

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-96SR18500 with the U.S. Department of Energy.

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Examination of 80 °C Desorption Isotherms of Tritium Aged Pd/k and LANA.75

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Metal hydrides, specifically Pd deposited on kieselguhr (Pd/k) and LaNi_{4.25}Al_{0.75} (LANA.75), have been used at the Savannah River Site for almost twenty years for hydrogen isotope separation and storage. Radiolytic decay of tritium to helium-3 in the metal matrix causes three classic changes in the performance of the hydride: the plateau pressure decreases, the plateau slope increases, and a heel forms, reducing the reversible capacity of the hydride. Deuterium and tritium isotherms were collected on the virgin materials, only tritium isotherms were collected at approximately 2 years, and both deuterium and tritium isotherms were collected at approximately 3.5 years of quiescent aging. Points of interest include those mentioned above as well as the effects of cycling the materials. The methods and results are presented.

I. INTRODUCTION

The Savannah River Site Tritium Facility has used Pd/k (palladium deposited on kieselguhr) and LaNi_{4.75}Al_{0.75} (LANA.75) in hydrogen isotope separation and storage processes for approximately 20 years. Unlike protium and deuterium, tritium is known to affect the performance of the hydride with time, as demonstrated in aged pressure-composition isotherms. Stresses caused by radiolytic decay of tritium to larger, virtually insoluble He-3 in the tritide lattice impinge on nearby hydrogen sites, changing the absorption and desorption characteristics of the hydride.

Pd/k and LANA.75 were selected for plant use for several reasons: high density storage, relatively fast gas transfer kinetics, sub-atmospheric plateau pressures at ambient temperature, and only moderate heating is required to deliver gas. In addition, both are capable of retaining large quantities of helium. Pd/k also has the advantages of a large separation factor and is relatively resistant to oxidation.

As a common choice for hydrogen isotope separation and storage, palladium tritide has been extensively studied¹⁻⁴. In both alpha and beta palladium hydride phases, hydrogen isotopes are located in octahedral sites

of the fcc lattice. The alpha to beta phase transition is accompanied by roughly a 12% increase in lattice volume. Helium-3 from radiolytic decay of tritium in palladium has been shown to precipitate into a uniformly distributed population of gas bubbles in the matrix. Initial bubble growth can be attributed to the clusters of helium-3 atoms located at vacancies and other defect structures. At higher bubble pressures, dislocation loops and networks may be punched out.

Several articles have been published describing the tritium aging effects on LANA.75⁵⁻⁹. LANA.75 has an hcp crystal structure and can accommodate hydrogen atoms in either octahedral or tetrahedral sites. Like palladium, alpha to beta phase transitions influence long range crystal structure with a 16.4% increase in lattice volume. Helium-3 behavior is not as well understood in LANA type materials as in palladium, though it is thought to be considerably less mobile.⁵

This paper compares 80°C desorption isotherms of virgin Pd/k and LANA.75 to those collected at approximately 2 years and 3.5-4 years of dormant tritium aging at ambient temperature. Changes in the isotherms due to cycling or exposure to elevated temperatures are also discussed.

II. EXPERIMENTAL

II.A. Materials

II.A.1. Pd/k

The Pd/k sample was supplied by Engelhard® and is nominally 50-wt% palladium. Palladium was deposited on Chromosorb P as a nitrate salt, then reduced under hydrogen, though as received Pd/k contained a significant amount of PdO. Supporting the hydride on kieselguhr significantly increases the surface to volume ratio, thereby increasing gas transfer rates and promoting He-3 release, reducing aging effects.

Approximately 5g of Pd/k was placed in a test cell consisting of two ½" schedule 40 pipe caps butt welded together. A Cajon® VCR4 tube fitting was butt welded perpendicularly to the pipe cap axis. The sample was

heated to 120°C under vacuum prior to activation and reduction with hydrogen. The material was exposed to hydrogen and baked out under vacuum five additional times with hydrogen prior to virgin isotherm data collection.

II.A.2. LANA.75

The LANA.75 sample was supplied by Ergenics® and contained less than 1.0 volume percent of secondary $\text{La}_z\text{Ni}_y\text{Al}_x$ phases with $z/(y+x) > 0.2$. Approximately 6 g was placed in a sample container as described above. The sample was cycled with hydrogen and baked out under vacuum similar to the Pd/k sample prior to virgin isotherm collection.

II.A.3. Gases

Deuterium was supplied via a compressed gas cylinder. Tritium was stored on a LANA.5 bed and was delivered as needed. Gas purities were typically >98.5% as determined by high resolution mass spectroscopy.

II.B. Apparatus

Aged isotherm measurements on both samples were performed on a Sievert's type manifold located in the Savannah River Site's Tritium Facility. Manifold pressure was measured with a Paroscientific 0-1375 kPa transducer accurate to ± 0.435 kPa. Manifold temperature was measured with a RTD calibrated to ± 0.11 °C. The sample cell was heated with a Glas-Col heating mantle paired with a Watlow F4P Series controller. A stick-on E type thermocouple monitored sample temperature to within ± 3 °C.

II.C. Approach

Each sample was examined in the virgin state prior to tritium aging. Two isotherms were performed on each sample after the first aging period. Between analyses, each sample aged quiescently at ambient temperature. Ages given represent total tritium exposure time, not time between analyses. A grab sample of the gas phase was taken on each sample at the end of the second aging period prior to isotherm determination. Isotherms were constructed using simple PVT material balances. After the second LANA.75 aging period, at the end of the second 80°C desorption isotherm, the sample temperature was increased to 120°C to observe the impact of elevated temperatures. A "cycle" in this article refers to desorbing the hydride stepwise (isotherm) followed by reloading the hydride with one large aliquot of gas. Heel size was determined on each sample after the second aging period via batch isotopic exchange. Equations describing single

as well as multiple isotopic dilutions have been developed.¹⁰

III. RESULTS AND DISCUSSION

III.A. Pd/k

A comparison of the virgin Pd/k isotherm with the 23 month isotherms is given in Figure 1. As expected, the

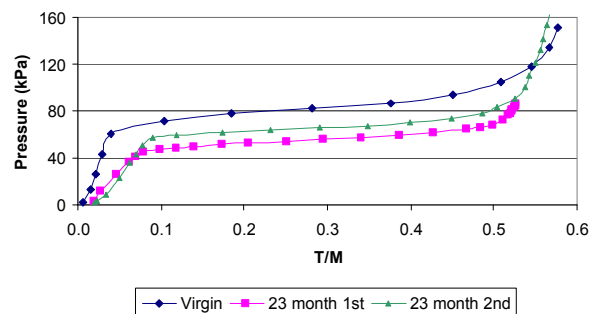


Fig. 1. Comparison of Virgin and 23 month 80 °C Pd/k Tritium Desorption Isotherms.

most pronounced feature is the decreased plateau pressure. In addition, the alpha phase slope is considerably lower than the virgin material, and a small heel of tightly bound tritium has formed. Cycling the material one time appears to have restored approximately 9.3 kPa to the plateau pressure.

At 40 months the sample remains surprisingly similar to the virgin sample. As can be seen in Figure 2,

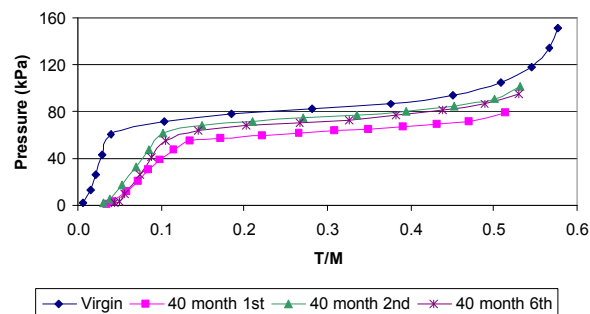


Fig. 2. Comparison of Virgin and 40 month 80 °C Pd/k Tritium Desorption Isotherms.

the plateau pressures appear to have recovered somewhat since the 23 month studies. This unexpected behavior is likely due to inconsistent heating of the sample and is within experimental error. As the heater placement around the sample was not changed between isotherm measurements, observations made in the same time period are more reliable than those made between time periods. As anticipated, the trapped hydrogen heel has grown to around 0.04 Q/M (where Q is any hydrogen isotope). There is essentially no change in plateau slope between the 40 and 23 month isotherms.

A number of other interesting phenomena were observed. Cycling the material restored 8-11 kPa of plateau pressure. Alpha phase slope decrease with the first isotherm is more pronounced and appears to partially heal itself in the second. Additional cycling had no significant effect on the resulting isotherm. The sample was cycled a total of 11 times with tritium or deuterium. Subsequent deuterium isotherms were virtually identical as the sample had been absorbed/desorbed several times with tritium.

Prior to processing the 40 month Pd/k, the overpressure was sampled at ambient temperature. High resolution mass spectroscopy determined the gas was 77.8 % helium with the balance tritium. This implies that 14-22% of the helium born in the metal was released during this time period. This is much higher than observed in other work on palladium powder¹¹, though it corroborates work done on similarly prepared Pd/k¹². Elevated helium-3 releases may help explain the relative stability of the hydride after 40 months of tritium aging.

Virgin and aged deuterium and tritium isotherms are given in Figure 3. As can be seen, the large isotopic

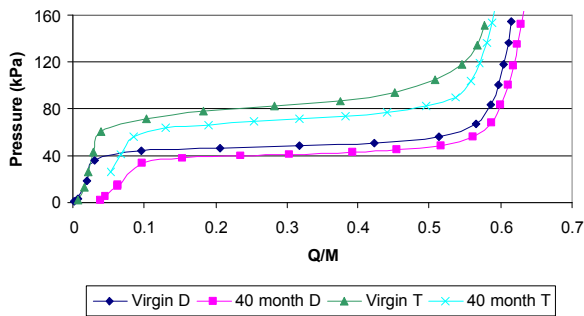


Fig. 3. Comparison of Virgin and aged 80 °C Pd/k Deuterium and Tritium Desorption Isotherms

effect characteristic of palladium is preserved. The tritium/deuterium plateau pressure ratios appear unchanged at approximately 1.7. Additional work utilizing absorption isotherms is needed to determine if the hysteresis loop has remained unchanged over the course of time.

III.B. LANA.75

A comparison of the virgin LANA.75 isotherm with the 23 month isotherms is given in Figure 4. While the concave up portion of the aged sample may represent the remnants of the beta phase transition, evidence of the alpha phase transition has been completely erased. The isotherm is approaching that for an amorphous material with respect to hydrogen. As expected, a large heel of deeply trapped tritium has significantly reduced the reversible capacity of the hydride. In accordance with literature, equilibrium pressures recovered markedly with one cycle, especially at higher stoichiometries.

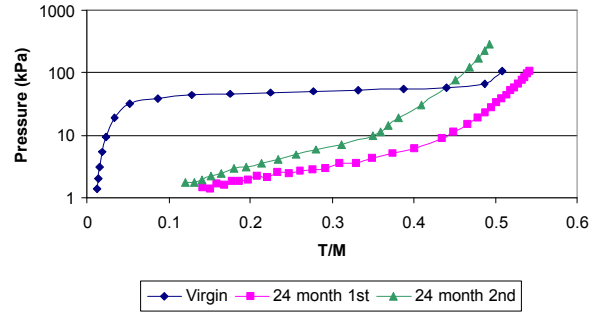


Fig. 4. Comparison of Virgin and 23 month 80 °C LANA.75 Tritium Desorption Isotherms.

The primary difference between the 23 and 40 month isotherm measurements is the continued decrease in reversible capacity, as can be seen in Figure 5. A slight

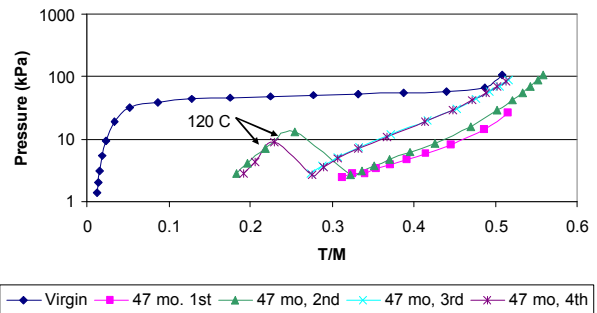


Fig. 5. Comparison of Virgin and 40 month 80 °C LANA.75 Tritium Desorption Isotherms.

recovery in isotherm pressure at higher T/M values is still evident between the first and second cycles, though not of the magnitude of the 23 month sample. At the termination point of the second isotherm, the test cell temperature was increased to 120°C and the isotherm continued. The next isotherm was shifted towards lower T/M values indicating a reduction in the amount of deeply trapped tritium (heel). Somewhat surprisingly, the shift remains almost parallel with the second isotherm, with no recovery of reversible capacity. Subsequent 80°C isotherms remained relatively constant. The fourth isotherm was performed in the same manner as the second. It can be seen that repeating this experiment had minimal effect on heel size.

High resolution mass spectroscopy of the 47 month LANA.75 overpressure determined the composition to be 86.3 % helium with the balance tritium. This implies that only 0-2% of the helium born in the metal was released during this time period.

Virgin and aged deuterium and tritium isotherms are given in Figure 6. Of note is the difference in plateau length for tritium and deuterium in the virgin hydride state. Otherwise, deuterium and tritium isotherms are essentially identical in both the virgin and aged materials.

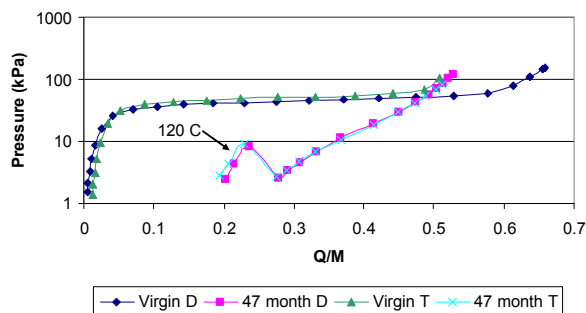


Fig. 6. Comparison of Virgin and aged 80 °C LANA.75 Deuterium and Tritium Desorption Isotherms

IV. CONCLUSIONS

IV.A. Pd/k

Tritium aging of this sample demonstrated two of the three anticipated results. The amount of deeply trapped hydrogen appears to grow over time. The isotherm plateau pressure decreased after 23 months of aging, though the 40 month plateau pressure appears to lie between the virgin and 23 month pressures. This is probably due to differences in heating blanket placement. No increase in plateau slope was observed, indicating the sample has retained a homogenous crystal lattice.

Several other interesting observations were made. A grab sample of the overpressure after 40 months of tritium exposure revealed that 14-22% of the helium-3 generated in the solid had been released to the gas phase. This may factor in how well the sample has held up to tritium. The ratio of deuterium to tritium plateau pressures remained constant over the course of this study. At both 23 and 40 month time intervals, one cycle appeared to partially restore both the alpha phase slope and plateau pressure. Additional benefits were not observed with additional cycling. It is thought that cycling the hydride promotes large helium-3 bubble growth at the expense of smaller bubbles. Given that helium-3 maintains good mobility in the palladium lattice, it is expected that minimal energy would be required for helium-3 to migrate to form larger bubbles.

IV.B. LANA.75

Helium-3 ingrowth due to tritium decay had a dramatically larger impact on the hydriding properties of LANA.75. By 47 months, the heel had grown to approximately half of the original reversible capacity of the hydride. The original plateau has been replaced with an isotherm that is almost linear on a log plot, indicating significant damage to the crystal lattice.

Like Pd/k, cycling the material impacted isotherm shape and possibly lateral position. Literature reports that additional cycling would continue to restore original hydriding characteristics to a point.⁵⁻⁷ Increasing the desorption temperature to 120°C after two 80°C

isotherms shifted subsequent isotherms toward lower Q/M values. A repetition of the temperature excursion did not produce additional changes. This seems to suggest a spectrum of stresses caused by helium-3 deposition. Heating the sample to 120 °C appeared more effective at relieving stresses than cycling the material at 80°C. The additional 0.08-0.09 Q/M desorbed from the hydride at the elevated temperature is indicative of the range of hydrogen trap energies. As expected, only 0-2% of the helium-3 generated in the solid had been released to the gas phase in the 47 month sample.

ACKNOWLEDGMENTS

The information contained in this article was developed during the course of work under Contract No. DE-AC09-89SR18035 with the U.S. Department of Energy.

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