ELASTIC CONSTANTS OF A Pd-H CRYSTAL WITH COHERENT INTERPHASES.

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ABSTRACT

Modeling hydrogen-induced embrittlement in metals requires a clear understanding of the effects of hydrogen on the elastic constants of the metal host and of the hydride phases that may form at the crack tip. We have used an ultrasonic spectroscopy technique to measure the three independent elastic constants of Pd as a function of the concentration of interstitial H. A notable result is that within the mixed ($\alpha + \beta$) two-phase range, C_{44} decreases monotonically with increasing hydrogen concentration, whereas $C' = (C_{11} - C_{12})/2$ shows a concave parabolic dependence on hydrogen concentration. It is shown that this difference is due to Zener-type anelastic relaxations involving μm-size coherent lenticular-shape precipitates (β-hydride precipitates in α-Pd(H) matrix, and α-hydride precipitates in β-hydride matrix). In the β-phase, C_{44} , C' and B decrease with increasing hydrogen content.

1 INTRODUCTION

Because of its small size, hydrogen can alloy with many metals, where it occupies interstitial lattice sites. At small hydrogen concentrations these sites are occupied at random. The hydrogen atoms cause both local distortions in the metal lattice and a homogeneous lattice expansion. Data for many metal-hydrogen systems indicate that the addition of one H atom increases the volume of the crystal by approximately $\Delta v = 2.9$ Å^3 , independent of the host metal [1].

The small size of the dissolved H atoms also gives them a high mobility in the metal-host lattice. This results from the ability of the H atoms to migrate via a direct interstitial mechanism, jumping into adjacent empty interstitial sites without the assistance of vacancies. The jump rate is very fast since the site exchange may be influenced by quantum mechanical tunnelling. For example, diffusion data for hydrogen in the dilute α-phase Pd-H$_{0.01}$ [2] and the hydride β-phase Pd-H$_{0.62}$ [3] tells us that at 300 K the "residence time" of a hydrogen atom at any given octahedral position in the lattice is on the order of 1 ns.

The H atoms interact via their elastic distortion fields with other H atoms, with point defects (e.g., vacancies, interstitial, substitutional solutes), with lattice defects (e.g., dislocations, grain boundaries), and with applied stress fields. The interaction of the H atoms with the stress field around a stressed crack tip is though to play an important role in the embrittelement of metals [4].

Hydrogen embrittlement does not affect all metallic materials equally. The most vulnerable are high-strength steels, titanium alloys, and aluminum alloys. Presently this phenomenon is not completely understood, partly because the role of hydrogen is difficult to characterize. Indeed, because of its high mobility, the H distribution near the crack, including the possible formation of hydride phases, is hard to visualize; hydrogen atoms are often able to leave the site of fracture once the stress field around the crack has been released by the advancement of the crack or by the removal of the applied stress.

Hydrogen embrittlement in the Group V transition metals has been attributed to the formation of a brittle hydride phase in front of the crack tip [4,5]. The hydride phase forms because the negative hydrostatic component of the stress field at the crack tip decreases the chemical potential for interstitial H atoms [5,6], inducing diffusion into the region. The effects of the shear-stress components are usually neglected and thus the effects of elastic anisotropy are also neglected.

Clearly, studies of H-embrittlement would benefit from a detailed knowledge of the effects of hydrogen on the elastic constants of the host and the effect of stress on the formation and shape of the hydride precipitates. The present paper summarizes a study of the elastic constants of the Pd-H system at 300 K, which serves as a model system for fcc metals.

2 ELASTIC CONSTANTS

The phase diagram for the Pd-H system has been characterized by many authors and the results have been summarized [7]. At ambient temperature, and for H concentrations less than $x_{\alpha,\max}$ = H/Pd ≈ 0.01 (throughout this paper, hydrogen concentrations, *x*, are in atom fractions, H/Pd), the H atoms reside at random octahedral-symmetry interstitial positions of type [0,½,0], forming a dilute solid solution, α. For higher H concentrations, some of the H atoms coalesce into an ordered palladium-hydride phase, β, having the composition $x_{\beta,\min} \approx 0.62$. In the β–hydride phase, the Pd atoms retain the *fcc* lattice of the α-phase, but the volume of the lattice expands by approximately 11%. The hydrogen atoms remain in [0,½,0]-type positions, occupying only a fraction of the available interstitial sites. For $x_{\alpha,\max} < x < x_{\beta,\min}$, the alloy is a two-phase mixture of the α and β phases. The width of this region decreases with increasing temperature, and vanishes at a critical temperature of approximately 290°C. At the critical point, the H_2 pressure is approximately 2 MPa (~ 20 Atm.). The dissolved H expands the Pd lattice and the lattice parameter, *a*, grows approximately proportionally to the H concentration, with a slope $(3/a)\, da/dx = 0.179$ [9].

The elastic constants of Pd(H) were measured on parallelepiped-shaped Pd single crystals of approximately 3 x 4 x 5 mm^3 , with surfaces normal to ‹001› and ‹110› axes. The elastic constants C', C_{44}, and B were measured by the Resonant Ultrasound Spectroscopy method [8]. The frequency of the ultrasonic signal was swept between approximately 150 kHz and 1.5 MHz. The α–phase Pd(H) single crystals were prepared by simply exposing the Pd crystals to the appropriate temperature and H pressure. The β–phase Pd hydride crystals were prepared through a more complicated charging procedure that took the crystals over and around the critical point, preventing them from traversing the two phase (α + β) region [9]. Single crystals of Pd-H are difficult to prepare within the two phase (α + β) region. This is because the lattice constants of the α and β phases differ by approximately 3.7% and thus the coherency strain between these phases can barely be accommodated elastically. As the volume fraction of the second phase increases, the precipitates emit dislocations and eventually become incoherent. We were able, however, to prepare Pd-H single crystals containing coherent α / β interfaces at the two compositions near the α / (α + β) and (α + β) / β solvi. We prepared crystals of majority α-phase and minority β-phase precipitates by quenching a single α-phase crystal, forcing it in the process to rapidly cross the α / (α + β) solvus. We prepared crystals of majority β–phase containing minority α–phase precipitates by letting the H escape slowly from a single-phase β–PdH_X crystal. For both cases, the minority phases developed as micron-size lenticular-shaped precipitates that were coherent with the majority phase. The large anisotropy in the elastic constants of Pd ($C_{44}/C' \sim 3$) is responsible for their lenticular shape. The α and β precipitates are parallel to {100}-type planes [10].

If the precipitates are incoherent their shape is no longer influenced by the coherency strain and thus they tend to have spherical shape, which minimizes the interface energy. The elastic constants of a two-phase crystal with *incoherent* interfaces can be calculated [11] and the predictions are rather uninteresting. The more interesting case, treated here, is that of *coherent* precipitates.

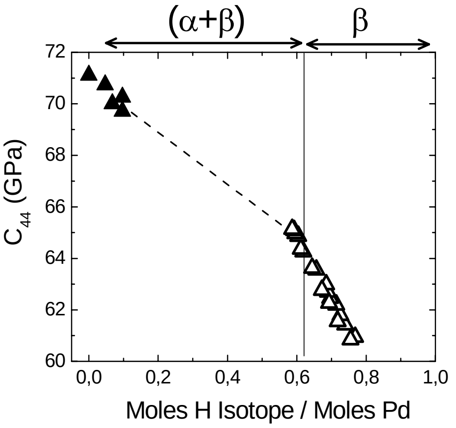

Figure 1.
Elastic constant C_{44} of Pd-H as a function of H content.

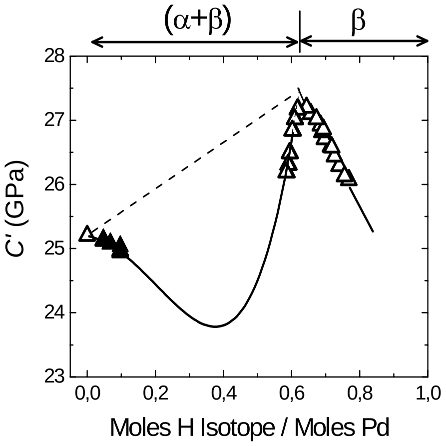

Figure 2.
Elastic constant $C' = (C_{11} - C_{12})/2$ as a function of H content.

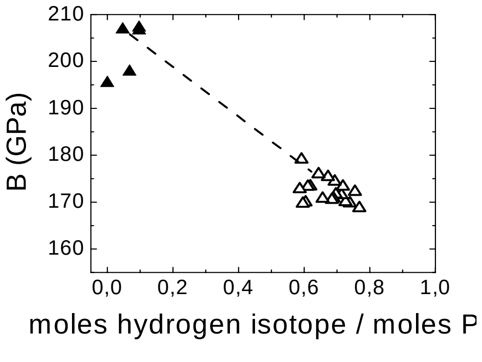

Figure 3.
Bulk modulus B of Pd-H, Pd-D, and Pd-T as a function of the H content in the crystal.

Figures 1, 2, and 3 show the room-temperature values of *C'*, C_{44} and *B* of Pd-H single crystals as a function of hydrogen concentration, *x*. The data covers the concentration ranges accessible at room temperature. These are: the dilute solid solution α for ($0 < x < 0.01$); the two-phase (α + β) range for ($0.01 < x < 0.62$); and the single-phase hydride β for ($0.62 < x < 1.0$). Within the two phase (α + β) range, the α and β precipitates are coherent. Because of the large coherency strains between these two phases, data within the (α + β) range could only be obtained near the terminal concentrations, as explained previously.

C_{44} and B show a monotonic decrease in value as a function of H concentration. This is the expected dependence, which is mainly due to lattice expansion caused by the interstitial H. The dashed curves in these two figures are the calculated elastic constants assuming *incoherent* precipitates [11]. These two curves are very close to a straight line joining the values of the elastic constants at the limiting compositions (Vegard-type average). Clearly, the values of C_{44} and B are not affected by the coherency strains.

Figure 2 shows the dependence of C' on H concentration. Of special interest is the peculiar behavior within the two-phase ($\alpha + \beta$) range. For compositions away from the terminal solubilities, where coherent precipitates could not be obtained, the data was interpolated by a parabola since there is theoretical justification to expect this dependence, as we will discuss below. The dashed curve in Fig. 2 gives the C' values expected for *incoherent* α/β interfaces. In contrast with the data for C_{44} and B, the presence of coherent precipitates has a pronounced effect on the value of C' .

3. DISCUSSION

The most important results of these measurements is that in the presence of coherent α / β interfaces, the two shear moduli, C_{44} and C', have quite different behavior. The difference is due to anelastic relaxations that change the shape of the coherent precipitates. These relaxations affect the value of C' but not C_{44}. To understand the effect, one must keep in mind the following:

- The diffusivity of H in the Pd lattice at 300K is so large (residence time of ~ 1 ns) that the H atoms can redistribute in the lattice in response to the applied ultrasonic stress used to measure the elastic constants, which is in the frequency range 150 to 1000 kHz. Thus, we are measuring the *relaxed* moduli.
- Within the $\alpha + \beta$ region and for concentrations near the terminal solubilities, the precipitates have lenticular shape, oriented in the {100}, {010}, and {001} lattice planes.
- C_{44} measures the elastic response of the lattice to a deformation equivalent to pulling the cubic lattice from two opposite corners (i.e. along a <111> - type direction).
- C' measures the elastic response of the lattice to a deformation equivalent to straining the lattice by, for example, $\varepsilon_{11} = e$, $\varepsilon_{22} = -e$, with all other strain elements set equal to zero.

Because the coherent lenticular-shaped precipitates are parallel to {100}-type lattice planes, the elastic distortion of each precipitate can be represented by an elastic dipole of tetragonal symmetry, having principal values λ_1, λ_2, and λ_3. Two of these values are equal for each of the there possible variants. In the absence of an applied stress, the precipitates populate the three variants equally. The same is true when the applied elastic deformation is that which corresponds to the shear constants C_{44} and B. The elastic distortion that corresponds to C' , however, lifts the degeneracy for one of the three variants. The ensuing redistribution of H atoms (either from one precipitate to another, or within each precipitate, so as to produce a slight change in their shape) causes an anelastic softening of C'. The effect is similar to a Zener-type anelastic relaxation in a cubic crystal containing tetragonal-symmetry atomic defects oriented along <100>-type axes. The difference with a Zener relaxation is that in the present case the "defects" are mesoscopic in size (the lenticular-shape precipitates). Notice that the relaxation only occurs because the precipitates are coherent with the matrix. Incoherent precipitates would tend to have spherical shape and would produce no elastic distortion distortion in the matrix which could then interact with the strain of the ultrasonic signal.

The size of the lenticular-shape precipitates is dictated by a minimization of the total energy, which includes the chemical energies of the phases and the lattice coherency strains.[12] Near the terminal solutions, the lenticular-shape precipitates are all approximately 1 μm in diameter and, because the precipitates are largely non-interacting, this size should change little with changing x. The density of precipitates, however, is expected to change in proportion to $x(1 - x_{\beta,\min})$, being zero at both terminal compositions of the two-phase field. Thus, the amplitude of the anelastic softening of *C'* (difference between the value of *C'* expected for incoherent precipitates, given by the dashed line in Fig. 2, and the data representing the *C'* values for coherent precipitates) should also change in proportion to $x(1 - x_{\beta,\min})$. This justifies the parabolic shape of the solid line used to interpolate the data.

Returning to the discussion in the Introduction on the influence of hydride formation on the fracture of a lattice that contains mobile H, one can see that a complete treatment of hydride formation at the crack tip must take into account not only the hydrostatic components of the stress field created by the crack, but also its shear components. Because in the dilute solid solution the interstitial H atoms are in octahedral-symmetry sites (of full cubic symmetry), the chemical potential of the H atoms depends mostly on the isostatic component of the stress, $\sigma_{11} + \sigma_{22} + \sigma_{33}$. But, once the hydride forms, the other stress components may become quite important. One can safely speculate that in an anisotropic *fcc* crystal the first hydride to form would be *coherent* with the matrix, lenticular in shape, and oriented along a {100}-type plane. For a mode I crack (tensile load perpendicular to the crack surface), the precipitate would form first on the {100} plane having the highest tensile stress normal to it. If the β phase is weaker than the matrix, decohesion would occur along this precipitate and the crack would propagate in brittle manner along this plane. Certainly, this is one of the many scenarios that have been proposed, and are under study, to explain the influence of H on the fracture of metals. For a summary, see for example Refs. 13,14.

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