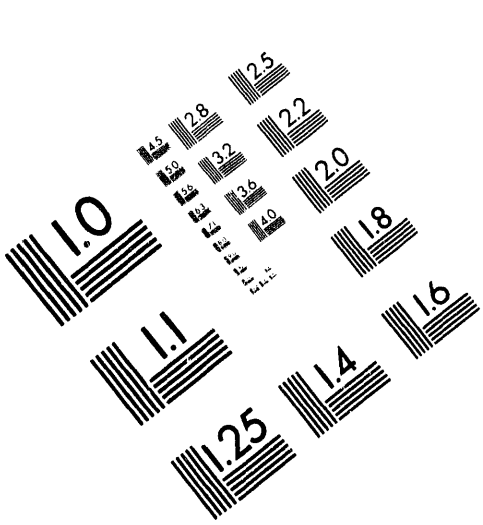

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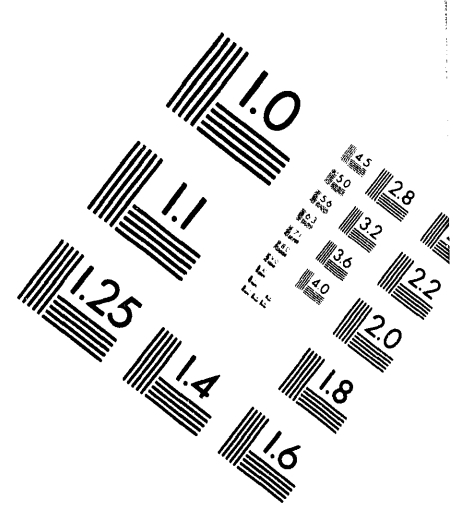

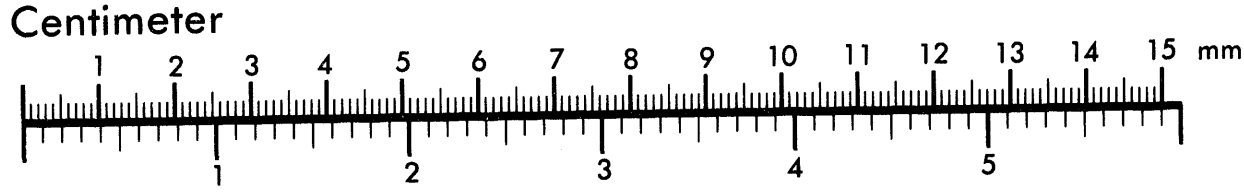

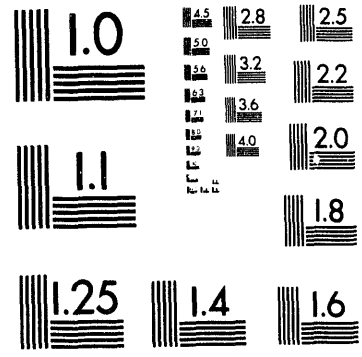

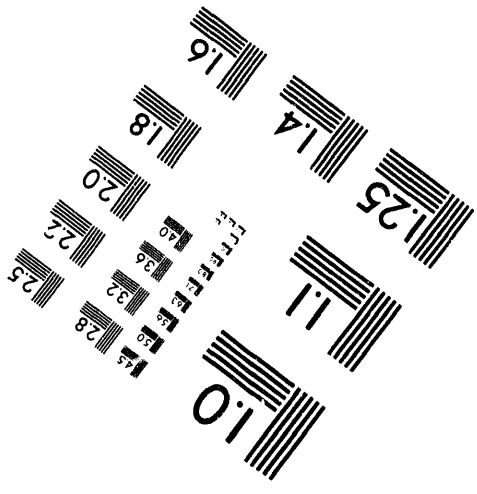

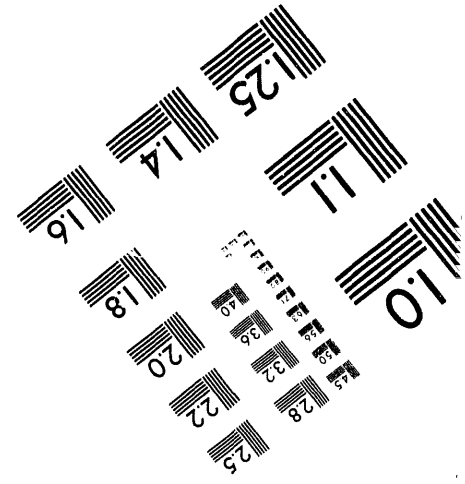

1 of 1

ANALYSIS OF $LANi_{4.25}Al_{0.75}$ (LANA.75) TRITIDE AFTER FIVE YEARS OF TRITIUM EXPOSURE (U)

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SUMMARY

Tritium aging studies have shown that $LaNi_{4.25}Al_{0.75}$ (LANA .75) tritide storage material undergoes significant degradation with tritium aging. After 5.4 years of dormant storage at full stoichiometry, which is considered a worst-case condition for this material, the performance is still acceptable for SRS tritium processing applications. The isotherms change, decreasing the desorption pressures, increasing the isotherm plateau slopes, and decreasing the total storage capacity. Eventually, the material will degrade with time to the point where it may no longer be useful for tritium processing applications. At the end of life, the tritium heel can be exchanged with protium or deuterium to produce a final material containing very little tritium.

INTRODUCTION

For the last several years, processes utilizing metal hydride technology have been successfully used in the SRS Tritium Facilities.[1,2] The 233-H Replacement Tritium Facility, which is currently in start-up phase and which will be on-line in 1993, utilizes this technology extensively. In addition, hydride technology is used for loading and purification operations in the current Tritium Production operations in buildings 232-H and 234-H. Metal hydrides are used in the Tritium Facilities for product pumping and storage, recovery pumping and storage, isotope separation, compression, and purification of hydrogen isotopes (Flow-Through Beds). The use of metal hydrides is also being investigated for use in the Plug Flow Reverser (PFR) for an advanced TCAP isotope separation system. The use of metal hydride technology has many advantages over conventional technology including (1) safe, low pressure, high density storage of tritium and (2) low maintenance pumps and compressors in which the only mechanical working parts are valves.

Tritium aging and compatibility studies have been underway for several years in the Materials Test Facility to determine the effects of tritium on these new materials.[3-9] The La-Ni-Al intermetallic materials used at SRS are based on $LaNi_5$ in which aluminum has been substituted for nickel to produce a compound having a general formula $LaNi_{5-x}Al_x$, where x = 0-1 (LANA.x). Aluminum substitution improves the stability of the compound and lowers the equilibrium isotherm pressure, allowing the formulation of alloys which exhibit a range of pressures over a given temperature range. LANA materials used for tritium processing retain helium-3 which is born in the metal lattice through radiolytic decay of tritium. The insoluble helium-3 strains the metal lattice and changes the thermodynamics of the metal-hydrogen system, leading to (1) decreases in the isotherm plateau pressure, (2) increases in the isotherm plateau slope, and (3) decreases in the

reversible hydriding capacity of the materials. The latter includes the retention of a tritium heel in these materials. Previous studies have demonstrated the removal of the tritium heel through an isotope exchange method.[12-14]

Previous studies examined the "21-Month Bed" and the LANA75T2 sample. The "21-Month Bed" was a large scale bed containing 1000 grams of $LaNi_{4.7}Al_{0.3}$ (LANA .30). This bed was used in tritium production for 21 months before being taken out of service. During this 21-month period, the bed was in dormant storage for 15 months. The bed was desorbed at 180°C and the tritium heel was exchanged with deuterium. The bed was then opened and the contents removed for materials characterization.[3-6] The LANA75T2 sample was a small test bed containing approximately 5 grams of $LaNi_{4.25}Al_{0.75}$ (Ergenics, heat 1158-V-2). This bed was exposed to tritium for 2.35 years. During this time three equilibrium desorption isotherms were determined. The bed was later desorbed and exchanged with deuterium. The bed was then opened and the contents removed for materials characterization.[11]

This paper describes the tritium exposure study and final analysis of sample LANA75T5. This intermetallic $LaNi_{4.25}Al_{0.75}$ alloy was obtained from Ergenics, Inc. as heat 1158-V-2. A total of seven desorption isotherms were collected over the storage lifetime of this material. The total integrated exposure time for this sample, stored at ambient temperature as $LaNi_{4.25}Al_{0.75}$ tritide with a stoichiometry of T/M = 0.6 is 5.4 years.

BACKGROUND

Metal hydride based tritium storage and handling systems have been of interest to the DOE Complex for many years. One of the remarkable properties of many metal tritides is the retention of decay helium-3 in the metal lattice. This property varies depending on the material. For instance, in uranium tritide helium-3 is released from the solid at the generation rate within one year.[10] On the other hand, palladium tritide retains the vast majority of the decay helium for 12-18 years before significant helium release occurs. LANA tritides also retain helium-3. The onset of helium release from LANA tritides has not yet been determined, however, data from the MTF indicates this occurs at times greater than five years. The retention of decay helium-3 is useful in tritium processing applications because it provides a source of high purity, helium-free tritium.

The retention of helium-3 in the metal lattice also has disadvantages. As helium-3 accumulates in the lattice from decay, this insoluble

component stresses the lattice. The stress is great enough to introduce short range order and to change the lattice constants. This effect also varies from one compound to another. Palladium tritide undergoes a reduction in the equilibrium desorption isotherm pressures and a change in slope of a portion of the isotherm plateau region. LANA 0.75 and LANA 0.30 intermetallics undergo a number of changes including a change in the equilibrium desorption isotherm pressures, a change in the isotherm α–β plateau slopes, and a reduction in the reversible absorption-desorption capacity. The latter effect is the result of the formation of tightly bound tritium which is often referred to as the tritium heel. This tritium cannot be easily removed under the normal processing conditions (150-200°C and full vacuum). In addition to the loss of production capacity, the formation of the heel also poses potential problems for the decommissioning and disposal of LANA tritium beds.

SAMPLE HISTORY

The history of the LANA75T5 sample is as follows. A total of seven desorption isotherms were collected over the storage lifetime of this material. The isotherms were determined using pure (>97%) tritium gas. Between isotherm determinations, the sample was held in dormant storage at ambient temperature with an approximate stoichiometry of T/M = 0.6. These activities and the dates on which they were carried out are listed below in Table 1.

Table 1. LANA75T5 Sample History

Date	Activity	Total Exposure (for Isotherms)
4/8/87	Sample vessel LANA75T5 loaded with 5.2 grams (12.7 mmoles) of $LaNi_{4.25}Al_{0.75}$ (Ergenics, Inc., heat #T-1158-V-2.	
4/8/87 to 4/10/87	Activated by vacuum bakeout at 120°C and by three D_2 absorption-desorption cycles.	
4/20/87	Unsuccessful T2 loading attempt. Sample did not absorb well.	
4/29/87	Baked out at 150°C. Loaded sample with tritium.	

Table 1 (continued). LANA75T5 Sample History

Date	Activity	Total Exposure (for Isotherms)
5/19/87 to 5/26/87	First 80°C Desorption Isotherm.	0.05 years
5/28/87	T_2 Loading after first isotherm.	
10/15/87 to 10/22/87	Second 80°C desorption isotherm.	0.44 years
10/22/87	T_2 Loading after second isotherm.	
11/28/90 to 12/7/90	Third 80°C desorption isotherm.	3.54 years
12/10/90	T_2 Loading after third isotherm.	
6/12/91 to 6/20/91	Fourth 80°C desorption isotherm.	4.05 years
7/1/91	T_2 Loading after fourth isotherm.	
4/15/92 to 4/21/92	Fifth 80°C desorption isotherm.	4.84 years
4/22/92	T_2 Loading after fifth isotherm.	
11/12/92 to 12/2/92	Sixth 80°C desorption isotherm.	5.40 years
4/26/93	T_2 Loading after sixth isotherm.	
4/29/93 to 5/3/93	Seventh desorption isotherm (150°C).	5.41 years
5/10/93 to 5/24/93	Seven deuterium exchange cycles.	
8/1/93	Sample passivated with air.	
8/1/93	Sample unloaded in air hood. 4.8 grams (11.7 mmoles) recovered from sample vessel.	

EXPERIMENTAL PROGRAM

The data presented here is based on small metal tritide sample containing 5.2 grams of $LaNi_{4.25}Al_{0.75}$ and 0.15 grams of tritium when fully loaded under the experimental conditions. After loading with high purity (>97%) tritium, tritium effects on the samples were characterized by determining the equilibrium desorption isotherms. Equilibrium isotherms relate the equilibrium pressure above the metal hydride to the composition of the solid at a given temperature. Desorption isotherms are determined by (1) loading a sample with the desired hydrogen isotope and (2) measuring the equilibrium pressure as aliquots of the gas are slowly withdrawn from the sample. The sample temperature is held constant during the experiment. Data relating the desorption equilibrium pressure to the composition of the solid, normally expressed in the ratio of hydrogen isotope atoms to metal atoms in the alloy (e.g. H/M, D/M, or T/M), are obtained from this experiment.

Following the final isotherm determination, the LANA75T5 sample was exchanged with deuterium to remove the tritium heel. The sample was then passivated by admitting air into the vessel. Following passivation the $LaNi_{4.25}Al_{0.75}$ powder was removed from the vessel in an air hood.

The recovered $LaNi_{4.25}Al_{0.75}$ powder was then subjected to several materials characterization tests including scanning electron microscopy (SEM), X-ray diffraction (XRD), particle size analysis, and quantitative determination of residual tritium and helium-3.

RESULTS

Gas Handling Experiments

Equilibrium Desorption Isotherms

The primary method of characterization of this and other metal tritide samples is the determination of equilibrium absorption or desorption isotherms. Isotherms are used to directly measure the performance of the metal tritides as these materials age. Desorption isotherms were used to characterize the $LaNi_{4.25}Al_{0.75}$ tritide material since the delivery of gas was believed to be the critical function of tritium storage beds. The $LaNi_{4.25}Al_{0.75}$ tritide is a low pressure storage material and no problems associated with charging the bed with tritium were anticipated. This assumption has been shown to be true through several years of testing. Any problems with loading have been

shown to be due to either poor activation of the material or tritium feed stocks containing high helium-3 contents.

Figure 1 shows the tritium equilibrium desorption isotherms for the LANA75T5 sample. The composition axis on these plots is expressed as a ratio of tritium atoms to metal atoms in the solid. The vertical axis is the gas phase tritium pressure in equilibrium with the solid metal tritide sample. Figure 2 shows isotherms at longer aging times. After the 80°C isotherm was determined, the sample was heated to 150°C to collect additional high temperature data points and to determine the tritium heel. Figure 3 shows two isotherms at 80°C and 150°C after 5.4 years of exposure. The tritium heel is defined as the amount of tritium left on the storage bed after desorption to 10 mm Hg pressure at a temperature of 150°C. The $LaNi_{4.25}Al_{0.75}$ tritide undergoes a number of changes as the material ages including a decrease in the equilibrium desorption isotherm pressures, an increase in the isotherm plateau slope, and a reduction in the reversible absorption-desorption capacity. The reversible storage capacity is defined as the region of the isotherm between pressures of 10 and 1000 mm Hg. These changes are further discussed in the Discussion section of this paper.

Helium Retention

One of the remarkable and useful properties of the LANA-tritide materials studied in the Tritium Exposure Program is the retention of the helium-3 decay product in the metal lattice. The LANA75T5 sample, as well as other $LaNi_{4.25}Al_{0.75}$ and $LaNi_{4.70}Al_{0.30}$ test samples and storage beds, has shown no release of the helium-3 decay product at total exposure times of greater than five years. A small amount of helium-3 is observed in the overpressure of these samples and storage beds, however, this is due to decay of gas phase tritium in the over-pressure.

Deuterium Exchange Experiment

A total of seven deuterium exchange cycles were conducted on the LANA75T5 sample. Analysis of the desorbed gas during each exchange cycle is presented in Table 2. The deuterium method has been previously described and the data is presented below:

Table 2 LANA75T5 Deuterium Exchange Experiment

Exchange Cycle	D_2 loaded (mmoles)	D_2 desorbed (mmoles)	T_2 desorbed (mmoles)	T/M
0				0.1752
1	17.054	12.202	4.482	0.0484
2	16.663	15.308	1.355	0.0129
3	16.255	15.895	0.360	0.0035
4	15.407	15.316	0.091	0.0011
5	15.860	15.832	0.028	0.0003
6	16.006	15.997	0.009	0.0001
7	15.834	15.830	0.004	0.0000

This data is displayed graphically in Figure 4. Additionally, data for this experiment on the LANA75T2 sample is included for comparison. The LANA75T2 sample was a 5 gram test sample of $LaNi_{4.25}Al_{0.75}$ which had been exposed to tritium for 2.36 years.

Materials Characterization of the Desorbed and Exchanged Powder

Sample Passivation and Removal of Powder

Following deuterium exchange to remove the tritium heel, the LANA75T5 sample was passivated with air. This was intended to react any active metals with air before unloading the powder from the vessel. The passivation was done by admitting air into the vessel under vacuum. On the initial passivation cycle the air in the void space of the sample vessel was sampled after 30 minutes. Three additional passivation cycles were also completed, however, the air was not sampled. The analysis of air from the first cycle by mass spectroscopy indicated that 0.055 mmoles of oxygen were consumed in the first cycle, accounting for approximately half of the oxygen admitted into the vessel. The temperature rise was also monitored during the passivation. During the first passivation cycle, the vessel temperature rose 4°C. No temperature rise was observed for the other three passivation cycles.

The powder was removed from the test vessel by inverting the vessel and tapping on it to transfer the powder into a glass vial. A total of 4.8 grams (11.7 mmoles) was recovered. Upon removal of the powder, the hood tritium activity increased to 150×10^{-5} μCi/cc for a short time. Within two hours the hood activity had returned to background levels (1×10^{-5} μCi/cc).

Determination of Residual Tritium Content

Residual tritium content of the exchanged $LaNi_{4.25}Al_{0.75}$ powder was determined by an acid hydrolysis method.[15,16] The powder is easily dissolved in 4.0 M nitric acid. This method hydrolyzes any residual hydrides in a closed container to form HD and HT gasses. These gasses then exchange with the water in the acid medium to form HDO and HTO. The quantity of tritium in the solution can then be determined using liquid scintillation counting (LSC) methods.

The residual tritium content as determined from this method is 19.5 ± 0.5 mCi/gram of powder. This amount is somewhat smaller than was determined for the 21-Month Bed powder which was determined to contain 270-350 mCi/gram.[6] This is presumably due to the fact that the LANA75T5 sample was subjected to seven exchange cycles as compared to four exchange cycles for the "21-Month Bed."

Scanning Electron Microscopy (SEM)

The powder was examined by mounting on carbon tape substrate. The SEM reveals a fine powder, irregularly shaped with sharp edges ranging in size from 1-2 μm up to >100 μm. Figures 5 and 6 show scanning electron micrographs of this material. Many of the particles were cracked, revealing the decrepitation process of the brittle alloy that occurs from absorption and desorption cycling of hydrogen isotopes on these materials.

Particle Size Distribution

The particle size distribution in the material was determined by a Microtrac® system. This system will measure individual particles as well as agglomerates consisting of several particle. The method uses a pump to suspend the particles in the measurement fluid. The average particle size for this material decreased as the sample was analyzed, beginning at about 33-34 μm and reaching a constant value of 21.8 ± 0.5 μm after 6 minutes. This is consistent with observations for protium cycled $LaNi_{4.25}Al_{0.75}$ powder. Figure 7 shows the results of this experiment as well as a comparison to a sample which was activated and subjected to four absorption-desorption cycles with protium.

X-Ray Diffractometry

Figure 8 shows x-ray diffraction patterns of LANA75T5 and reference $LaNi_{4.25}Al_{0.75}$ Heat 1158-V-2 recorded under the same conditions. In Figure Xb the intensity scale for LANA75T5 has been expanded to show the shapes of the diffraction peaks more clearly.

Determination of Residual Helium-3 Content

A quantitative analysis of the helium-3 content of the tritium-aged $LaNi_{4.25}Al_{0.75}$ powder was obtained by high temperature desorption. Additional gas liberation was achieved by fusing the material with molten tin metal. Grab samples of evolved gasses were analyzed by mass spectroscopy.

In one experiment, a quartz crucible containing 280 mg of powder was heated to 404°C under vacuum. A total of 0.223 mmole of gas was evolved during this run, sampled, and pumped away. An excess amount of granular tin metal (2.55 grams) was then added to the crucible and the sample was again heated to 399°C under vacuum. Vigorous evolution commenced at about 250°C. A total of 0.802 mmole of gas was evolved and sampled. Further heating of the sample to 642°C evolved an additional 0.017 mmole of gas, which was not sampled.

In a second experiment, 296 mg of the $LaNi_{4.25}Al_{0.75}$ powder and 2.67 grams of tin were added to a quartz crucible. The vessel was heated to 446°C and maintained at that temperature until gas evolution ceased. The gas was then sampled and pumped away. A total of 1.052 mmole of gas was evolved. The results of these two tests is summarized in Table 3.

Table 3. Tritium Heel Formation as a Function of Cumulative Exposure Time for La-Ni-Al Materials.

Trial	Temp. (°C)	Total Gas (mmoles)	Analysis Results (mmoles) He-3	T2	D2	H2
1	404	0.223	0.039	0.001	0.153	0.029
	399 (fused)	0.802	0.662	0.002	0.098	0.040
	642 (fused)	0.017				
2	446 (fused)	1.052	0.738	0.001	0.266	0.044

Analysis of the Stainless Steel Container

After the $LaNi_{4.25}Al_{0.75}$ powder was unloaded from the vessel, the vessel was cut open and examined using a scanning electron microscope (SEM). No evidence for interaction of the $LaNi_{4.25}Al_{0.75}$ powder with the vessel walls was observed in this examination. These results are consistent with previous examination of the "21-Month Bed."[17]

DISCUSSION

Gas Handling Experiments

Effects of Aging on Tritium Desorption Isotherms

Changes in the equilibrium desorption isotherms of these materials have been previously reported. The typical tritium aging effects of lowered α–β plateau pressure, increased plateau slope, decreased reversible capacity, and the formation of a tritium heel are also observed in the LANA75T5 sample. Table 4 shows a compilation of these effects.

Table 4. Aging Effects on Tritium Desorption Isotherms of LANA75T5

Exposure (Years)	Isotherm Date	Plateau Slope (mm Hg/T/M)	Reversible Capacity (T/M)	$P_{(T/M = 0.35)}$ (mm Hg)
0.05	5/19/87	339	0.603	573
0.44	10/15/87	392	0.591	306
3.54	11/28/90	248	0.315	22.6
4.05	6/12/91	552	0.397	74.0
4.84	4/15/92	752	0.348	71.3
5.40	11/12/92	823	0.347	60.3

A decrease or shift in isotherm pressures is evident even at short aging times begins. For instance, consider the α–β plateau pressure at a composition of T/M = 0.35. At 80°C, this pressure decreases from 573 to 306 mm Hg after 0.44 years (161 days). As the aging process proceeds the pressure at this temperature and composition stabilize somewhat at 60-75 mm Hg for periods of 4-5.4 years.

During the aging process, the plateau slope increases significantly. A small positive or zero indicates that the gas pressure at a particular temperature will be nearly constant over a large loading or

composition range of the $LaNi_{4.25}Al_{0.75}$ tritide material. With a larger slope, greater heat input is required to maintain a constant delivery pressure from a metal tritide storage bed as tritium is desorbed.

The other primary effect is the reduction of reversible storage capacity due to the growth of a tritium heel. The storage capacity decreases significantly to a final value of 57% of the original capacity for this sample. Table 5 shows the growth of the tritium heel in LANA75T5 sample:

Table 5 Tritium Heel Formation in LANA75T5 Sample as a Function of Cumulative Exposure Time

Exposure Time (Years)	Tritium Heel (T/M)
0.05	0.0047
0.44	0.0175
3.54	0.1505
4.05	0.1194
4.84	0.1708
5.40	0.1752

From the plot of the isotherms and from the data listed in Tables 4 and 5, it can be readily seen that the 3.54 year isotherm is anomalous. This is apparently due to the extended dormant storage period of 3.1 years between the second and third isotherms. It had been previously shown that absorption-desorption cycling increases the α–β plateau pressure. The large size of the tritium heel in this isotherm is largely a function of the low plateau pressure. One desorption-absorption cycle is sufficient to increase the plateau pressure significantly. Very frequent absorption-desorption cycling, such as that required in many tritium loading operations, should improve the performance of the process storage beds over the samples in this study. This will allow the materials to be in service for a longer time period.

Before the sample was passivated with air and unloaded from the vessel, a final 150°C isotherm was determined. This isotherms shows the same value for the heel as previously determined (T/M = 0.175). The 150°C isotherm also demonstrates the ability of the bed to deliver tritium at a pressure of >2000 mm Hg over a significant portion of the bed capacity. This indicates that a production-scale bed should have acceptable performance after 5.4 years.

Additionally, the conditions under which the LANA75T5 sample was tested is a worst case. The bed was loaded to full stoichiometry (T/M = 0.6) with pure tritium and held in dormant storage between isotherm determinations. This sample was cycled only seven times during the 5.4 year tritium exposure history. Storage bed which are frequently cycled or maintained at a lower average tritium loading should exhibit a considerably longer lifetime in tritium processing applications.

Helium Retention

The residual helium-3 analysis, as well as operating experience, indicates that $LaNi_{4.25}Al_{0.75}$ retains most if not all of the decay helium-3 generated within the solid lattice. The amount of helium-3 determined from thermal desorption was He/M = 0.17 as compared to a calculated value of He/M = 0.18 for a bed loaded at full stoichiometry for 5.4 years. Also, no problems with helium-3 release have be encountered using this and other $LaNi_{4.25}Al_{0.75}$ samples and storage beds in the Materials Test Facility laboratories. The retention of all decay helium-3 over the 5.4 year period will simplify operation of these storage beds by delivering helium-free tritium gas to the processing and loading operations.

Isotope Exchange of the Tritium Heel

Exchange of the tritium heel with the lighter isotopes deuterium or protium is an effective method for removal of residual tritium from $LaNi_{4.25}Al_{0.75}$ storage beds. The tritium heel as determined by isotope exchange and mass spectroscopic analysis of the desorbed gasses is in good agreement with the inventory based on gas phase (P-C-T) accounting methods.

In this experiment, seven deuterium exchange cycles were effective in reducing the tritium inventory from >10000 Ci/kg to <20 Ci/Kg of $LaNi_{4.25}Al_{0.75}$. Additional exchange cycles should be able to further reduce the inventory, if necessary for disposal of spent materials. These results were in good agreement with previous studies.[12-14]

Materials Characterization of the $LaNi_{4.25}Al_{0.75}$ Powder

Determination of Residual Tritium and Helium-3

The determination of residual tritium using the acid hydrolysis method proved to be an effective method for determining residual tritium content in exchanged metal tritides. The residual tritium levels of 19.5

± 0.5 Ci/kg of $LaNi_{4.25}Al_{0.75}$ shows the effectiveness of the isotope exchange technique and will allow classification of the waste metal tritide from spent metal tritide materials. The hydrolysis technique showed excellent sensitivity for residual tritium and may prove very useful for waste characterizations at the end of life for storage beds or other tritium-bearing components or materials.

The helium-3 analysis can be used to determine the total integrated storage time of the $LaNi_{4.25}Al_{0.75}$ tritide material, since helium-3 generated in the solid lattice is not released to the gas phase. The amount of helium-3 calculated from storage for 5.4 years with an average stoichiometry of T/M = 0.6 is He/M = 0.18. The average amount of helium-3 determined from two thermal desorption experiments was He/M = 0.17. This number is in good agreement with the calculated value, especially considering the storage history of this sample. During the long period of time (3.1 years) between the second and third isotherm, the stoichiometry of the sample decreased due to the depletion of the gas phase overpressure in the sample. The good agreement between the calculated and experimental number is also further evidence that there is no release of helium-3 during the 5.4 year storage period.

Scanning Electron Microscopy

Analysis using the scanning electron microscope (SEM) reveals a morphology similar to that seen previously in La-Ni-Al metal hydride materials. The particles are irregularly shaped, revealing the decrepitation process of the brittle material. Very few particles are spherical; rather most are oblong shaped with sharp, jagged edges. The particles show internal cracking from incomplete fracturing during the decrepitation process caused by hydriding these materials. There is some tendency of the powder to clump together, as observed by a macroscopic examination of the material. This may be due to the formation of agglomerates, probably due the roughness of the particles.

X-Ray Diffractometry

Tritium exposure has caused considerable broadening of the diffraction peaks of LANA75T5 caused by strain introduced into the crystal lattice by internal helium produced by radioactive decay of absorbed tritium. The line broadening for LANA75T5 was anisotropic as observed for other tritium exposed LANA samples. Broadening for LANA75T5 was about four times that of $LaNi_{4.7}Al_{0.3}$ exposed 21 months, about 2.5 times that of LANA75T2 exposed 2.36 years, and about 1.3 times that of LANA75T1 exposed 2.34 years. Line broadening does not correlate directly with tritium exposure time since different degrees of

structural recovery probably occurred when the samples were heated in vacuum or cycled in deuterium to remove residual tritium.

CONCLUSIONS

1. Although significant changes were observed, the performance of $LaNi_{4.25}Al_{0.75}$ tritide after 5.4 years is acceptable for tritium processing applications. The actual lifetime of the beds will be dependent upon the average tritium loading and frequency of cycling. The retention of helium-3 in the material will eventually affect the thermodynamics to the point where the material will no longer provide satisfactory performance.

2. Helium-3 is retained in the solid for periods of >5.4 years, allowing a $LaNi_{4.25}Al_{0.75}$ storage bed to deliver tritium free of the helium-3 decay product.

3. Some improvement in desorption isotherm pressure is achieved by absorption-desorption cycling.

4. Although retention of helium-3 causes changes in the thermodynamics of the $LaNi_{4.25}Al_{0.75}$ tritide due to increasing lattice stress, the average particle size of the powder is unaffected by long aging times.

5. The tritium heel can be reduced to <20 Ci tritium per kilogram of $LaNi_{4.25}Al_{0.75}$ by exchange with protium or deuterium.

6. Long tritium aging times has little effect on particle size distribution of the $LaNi_{4.25}Al_{0.75}$ powder.

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REFERENCES

1. Ortman, M. S. Heung, L. K., Nobile, A., and Rabun, R. L., Tritium Processing at the Savannah River Site: Present and Future," *J. Vac. Sci. Technol.* A8(3), 2881 (1990).

2. Nobile, A., Jr. Experience Using Metal Hydrides for Processing Tritium in the Present Tritium Facilities, WSRC-TR-90-475.

3. Walters, R. T., "Tritium Storage Effects on La-Ni-Al Alloys: Preliminary Results," DPST-88-756.

4. Lee, S. C., "Tritium Storage Beds, $LaNi_{4.7}Al_{0.3}$," DPST-87-274.

5. Hsu, R. H., "Significance of LANA Tritium Data for RTF," DPST-87-317.

6. Walters, R. T., Mosley, W. C., "Metal Hydrides for Pumping and Storing Tritium: Studies of $LaNi_{4.7}Al_{0.3}$ after 21 Months of Tritium Exposure," DPST-89-366.

7. Mosley, W. C., "X-Ray Diffractometry of Lanthanum-Nickel-Aluminum Alloys," DPST-88-763.

8. Nobile, A., Walters, R. T., Wermer, J. R., "Aging Effects in Palladium and $LaNi_{4.25}Al_{0.75}$ Tritides," WSRC-MS-91-076.

9. Walters, R. T., "Helium Dynamics in Metal Tritides I. The Effect of Helium from Tritium Decay on the Desorption Plateau Pressure for La-Ni-Al Tritides," *J. Less Common Metals*, 157, 97-108 (1990).

10. Carlson, R. S., "Uranium-Tritium System: Storage of Tritium," in *Radiation Effects and Tritium Technology for Fusion Reactors, Vol. IV, CONF-750989*, Edited by J. S. Watson and F. W. Wiffen, p. IV-36, March, 1976.

11. Nobile, A.,Walters, R. T., Mosley, W. C., "Effects of Radiolytic Tritium Decay on the Thermodynamic Behavior of $LaNi_{4.25}Al_{0.75}$ Tritides," *J. Less Common Metals*, 174, 1352 (1991)

12. Nobile, A. "Recommendation of a Method for Disposal of Tritium-Exposed Metal Hydrides," WSRC-TR-91-391.

13. Wermer, J. R., "Removal of Tritium from Aged La-Ni-Al and Pd Metal Tritides," WSRC-MS-91-513.

14 Wermer, J. R., "Quantification of Tritium 'Heels' and Isotope Exchange Mechanisms in La-Ni-Al Tritides," WSRC-TR-92-368.

15. Wermer, J. R., "Hydrolysis of Metal Tritides as a Method of Residual Tritium Analysis," SRT-HTS-93-0194.

16. Wermer, J. R., "LANA Dissolution Experiments," WSRC-TR-93-379.

17. Clark, E. A., "Formation of Intergranular Surface Ditching on Annealed Type 304L Stainless Steel by Acid Cleaning," WSRC-TR-90-600.

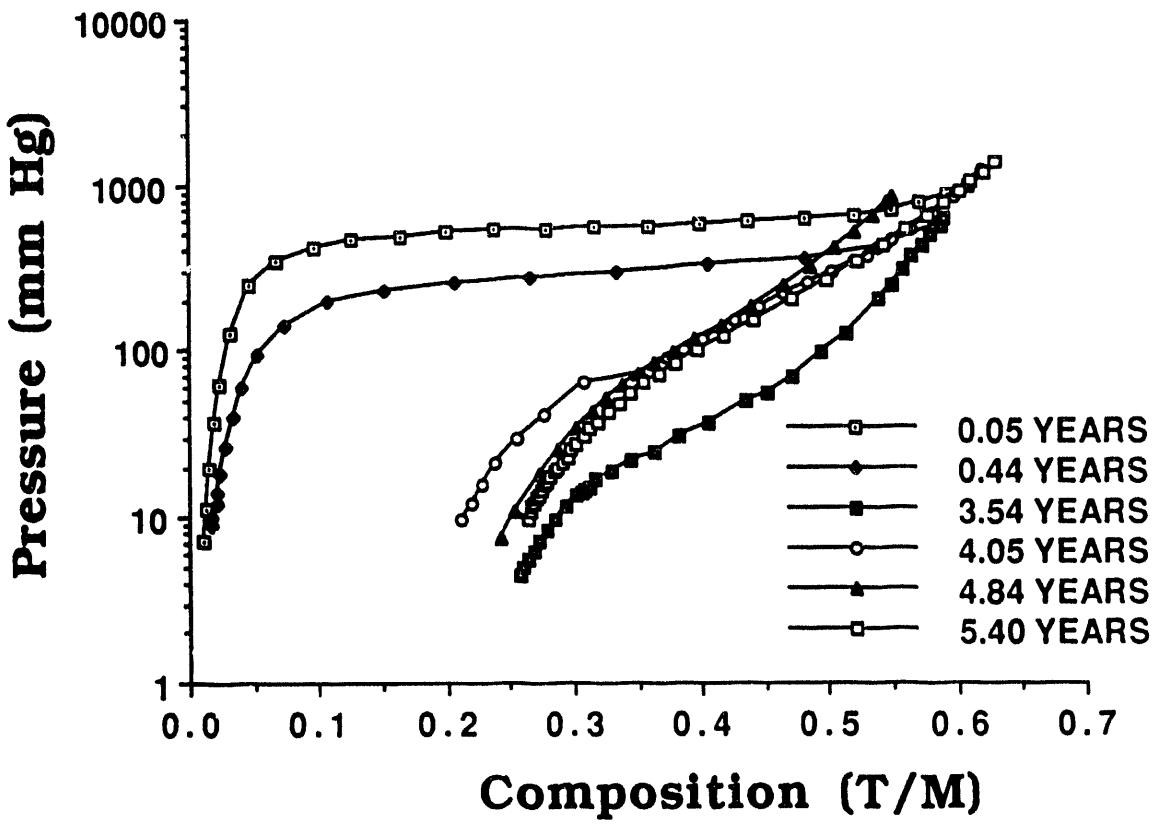

Figure 1. Equilibrium Desorption Isotherms at 80°C of Tritium Aged LANA 0.75.

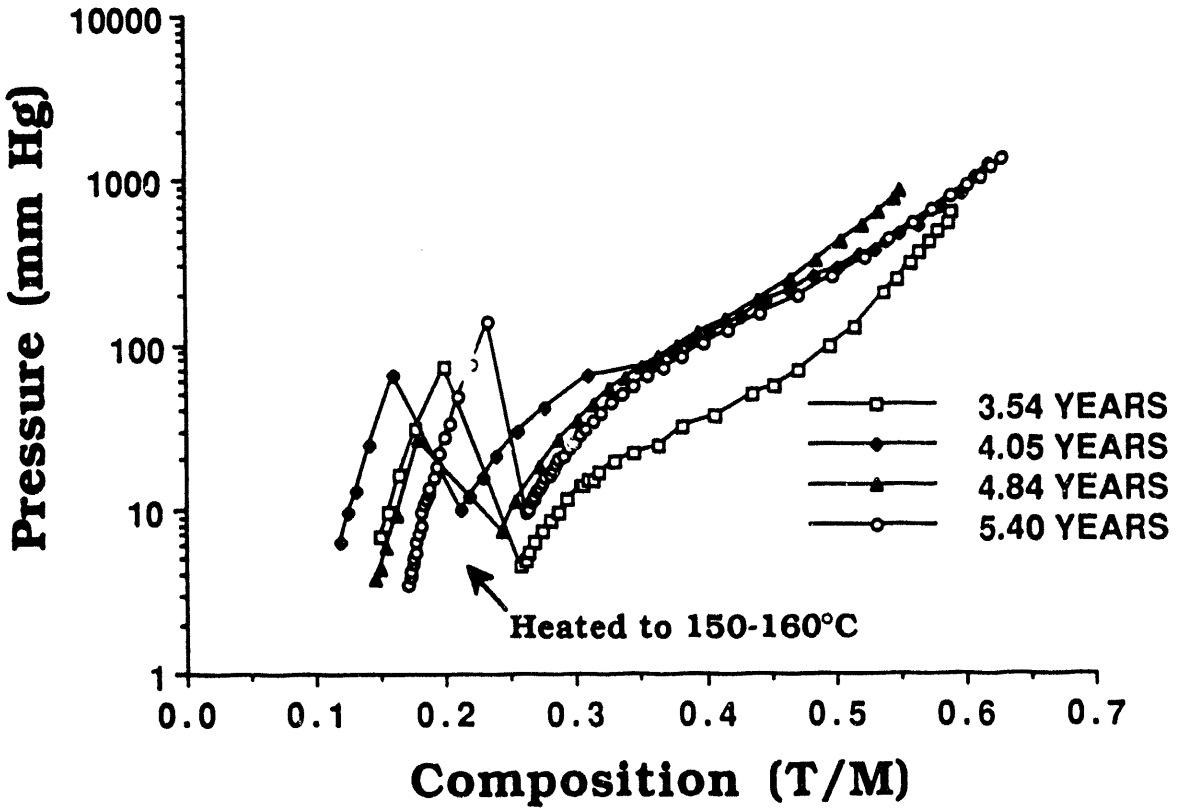

Figure 2. Isotherm Plots of Tritium Aged LANA 0.75. The initial points in the aged plots were determined at 80°C. When the equilibrium pressure reached 10-20 torr in the isotherm, the samples were heated to 150-160°C, and a second set of isotherm points were determined. The lower points on the 150-160°C data indicates the tritium "heel."

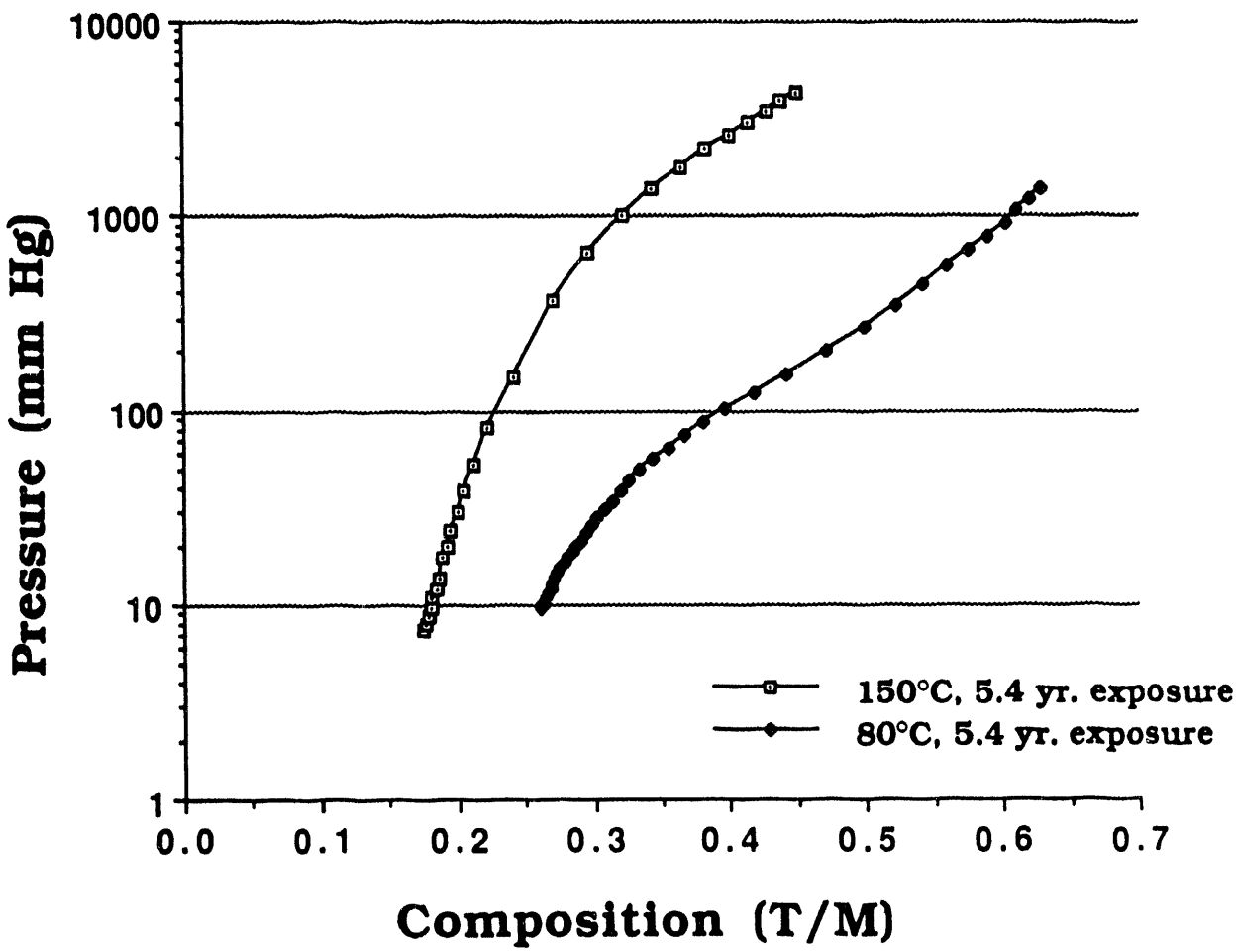

Figure 3. Isotherms of LANA75T5 sample aged 5.4 years. The isotherms were determined at 80°C and 150°C.

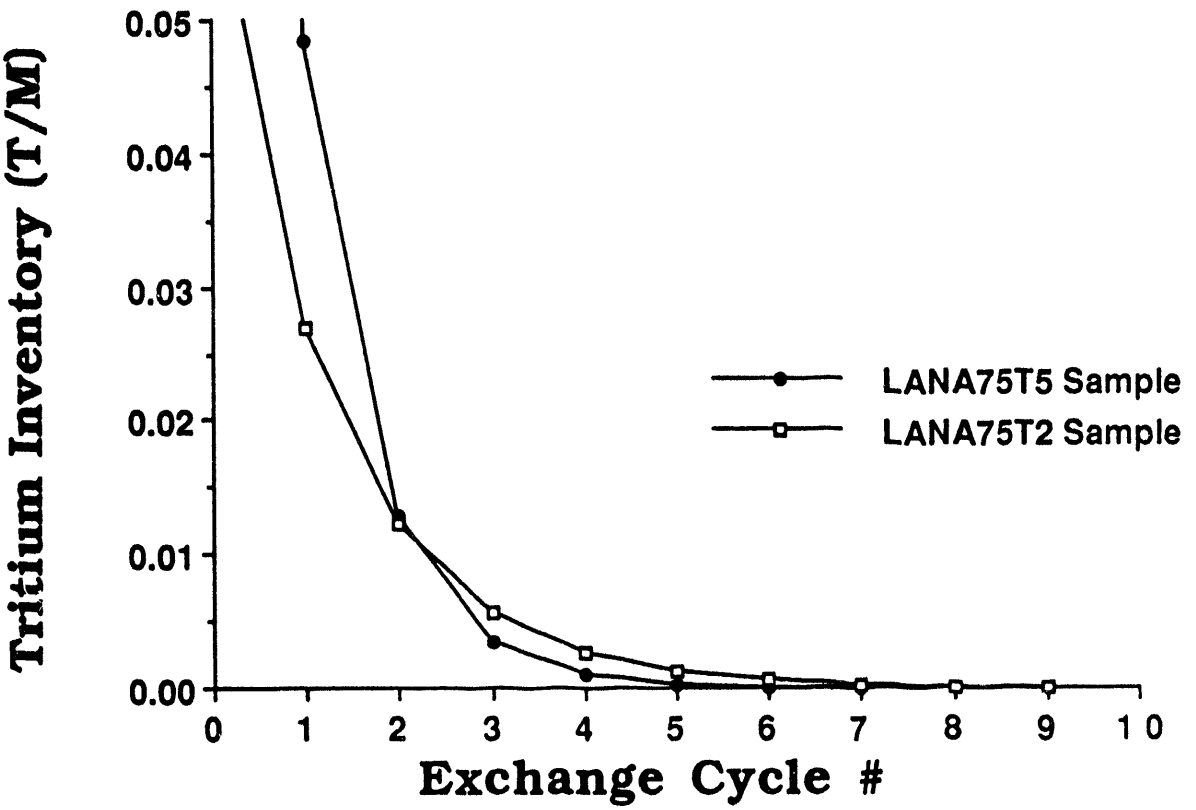

Figure 4. Deuterium Exchange Experiments of the LANA75T5 and LANA75T2 Samples.

Figure 5. Scanning Electron Micrograph at 513X magnification. Note the many irregularly shaped and cracked particles.

Figure 6. Scanning Electron Micrograph at 2100X magnification.

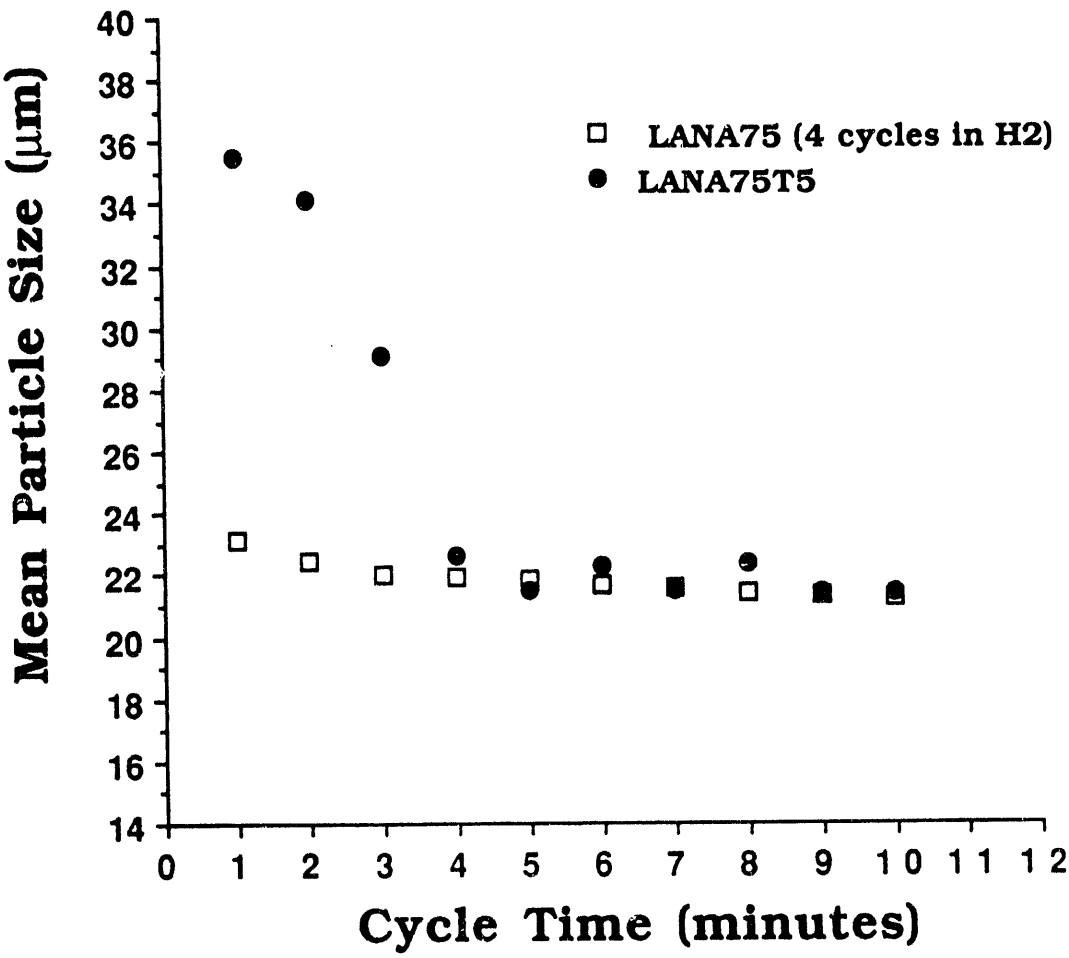

Figure 7. Microtrac® particle size analysis as a function of cycle time. The longer cycling causes a breakdown of the initial material down to a constant average particle size which is in good agreement with the results for a $LaNi_{4.25}Al_{0.75}$ which was actived and cycled in protium.

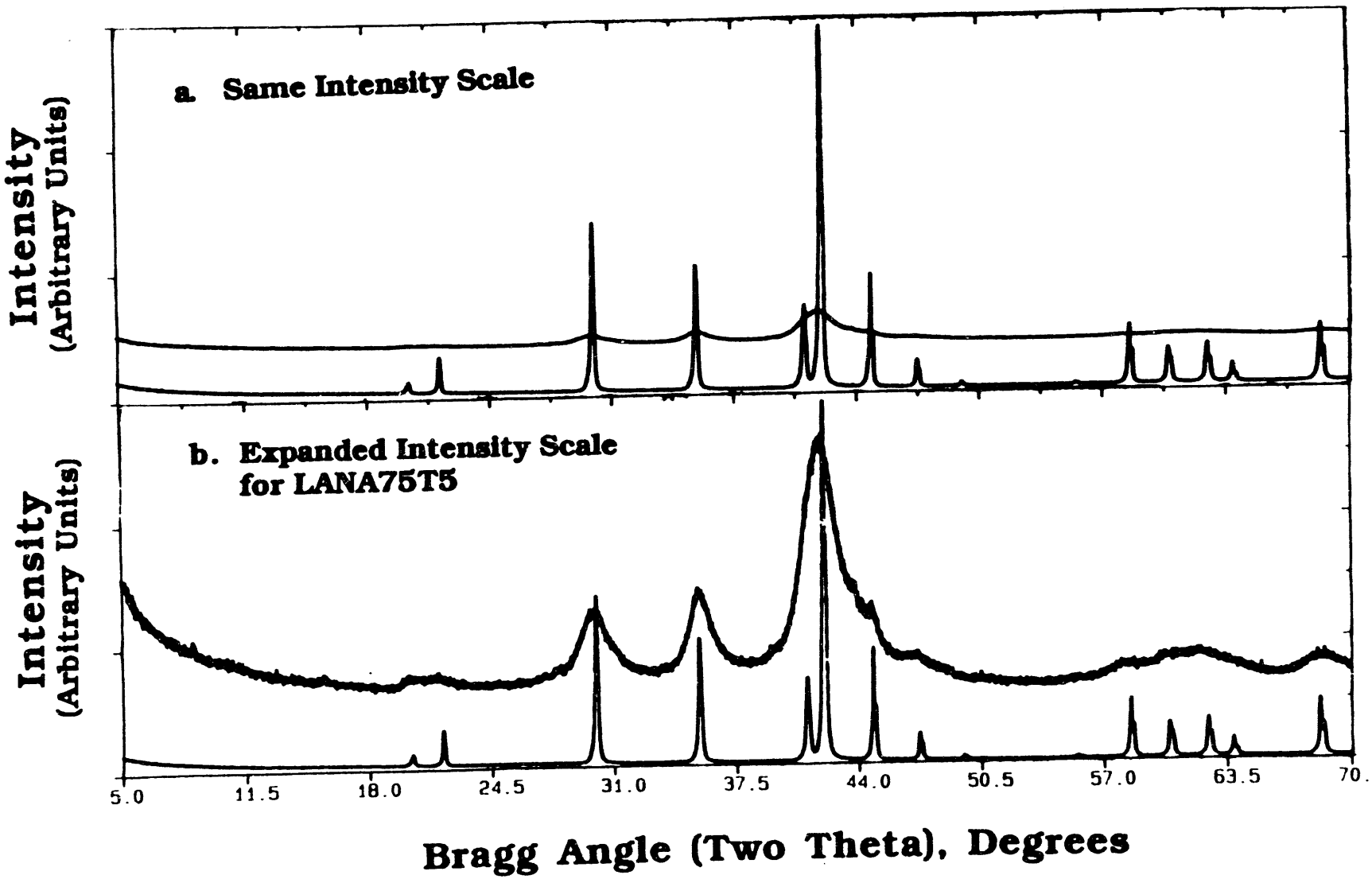

Figure 8. X-Ray Diffractometry of LANA75T5 and Reference $LaNi_{4.25}Al_{0.75}$ (Heat 1158-V-2).

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