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Performance Restoration of a Tritium-Aged $LaNi_{4.25}Al_{0.75}$ Sample

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Abstract — *Hydride beds containing $LaNi_{4.25}Al_{0.75}$ (LANA.75) are used to store significant quantities of tritium. These hydride beds have a limited service life due to radiolytic decay of tritium to ^3He within the metal matrix. The crystal structure of the hydride is altered by trapped ^3He, which has a very low solubility in the metal. The altered structure induces the formation of a heel of trapped hydrogen isotopes and diminishes the reversible capacity of the hydride. With sufficient tritium exposure, the bed loses the ability to deliver ^3He-free tritium, and replacement is needed. Demonstration of a means to regenerate tritium-aged LANA.75 in situ would delay or even eliminate the need to replace lanthanum nickel aluminum (LANA) hydride beds. This paper presents test results obtained during regeneration testing. The efficacy of regeneration testing was evaluated by comparing tritium desorption isotherms collected on the hydride before and after exposure to regeneration conditions. Testing was performed on a bench-scale tritium-aged LANA.75 sample that was previously isotopically exchanged (from tritium to deuterium), passivated, and recovered. Once transferred to a high-temperature test cell, the deuterium heel of the sample was isotopically exchanged with tritium, and a baseline desorption isotherm was collected for comparison purposes. The sample was then heated under vacuum, and comparative isotherms were gathered between regeneration evolutions. Shifts in isotherms show progressive improvements with higher-temperature exposure over the tritium-aged baseline. The heel was significantly reduced, and the reversible capacity of the hydride was essentially restored to near virgin values. For all tested conditions, the plateau pressure remained higher than virgin LANA.75.*

Keywords — *LANA.75, regeneration, hydride storage, isotherm performance.*

Note — *Some figures may be in color only in the electronic version.*

I. INTRODUCTION

Lanthanum nickel aluminum (LANA) hydride storage beds are limited life components due to decay of tritium to ^3He in the hydride metal matrix. Decay impacts hydride performance over time by reducing the reversible capacity of the material and causing the development of a heel or holdup of hydrogen isotopes that are not accessible under normal conditions.[1,2] Depending on conditions, up to half of a hydride storage bed's tritium inventory could be trapped in the hydride heel. Replacement is required when the material can no longer provide helium-free tritium.

As part of an effort to recover ^3He from retired LANA beds at Savannah River Tritium Enterprise (SRTE), previous testing was performed to determine the thermal release characteristics of ^3He from tritium-aged $LaNi_{4.25}Al_{0.75}$ (LANA.75) (Ref. 3). A tritium-aged LANA.75 sample was isotopically exchanged, passivated, recovered from its original test cell, and heated in argon in a thermogravimetric analyzer (TGA). Gases evolved from the sample were quantified with a mass spectrometer (MS), and test data showed two primary peaks. The first peak consisted of both hydrogen isotopes and ^3He. The second peak was primarily ^3He.

Additional testing was performed on a tritium-aged LANA.75 sample to determine whether LANA.75 could be completely oxidized in a controlled manner to release trapped gases at temperatures lower than measured previously.[4] A different tritium-aged LANA.75 sample was isotopically exchanged, passivated, and recovered from the test cell. Portions of the sample were heated in the TGA-MS to various temperatures in either argon or

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a dilute oxygen/argon environment. X-ray diffraction (XRD) patterns were obtained on selected samples recovered from the TGA-MS. These XRD patterns indicated a relationship between exposures to higher temperatures under argon and improved LANA.75 crystallinity.

LANA.75 acts as a hydride by storing hydrogen atoms in interstitial sites within its crystal lattice. Therefore, improved LANA.75 crystallinity suggested that the hydride performance may be at least partially restored. The objective of this testing was to verify whether hydride performance could be restored by heating to higher than normal conditions under vacuum. Performance restoration would likely include a reduction in the amount of unusable tritium trapped in the metal. An additional benefit of regeneration includes recovery of significant quantities of ^{3}He from the tritium-aged LANA.75. Helium-3 is a valuable by-product used predominantly in neutron detectors, ultra-low-temperature cryogenics, and medical imaging.

II. EXPERIMENTAL PROCEDURE

II.A. Apparatus Description and Test Cell Design

Testing was performed on the sample assay system, an experimental tritium-handling manifold located in the SRTE. The manifold is equipped with calibrated volumes, temperature and pressure instrumentation, an inert gas supply, and vacuum capabilities for precise pressure, volume, and temperature (PVT) measurements. Tritium is supplied to the manifold at >99% purity. Gas composition is determined via high-resolution mass spectrometry.

A novel test cell was designed and fabricated to accommodate the high temperatures required for testing. The test cell is shown in Fig. 1. A 200-cm^3 unheated buffer was added to ensure that the design pressure of the test cell was not exceeded given the significant thermal swings to which the cell would be exposed. Uniform heating of the hydride was provided by three cartridge heaters embedded in a nickel block surrounding the sample. The heater block included bores for placement of thermocouples and a resistance temperature detector used for control and overtemperature protection.

II.B. Test Approach

Hydride behavior can be compared using pressure-composition response curves collected at constant temperature (isotherms). The composition of a hydride is typically expressed as the hydrogen-to-metal atomic ratio Q/M (where Q represents hydrogen isotopologues protium, deuterium, or tritium). For an absorption isotherm, equilibrium pressure measurements are taken after an aliquot of gas is added to the system. Likewise, for a desorption isotherm, equilibrium pressure measurements are taken after an aliquot of gas is removed from the system. The quantity of tritium absorbed or desorbed by the hydride is inferred from changes between before and after PVT measurements of the gas phase. Isotherms reveal the plateau pressure, reversible capacity, and heel of a material.

Fig. 1. Hydride test cell and heater block assembly.

The LANA.75 sample selected for testing was initially exposed to tritium in 1987. The sample was used for over a decade for characterization testing with tritium. Because of temperature limitations of the original test cell materials, the sample underwent an isotope exchange process with deuterium to remove as much tritium as practical and was passivated prior to being transferred to the new test cell. The sample was then subjected to another isotope exchange to restore the tritium heel. This was done to remove potential isotope effects as a test variable. After the heel was >98% tritium, a baseline tritium desorption isotherm was collected at 80°C. The isotherm was repeated to ensure sample stability.

Following baseline isotherm collection, regenerative testing began. The sample was evacuated, heated to 450°C, and held under vacuum at 450°C for approximately 8 h before it was allowed to cool to ambient temperature overnight. The sample was loaded with tritium, and an 80°C desorption isotherm was obtained to determine whether material performance had changed. The sample was then heated to 600°C under vacuum for 8 h and cooled to ambient, and another 80°C desorption isotherm was collected. Finally, the process was repeated at 750°C.

III. RESULTS AND DISCUSSION

The 80°C baseline desorption isotherm collected on the tritium-aged sample is shown in Fig. 2. The sample exhibits severe tritium aging (no discernable plateau region, presence of a significant heel, and greatly diminished reversible capacity) compared to a representative virgin tritium desorption isotherm (also shown in Fig. 2) performed on a different sample of LANA.75. The baseline isotherm was repeated (not shown in Fig. 2) to verify stability within analytical techniques. Location of the baseline isotherm on the *x*-axis was accomplished using PVT and MS measurements obtained during isotope exchange of the heel. Isotherm placement on the *x*-axis for subsequent isotherms was approximated by assuming that all the hydrogen isotopes were removed from the sample under regeneration conditions.

Heating the sample under vacuum to 450°C for approximately 8 h moderately restored hydride performance as is shown in Fig. 3. The heel of trapped hydrogen isotopes was dramatically reduced, and the reversible capacity was significantly improved. The two-phase plateau region, however, retained a noticeable slope and was unexpectedly higher than that of a virgin LANA.75 sample. This 80°C isotherm was also repeated (not shown) to ensure accuracy. Previous testing had shown the hydrogen heel would depopulate at temperatures less than 450°C (Ref. 3). Repeating the isotherm demonstrated that the heel is not immediately repopulated when the sample is exposed to tritium.

Desorption isotherms collected at 80°C after the sample was subjected to regeneration temperatures of 600°C and then 750°C are shown in Fig. 4. Included in Fig. 4 are comparative baseline and 450°C isotherms and the prototypical virgin isotherm. Higher regeneration temperatures corresponded to lower heels, larger reversible capacities, and lower isotherm plateau pressures. The effects of exposure to various regeneration conditions on the heel and reversible capacity, as compared through 80°C desorption isotherms for the given stochastic bake-out conditions, are presented in Table I.

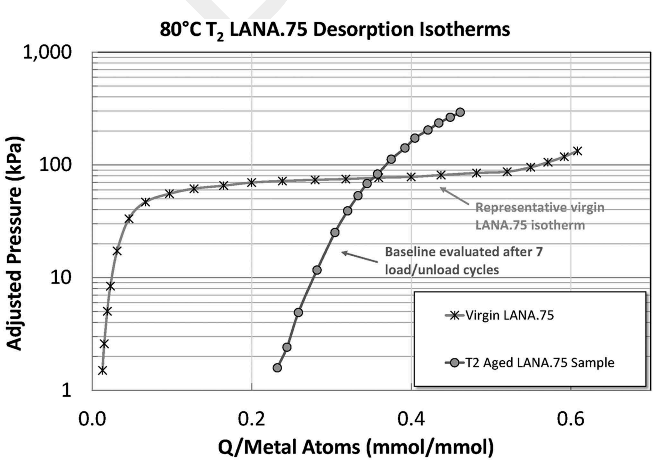

Fig. 2. Baseline desorption isotherm.

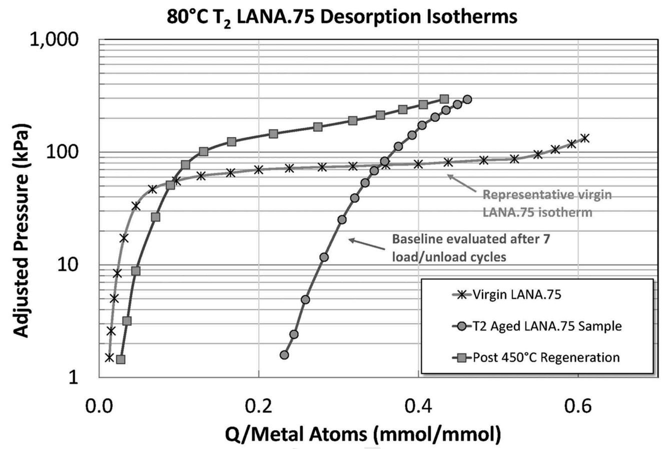

Fig. 3. Post 450°C regeneration isotherm (see Fig. 2).

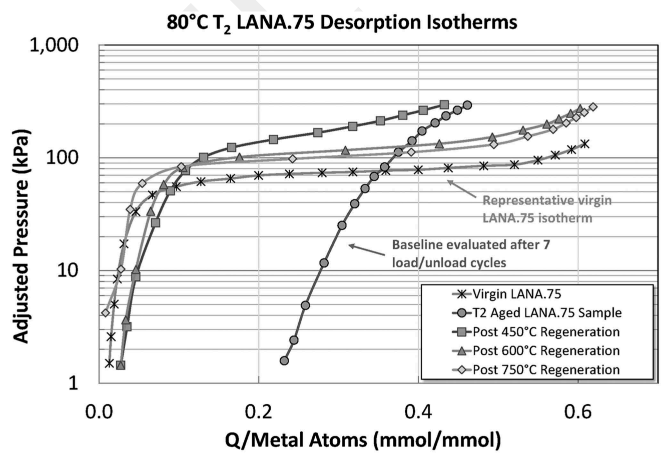

Fig. 4. Regeneration isotherms at 450°C, 600°C, and 750°C (see Figs. 2 and 3).

As shown in Fig. 4 and in Table I, regeneration at 600°C shows marked improvements over regeneration at 450°C. These improvements are likely due to removal of the bulk of the remaining ^3He trapped in the metal. Regeneration at 750°C showed slight additional improvements over regeneration at 600°C, but the plateau pressure remained approximately ~33.3 kPa greater than that measured for the virgin LANA.75 sample. These changes may be due to stress releif within the metal matrix beyond those obtained by simply releasing the ^3He.

While regeneration testing produced extremely promising results, observation of a plateau pressure higher than that for a virgin LANA.75 sample was unexpected and is not well understood. One characteristic of early

TABLE I

Regeneration Effects in Terms of Q/M

Q/M Evaluated at 80°C	Heel at ~13 kPa	Reversible Capacity ~13 to ~267 kPa
Baseline Aged Sample	0.28	0.17
450	0.05	0.36
600	0.05	0.55
750	0.03	0.58

LANA.75 tritium aging is plateau pressure depression. When regeneration of tritium-aged LANA.75 was conceived, it was anticipated that hydride performance restoration would mimic tritium aging in reverse. There are several potential explanations for the pressure discrepancy: sublimation of aluminum at high temperatures, disproportionation of the hydride at high temperatures, and/or the presence of residual stresses in the hydride. The fact that plateau pressures decrease with exposure to higher regeneration temperatures suggests that aluminum is likely not subliming during regeneration; aluminum sublimation would cause plateau pressures to increase, not decrease. Likewise, disproportionation would be expected to be exacerbated at higher temperatures and induce a greater slope in the plateau region of the isotherm. Perhaps the most promising explanation for the elevated plateau pressure is the presence of residual stresses within the crystal lattice. Exposure of the hydride to subsequently higher regeneration temperatures produced plateau pressures that approached that of a virgin annealed LANA.75 sample. However, if one assumes that the stresses remaining after ^3He release were simply a fraction of the stresses built in during tritium decay, the regenerated isotherms should resemble those of LANA.75 beginning to undergo tritium aging. Clearly, this area requires additional investigation.

IV. CONCLUSIONS

Regeneration of tritium-aged LANA.75 was successfully demonstrated by heating the hydride under vacuum to temperatures significantly higher than those used for normal processing. This treatment releases both the heel of trapped hydrogen isotopes and ^3He. Heating the sample to 600°C showed significant improvement over heating to 450°C. These improvements are likely due to the release of the bulk of the remaining trapped ^3He. It is suspected that relieving the stresses in the metal matrix caused by the accumulation of insoluble ^3He due to tritium decay allowed the hydride to return to near virgin performance. Based on tritium-to-metal atomic ratios, exposure of the sample to a regeneration temperature of 750°C for 8 h reduced the heel of hydrogen remaining in the hydride at 80°C and ~13 kPa to 0.03 T/M from the baseline value of 0.28 T/M. Likewise, the reversible capacity between ~267 and ~13 kPa increased from 0.17 to 0.58 T/M during regeneration testing. This represents an almost complete elimination of the trapped hydrogen heel and an almost complete restoration of the reversible capacity of the bed. Unexpectedly, the 80°C desorption plateau pressures for the regenerated LANA.75 were higher than the virgin plateau pressure for all regeneration temperatures tested, though higher regeneration temperatures produced smaller differences.

Only one tritium-aged LANA sample underwent regenerative testing; the bias effects of the stochastic regenerative testing methodology are assumed to be negligible. Further investigation is planned to demonstrate repeatability.

Acknowledgments

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