Contract No:

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy (DOE) Office of Environmental Management (EM).

Controlled Oxidation of Tritium-Aged $LaNi_{4.25}Al_{0.75}$ Hydride to Support Retired Bed Disposition

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INTRODUCTION

The Savannah River Tritium Enterprise (SRTE) has included $LaNi_{4.25}Al_{0.75}$ (LANA.75) hydride in their processing facility for approximately two decades. Beds containing LANA.75 have a limited service life due to radiolytic decay of tritium to He-3 within the metal matrix. He-3 has a very low solubility in the metal, so it becomes trapped and alters the crystal structure of the hydride. The altered structure, in turn, adversely impacts the performance of the hydride under normal processing conditions. Eventually, either the reversible capacity of the hydride will impact process throughput or the hydride will begin to weep He-3. When either happens, the bed is replaced. Spent beds still contain considerable quantities of hydrogen isotopes as well as trapped He-3. The SRTE has a number of these beds in storage that have been removed from service.

There are two concerns related to the final disposition path for retired hydride beds. The first is that LANA.75 is considered pyrophoric until it has been "passivated", or made practically insensitive to air under ambient conditions. Passivation is typically accomplished by exposing the hydride to air in a controlled manner until a thin oxide layer is formed on the surface of the particles. The second concern is related to pressure generation in the bed due to decay of residual tritium. Alleviation of the second concern can be accomplished by removing a sufficient amount of residual tritium.

This project sought to address both concerns by examining the conditions necessary to cause bulk oxidation of LANA.75 under controlled conditions. It was believed that destruction of the metal matrix and accompanying volume change would promote the release of both He-3 and residual hydrogen. If proven successful, retired hydride beds could be prepared for disposal using a single step process involving temperatures much lower than those needed to release the trapped gases in an inert environment. The desorbed, oxidized bed could then be disposed of as normal contaminated process waste.

DESCRIPTION OF THE ACTUAL WORK

The Savannah River National Laboratory (SRNL) conducted a series of tests on a tritium-aged LANA.75 sample. Sample preparation included removal of the bulk of tritium through isotope exchanges with deuterium and passivation before the hydride was recovered from the Tritium Exposure Program (TEP). Testing included thermogravimetric analysis coupled with mass spectrometry (TGA-MS) in argon and argon/oxygen environments with various one hour hold temperatures before continuing the ramp to 1000 °C as shown in Fig. 1 below. One inert test was performed to 1200 °C, closer to the administrative limit of the instrument.

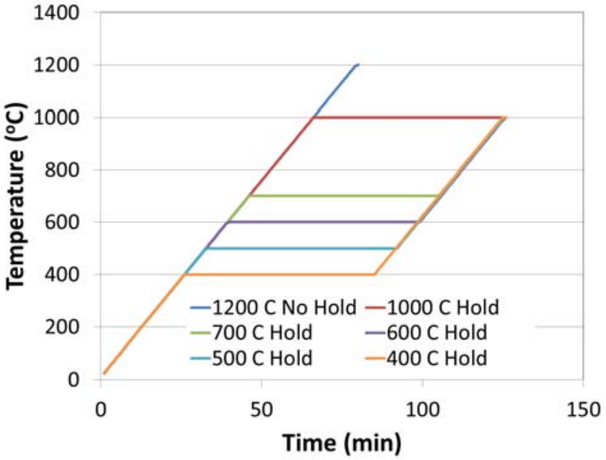

Fig. 1. Temperature Profiles Tested

Both He-3 and hydrogen isotopalogs were tracked during inert testing. Testing with oxygen did not attempt to quantify hydrogen due to the likelihood of oxidation to D_2O and interference with the high MS background associated with a doubly ionized Ar-40 peak. In addition, X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), and Transmission Electron Microscopy (TEM) were performed on As-received and selected post TGA-MS samples.

RESULTS

Analysis of gas evolution from each sample in an argon environment demonstrated that He-3 and deuterium began evolving from the solid around 120 and 160 °C, respectively. Very small quantities of other hydrogen isotopalogs were detected, in accord with sample history. Essentially all of the hydrogen isotopes are released by the end of the 400 °C hold period. Not surprisingly, the fraction of the He-3 released by the end of the hold time increased with increasing temperature. Nearly all of the He-3 was released by the hold at 600 °C; testing up to 1200 °C showed no additional He-3 release peaks. The presence of multiple mass 3 peaks suggests depopulation of He-3 trap sites of different energies. Signals were normalized to Ar-36 to compensate for any minor pressure fluctuations inside the MS. Results for the sample heated to 1000 °C in argon are given in Fig. 2.

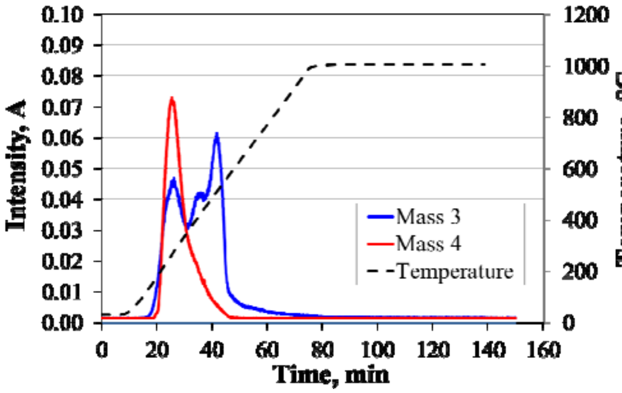

Fig. 2. MS Results for Argon Testing

Analysis of gas evolution from each sample in a dilute (~0.75 %) oxygen environment showed that He-3 began evolving from the solid around 115 °C, slightly lower than using argon alone. As observed during inert testing, the fraction of the He-3 released by the end of the hold time increased with increasing temperature. Very little additional gas was released between 600 and 1000 °C, the highest temperature tested. Signals were normalized to Ar-36 to compensate for any minor pressure fluctuations inside the MS. Results for the sample heated to 1000 °C in argon are given in Fig. 3.

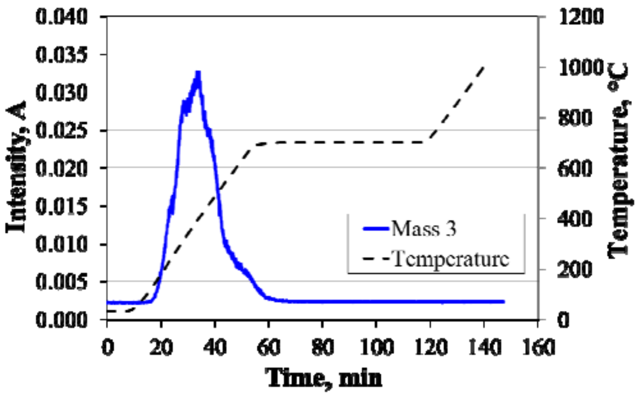

Fig. 3. MS Results for Argon/Oxygen Testing

X-Ray Diffraction performed on the as-received tritiated LANA.75 as well as portions heated in argon to various temperatures. The As-received sample spectrum, Fig. 4, was considerably different from the overlaid reference spectra of the base LANA.75, demonstrating the severe damage caused by tritium aging. Samples held at increasing temperatures in argon showed a clear transition to a more crystalline structure. Heating the sample to 1000 °C in argon appears to have undone a significant portion of the damage caused by tritium aging, shown in Fig. 5 with the library spectrum of LANA.75. Heating the sample to 1000 °C in argon/oxygen appears to have completely oxidized the sample, shown in Fig. 6 with various library spectra of constituent oxides.

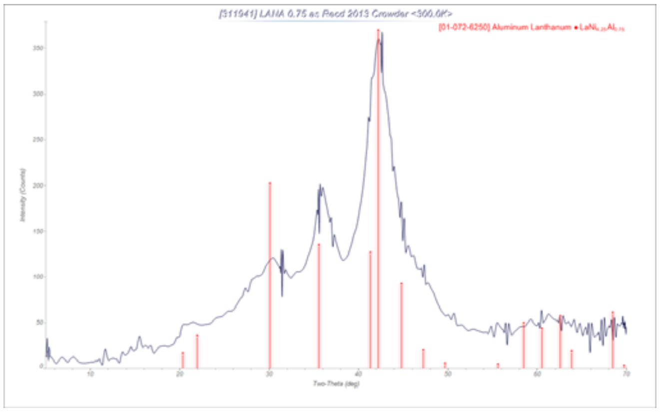

Fig. 4. XRD of As-received LANA.75

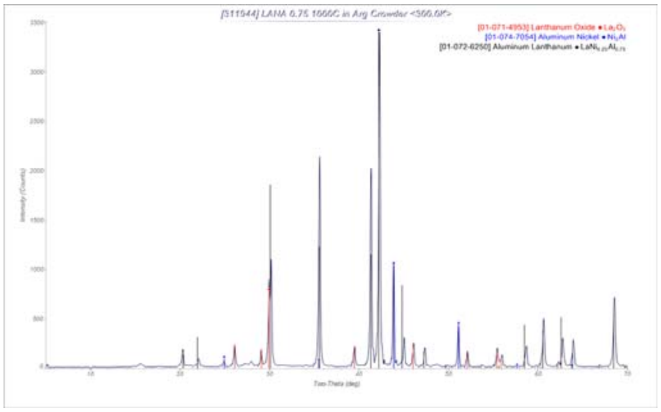

Fig. 5. XRD of LANA.75 Heated in Ar to 1000 °C

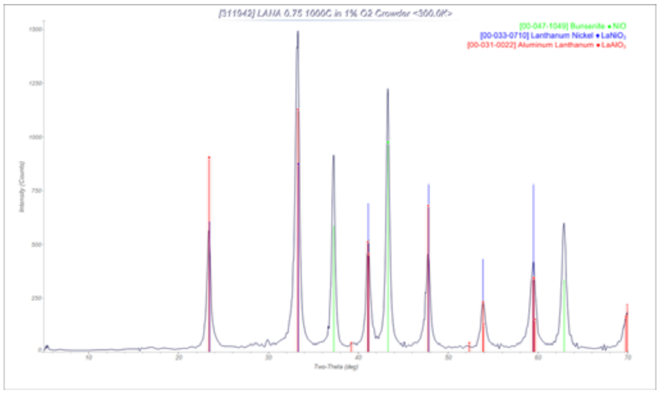

Fig. 6. XRD of LANA.75 Heated in Ar/O_2 to 1000 °C

As with the XRD, TEM results showed a progression from more amorphous to more crystalline materials with heat in either argon or argon/oxygen. Fig. 7 is an electron diffraction pattern of the as-received LANA.75. This pattern consists of concentric diffraction rings, few, if any, discrete reflections, and considerable, diffuse background intensity. The absence of diffraction spots and the presence of significant background intensity may indicate that the LANA.75 is, at least partially, amorphous. This is most likely due to the large number of He-3 bubbles in this material distorting the metal matrix.

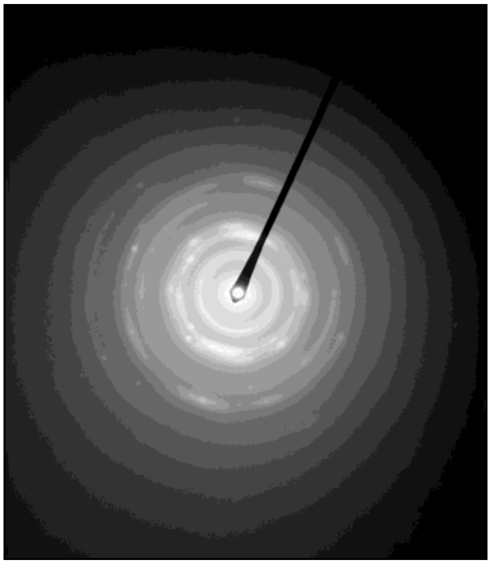

Fig. 7. TEM of As-received LANA.75

The diffraction pattern of LANA.75 heated to 1000 °C in argon (Fig. 8) is indicative of many small grains in a polycrystalline material. Although a very complex pattern, some of the diffraction rings did match LANA.75 while others matched La_2O_3. Some of the rings present originated from unidentified phases/compounds.

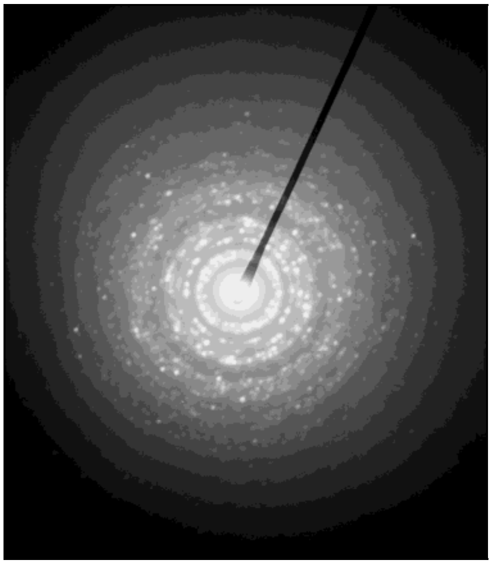

Fig. 8. TEM of LANA.75 Heated in Ar to 1000 °C

Fig. 9 is an electron diffraction pattern of LANA.75 Heated in Ar/O_2 to 1000 °C. This extremely complex diffraction pattern shows that the material is definitely polycrystalline and that the many small grains are randomly oriented. No attempt was made to fully analyze this pattern due to the large number of diffraction rings and spots present.

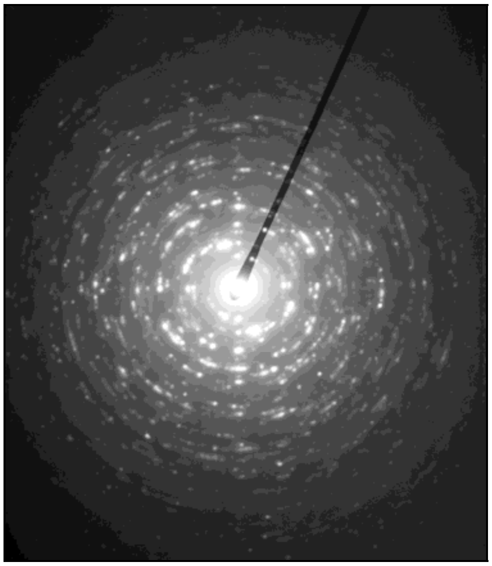

Fig. 9. TEM of LANA.75 Heated in Ar/O_2 to 1000 °C

When oxygen was present, a minor advantage was realized with respect to lowering processing temperatures. However, this advantage is lost by complicating downstream gas processing through the deliberate formation of tritiated water. Formation of tritiated water could be largely avoided by performing an initial heat up to desorb the trapped hydrogen followed by processing with an oxygen containing gas. The use of oxygen at elevated temperatures would recover slightly more He-3 at the expense of a more complicated process.

The recommended strategy to safely prepare a retired LANA.75 hydride bed for disposal is to desorb the residual hydrogen isotopes by heating in an inert environment followed by passivation of the hydride surface at ambient temperature. Heating the bed to at least 500 °C for an hour will remove essentially all of the residual trapped hydrogen isotopes. Additional He-3 could be removed by heating to higher temperatures. After removal of the hydrogen, the bed is cooled while maintaining an inert environment. Cooling the bed is performed as a precautionary measure before introducing oxygen. Finally, the surface of the LANA.75 is oxidized, or passivated. Options for passivation include either adding and evacuating appropriately sized aliquots of an oxygen containing gas to dead-ended beds or flowing a sufficiently dilute oxygen containing gas through the bed where design allows. This approach will allow the bed to be disposed of as normal process waste by elimination of the source for pressurization (residual tritium) and rendering the contents non-pyrophoric.