

available solely with atomic cations suggests that materials with unit cells large enough to identify the maximum possible T_c , and the expected metal-insulator transition beyond this, may be accessible synthetically. □

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Computer simulation of hydrogen embrittlement in metals

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IT has been long known that hydrogen can substantially reduce the mechanical stability of transition metals under tensile stress^{1–3}. This phenomenon of ‘hydrogen embrittlement’ has important consequences for the safety of fusion reactors and for space technology; but there remains considerable uncertainty about its microscopic origin^{2,3}. Here we report the results of a study of fracture of hydrogen-loaded palladium under tensile stress which uses Parrinello–Rahman molecular dynamics based on a many-body alloy hamiltonian. A rather unexpected result is that the apparent hydrogen embrittlement results from a local enhancement of ductility in hydrogen-saturated regions of the metal which causes a reduction of the critical tensile stress at which failure occurs.

One of the oldest proposed mechanisms of hydrogen embrittlement is the ‘decohesion mechanism’ which associates this effect with a decreased metal bond strength in the presence of hydrogen^{4–7}. The ‘hydrogen-related phase change mechanism’ has been suggested as the origin of hydrogen embrittlement in those systems where a brittle hydride phase is stabilized by the presence of hydrogen and the crack-tip stress fields^{8,9}. The ‘hydrogen-enhanced local plasticity’ (HELP) mechanism postulates a ductility enhancement at crack tips which facilitates the initiation and propagation of fracture^{10–12}.

We elected to study the effect of hydrogen on the mechanical stability of Pd because this system shows a large variety of interesting effects when exposed to hydrogen, such as hydride formation and surface reconstruction, and has been studied extensively by *ab initio* techniques^{13–15}. To understand the microscopic processes associated with hydrogen-assisted crack formation, we used a molecular dynamics (MD) calculation¹⁶. This technique describes the evolution of the system in time by direct numerical solution of the equations of motion for individual atoms. We used the Parrinello–Rahman MD method^{17–19} to study specifically the elastic response (and mechanical stability) of bulk Pd to uniaxial tensile stress at different temperatures and concentrations of hydrogen. This approach provides the

framework for treating a canonical ensemble, exposed to an arbitrary stress field at a fixed temperature, by introducing 10 extra degrees of freedom for the coupling of the system to an external heat bath and a corresponding pressure reservoir. Specifically, this method can determine the deformations of the unit cell which occur during the fracture process, in response to an anisotropic stress field.

A precise description of atomic interactions is of critical importance to a successful description of the fracture process. In single-component systems with a close-packed structure, the embedded-atom method (EAM)^{20,21} has proved to be quite successful in describing structural and dynamical properties^{22,23}. Recently we developed a model many-body alloy (MBA) potential²⁴ based on *ab initio* calculations for alloy systems, and used this potential successfully to study the structure and dynamics of bulk Pd, clean and hydrogen-covered Pd surfaces at zero temperature²⁴ and the melting transition of Pd (ref. 25). The main advantage of the MBA over the EAM hamiltonian in alloys is that the MBA distinguishes neighbouring sites by both the atom type and the atomic charge density. It also does not assume local charge neutrality.

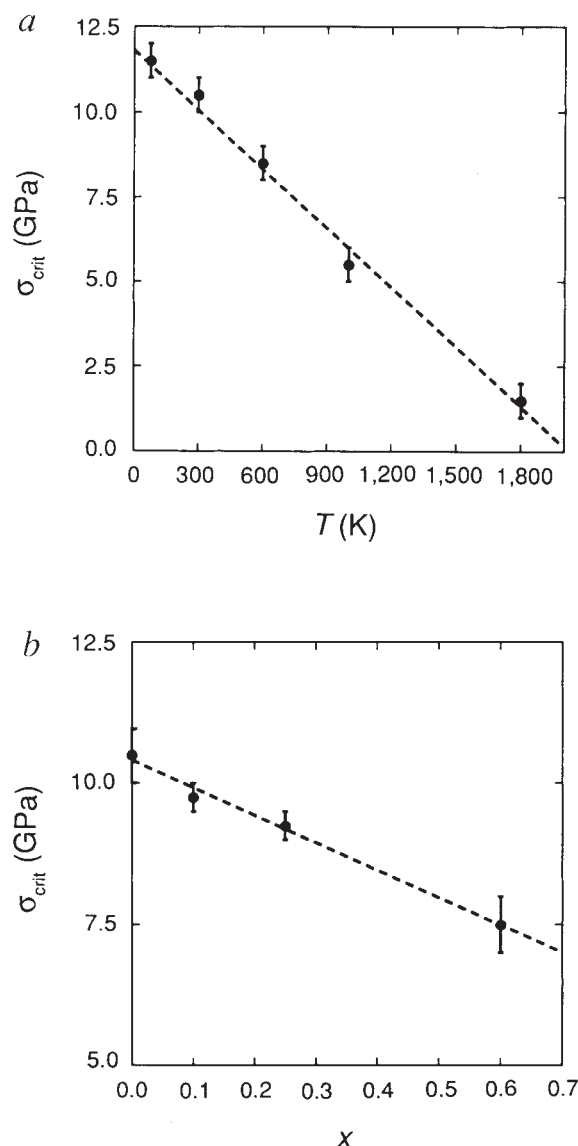


FIG. 1 Calculated critical tensile stress σ_{crit} for (a) hydrogen-free bulk Pd at different temperatures and (b) PdH_x at different hydrogen concentrations x . The dashed lines serve as guides to the eye.

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The parameters for the MBA hamiltonian appropriate for the Pd-H systems have been given in ref. 24. The dynamics of the system is obtained by integrating the equations of motion, which result from the Parrinello-Rahman lagrangian¹⁷⁻¹⁹. In a typical MD simulation of the bulk crystal, we consider a periodic arrangement of unit cells (with originally cubic shape) containing 500 Pd atoms. The effect of hydrogen concentration on the mechanical stability of PdH_x is investigated at four hydrogen concentrations, $x = 0.0, 0.1, 0.25$ and 0.6 . Initially, we let the system equilibrate at zero external pressure and a specific temperature. Then, we apply a uniaxial tensile stress σ to the system, which we gradually increase in small steps. Following each pressure increase, we let the system equilibrate. The critical tensile stress for fracture (σ_{crit}) is reached when the length of the unit cell along the direction of the tensile stress increases dramatically. This elongation is typically associated with the development of a large crack which makes the system unstable. At this point, the shape of the unit cell is frozen in and we monitor the time evolution of the crack. This leads to information on the mechanical failure process at a microscopic level.

We first address the effect of temperature on the mechanical failure in bulk Pd. In Fig. 1a we show the critical tensile stress σ_{crit} as a function of temperature T . Our results indicate a rapid linear decrease of σ_{crit} with increasing temperature. Note that the extrapolation of our data yields the reasonable result that the critical tensile stress vanishes near the calculated²⁵ melting point $T_m = 2,050$ K (which in turn is close to the experimental²⁶ value of 1,827 K). We expect our simulation to give an upper limit (rather than a realistic estimate) to the observed tensile stress in real materials, due to our use of an initially defect-free lattice and relatively large strain rate, which is reminiscent of a shock wave.

Next, we determine the effect of hydrogen concentration (x in PdH_x) on σ_{crit} . Figure 1b shows a linear decrease of the critical tensile stress with increasing hydrogen concentration. This behaviour is very similar to the dependency of σ_{crit} on temperature, as discussed above.

The similarity between Fig. 1a and b implies that presence of hydrogen may have a similar effect on σ_{crit} as a temperature increase. This behaviour may be due to a plasticity enhancement which eventually should lead to melting. To investigate whether the presence of hydrogen may cause local pre-melting of the system, we calculate the Pd-Pd pair correlation function $g(r)$ at the point of fracture for Pd at different temperatures and concentrations of hydrogen. Our results are shown in Fig. 2. The pair correlation function for pure Pd at 300 K (Fig. 2a) shows only weak vibrational broadening of the 'Bragg peaks' (associated with a crystalline solid) with visible structure up to very large values of r . As the temperature rises to 1,000 K (Fig. 2b), the nearest-neighbour peak in $g(r)$ still remains sharp. At large r , however, $g(r)$ gradually loses structure and approaches unity. This behaviour, together with a second split peak at $r \approx 5 \text{ \AA}$, indicates an amorphous structure, which has been formed under critical levels of tensile stress. Because melting is a typical prerequisite for glass formation, we conclude that stress-

induced pre-melting occurs in our system at a temperature well below the bulk melting point²⁶ ($T_m = 1,827$ K).

A striking result is the similarity between the Pd-Pd pair correlation functions of pure Pd at 1,000 K and that of PdH_{0.25} at 300 K (Fig. 2b and c respectively). This indicates that the atomic structures of bulk Pd and PdH_x at the point of fracture are very similar and may be amorphous. We conclude that hydrogen loading and an increase of temperature have a similar effect on the formation of cracks and subsequent mechanical failure. A possible cause of both these effects could be stress-induced pre-melting of the system.

The easiest way to verify this is to inspect the motion of the individual atoms in Pd and PdH_x at different temperatures during the fracture process. We have followed the atomic motion under tensile stress in a computer-animated movie. Characteristic atomic arrangements in a system subject to tensile stress along the horizontal direction are presented in Fig. 3, depicting three adjacent layers in bulk Pd (out of ten layers in the MD unit cell).

At 300 K, the atomic structure of pure Pd at a moment preceding the fracture, shown in Fig. 3a, is very regular and contains no explicit indication of where a crack might start forming. Upon applying tensile stress, we first observe an increased lattice spacing in the stress direction, and finally a disintegration of the system into isolated monolayers at σ_{crit} . These monolayers subsequently recombine to give thicker slabs with a very regular and smooth surface (see Fig. 3d). No significant atomic diffusion is observed in the crack area, indicating a brittle fracture.

At the higher temperature of 1,000 K, Pd shows increased atomic disorder (Fig. 3b). Thermal fluctuations induce defects which are potential seeds of microcracks under tensile stress. On the microscopic scale, fracture proceeds in a ductile manner, and occurs much faster than at room temperature. At the moment following the fracture, (Fig. 3e), we find a large atomic diffusion along the crack surface, indicating melting well below the bulk melting point. This diffusion smooths the originally rough crack surface, and leads to the amorphous structure discussed above.

The most important part of our study is the crack formation in PdH_{0.25} at 300 K, shown before and after the fracture in Fig. 3c and 3f, respectively. Before the point of fracture, we observe a large number of defects especially in regions saturated by hydrogen. These defects act as seeds for crack formation (see the arrow in Fig. 3c). Because hydrogen atoms are most stable in an expanded lattice²⁷, the strained lattice at the crack tip facilitates local accumulation of hydrogen. As discussed below, presence of hydrogen enhances ductility locally. This is associated with a local pre-melting, which in turn accelerates the crack propagation. Our computer animation shows that hydrogen strongly enhances the diffusion of Pd atoms near the crack surface, leading to a faster healing of a formed crack. As we see in the 'snapshot' in Fig. 3f of the geometry following the fracture, the presence of hydrogen leads to a microscopically plastic behaviour and a ductile fracture. This interpretation of the processes is obvious from a comparison of hydrogen-free

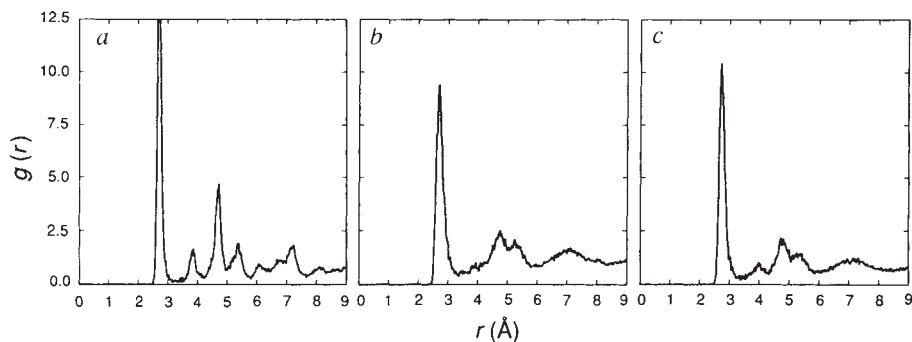


FIG. 2 The Pd-Pd pair correlation function $g(r)$ at the point of fracture for (a) bulk Pd at 300 K, (b) bulk Pd at 1,000 K, and (c) bulk PdH_{0.25} at 300 K.

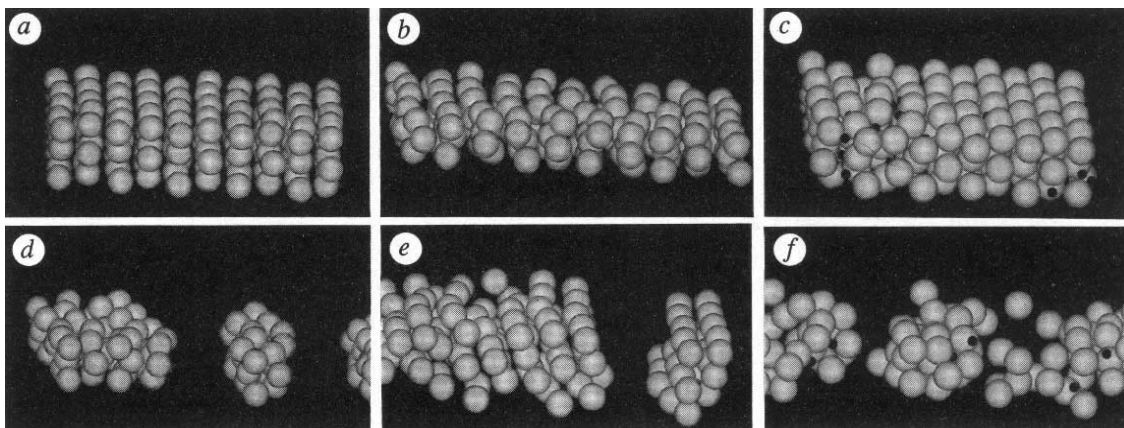


FIG. 3 Momentary atomic arrangement in three adjacent layers of the bulk metal before the point of fracture for (a) Pd at 300 K, (b) Pd at 1,000 K, and (c) PdH_{0.25} at 300 K. The corresponding geometries after fracture are

given in d, e and f. The Pd atoms are shown as white spheres with a radius of 1.3 Å and hydrogen atoms are given by black spheres with a radius of 0.4 Å.

bulk Pd (Fig. 3d) and bulk PdH_{0.25} (Fig. 3f) at the same temperature $T = 300$ K, at the moment following fracture.

We can explain the microscopic origin of the local hydrogen-induced ductility enhancement as follows. Based on our previous LDA calculations, we found that the occupation of the Pd 5s band decreases near hydrogen atoms, whereas the filling of the Pd 4d band increases to a near-noble-metal configuration¹⁵. The latter effect decreases the contribution of 4d electrons to anisotropic bonding, reducing the shear modulus and increasing ductility. Similar behaviour is expected in other metals with a similar electronic configuration, such as Ni. (Our results can not be easily generalized to other systems with near half-filled d band, such as Fe. There, independent of hydrogen loading, the anisotropic d orbitals play a significant role in the mechanical response to applied tensile stress. The origin of hydrogen embrittlement in such systems is still an open question).

Hydrogen atoms have a very small mass and size, and an accordingly large diffusion coefficient. As hydrogen atoms are most stable in an expanded lattice, they accumulate rapidly near fluctuation- and stress-induced defects in the Pd matrix. Such defects are the mechanical weak points of the structure, as they can deform easily. This results in a locally enhanced ductility or plasticity.

In a system under tensile stress, the defects are often near strain singular points such as crack tips. Rapid accumulation of hydrogen at the crack tips results in a strongly inhomogeneous

hydrogen concentration, associated with local plasticity variations. Under tensile stress, fracture will occur at these hydrogen-saturated weak links, while the bulk of the matrix is not strongly affected. This mechanism leads to a fracture morphology which is indistinguishable from brittle fracture (because brittle fracture implies no crystal shape changes outside the crack region, whereas a typical ductile fracture is accompanied by large-scale shape deformations). Our findings are in agreement with the hydrogen-enhanced local plasticity mechanism of fracture¹⁰⁻¹², which had originally been proposed¹⁰ to explain fracture of hydrogen-loaded steel under tensile stress. Our results do not provide any evidence for the 'decohesion' or 'hydrogen-related phase-change' mechanisms of hydrogen embrittlement in PdH_x.

Although our numerical results have been obtained for idealized defect-free lattices, we expect the HELP mechanism also to apply in realistic systems. There, hydrogen accumulates preferentially in regions of extremely high local stresses, increasing ductility locally and allowing the system to relax by forming cracks. The presence of such cracks with ductile tips lowers the critical tensile stress substantially when compared to the defect-free system. In realistic crystals, deformation occurs by dislocation motion. The locally increased plasticity near hydrogen-loaded dislocations clearly lowers the friction stress for dislocation motion and hence the material's resistance to cleavage. It would be instructive to investigate experimentally the effect of extremely high stress loading rates on the critical tensile stress, and to test our corresponding predictions. □

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