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Tritium aging effects in $LaNi_{4.25}Al_{0.75}$

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Abstract

Tritium desorption isotherms and helium release properties are reported for three different $LaNi_{4.25}Al_{0.75}$ samples having seen 11.5 and 13 years of tritium exposure, and are compared to earlier data from similar samples with less exposure. The isotherms show a complete loss of the typical plateau structure, and a decreasing absorption capacity. However, the capacity loss is not due to further increase in heel content. Helium breakout is show to occur in one sample when the T content became low.

Keywords: Intermmetallic material; Radiolytic decay; Tritium processing

1. Introduction

The Savannah River Site (SRS) tritium processing facilities use $LaNi_{4.25}Al_{0.75}$-tritide as the primary tritium storage medium [1–4]. This intermetallic material was chosen because it can store large amounts of tritium, the material is easily activated, the storage pressure is subatmospheric, and a delivery pressure of >200 kPa is easily achieved by moderate heating. In addition, the material captures nearly all of the ^3He formed from radiolytic decay of the solid tritide. As part of the development for large-scale tritium processing using $LaNi_{4.25}Al_{0.75}$, a number of bench-scale storage samples were loaded in 1986–87. Characterization of samples having a cumulative aging time of >11 years has now been attempted. Some of these samples have or nearly have reached the point of He saturation, and one has shown significant He pressure buildup and He release.

When first loaded, the equilibrium desorption isotherm of $LaNi_{4.25}Al_{0.75}$-tritide showed a flat, well-defined phase transition (as indicated by the plateau in the pressure–composition isotherms), and the total reversible tritium storage capacity spanned a tritium to metal atom ratio of ~0.6 with no tritium heel. With time, $LaNi_{4.25}Al_{0.75}$-tritide degrades significantly, causing a decrease in the plateau pressure, an increase in the plateau slope, and the formation of a heel. Several prior reports on samples from the 1986–87 group and related materials have been issued [5–11]. This report describes the partial characterization of some of the oldest aged samples of $LaNi_{4.25}Al_{0.75}$-tritide ever studied.

2. Experimental

Tritium gas is supplied from the production process at WSRC, and composition is routinely >97% pure T_2. T_2 is stored on a $LaNi_{4.5}Al_{0.5}$ bed and delivered as needed, minimizing the ^3He contaminant. Load gas is sampled and analyzed mass spectrometrically to determine exact purity of load gas on each sample. Deuterium was supplied as bottled gas (Matheson lab grade).

The Sieverts' apparatus used were constructed of 1/4 in. stainless steel tubing connected by Cajon VCR fittings. Pressure was monitored with MKS 10 000 Torr Baratrons. Temperatures were monitored with various type K thermocouples. Recent data was collected by computer logging with a LabView program installed on a DEC 400 MHz PC.

$LaNi_{4.25}Al_{0.75}$ alloys were purchased from Ergenics, Inc. (Hy-Stor custom alloys). Three specific samples will be discussed. LANA75-SP1 and LANA75-T6 were approximately 11.5-year-old samples when last examined.

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LANA75-T4 was ~13 years old when examined. All samples were from the same lot of material.

Various samples have had varying exposure histories, with some samples having perhaps one isotherm taken early in their life, and others having had multiple isotherms acquired from them at differing times. Sample designations routinely include the Al content, i.e. LANA75-SP1 is nominally a $LaNi_{4.25}Al_{0.75}$ alloy. The specific sample history will be described as needed. In general, the sample weights were ~5 g. Sample cell free volumes were roughly 15 cc, and were determined individually by Ar expansions (as were all system volumes). La–Ni–Al alloys typically need multiple cycles of absorption/desorption to obtain reproducible behavior, as the samples decrepitate and the surface to volume ratios change. All the samples discussed herein have been activated in this fashion and baked out prior to use.

3. Results and discussion

Fig. 1 shows 80 °C desorption isotherms characteristic for the material. The primary observation is the loss of the plateau experienced by the most aged material. Also of note is the observation that the heel is thermally depopulated by raising the isotherm temperature to 150 °C. (a 150 °C desorption isotherm is shown for comparison.) However, even in that case some heel remains. The two isotherms shown for the 11.5-year-old material are replicate runs on LANA75-SP1. LANA75-T6 showed similar behavior. Earlier isotherms have been published previously [7–11].

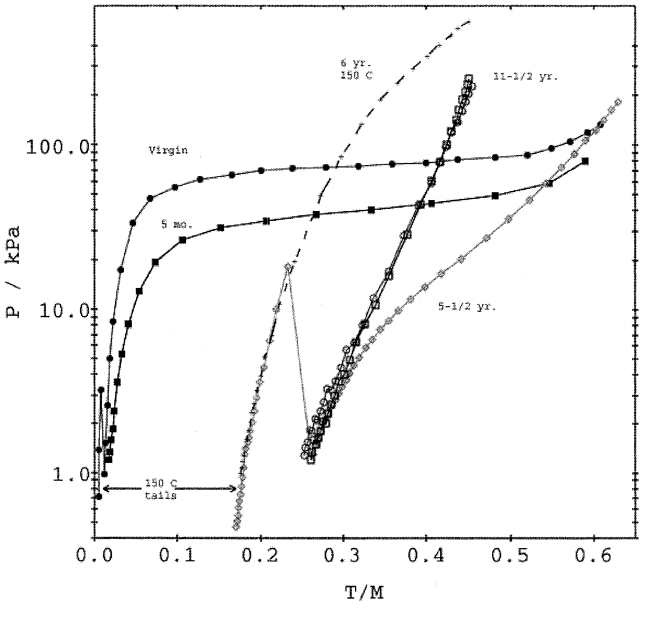

Fig. 1. Tritium desorption isotherms (80 °C unless noted) for $LaNi_{4.25}Al_{0.75}$ for various aging times. (●) Virgin material; (■) aged 5 months in tritium; (○) aged 5.5 years in T_2; (+) aged 6 years in T_2 (isotherm at 150 °C); (□, ○) aged 11.5 years in T_2. Note that the 5.5 year and virgin material isotherms show tails where the temperature was increased from 80 to 150 °C, demonstrating that the heels can be thermally depopulated.

Some concern existed that a disproportionation of the material may have occurred over time, forming a strongly bound hydride such as LaT_2 or LaT_3. Thus the heel exchangeability was probed with deuterium heel exchange experiments and high temperature desorptions of small parts of one sample (LANA75-SP1). Fig. 2 shows the results of mass spectral analysis for T content of the gas desorbed from the aged samples after full loading with pure D_2. Clearly, the T in the heel mixes with the freshly absorbed D in a simple dilution process, and is subsequently desorbed. Loading was typically conducted at room temperature, and desorption was at 80 °C. A consistent terminal pressure was used in each cycle to make the data points as comparable as possible. The total T heel was determined by integrating the T removed in all cycles, and this was found to lead to a T/M value of ~0.25 in two different samples (LANA75-T6 and LANA75-SP1). Isotherms in Fig. 1 are adjusted to this point, based on these heel content determinations.

With material this old, the solid phase He content is expected to have approached the point where the total bulk He capacity could be exceeded. Typically at that point, 'breakout' occurs and any excess He formed by decay is released at the generation rate. Thus careful sampling and analysis of the gas remaining in the cells after the extended aging period was conducted. The cell gas was nearly 100% ^{3}He in all cases, indicating the T content of the material had decayed to the point where all T was in the heel and none remained in the gas phase. Computation indicated the

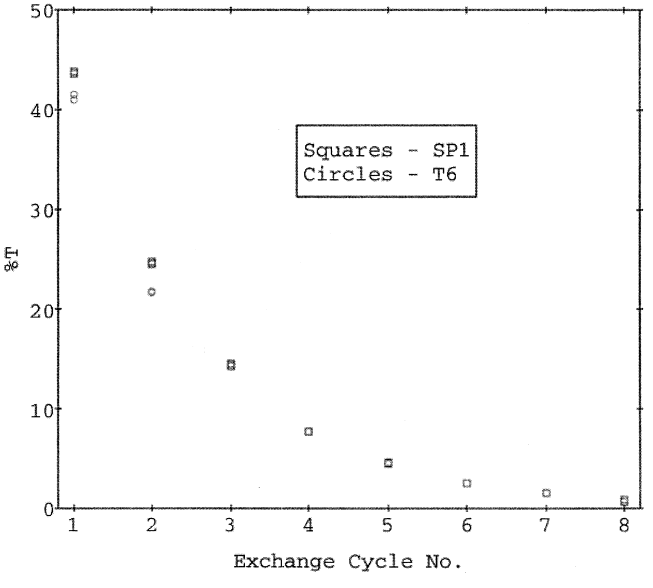

Fig. 2. Deuterium exchange experiment result, %T in D_2 evolved from aged materials. The data shows simple dilution of the initially fully tritiated heel. (□) Data for sample LANA75-SP1; (○) data for sample LANA75-T6.

He/M ratio of samples SP-1 and T6 was 0.34 in both cases. Since the healing of the aging damage observed in a Pd–Rh–Co foil [12] was not anticipated, all isotherm work usually began with a full reloading of the alloy. Subsequent isotherms were reproducible, as shown in Fig. 1, but the possibility of a first cycle shift remains and will be investigated on remaining samples.

An interesting He release behavior was noted with sample LANA75-T4. Initially no continuous He release was noted. Starting sample cell overpressure was analyzed after a 13-year storage period, and found to be 99.9% ^{3}He. However, the sample cell pressure was calculated to be 1.14 MPa, which indicates complete breakout was occurring. The theoretical He/M ratio would have been 0.43 if no release had occurred. Reducing the He/M ratio by the released amount indicated a final He/M ratio of 0.34 in agreement with the other two samples.

During a subsequent 80 °C desorption isotherm determination, the first 10 points on this curve, which reduced the equilibrium pressure from 495.3 to about 28.1 kPa, showed typical tritium desorption behavior in that the pressure would eventually equilibrate. The pressure time profile for both the tenth and 11th points are shown in Fig. 3. The 10th point is discontinuous (flat portion) because the sample cell valve was closed overnight, but the data logger continued running. Since the pressure sensor was isolated from the sample, it remained constant until the sample cell valve was reopened the next morning, and the released tritium was allowed to flow into the manifold. A brief equilibration period then occurred before the sample cell was again isolated and the aliquot for the next equilibration point was removed from the manifold.

However, as shown in Fig. 3, while allowing equilibration for the 11th point, the pressure began increasing continuously. Because this was unexpected, the system was allowed to attempt to equilibrate for an extended period without isolating the sample from the manifold. As can be seen the pressure continued to increase. Two gas samples were taken, and are indicated in Fig. 3. The first was collected approximately 75.2 h after equilibration began, and was analyzed as containing 11.4% ^{3}He. After another 89.4 h, the gas was sampled again, and the ^{3}He content had increased to 17.2%, clearly indicating He release was occurring. Samples LANA75-T6 and LANA75-SP1 did not show similar He release behavior, and were used in isotherm and heel exchange studies.

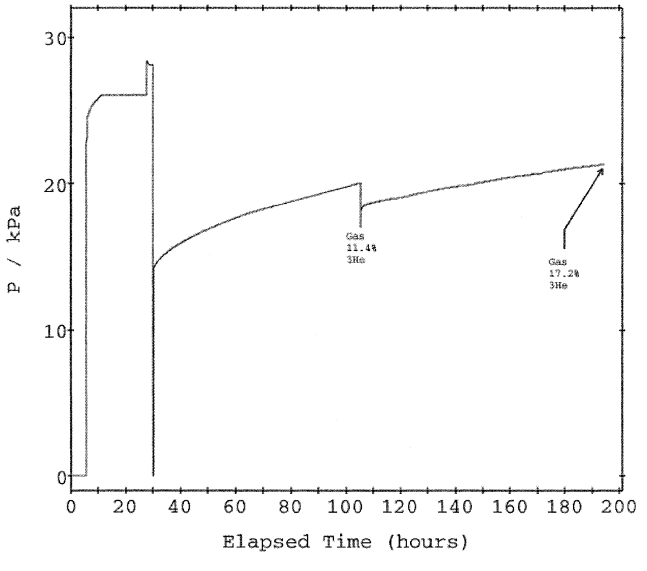

Fig. 3. Pressure–time profile for sample LANA75-T4 for the tenth and 11th desorption step of an 80 °C desorption isotherm. Gas ^{3}He content indicated in two places.

During a 6-month period where the D_2-exchanged LANA75-SP1 was stored without tritium content, it suffered from an air in-leakage. This sample was passivated by further exposure to an aliquot of room air, and then was removed from the sample cell for additional studies. Three separate small 0.345-g samples were placed in a glass tube inside a stainless steel test cell and heated to ~450 °C on at least two separate occasions. The evolved gas pressure was measured and sampled for mass spectrometry analysis. Three samples thus tested showed no appreciable T in the evolved gas, suggesting no appreciable T remained in the heel after multiple D_2 exchanges.

Upon finding that some LANA75-T4 had already released significant quantities of He, several other samples that were also ~13 years old were checked for high sample cell pressure by gas sampling at room temperature. No other excessive pressure buildup was detected, no isotherm work was attempted on these samples, and no continuous He release was observed, however, it may well be that elevated temperatures and low T/M ratios are required to induce He release. One sample had a broken valve that could not be fully opened. Instead just enough seal pressure could be removed that a slow pressure leak into the manifold was observed. However, this would eventually equilibrate, indicating no continuous release was ongoing.

4. Conclusions

Several La–Ni–Al alloy samples have been aged with tritium for several years and subsequently examined. While the material still shows hydrogen absorption capability, the material capacity has been severely decreased at a given pressure. The clear phase change behavior that typically produces plateaux in isotherms has given way to what could be interpreted as a totally heterogeneous behavior. Heel growth has apparently stopped, based on measurement of the current heel content by deuterium exchange demonstrating the same T content as observed approximately 6 years prior. Instead, the upper capacity value is now falling with age. High temperature desorption of D-exchanged sample has shown that all T is exchangeable (within experimental error).

Unfortunately, the first cycle after storage was not observed, so whether or not some healing of age damage has occurred remains to be determined.

One 13-year-old sample has shown interesting He release behavior. While initially showing excessive He in the sample cell overpressure, during isotherm determination the pressure was observed to equilibrate, implying no rapid release was occurring. However, once the T content had been reduced significantly, He release became noticeable. Several other similar samples were checked for excessive He pressures, but none were found. However, several other samples remain unexamined, and computed cell pressure in LANA75-T6 may indicate some release.

Clearly, more work is required to quantify the He content of the samples. This computation is made difficult by the grossly changing isotherm characteristics coupled with the long storage times these samples have seen. Careful examination of the high temperature desorption results should be able to shed some light on this problem. Presuming some samples will not show He breakout, tritium aging of those samples will continue with the intent of further studying the He release properties of these aged materials.

Acknowledgements

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References

[1] M.S. Ortman, T.J. Warren, D.J. Smith, Use of metal hydrides for handling tritium, Fusion Technol. 8 (1985) 2330.
[2] M.S. Ortman, L.K. Heung, A. Nobile, R.L. Rabun III, Tritium processing at the Savannah River Site: present and future, J. Vac. Sci. Technol. A 8 (3) (1990) 2881.
[3] R. Lasser, T. Schober, Some aspects of tritium storage in hydrogen storage materials, Mater. Sci. Forum 31 (1988) 39.
[4] T. Motyka, The replacement tritium facility, Fusion Technol. 21 (2) (1992) 247.
[5] J.L. Flament, G. Lozes, Localisation de l'helium forme dans les composes trities, in: Proceedings of the Third International Congress on Hydrogen and Materials, Paris, France, 1982.
[6] R.C. Bowman, R.H. Steinmeyer, L.K. Matson, A. Attalla, B.D. Craft, Long-term behavior of the tritides formed by nickel-based intermetallic compounds, Fusion Technol. 8 (1985) 2337.
[7] R.T. Walters, I. Helium Dynamics in Metal Tritides, The effect of helium from tritium decay on the desorption plateau pressure for La–Ni–Al tritides, J. Less-Common Metals 157 (1990) 97.
[8] R.T. Walters, A. Nobile Jr., W.C. Mosley, Helium dynamics in metal tritides. II. The significance of microstructure in the observed helium behavior for La–Ni–Al tritides, J. Less-Common Metals 170 (1991) 63.
[9] A. Nobile, R.T. Walters, W.C. Mosley, Effects of radiolytic tritium decay on the thermodynamic behavior of $LaNi_{4.25}Al_{0.75}$ tritides, J. Less-Common Metals 172–174 (1991) 1352.
[10] A. Nobile Jr., Experience using metal hydrides for processing tritium, Fusion Technol. 20 (1991) 186.
[11] A. Nobile, J.R. Wermer, R.T. Walters, Aging effects in palladium and $LaNi_{4.25}Al_{0.75}$ tritides, Fusion Technol. 21 (1992) 769.
[12] K.L. Shanahan, J.S. Hölder, Tritium aging effects in a $Pd_{0.94}Rh_{0.05}Co_{0.01}$ foil, J. Alloys Comp. 348 (2003) 72.