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RECOVERY OF DEFORMED AND HYDROGEN-CHARGED PALLADIUM*

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Positron lifetime and Doppler-broadening studies made at 300 K have been used to investigate the interaction between interstitial hydrogen and lattice defects in deformed Pd. Specimens were charged with hydrogen at 300 K to levels up to 0.1%. The presence of hydrogen was found to have no effect on the recovery curves of Pd upon annealing to 400°C. By 400°C the values for both lifetime and Doppler-broadening for both cold worked and cold worked plus hydrogen were below the values obtained for annealed pure Pd. This can be interpreted as gaseous-impurity-trapped vacancies being present after the 1200°C anneal, but being swept away by the dislocation microstructure recovery between 200-400°C. Although the specimens hydrided to the β phase and outgassed back to the α phase showed continual recovery up to 400°C, complete recovery was not achieved as with the deformed specimens. The lifetime results indicate the presence of defects more open than single vacancies. One possibility would be the formation of cavities, possibly hydrogen filled, during the hydriding that are stable at 400°C.

The defect concentration and type in the host lattice can be a major determining factor in both the solubility of hydrogen in metals and the diffusion rate of hydrogen in the metals. Flanagan et al. [1,2] demonstrated that in the low-H-content α phase of Pd the solubility of H as determined by absorption isotherms increased with increasing prior cold work. They attributed this increased solubility to trapping of H in the strain fields of the dislocations present. The role of vacancy agglomerates in the trapping process is not clear, but is not believed to play a major role. Cold work does decrease the diffusivity of hydrogen in Pd [2-4]. The decreased diffusivity of hydrogen in Pd after cold work is associated with the H trapping at the dislocation strain fields. For Pd hydrided to the β phase and degassed to the α phase at low temperatures, an enhanced hydrogen absorption is observed upon further low-concentration H charging. Trapping at dislocations generated during the phase charge is the currently favored explanation [2].

We have used positron techniques to get information on (1) role of vacancy-type defects on hydrogen trapping, (2) effect of H on the dislocation recovery upon annealing, and (3) the defects produced by hydriding Pd. Samples were studied in the following states: (1) cold worked, (2) cold worked + H charged, and (3) cold worked + annealed to 1200°C and were made from a Pd (99.99+%) sheet cold-rolled to 95% reduction. Identical pairs sandwiched ~10 uCi of $^{22}NaCl$ deposited directly on one face for measurement of lifetime and Doppler broadening. Standard techniques were employed. The hydrogen charging was done at room temperature under pressure to a hydrogen level of H/Pd ~0.006 for the cold work + H specimens. For the specimens hydrided and degassed to the α phase the charging was done at room temperature to a level of H/M ~0.7 and then held under vacuum for 12 h.

In Fig. 1 the results are presented for a single-variable-lifetime (τ_1) fit for cold worked + H charged specimens. Isochronal anneals were made at 100, 200, 300, and 400°C for 2 h. A second lifetime component was fixed (570 psec at 0.78%) to account for source and surface annihilations. This component was determined from fits to the "well-annealed" and high-temperature-annealed cold-worked specimens. Single-lifetime fits such as this do not yield quantitative results as a rule but are useful as qualitative indications of defect changes.

From this Fig. some small amount of recovery is indicated from the annealing to 200°C with a large change between 200 and 300°C. The curve is drawn as a guide for the eye. The lifetime data show no difference between the recovery of the cold-worked specimens and the cold-worked + H specimen. The values of the room temperature τ_1 for both treatments were essentially the same (166 vs 168 psec).

The surprising result from the recovery depicted in Fig. 1 is that the value of τ_1 after 300 or 400°C annealing (96 and 98 psec, respectively, at 400°C) is below that obtained for the "well annealed" (120 psec). The latter is represented by the horizontal dashed curve. The interesting implication here is that the "well annealed" specimen has a defect population greater than that of the two treatments shown after they are annealed at 300°C or above. This suggests that the 1200°C anneal and subsequent cooling introduces some

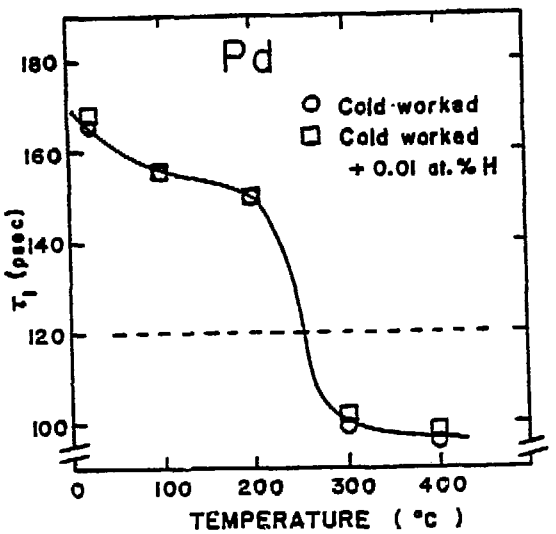

Figure 1: Single-variable-lifetime fit τ_1 vs annealing temperature for cold-worked and cold-worked + H-charged Pd. The horizontal dashed line denotes the 1200°C "well-annealed" value.

type of trapping center that is not present after annealing the two treated pairs to 400°C.

A two-lifetime fit was made to the cases shown in Fig. 1 and the "well-annealed" specimens. For the annealed specimens, the results gave two similar components with comparable statistical fits. Only for the as-treated cases were two different components resolved. For the CW, two lifetimes of 61 and 171 psec were resolved, with the latter intensity being 76%. For the CW + H we obtained 600 and 177 psec, with the latter intensity at 69%. The major positron trapping site then has a lifetime ~175 psec. For the as-treated specimens the fit was significantly better (~1.1) than the single-lifetime fits. The 600-psec value (±100 psec) in the CW + H is anomalous to these results. It is not resolved, however, after annealing to 100°C.

For the "well-annealed" case the results were 75±5 and 173±3 psec with an intensity of the latter component of 37%. The first 1200°C anneal was done in air. To see if gaseous impurities absorbed during the anneal could explain the higher lifetime observed, a second set was annealed at 1200°C for 2 h in a vacuum of ~1×10^{-6} torr. Lifetime results were the same for the two treatments with the exception that the intensity of the 173-psec component changed from 37% to 22%. From this difference one could conclude that gaseous impurities might be involved in the trapping phenomena in "well annealed" Pd.

In Fig. 2 we present the results of a peak-to-wings parameter analysis of the Doppler-broadening data for the two cases CW and CW + H. As with the Fig. 1 there is little difference between the two treatments. The small recovery evidenced by lifetime upon annealing to 200°C is evidenced in the CW but not the CW + H case. The major recovery stage between 200 and 300° C reproduces the lifetime behavior. Also note that the value of P/W falls below the "well annealed" value, depicted by the horizontal dashed line.

When the hydrogen concentration in Pd approaches 0.02, the hydride β phase forms [5] with complete transformation to the β phase at n = 0.60 [6]. To investigate the nature of these defects produced during the phase changes and compare them with the cold-work-produced defects, specimens of Pd cycled α → β → α were investigated using identical measuring techniques on as discussed before. Fig. 3 shows the lifetime and Doppler-broadening results.

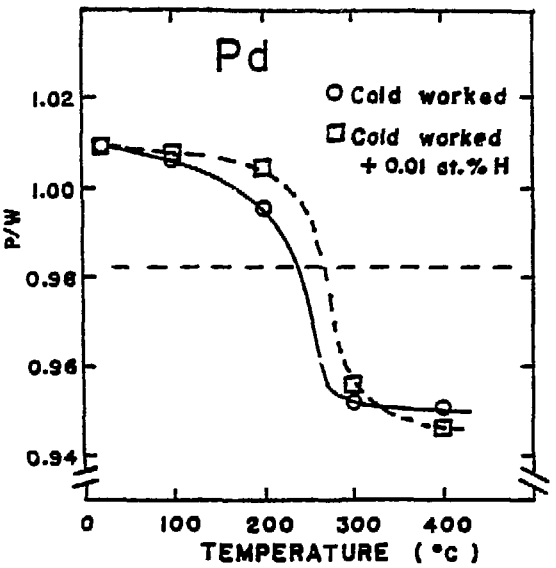

Figure 2: The peak-to-wings Doppler-broadening parameter of cold-worked and cold-worked + H charged Pd on a function of annealing temperature. The horizontal dashed line denotes the well-annealed value.

In this case the lifetime τ plotted is the lower of two fitted lifetimes (a third component due to source subtracted). The higher lifetime was ~400 psec with an intensity of ~5% for all cases. Note that the initial value of τ is 171 psec, comparable with the value consistently obtained for the major trap in the CW and CW + H cases. For this case we see continual recovery up to 400°C annealing with no well-defined recovery stage.

Also the value of τ remains well above the "well annealed" value of 120 psec and of course the "bulk" value of ~97 psec. Although apparently complete recovery of the defect structure introduced by 95% reduction cold

work is recovered by annealing to 400°C, only partial recovery of the defect structure introduced by hydriding and degassing is accomplished by the same anneal. The higher-lifetime, presumably void (bubble)-like defect, appears to be unaffected by the anneals. The Doppler-broadening results also shown on Fig. 3 show the same incomplete recovery.

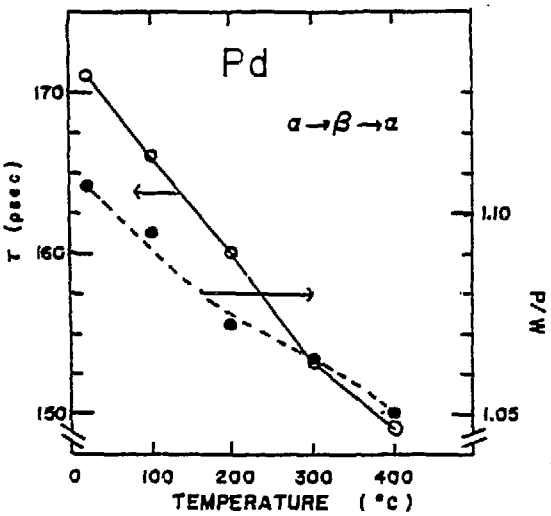

Figure 3: The lower of two fitted lifetimes (τ) and the Doppler P/W parameter for Pd hydrided to the β phase and degassed back to the α phase. They are plotted as a function of annealing temperature.

The value of τ and P/W is smaller in CW and CW + H after annealing than the values for "well annealed" Pd. Moreover, the "well annealed" lifetime spectrum could be analyzed on terms of one component due to traps (173 psec) and a bulk lifetime (97 psec). Therefore the conclusion is reached that trapping sites are present after annealing at 1200°C which are not present after annealing at 400°C. We prefer the tentative identification of these traps as vacancies (generated thermally at 1200°C) trapped at gaseous impurities upon the cooling of the specimen. The higher intensity of the trap component after air annealing than after vacuum annealing levels supports this view. These traps are removed in the 300 and 400°C anneal by the dislocation recovery taking place sweeping them to tangles and grain boundaries. The identity of the impurity (O or N or both) is, of course, unknown at this stage. Flanagan et al., [1] also quenched Pd from near the melting point to 273 K to investigate the role of vacancies in enhanced hydrogen absorption. No change was found. Since quenched and cold-worked Pd [7] recover between 200 and 300°C with an activation energy of 1.57 eV, this was assigned to single vacancies. This is the same temperature range to which we attribute dislocation recovery as seen in Figs. 1 and 2. Also the value Flanagan et al., [1] and Koster et al., [8] obtain for the migration energy (1.57 eV) seems to be too high when compared with the self-diffusion energy E_{SD} = 2.76 eV [8], and with the formation energy E_{IV} = 1.85±0.25 eV determined by Maier et al. [9] This gives a value of $E_m = E_{SD} - E_{IV}$ = 2.76-1.85 = 0.91 eV which is much lower than the 1.57 eV for the 200-300°C process and would argue for the placement of Stage III vacancy migration near 300K. With this uncertainty of where "Stage III" takes place in Pd, we feel that the role of vacancies on hydrogen trapping in Pd is a completely open issue.

It has been observed [6] that enhanced uptake of hydrogen occurs in hydrided-dehydrided Pd similarly to cold-worked Pd. This was attributed to hydrogen trapping at the dislocations generated during the phase changes. From the incomplete recovery of the shorter lifetime component and Doppler-broadening of Fig. 3 we conclude that the nature of the defect state is much different after hydriding-dehydriding than after cold working (Figs. 1 and 2) [10]. This is further attested to by the presence of a second higher-lifetime component in the α→β→α specimens (~400 psec at 5%) which is most probably a bubble-like defect. This defect remains after the completion of the annealing schedule reported here. The recovery of the shorter component is not complete at 400°C indicating that the other microstructure generated during the phase transformations is more stable than that produced by the 95% cold work. The evidence from the CW + H that a higher-lifetime component was present that was absent in the CW case would seem to argue that the presence of hydrogen on the microstructure enabled the stabilization of three-dimensional bubble-like defects. Whether the hydrogen is still in the defects after the annealing is an unknown.

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