancy site in Al), the binding energy was found to be $+0.02$ eV [16]. Similarly, one can calculate the binding energy of multiple H atoms trapped at a single vacancy site, which turn out to be positive as well. Based on these results, we conclude that if the single vacancy concentration C_V is greater than the H concentration C_H , each vacancy in equilibrium should contain no more than 1 H atom.

On the other hand, if C_H is greater than C_V , the question arises as to where will the extra H atoms be situated, at interstitial or at vacancy sites? Experimental measurements for the ratio C_H/C_V in Al range from 0.25 to 4, depending on H charging conditions, with the most probable value close to 1 [6]. To answer the above question, we have calculated the trapping energy E_{trap} of multiple H atoms at a single vacancy site, which is defined as

$$E_{\text{trap}}(n) = \frac{1}{n} [E_c(V_{\text{Al}} + n\text{H}) - E_c(V_{\text{Al}})] - [E_c^0(\text{H}) - E_c^0], \quad (2)$$

where $E_c(V_{\text{Al}} + n\text{H})$ is the cohesive energy of a system with n H atoms each situated at a single vacancy site, $E_c^0(\text{H})$ is the cohesive energy of bulk Al with a H atom at the tetrahedral interstitial site, and E_c^0 is the cohesive energy of the ideal bulk without H. A negative value for the trapping energy represents the energy gain when the H atoms are trapped at a single vacancy site relative to being dispersed at n different tetrahedral interstitial sites. The results for E_{trap} as a function of n are summarized in Fig. 2. Consistent with the binding energy calculations, it is energetically most favorable for each vacancy to trap a single H atom. At the same time, it is also energetically favorable for multiple H atoms to be trapped at a single vacancy site relative to being dispersed at interstitial sites as individual atoms. In fact, up to *twelve* H atoms can be trapped at a single vacancy in Al, twice the highest number of H atoms (six) that can be trapped in Fe [5]. The atomic arrangement of the 12 H atoms trapped at a single vacancy is indicated in Fig. 1(b). There are two H_2 units in each $\langle 100 \rangle$ direction surrounding the vacancy, and the bond length is 1 Å for all six units. The intermolecule distance in each direction is 3 Å, and the NN distance between H and Al in each direction is 2 Å (the lattice constant of Al is 3.99 Å). The ordered arrangement of the H atoms is necessary to minimize the electrostatic energy. The greater H-trapping capacity of Al compared to Fe, can be attributed to its larger lattice constant and more delocalized nature of electrons. It is observed that the volume change of the supercell owing to the H additions is negligible.

The fact that the H_2 units at a single vacancy site attract the conduction electrons from the edge of the vacancy, raises the interesting possibility that the covalent or metallic bonds between the first shell of NN Al ions around the vacancy site may be disrupted enough to permit a coalescence of multiple vacancies. To check this possibility, we carried out calculations for a number of relevant configurations. Specifically, we have examined: (i) two vacancies,

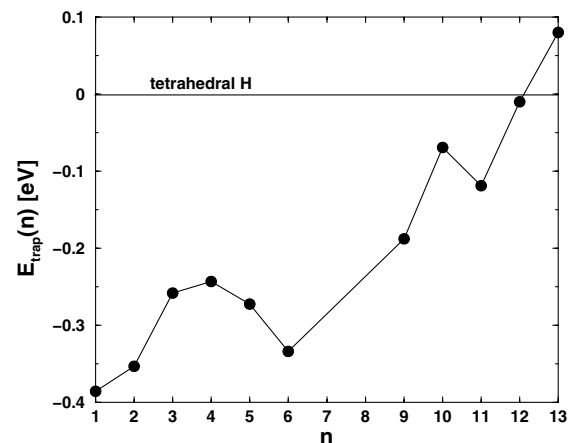
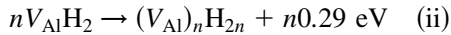
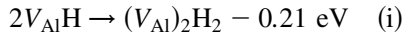


FIG. 2. Trapping energy per H atom in eV as a function of the number of H atoms being trapped at a single vacancy site. The zero energy corresponds to the energy of a H atom at the tetrahedral interstitial site.

each with 1 H atom, forming a NN divacancy with 2 H atoms trapped; (ii) n vacancies, each with 2 H atoms, forming a complex of NN multivacancies with $2n$ H atoms trapped, for $n = 2$ and 3. To summarize the results, we use the notation of chemical reactions:



where the last number in each equation represents the reaction enthalpy ΔH . A positive value of ΔH means the reaction is exothermic, that is, the process from left to right is energetically favorable. ΔH is defined as follows for reaction (i):

$$\Delta H = 2E_c(V_{\text{Al}}\text{H}) - E_c[(V_{\text{Al}})_2\text{H}_2] - E_c^0, \quad (3)$$

where $E_c[(V_{\text{Al}})_2\text{H}_2]$ is the cohesive energy of a system with 2 H atoms trapped at a divacancy, with analogous definitions for reaction (ii). Consistent with our earlier discussion, we find reaction (i) to be unfavorable (endothermic) because the effect of a *single* H atom on the covalent or metallic bonding of the NN Al atoms around the vacancy site is small and localized. On the other hand, reaction (ii) is favorable for $n = 2$ and 3, because the H_2 units can attract more conduction electrons from the nearby Al atoms, weakening the bonding among the NN Al atoms, which in turn drives the formation of multivacancies. The large energy gain in forming the trivacancy ($n = 3$) is of particular interest. First, it is consistent with the experimental observation that the single vacancy defects occupied by H atoms can coalesce to form platelets on $\{111\}$ planes of Al. Although our calculations primarily concern the formation of the trivacancy, it is likely that even larger vacancy clusters can also be formed based on the same mechanism. In support of this claim, we mention that the increase in positive enthalpy associated with reaction (ii) is linear in the number of vacancies for $n = 2$ and 3. Second, these vacancy clusters can serve as embryos of cracks and microvoids with local H concentrations much higher than the average bulk value.

Next we discuss the implications of our results on hydrogen embrittlement phenomena. It was generally believed that H-induced embrittlement in metals takes the form of plastic rupture rather than brittle fracture, consistent with the notion of H-enhanced local plasticity (HELP). It was widely observed that the fracture surface is along the active slip planes where shear localization occurs. For fcc metals, the slip planes are the $\{111\}$ planes. In many cases, microvoids open up along these active slip planes in front of the crack tip; these microvoids can open and close in response to the local stress. Plastic rupture occurs when these microcracks are joined to the crack tip, upon reaching the critical stress. Our results clearly suggest that H-enriched microvoids may be created along the slip planes by the coalescence of vacancies with trapped H. These microvoids can

be formed *only* in the presence of H, which produces an *additional* source of microcracks necessary for the H embrittlement. The fact that there is a strong binding between H and dislocation cores, and H can enhance dislocation motion along the slip planes [17], provide a means of rapid transport of H atoms to the crack front. On the other hand, the apparent lattice mobility of H atoms is also enhanced since multiple H atoms may be trapped at a single vacancy. All these vacancy-based mechanisms contribute to the H embrittlement as they increase the rate of crack growth. Finally, the significant H trapping at vacancies provides a scenario by which drastic increase of local H concentration may occur without improbable accumulation of H at bulk interstitial sites [5]. This new feature resolves the long-standing problem of how a sufficiently high H concentration can be realized to successfully induce H embrittlement in materials such as Al, where the equilibrium H concentration in bulk is extremely low.

We acknowledge the support from Grant No. F49620-99-1-0272 through the U.S. Air Force Office for Scientific Research.

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