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Author(s):

H. T. Bach, R.B. Schwarz, and D. G. Tuggle

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HYDROGEN, DEUTERIUM AND TRITIUM IN PALLADIUM: AN ELASTIC CONSTANTS STUDY

H. T. Bach [1*], R.B. Schwarz [2], and D. G. Tuggle [1]

[1*] *Engineering Science and Application Division, Tritium Science and Engineering Group, MS C927, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, email: hbach@lanl.gov*

[2] *Material Science and Technology Division, Structure and Property Relation Group, MS G755, Los Alamos National Laboratory, Los Alamos, New Mexico 87545*

We have used resonant ultrasound spectroscopy to measure the three independent elastic constants of Pd-H, Pd-D, and Pd-T single crystal at 300K as a function of hydrogen, deuterium, and tritium concentration, respectively. The addition of interstitial H (D, or T) atoms, located at (0,½,0) in the fcc Pd lattice, affects all three elastic constants C', C_{44}, and B. In the mixed (α+β) phase, and with increasing H isotope, the shear modulus C' shows an abnormal softening whereas C_{44} and B do not. This is explained in terms of Zener-type anelastic relaxations affecting the shape of the hydride phases in the coherent(α+β) two-phase mixture In the single β-phase, C' shows a strong isotope dependence whereas C_{44} and B show none. This behavior is explained in terms of differences in the excitation of optical phonons. In Pd-T, ^{3}He is produced by the radioactive decay of tritium. We have measured in situ the swelling and the change in the elastic constants in Pd-T as a function of aging time. Aging (^{3}He formation) affects all three elastic constants. These measurements are being used to understand the early stages of ^{3}H-^{3}He cluster formation in aged Pd-T crystal.

I. INTRODUCTION

Depending on temperature and pressure, the Pd-H system shows three distinct phases: a dilute Pd-H solid solution or α-phase, an ordered palladium hydride or β-phase, and a mixed (α+β)-phase [1]. At near room temperature and one atmosphere H pressure, the α phase forms for H/Pd in the range 0 to 0.03, the mixed (α+β)-phase exists for H/Pd between 0.03 and 0.62, and the β-phase exists for H/Pd > 0.62. The α and β phases are both *fcc*, with the H atoms occupying lattice positions of the type (0,½,0). Whereas the H atoms in the α phase form a dilute solid solution, the H atoms in the β-phase form an ordered sub-lattice. The precipitation of the β-phase expands the volume of the Pd lattice by approximately 12%. Because of this large volume difference, it is difficult to prepare two-phase (α+β) single crystals with coherent interfaces. However, by carefully adding hydrogen to an α-phase Pd-H single crystal forcing it to cross the α/(α+β) solvus, or by slowly removing hydrogen from a β-phase Pd-H single crystal forcing it to cross the (α+β)/β solvus, one can prepare two phase (α+β) single crystals that have coherent interfaces. This procedure allowed us, for the first time, to measure the single crystal elastic constants within the coherent (α+β) range.

The Pd-H and Pd-D systems have been extensively studied and the elastic constants of these two alloys in single α and β phases have been reported [2,3,4]. The present study presents the first measurements of elastic constants in the mixed (α+β) phase where the two phases are coherent. We show that the coherency introduces a strong softening in *C'* which is not expected for the case that the two phases are incoherent. Furthermore, we present the first measurements for the Pd-T system. Finally, we discuss the effects of aging (incorporation of ^{3}He into the β-phase Pd-T lattice from the radioactive decay of tritium). It is shown that measurements of the three independence elastic constants of Pd-T single crystals provide detailed data on the early stages of ^{3}He agglomeration and bubble nucleation. Further details of this work will be published separately [5].

II. EXPERIMENTAL

Palladium single crystals in the shape of parallelepipeds, approximately 3 x 4 x 5 mm^3 were used in this study. These were charged with H (D, T) using standard gas equilibration techniques. The α-phase single crystals were the easiest to prepare. To prepare the β-phase Pd-H (D, T) single crystals we needed to avoid traversing the two-phase (α+β) region of the phase diagram since otherwise the large difference in molar volume between the α and β phases would have fractured the single crystals. Thus, these crystals were prepared using a pressure-temperature path that circumvented the critical point (critical H pressure about 20 atm.; critical temperature about 300°C). Having single crystals of α-

PdH and β-PdH, we were then able to prepare single crystals inside the mixed (α+β) region, as explained next.

At ambient temperature and pressure, a β-phase Pd-hydride crystal losses hydrogen slowly. This loss enabled us, over a period of several days, to measure the elastic constants of the β phase as a function of the molar ratio H/Pd. After a few days, the sample entered the hydrogen-rich end of the (α+β)-phase, causing the formation of a small density of α-phase precipitates in the majority β-phase Pd-H matrix. These precipitates have thin lenticular shape, as visualized by transmission electron microscopy (TEM) [6]. To prepare a Pd-H crystal at the hydrogen-poor end of the (α+β)-phase we heated a Pd crystal in vacuum to between 60 °C to 100 °C. We then increased hydrogen pressure slowly to form a homogeneous α-phase Pd-H [7]. Finally, we quenched the crystal to room temperature while under a suitable hydrogen overpressure. The fast cooling prevented the H form leaving the crystal while forcing it to cross the α/(α+β) solvus. This caused the precipitation of β-phase hydride inside the majority α-phase. Again, the precipitates were coherent with the matrix and had lenticular shape, as revealed by TEM. We allowed the samples to reach thermal equilibrium at room temperature before measuring the elastic constants.

The elastic constants C', C_{44}, and B were measured using a resonant ultrasound spectroscopy (RUS) technique. The crystals were held at opposite corners between a pair of ultrasonic transducers (Pinducers from Valpey Fisher, Hopkinton, MA 01748). One transducer applied an ultrasonic signal of constant amplitude and varying frequency to the crystal, whereas the other transducer detected the frequencies at which the crystal entered into mechanical resonances. We scanned the excitation frequency from about 170 kHz to 700 kHz and computed the elastic constants from the first 40 resonance frequencies. The details of this technique have been published elsewhere [8,9]. We determined the H (D, or T) concentration in the Pd-H (D, or T) by the difference in weights before and after H (D, or T) charging.

We measured elastic constants of the Pd-H and Pd-D crystals in air and Pd-T crystal inside a nitrogen glovebox at room temperature. For this, we moved the pre-amplifier of the RUS equipment inside the glovebox and transferred the electronic signals to a computer located outside the glovebox via special coaxial cables assembled for this purpose. The measurement of elastic constants was quite cumbersome because it was difficult to handle the small single-crystal sample using the triple-set of plastic gloves required to protect personnel from the tritium-contaminated atmosphere inside the glovebox. When the Pd-T crystal is not being used, we stored it under a pressure of 35 atm of tritium at room temperature to keep the sample in the β-phase and allow ^{3}He concentration to build up. The elastic constants were measured as a function of both tritium and ^{3}He concentration.

III. RESULTS

Our measurements of C_{44}, C', and B for Pd-H, Pd-D, and Pd-T as a function of hydrogen isotope concentration are plotted in Figures 1-3. The figure also shows literature data (solid symbols) for the elastic constants of Pd-H and Pd-D in the β-phase. Our C_{44} and C' values for Pd-H are in good agreement with the data of Hsu and Leisure [2] and Geerken *et al* [3] and also in reasonable agreement with data of Nygren and Leisure [4]. Our C_{44} and C' for Pd-D are higher than the value reported by Geerken *et al* [3]. We attribute the discrepancy to an error in the D/Pd value (abscissa) reported in [3].

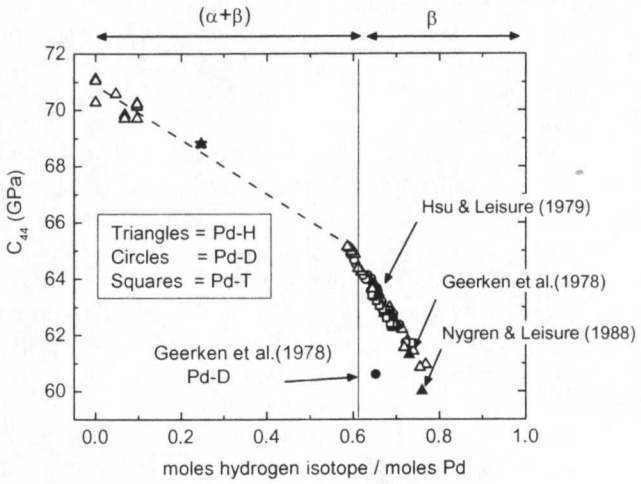

Fig. 1. Elastic constant C_{44} of Pd-H, Pd-D, and Pd-T single crystals.

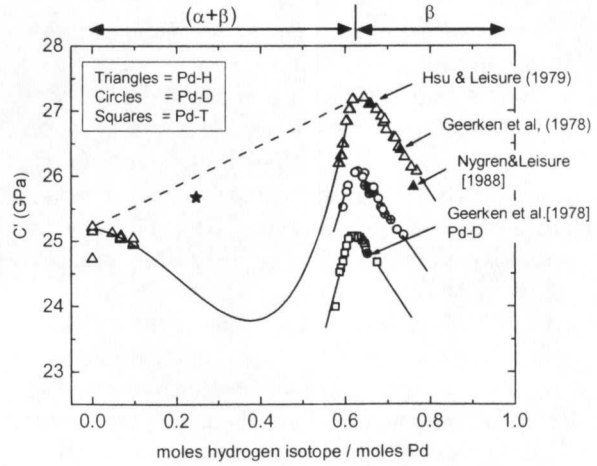

Fig. 2. Elastic constant C' of Pd-H, Pd-D, and Pd-T single crystals.

C_{44} decreases monotonically with increasing H concentration (Fig. 1). This is the expected concentration dependence because the expansion of the Pd lattice with the addition of interstitial H (D, or T) atoms should cause a monotonic decrease in all the elastic constants. For the single β-phase hydride the figure shows a superposition of data for Pd-H (open triangles), Pd-D (open circles), and Pd-T (open squares). There are also data for the mixed (α+β) region, but only near the terminal solubility of this mixed phase since, as explained earlier, single crystals with coherent α/β interfaces could only be prepared at these limits. The solid star at H/Pd = 0.25 is for a Pd-H crystal with incoherent interfaces.

C', on the other hand, shows unexpected dependence on H concentration (Fig. 2). The main differences with the behavior of C_{44} are: (1) C' for H/Pd=0.62 is higher than for pure Pd, (2) within the (α+β)-phase C' has a concave parabolic dependence, and (3) C' has a strong isotope dependence whereas C_{44} has none. The elastic constants of Pd-D and Pd-T have only been measured for $0.58 < H/Pd < 0.75$ but there should be little doubt that the isotope effect is present for all isotope concentrations. The parabolic-shape solid curve traced through the Pd-H data is an interpolation of the data obtained near the terminal solutions of the (α+β) phase, since no crystals with coherent interfaces could be obtained at other compositions within this phase. The solid triangle is the C' value at H/Pd = 0.25, but in this crystal the α and β precipitates had grown too large and had become incoherent. The measurement accuracy of the elastic constants C' and C_{44} is much better than that of the bulk modulus B. This is an inherent limitation of the RUS method [4-5].

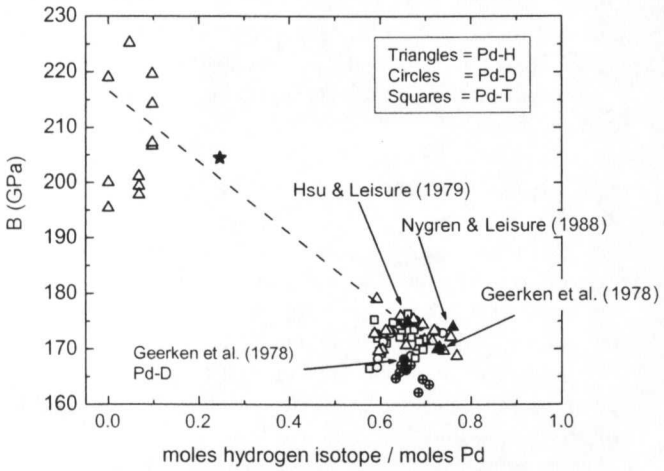

Fig. 3. Bulk modulus B of Pd-H, Pd-D, and Pd-T single crystals.

Figures 4, 5 and 6 show the C', C_{44} , and volume of aged Pd-T single crystal as a function of tritium and ^{3}He concentrations measured over a period of 400 days. Both C' and C_{44} decrease linearly with increasing tritium concentration but non-linearly with helium concentration. In the early aging stage, C' and C_{44} decrease ~10 times faster with respect to helium concentration than with respect to tritium concentration.

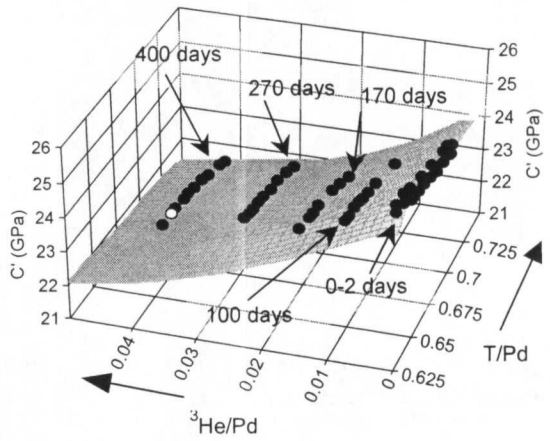

Fig. 4. Elastic constant C' of Pd-T single crystal as a function of tritium and helium concentration.

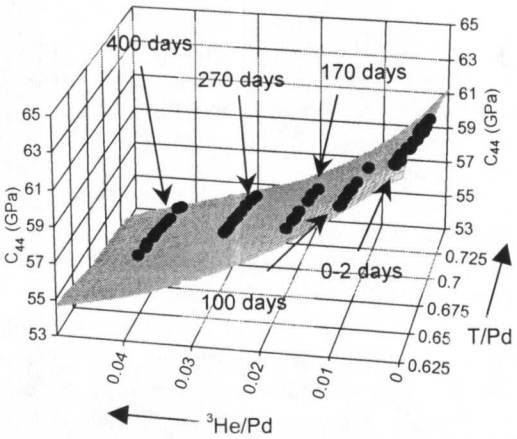

Fig. 5. Elastic constant C_{44} of Pd-T single crystal as a function of tritium and helium concentration.

The volume of the aged Pd-T crystal increases linearly with increasing tritium concentration but non-linearly with helium concentration. There is a sharp break at ~1.5% of ^{3}He corresponding to ~ 150 days.

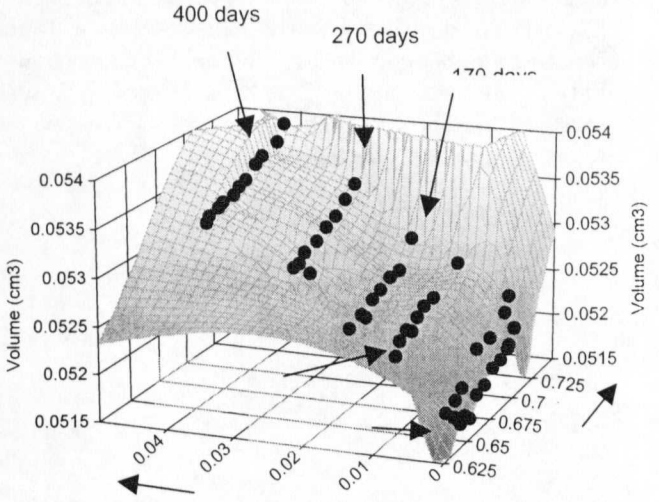

Fig. 6. Volume of Pd-T single crystal as a function of tritium and helium concentration.

IV. DISCUSSION

IV.A. Hydrogen, deuterium, and tritium concentration dependence

Geerken *et al.* [3] proposed a simple spring model for the *fcc* lattice of Pd that can explain qualitatively why C' is larger in β-phase Pd-H than in pure Pd, whereas C_{44} shows the opposite effect. In this model, the Pd atoms are interconnected by nearest-neighbor $K1$ springs and next-nearest-neighbor $K2$ springs. The evaluation of the elastic constants of this spring solid gives $C' \sim K1 + 4\,K2$, $C_{44} \sim K1$, and $B \sim K1\text{-}K2$. The addition of interstitial hydrogen atoms, at locations (0,½,0), should mainly stiffen the $K2$ springs, leaving the $K1$ springs largely unchanged. Thus, the spring model suggests that the increase in C' due to the stiffening of $K2$ overcompensates the decrease in C' caused by the volume expansion. Since $K1$ remains largely unchanged, the main effect of H on the C_{44} value of Pd-H would come from the lattice expansion, which softens all the springs and thus causes C_{44} to decrease with increasing H. This model cannot explain why C' continues to decrease in the single β-phase with increasing in H (D or T) concentration.

IV.B. Aneslatic relaxation in the two-phase (α+β) region

The parabolic dependence of C' on H/Pd ratio within the two-phase (α+β) region is the result of an anelastic relaxation involving a change in the shape of the coherent precipitates. Ho *et al.* [5] used TEM to examine morphology of the two phase (α+β)) alloys and observed that the near terminal solubility of the (α+β) homogeneity range, the precipitates had lenticular shape (β precipitates embedded in a majority α phase and, at the other end, α precipitates embedded into a majority β phase). The lenticular shape precipitates are oriented along the three equivalent <100> crystallographic planes. In the absence of an applied stress, the lenticular shape precipitates occupy equally all three variants. The precipitates will be affected equally by a longitudinal stress along a <111> direction (which causes an elastic distortion characterized by C_{44}) or by an isotropic dilatation or compression (which causes an elastic distortion characterized by B), but unequally by a shear stress σ_{xx}-σ_{yy} (which causes an elastic distortion characterized by C'). Because of symmetry, the first two types of stresses will not induce a change in the shape of the precipitates, and therefore there will be no anelastic relaxation in C_{44} or B. On the other hand, the shear stress σ_{xx}-σ_{yy} will cause a change in the shape of some of the precipitates and the ensuing anelastic strain will cause a relaxation in C'. The magnitude of change in C' is predicted to be proportional to the density of α precipitates in the β matrix, and of β precipitates in the α matrix. Overall, the density of precipitates follows a $x(1\text{-}x)$ dependence, where x stands for H/Pd, and this explains the parabolic dependence of C' within the (α+β) region. In the absence of anelastic relaxations, the C' value within the (α+β) phase would be close to the dashed line that joins the C' values at the extreme concentrations of this phase. The anelastic relaxations cause a softening of C' form the values given by the dashed line. Microscopically, the anelastic relaxation results from small changes in the shape of the precipitates, which occurs by a migration of H atoms through the matrix. There is ample time for this migration since the measurements are done at frequencies of less than 1 MHz and the residence time for a H atom at any given lattice site at 300 K is on the order of 1 ns [10,11]. The C' data for Pd-D and Pd-T is expected to follow a similar parabolic shape dependence on H isotope concentration.

IV.C. Isotope dependence

C' in the single β-phase show strong isotope dependence, whereas C_{44} and B show none (Figs. 1-3). Only one of the three shear elastic constants shows an isotope dependence may suggest that the isotope dependence of C' is due to an anelastic relaxation. If the change in C' were due to relaxation, then the effect for all three isotopes should vanish at concentration of 1. At this concentration all the (0,½,0)-type interstitial sites are occupied and thus there are no vacant sites to enable the motion of H atoms. The C' data for the three hydrogen isotopes is well fitted by parallel lines, which do not extrapolate to a single point. The data provides evidence that C' in β-phase is not affected by a relaxation.

The current accepted explanation of isotope effect on C' is based on the optical phonons and their strong dependence on isotope mass. In Pd hydrides, because hydrogen isotopes have small masses they can easily follow the low energy vibrations of the surrounding Pd lattice atoms (acoustical branches). Hydrogen atoms also vibrate against the Pd lattice atoms at higher vibration energy (optical branches). From the neutron scattering data [12], the energies of transverse optical phonons with k=0 for Pd-H, Pd-D, and Pd-T are 63, 43, 34 MeV, respectively. At room temperature (25 MeV) the optical phonons are readily excited. With the same excitation energy, the number of excited optical phonons increases significantly on going from Pd-H to Pd-D to Pd-T. Because the transverse optical phonons delocalize the H isotope atoms, the excited optical phonons should soften the next-nearest-neighbor *K2* springs [3], and thus soften C'. The softening of C' should be more pronounced for tritium than for hydrogen.

IV.D. Aging effect (^{3}He concentration dependence)

The changes in the elastic constants seen in Figures 4 and 5 are due to two factors: (1) the slow loss of tritium, and (2) the incorporation of helium into the Pd-T crystal. The first factor has been discussed above. The second factor is discussed next.

Tritium decays with a lifetime of about 12.3 years, producing a ^{3}He atom. Because the recoil energy is only on the order of electron volts, each ^{3}He atom is likely to remain in the same position previously occupied by the parent tritium atom, namely in a (0, ½, 0) position. Since the ^{3}He atoms have a larger atomic volume than tritium atoms, the ^{3}He atoms create local elastic distortions in the Pd tritide lattice, and this should change the values of the elastic constants.

In the early aging stage (less than 130- 170 days), the changes of C', C_{44}, and sample volume with helium concentration are more than that in the later stage. What do these changes in C', C_{44}, and sample volume with helium concentration correspond to? We will use elastic constants to further study: 1) the coalescence of ^{3}He atoms into dimmers and higher order aggregates, 2) the shape of these aggregates while they are small and are still coherent with the Pd matrix, and 3) the aging time when the ^{3}He precipitates change from being coherent to being incoherent (i.e., bubbles).

V. CONCLUSIONS

1) All three elastic constants C', C_{44}, and B depend on H (D, or T) concentration.
2) In the two-phase (α+β) region, C' is affected by anelastic relaxation, C_{44} and B are not.
3) Isotope (H, D, T) affects C' but not C_{44} and B due to the differences in the excitation optical phonons.
4) Aging (^{3}He formation) affects all three elastic constants.

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