Contract No.:

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Tritium 2016 Abstract Log Number: **17017** **FST16-163**

Title: **Tritium Aging of LaNi4.15Al0.85 (LANA.85)**

Author List:

David W. James – Savannah River National Laboratory

Gregory C. Staack – Savannah River National Laboratory

Simona Hunyadi-Murph – Savannah River National Laboratory

Corresponding Author: **David W. James**

Corresponding Author Contact Information:

Savannah River National Laboratory

Savannah River Site, Building 999-2W

Aiken, SC, 29808

(803) 646-7576

david.james@srnl.doe.gov

Total Number of Pages Including Cover Page: **13**

Number of Tables**: 0**

Number of Figures: **4**

Key Words: **Hydride Storage; LANA.85; Tritium Aging; Isotherm Performance**

SRNL Document Number: **SRNL-STI-2016-00212**

Tritium Aging of $LaNi_{4.15}Al_{0.85}$ (LANA.85)

David W. James*, Gregory C. Staack, Simona Hunyadi-Murph

The Savannah River Tritium Enterprise (SRTE) has used hydride beds to store and process hydrogen isotopes for over two decades. New beds are being designed to use a hydride material, - $LaNi_{4.15}Al_{0.85}$ *(LANA.85) - that has a lower plateau pressure than the material previously employed. LANA.85 is expected to have a limited service life due to radiolytic decay of tritium to He-3 within the metal matrix, which will result in degradation of hydride performance. Tritium aging was initiated on a LANA.85 metal hydride sample to look for changes in desorption isotherm performance which occur with aging. Desorption isotherms were collected at 120, and 160 °C annually. A lower temperature isotherm was collected at 100°C after 2 years of aging. A single absorption isotherm was collected each year at 120°C. After testing, each sample was reloaded with tritium for quiescent aging until the following year. Samples were stored in the beta phase.*

Results collected on the virgin material and annually for two years of tritium exposure are presented and discussed. The results have shown no unexpected behavior of the LANA.85 materials over the course of tritium exposure. As the service life of a the new hydride bed being designed is greater than eight years, further annual monitoring and evaluation is recommended to track the effects of tritium exposure on isotherm behavior. Continued evaluation of will reduce the likelihood that unanticipated behaviors will be encountered in full scale production beds within the SRTE Tritium Facility.

I. INTRODUCTION

The SRTE has used lanthanum-nickel-aluminum $LaNi_{4.25}Al_{0.75}$ (LANA.75) metal hydride beds for over two decades for high density storage of hydrogen isotopes.[1] LANA materials reacts with hydrogen isotopes reversibly to form a metal hydride. When the hydrogen partial pressure is higher than the equilibrium pressure, hydrogen is absorbed by the metal. The absorption reaction is exothermic which means cooling is needed to sustain the reaction. Desorption is endothermic, meaning that heat must be supplied to release the hydrogen isotopes. Early SRTE bed designs depended on a problematic Hot and Cold Nitrogen (HCN) system to provide the heating or cooling required for desorbing and absorbing hydrogen isotopes. Later bed designs utilized electrical heating and forced glovebox nitrogen cooling to reduce reliance on the problematic HCN system. While electrical heating is significantly more effective than hot nitrogen for gas delivery, the use of glovebox nitrogen for cooling to induce gas absorption is less effective. To compensate for less effective cooling, a lower pressure material, $LaNi_{4.15}Al_{0.85}$ (LANA.85), was selected for use in next-generation hydride beds.

LANA.85 is a slightly modified alloy of the LANA.75 hydride currently employed in the SRTE and is expected to meet the prescribed hydrogen absorption and desorption performance criteria of operating at a lower plateau pressure. Substitution of Al for Ni serves to lower the plateau pressure of a formed tritide.[2] With the increased aluminum content of LANA.85 over LANA.75, both the plateau pressure and reversible capacity of the hydride are slightly decreased.[1] The decrease in reversible capacity is overcome by the addition of more hydride material for a given bed.

LANA.85 is expected to have a limited service life due to radiolytic decay of tritium to He-3 within the metal matrix. Tritide metal hydrides are unique compared to other hydride materials in that He-3 will accumulate in the lattice of material.[3] This decay causes changes in the phase transition $\alpha + \beta$ plateau (depression and slope), reduces the reversible capacity of the bed through the formation of a 'heel' of trapped hydrogen isotopes, and eventually leads to He-3 saturation of the metal.[3, 4] Bed failure typically occurs when either (a) the bed reversible capacity adversely impacts process throughput or (b) it can no longer deliver He-3-free hydrogen isotopes. With LANA.75, these changes take place over approximately 8-12 years, (depending on the quantity of tritium to which the hydride is exposed).[4] The behavior of LANA.85 in a tritium environment over time is unknown.

This document describes tritium aging of LANA.85 materials over 2 years. The behavior of metal hydrides is most commonly measured by isothermal pressure composition response curves (isotherms). From isotherms, thermodynamic properties may be determined. While testing on LANA.85 has been performed using protium and deuterium, negligible information is available pertaining to its long term performance in tritium service. By tracking the aging behavior of small samples, SRNL and SRTE personnel are able to monitor LANA.85 performance degradation years in advance of these behaviors presenting themselves in full-scale-process beds.

II. EXPERIMENTAL PROCEDURE

To collect isotherms, at a given constant temperature, a known amount of gas is either introduced or withdrawn from a system containing a metal hydride sample, and the pressure is measured after the new solid-gas equilibrium is achieved. A series of hydrogen additions results in an absorption isotherm; a series of subtractions produces a desorption isotherm. The difference in pressures before and after hydrogen exposure allows calculation of the amount of gas absorbed or desorbed from the hydride. The hydride material undergoes a phase transition ($\alpha \rightarrow \beta$ or vice versa) as hydrogen is either absorbed or desorbed. The length and slope of the transition plateau region is indicative of the capacity and homogeneity of the hydride, respectively. The solid phase composition is presented as the ratio of hydrogen atoms to metal atoms.

Two samples of LANA.85 were loaded with tritium to initiate tritium aging and examine aging effects. The first sample was used to monitor He-3 saturation. Results from the second sample, which was loaded to monitor isotherm performance, are discussed in this work.

II.A. LANA.85 Sample Description

The tested LANA.85 material was purchased from GfE (GfE Metalle und Materialien GmbH, Germany). The hydride was sent to Hydrogen Consultants, Inc. for annealing under argon at ~900-1000°C for 100 hours to produce an alloy with uniform composition. All sieved particulate passed a 10 Mesh screen and a maximum of 20% of the sieved particulate passed a 100 Mesh screen. Extra fine material was not used. Isotherms generated using the annealed LANA.85 showed a characteristic $\alpha \rightarrow \beta$ phase transition and XRD results indicated that the hydride was largely homogenous.[5]

Approximately 4.0 g of LANA.85 were weighed and placed in a new test cell for aging studies. Test cells consist of two schedule 40 pipe caps butt welded together, a spool piece, and two B series Nupro valves and have a design temperature rating of 800°C.

II.B. Sample Activation

Prior to tritium aging, materials were activated by cycling in deuterium at 80°C a minimum of ten times. Activation reduces and removes oxides from the surface of the hydride, allowing it to readily absorb hydrogen isotopes. A cycle consists of loading and unloading gas from the hydride. Cycling was performed to generate the particle size distribution that would be present in a future process bed by causing it to decrepitate, or break down into smaller particles. The LANA.85 used for testing was roughly millimeter sized when loaded into the test vessels, but after several cycles the particle size should be on the order of microns. Following cycling, the sample was evacuated at elevated temperature to remove residual deuterium before transferring from SRNL ‘non-rad facilities’ to SRTE where tritium exposure occurs.

II.C. Sample Assay System Description

Tritium isotherm collection is performed on the Low Pressure Manifold (LPM) portion of the sample assay system (SAS) located in the SRTE. The SAS is equipped with: pressure transducers, resistance temperature detectors (RTDs), thermocouples, calibrated volumes, heaters, temperature controllers, and sample bombs required to perform tritium isotherm studies. Pressure measurements are provided by a Paroscientific 31K transducer. Manifold and sample temperatures are provided by Thermo Electric RTDs. Uniform sample heating is obtained by placing the test cell in a nickel block wrapped with a resistance heater. Tritium is supplied from the SAS storage bed at >99% purity. Sample bombs are used to collect gas samples for analysis using a high resolution mass spectrometer.

II.D. Test Approach

The behavior of metal hydrides is commonly measured by isothermal pressure-composition response curves (isotherms). Isotherm performance was monitored annually. Tritium desorption isotherms were initially collected at 80, 120, and 160°C. In the first year of aging, it was discovered that isotherm collection at 80°C was not possible because the $\alpha + \beta$ to α transition had dropped below the analytical capabilities of the SAS manifold. As a result, the lowest temperature isotherm was increased from 80°C to 100°C. Prior to gathering each isotherm, the sample was loaded into the β phase (the region on the isotherm where the slope of the curve concaves upward which is generally at higher T/M values) with a single tritium charge. A single absorption isotherm was performed at 120°C to recharge the sample for storage.

The comparative changes in aging due to cycling the material through isotherm collection are not explored in this work. Collection of isotherms induces a small degree of cycling on the LANA material. Cycling of LANA material has been suggested as a means of removing some aging effects.[6] Cycling will directly relieve stresses on the crystal lattice through the removal of He-3 but this is minimal, in this case, due to the low operating temperatures of the test system.

Isotherm plateau pressures were used to generate a van't Hoff plot for virgin LANA.85. This plot is used to estimate the enthalpy and entropy of the hydride system as well as predict hydride performance at other temperatures.[2]

III. DISCUSSION AND RESULTS

III.A. LANA.85 Isotherms

When tritium decay occurs within LANA materials, larger He-3 atom "born" in the hydride becomes trapped and stresses the surrounding metal crystal lattice.[3, 7] The He-3 accumulates over time and eventually the metal becomes saturated so that it can no longer deliver He-3-free hydrogen isotopes. When either the bed begins weeping He-3 or the loss of reversible capacity adversely impacts process throughput, the hydride bed is removed from service. Previous studies on LANA.75 showed that the crystalline stresses: (a) damage the intermetallic compound structure and thus lowers the plateau pressure of the hydride at a given temperature, (b) increase the slope of the plateau, and (c) decrease the reversible tritium storage capacity.[6-10]

Initial characterization of virgin LANA.85 using pressure-composition-temperature curves with tritium produced well-formed desorption isotherms. Desorption isotherms were collected after one year of aging, but a leaking valve seat on the test vessel caused the isotherms to be artificially elongated along the x-axis and are therefore not included. During testing the following year, the valve seat was confirmed to leak, and the second test vessel valve was used as the boundary for isotherm collection to compensate. Desorption isotherm behavior of the sample after two years of tritium aging is shown in Fig. 1 for 100, 120 and 160°C isotherms. The α + β plateau of the 120°C desorption isotherm is identified.

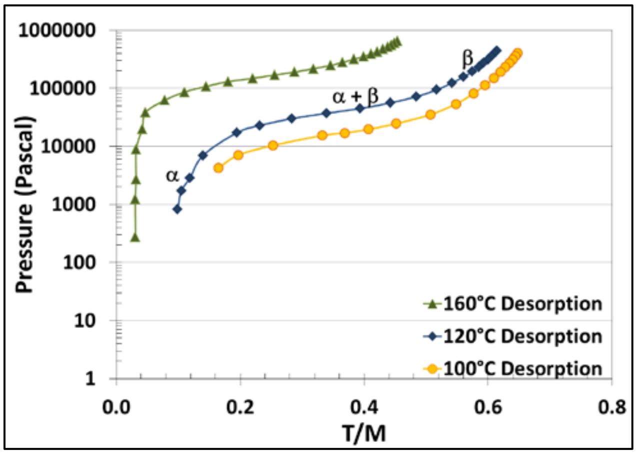

Fig. 1. LANA.85 T_2 desorption isotherms after 2 years of aging.

Because the mass balance of the gas in the test vessel was lost due to the leaking valve, the exact placement of the isotherms on the x-axis in Fig. 1 is unknown. Placement was arbitrarily chosen to give a 'heel' near 0.04 T/M at 160°C where T/M represents the mmol of elemental tritium desorbed per mmol of metal hydride.

The effects of tritium on isotherm performance are evident after only 2 years of aging as demonstrated by changes in plateau pressures in the 160°C and 120°C desorption isotherms shown in Fig. 2 and Fig. 3 respectively. The shapes of the curves and depression of plateau pressure shows similar trends to LANA.75 materials. Three main similarities between LANA.85 and LANA.75 curves are the decreased isotherm pressure, increased isotherm plateau slope, and the increased 'heel' of trapped tritium which is indicated by the shift of the curves along the x-axis.[8]

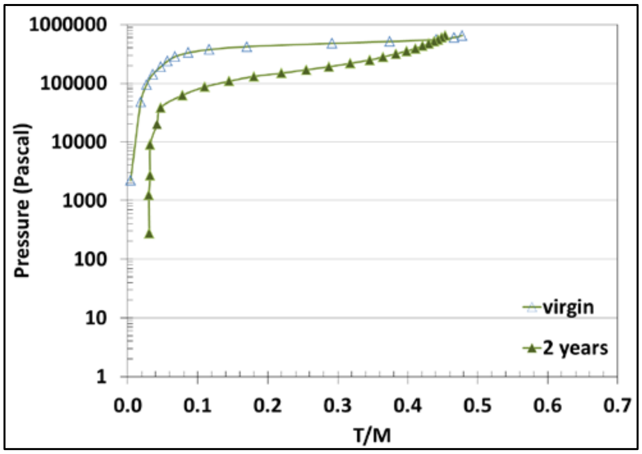

Fig. 2. LANA.85 T_2 160°C desorption isotherms see Fig. 1.

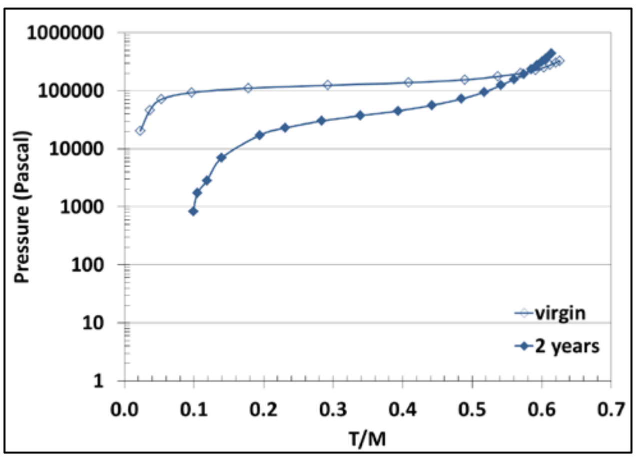

Fig. 3. LANA.85 T_2 120°C desorption isotherms see Fig. 1.

After collection of the desorption isotherms, the sample was heated to 160°C under vacuum, and the valve assembly on the vessel was replaced. During valve replacement the sample was exposed to the nitrogen glovebox atmosphere. The material balance of the test cell will be restored through a partial isotope exchange followed by gas analysis. This is accomplished by quantitatively loading a known aliquot of deuterium onto the LANA.85 and then desorbing the gases by heating. The tritium content (measured using mass spectrometry) in conjunction with the pressure values establishes the composition of absorbed gases.[3]

III.B. LANA.85 van't Hoff Plot

A van't Hoff plot is a semi-log plot of pressure (P) versus the inverse of the absolute temperature (T) for a given hydride loading. The hydride loading is usually selected as the midpoint of the isotherm plateau, because it is least sensitive to small errors. The plot generates a straight line that can be used to estimate the enthalpy and entropy of reaction using the equation:[2]

$$ln\left(\frac{P,(Pa)}{101325Pa}\right) = -\frac{\Delta H}{RT} + \frac{\Delta S}{R},$$

where R is the universal gas constant (8.3145E-3 J/(mol*K)). The van't Hoff plot shown in Fig. 4 was generated using the isotherm data from the virgin material at 80, 120, and 160°C

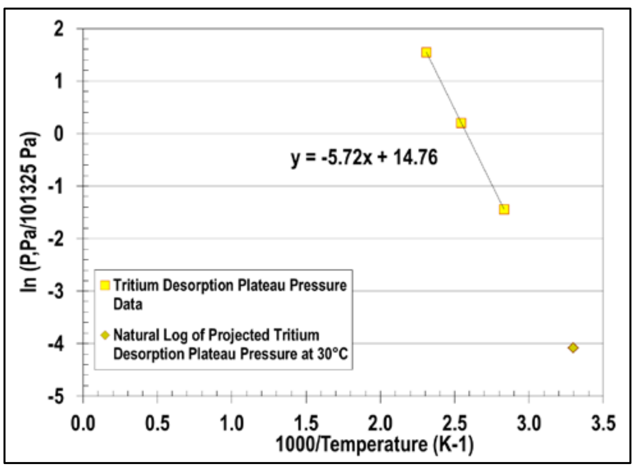

Fig. 4. van't Hoff plot of LANA.85 T_2 desorption

The values of the linearly derived enthalpy (ΔH) and entropy (ΔS) are ~47.59 kJ/mol and ~1.78 kJ/mol*K respectively.

The van't Hoff parameters predict that the mid-point desorption plateau pressure of a LANA.85 bed at 30°C (approximate glovebox temperature) will be ~1.65 kPa. This compares to the ~4.93 kPa plateau pressure of LANA.75. It is noted that this estimate involves an extrapolation of the available temperature data, but is expected to be reasonably accurate.

IV. CONCLUSIONS

Isotherm results have shown no unexpected behaviors after two years of tritium aging. Restoration of the material balance in the cell is expected through a partial isotope exchange followed by gas analysis. Next generation hydride bed service life is expected to be 8+ years. Further evaluation is continuing on an annual basis to track the effects of tritium exposure on both isotherm performance and He-3 release before this material is incorporated in full scale process beds.

ACKNOWLEDGEMENTS

Funding was provided by the SRTE Engineering and Operations, Savannah River Field Office, and National Nuclear Security Administration (NNSA) Technology Maturation Division (NA-123.2) for the Plant Directed Research and Development (PDRD) program funding of projects. This manuscript has been authored by Savannah River Nuclear Solutions, LLC under contract No. DEAC09-08SR22470 with the U.S. Department of Energy.

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Fig. 1. LANA.85 T_2 desorption isotherms after 2 years of aging.

Fig. 2. LANA.85 T_2 160°C desorption isotherms.

Fig. 3. LANA.85 T_2 120°C desorption isotherms.

Fig. 4. van’t Hoff plot of LANA.85 T_2 desorption