

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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Helium Release Behavior of Aged Titanium Tritides (U)

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Abstract

One sample of bulk Ti has been loaded with a 50%/50% deuterium/tritium (D/T) mixture and statically aged for 6.5 years. Thermal desorption of the sample shows an initial release of hydrogen isotopes followed by ^3He release. Subsequent D_2 loading/desorption was used to quantify the trapped tritium heel. The sample shows an excess hydrogen capacity as a second thermal desorption peak that partially disappears and shifts with annealing at 923-973K. The main hydrogen desorption peak also shifts to higher temperature, indicating a partial reversal of the tritium-decay induced damage by annealing.

Introduction

The Savannah River Site has been interested in studying tritium decay processes in metal hydrides for many years [1, 2, 3]. Tritium decay in metal tritides produces ^3He in the bulk. This He is highly insoluble, and typically nucleates and forms internal bubbles. The bubbles and dissolved He are thought to induce strain in the metal, which alters the thermodynamics of hydrogen absorption/desorption and forms trapped hydrogen that is more difficult to thermally desorb. This manifests as reduced plateau pressures, loss of hysteresis, and capacity reduction.

Prior work on tritium aging effects in Ti thin films by Rhodin and Surenyants has shown that the thermal desorption of He shows two peaks [4]. As the He content is increased these peaks move to lower desorption temperatures. (In those experiments the hydrogen isotopes were gettered out of the gas and did not appear in the thermal desorption spectrum.) It is of interest to examine bulk Ti and compare its behavior to that of thin films and other hydride materials.

The Savannah River Site has been using titanium as a tritium storage material for several years, and several research samples were prepared for tritium aging effects studies. One sample has been extensively examined at this time. The primary techniques used in these studies are thermal desorption and isotopic heel exchange. In the typical thermal desorption experiment the sample is loaded at room temperature and then subjected to increasing temperature. Pressure developed as the hydrogen isotopes desorb is monitored, along with sample temperature. Isotopic heel exchange experiments are modifications of the thermal desorption experiment, where gas samples are taken and mass spectrometrically analyzed for isotope content.

Experimental

The Ti used in this experiment was specially manufactured by Ergenics, Inc., and consisted of large particles of x to y mesh size. The samples were placed in stainless steel test cells equipped with stainless steel Nupro valves using Cajon VCR connections. In some cases, the particle size had to be reduced by fracturing the chunks in order to get the sample to pass through the VCR weld gland. The sample was loaded with a 50/50 mix of D/T isotopes, and allowed to age. At that point the sample was mounted on a Sievert's apparatus equipped with MKS 10000 torr Baratron pressure sensors for these studies. Gas grab samples were collected and analyzed for isotope and ^3He content at appropriate points during experimentation. The test cell was not equipped with any method to directly measure sample temperature internally. Temperature measurement was accomplished by attaching a Type K thermocouple to the exterior of the cell near where the Ti was located. Isotope exchange experiments used commercial high-purity deuterium gas.

Results and Discussion

The Ti sample was loaded with a 50/50 D/T mix and the final loading $(\text{D}+\text{T})/\text{M}$ ($= \text{Q}/\text{M}$) was 1.8., where it is assumed that all hydrogen isotopes were eventually absorbed by the Ti leaving a very low overpressure. After storage for 6.46 years (half-life of T is 12.6 years), the Ti sample was found to have a small amount of gas overpressure which was analyzed and found to be 100% ^3He . The sample then was thermally desorbed and results are shown as a time plot in Figure 1, where two peaks are evident. Three grab samples were taken during this experiment (indicated by the asterisks in the Figure). The first was acquired on the early part of the first peak, the second was collected at the minimum between the peaks, and the third at the very end of the experiment. Mass spectrometric analysis of the samples showed that the first sample was 1.53% ^3He and 98.0% hydrogen isotopes (41.4% T). The second sample was 1.12% ^3He and 98.9% hydrogen isotopes (41.5% T), indicating a slight dilution of the ^3He . The third sample however was 42.3% ^3He and 57.2% hydrogen (41.5% T), which defines the second peak as being due to ^3He evolution. Initial He/M ratio was 0.28, and the location of the He peak maximum is roughly consistent with [4], where a 30 at% He content produced an initial peak at ~850K and a 22 at% He content produced an initial peak at ~1050K. Gas evolution was still increasing when the temperature stabilized at ~923K, the upper limit for that run.

The sample was isolated at that point and the small residual hydrogen isotopes found in the ~25cc test cell gas space were allowed to reabsorb. Subsequently a second thermal desorption was undertaken, with very little pressure being developed, with 28.2% being ^3He . Computations based on the calibrated system volumes, temperatures, and pressures indicated that the He/Pd ratio had decreased from 0.28 to 0.05 in the first desorption. The second desorption further released approximately 0.005 He/Pd units, but that number is the approximate experimental error. Final Q/Ti ratio was computed to be 0.97. The sample was reloaded with deuterium and desorbed. The third desorption was computed to reduce to He/Ti ratio to approximately zero, but some small amounts of He were still observed in the next (fourth) desorption's offgas.

The third desorption's offgas had 9.45% ^3He in it, and the hydrogen isotopes consisted of 73.0% D and 17.0% T. The isotope exchange process reduced the heel to 0.83 Q/M by extended heating and desorption followed by evacuation of the gas from calibrated volumes. A second exchange (fourth desorption) produced 2.1% ^3He , 93.7% D, and 3.4% T in the gas and a final Q/M of 0.85. The third exchange (fifth desorption) produced 0.25% ^3He , 0.28% H, 99.2% D, and 0.32% T in the gas and 0.81 Q/M in the heel. The computed and found %T in H isotopes was 19.4% and 18.7% in the first exchange; 8.4% and 3.5% in the second, and 1.5% and 0.3% in the third. It is unknown why the observed percents are lower than expected.

The first and second exchange experiments used just enough D_2 to load the Ti to its theoretical maximum (Q/M=2.0). However, the third exchange was conducted by loading with twice that pressure. Surprisingly, a new desorption peak was observed, and computed loading level was 2.68 Q/M, evidencing a 34% excess capacity. Two subsequent isotope exchange experiments were conducted after the third, using higher loading pressures. Since the T content of the third exchange experiment was so low, gas composition analysis of the subsequent exchanges were of little value, however, these experiments determined that 2.68 was the maximum capacity. The origin of this excess capacity is unknown at this time.

The change in pressure vs. temperature for the first, third, and fourth exchange are shown in Figures 2, 3 and 4, respt. Of note is the large extra peak with maximum at about 725K seen in Figure 3. With each exchange cycle, that peak is seen to decrease slightly and move to higher temperature. The primary hydrogen isotope peak that occurs near 750K in the first desorption also moves up to nearly 925K in the latter desorptions. This is indicative of an annealing out of T-induced damage in the material, and has been noted in other hydride materials. However, the excess capacity is still present after up to 24 hours of annealing at 973K.

Conclusions

Tritium aging damage in Ti has been observed, and plateau pressure depression has been shown to be removed by annealing since thermal desorption maxima for the primary H isotope desorption moves up in maximum. The damage includes the formation of a large heel, up to ~1.0 Q/M units, but this heel content does not seem to be affected much by annealing. The initial He content introduced by T decay was removed thermally, but the heel content remained unchanged, indicating the Ti structural damage is the cause of the heel, and not the actual presence of He. A 34% excess hydrogen capacity was discovered, that seems to respond to annealing as well. Clearly, the nature of this excess capacity needs to be investigated further. At this time it could be attributed to many possible sources, including contaminants and/or small particulates formed by decrepitation.

References

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Acknowledgement

This work was supported by Westinghouse Savannah River Company under U. S. DOE contract number DE-AC09-96SR18500.

Figure captions

Figure 1. Change in pressure with respect to time for initial desorption of mixed hydrogen isotopes and helium from 6.5 year old TiQ2. Initial Q/Ti (after decay) = 1.55 (41.0% T), initial He/Ti=0.28. Found 41.0% T, expected 41.5% T.

Figure 2. Change in pressure as a function of temperature for third desorption (1st exchange experiment). Initial Q/Ti = 2.06, initial He/Ti~0, found 18.7%T, expected 19.4% T.

Figure 3. Change in pressure as a function of temperature for fifth desorption (3rd exchange experiment). Initial Q/Ti = 2.68, final Q/Ti=0.81, initial He/Ti~0, found 0.3%T, expected 1.5% T (0.3%T is the approximate noise level of the experiment).

Figure 4. Change in pressure as a function of temperature for sixth desorption (4th exchange experiment).

Figure 1.

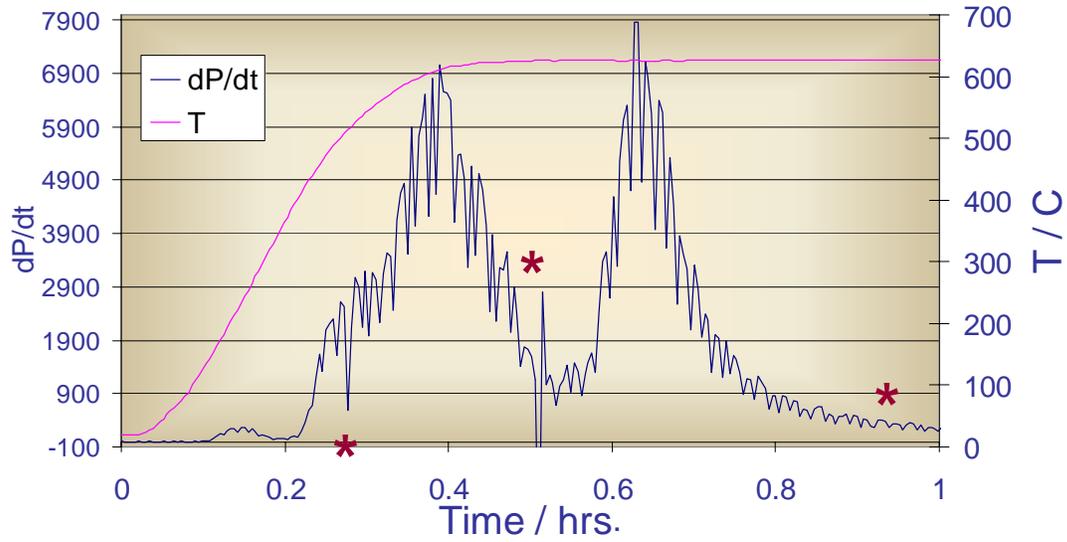


Figure 2.

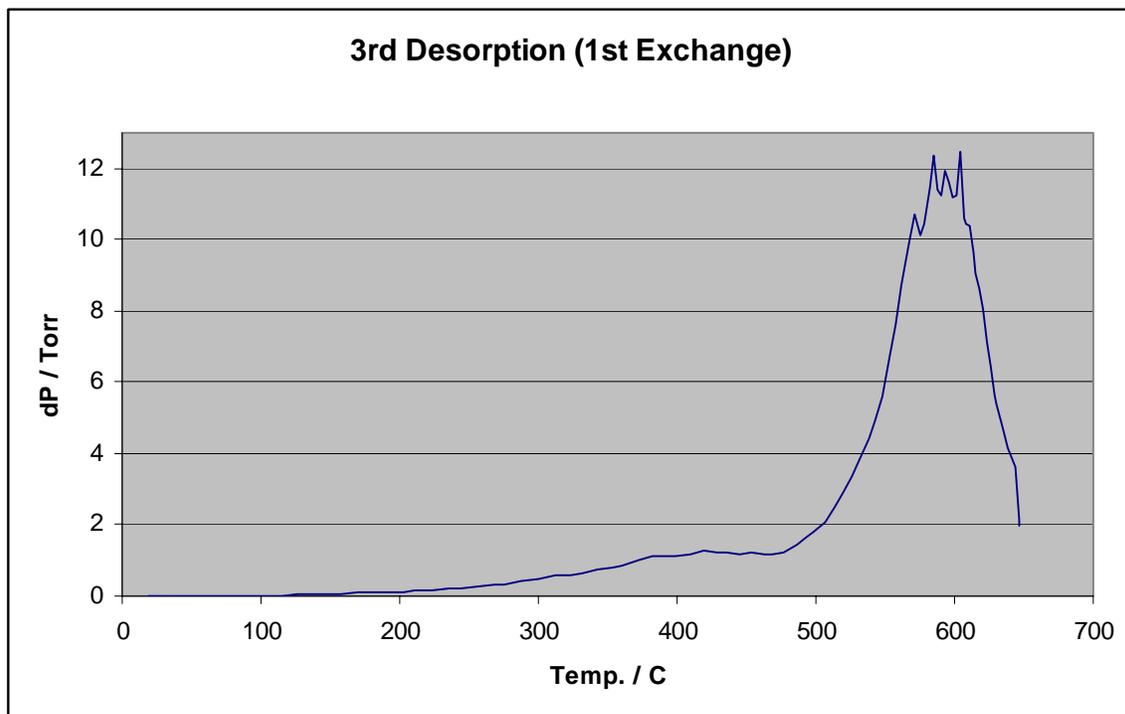


Figure 3.

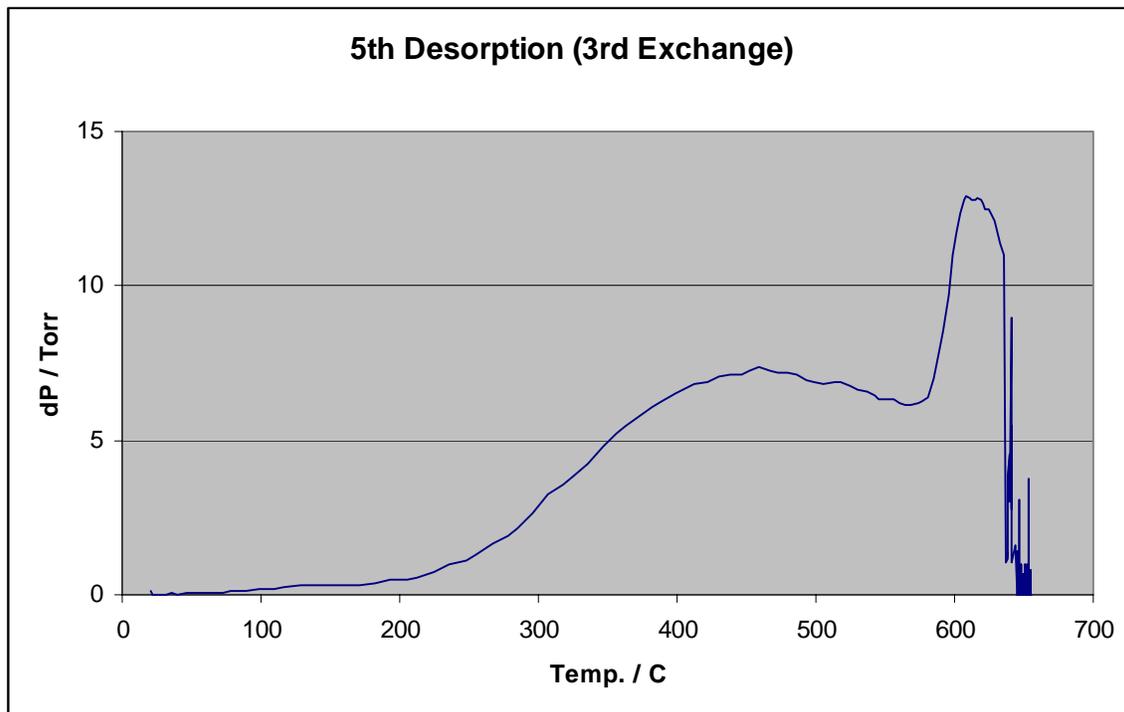


Figure 4.

