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Short Term Aging of LaNi4.25Al0.75 Tritide Storage Material (U)

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Short Term Aging of $LaNi_{4.25}Al_{0.75}$ Tritide Storage Material†

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Introduction

In support of the Tritium Facilities at the Savannah River Site (SRS), the Tritium Exposure Program (TEP) was initiated in 1986 to investigate the effects of tritium aging on metal hydride materials used in tritium processing applications. The primary material selected for tritium storage was the substituted $LaNi_5$ alloy, $LaNi_{4.25}Al_{0.75}$ (LANA.75). The substitution of Al for Ni served to lower the plateau pressure of the tritide, and to stabilize the material to cycling and tritium aging effects. The sub-atmospheric plateau pressure, of LANA.75 tritide at room temperature, made it a safe tritium storage medium, and the tritium aging effects were reduced from that of $LaNi_5$ tritide, but not eliminated.

LANA.75 tritides retain the ^3He decay product of absorbed tritium in the metal lattice. As the concentration of ^3He grows, the lattice becomes strained due to the insoluble species. This strain is manifest in tritium aging effects, which may be observed in the desorption isotherms for the tritide. These effects include (1) a decrease in the equilibrium plateau pressure, (2) an increase in the plateau slope, (3) a reduction in the reversible storage capacity, and (4) the evolution of a tritium heel.[1] The long term aging effects have been studied over the years,[2] however the short term (less than one year) tritium aging effects have not been investigated until now.

The acquisition of desorption isotherms at more than one temperature allows the thermodynamic parameters of change in enthalpy, ΔH, and change in entropy, ΔS, for the $\beta-\alpha$ phase transition of the metal tritide to be determined. These parameters are related to the equilibrium pressure, P, and the isothermal temperature, T, through the following relation:

$$\frac{1}{2}\text{Ln}(P) = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \qquad (1)$$

where R is the gas constant, and the factor of 1/2 yields results per mole of atomic tritium. A van't Hoff plot of 1/2 Ln(P) versus 1/T may be fitted to a straight line, with the slope and intercept used to determine ΔH and ΔS through equation (1).

Experimental

The LANA.75 sample (5.66 g) was taken from lot #T-1158-V-2, which was purchased from Ergenics, Inc., in 1987 as a La-Ni-Al Hy-Stor® Custom Alloy. Experiments were performed in the SRTC Materials Test Facility on the Experimental Tritium Manifold. Tritium was supplied from a $LaNi_{4.5}Al_{0.5}$ storage bed with the following composition: 97.2% T, 1.8% D, 0.9% H, and 0.0% ^3He. Deuterium was supplied at 99.5% purity from a lecture bottle.

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The sample was activated with deuterium, vacuum desorbed at 150°C, and loaded with tritium via a one-step absorption procedure to prepare for the first isotherm. Three tritium desorption isotherms were collected on the sample in the as received or "virgin" state at 80, 40, and 115°C. The sample was loaded to a composition of T/M = 0.7 and stored at room temperature for 202 days. A second set of tritium desorption isotherms were acquired on the tritium aged sample at temperatures of 80, 40, 115, and 80°C. The sample was finally desorbed at 150°C and exchanged with deuterium three times to determine the magnitude of the tritium heel.

Results and Discussion

The "virgin" LANA.75 sample was easily activated and readily absorbed tritium up to a composition T/M = 0.7 at room temperature. The tritium desorption isotherms were well behaved with wide flat plateau regions and no sign of irreversible tritide formation. The isotherms collected after 202 days of tritium aging showed significant change from the "virgin" isotherms. Most notable was the decrease in the plateau pressures and the development of a tritium heel. It was also found that the capacity was reduced, the plateau slope increased, and the thermodynamics of the phase transition were altered.

This is illustrated in Figure 1, where the 80°C desorption isotherms for the "virgin" and tritium aged LANA.75 sample are plotted. Two aged isotherms are shown, with the one corresponding to the fourth absorption/desorption cycle after tritium aging exhibiting a slightly higher plateau pressure than the one recorded on the first cycle. The tritium aging resulted in a decrease from 545 to 167 torr in the plateau pressure at the mid-point (T/M = 0.3), however some recovery was observed with cycling. Figure 1 also shows that an appreciable heel of tightly bound tritium has developed as a result of aging. The heel is defined as that tritium which is retained by the sample after desorption at 150°C, and may be removed by exchange with deuterium. Mass spectroscopic analysis of the exchange gas revealed the tritium heel to be equivalent to a T/M = 0.02.

The capacity, C, is defined as the difference in the composition of the tritide at $10 \cdot P_{mid}$ and $0.1 \cdot P_{mid}$, where P_{mid} is the equilibrium pressure at the mid-point of the plateau region. Thus, the capacity includes both α– and β–phase tritide. The slope, s, is calculated from the change in pressure between two points on either side of the mid-point, separated by C/2. An isotherm with a plateau slope of less than 1.0 is considered flat. These parameters were calculated from the "virgin" and aged isotherms at each temperature, and are listed in Table 1. The capacity decreased by 9% and the slope nearly doubled with aging.

The thermodynamic parameters for the β–α phase transition in the "virgin" and tritium aged LANA.75 tritides were calculated from the lines of best fit to the van't Hoff plots of the desorption data and comparison to equation (1). These determinations were made at three compositions: T/M = 0.14, 0.30, and 0.46, where T/M = 0.30 was the plateau mid-point. These results are shown in Table 2. ΔH and ΔS exhibited a slow increase with composition in the "virgin" tritide, however this trend was accentuated in the aged tritide. This is a result of the increased slope in the plateau region, and indicates the energetics of the phase transition are a function of the composition. The increase in ΔH for the aged sample indicates that the aged tritide is more stable than the "virgin" one, and is reflected in the lowering of the plateau pressure.

Conclusions

The tritium aging characteristics of $LaNi_{4.25}Al_{0.75}$ (LANA.75) have been determined by the acquisition of tritium desorption isotherms at three temperatures before and after storage of the sample in the tritided state for 202 days. A significant decrease in the plateau pressure and the development of a tritium heel were found in the aged sample. Tritium aging was also responsible for a 9% decrease in the material's capacity for tritium, an increase in the slope of the P-C-T curve in the plateau region, and an increase in ΔH for the β–α phase transition of the tritide.

References

[1]A. Nobile, Jr., R. T. Walters, and W. C. Mosley, *J. Less-common Met.*, **174** (1991) 1352.

[2]A. Nobile, Jr., R. T. Walters, and J. R. Wermer, *Fusion Technol.*, **21** (1992) 769.

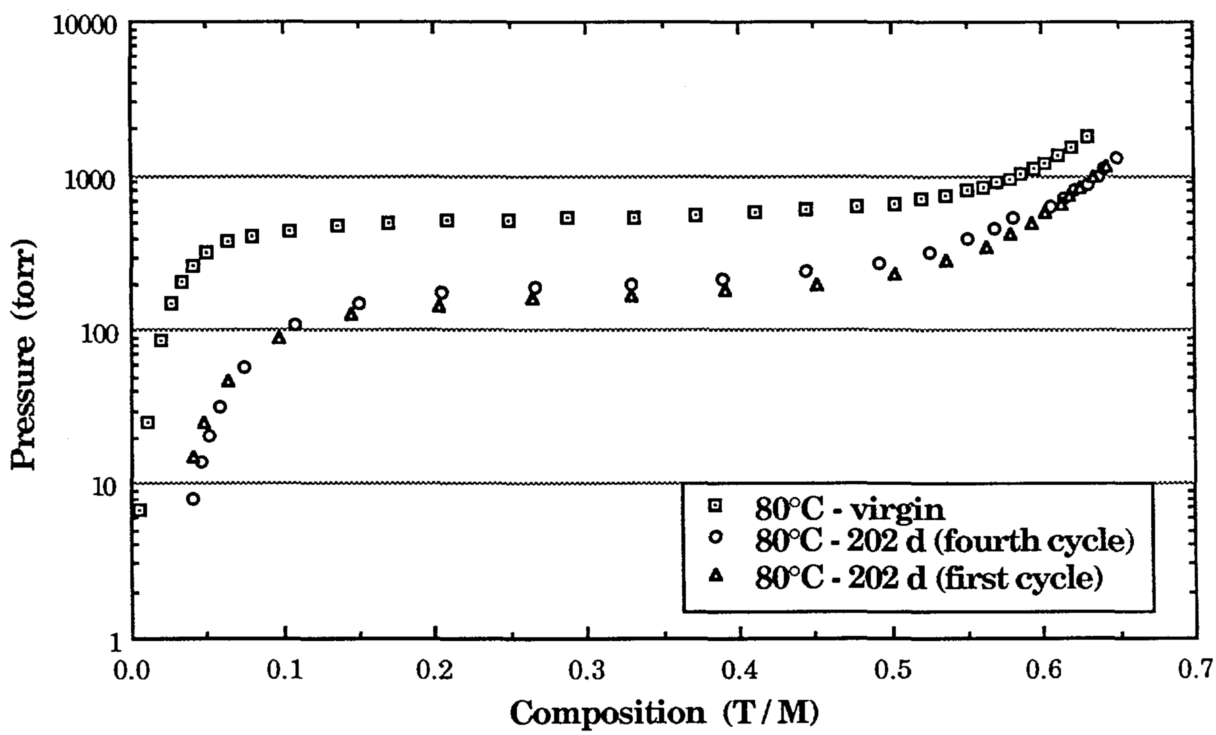

Fig. 1. Tritium desorption isotherms from LANA.75 at 80°C in the "virgin" state, and after 202 days of tritium aging (first and fourth isotherms after aging).

Table 1. Capacities and slopes for "virgin" and tritium aged LANA.75 tritide as a function of temperature.

Temp (°C)	C (T/M)[a]	s (T/M^{-1})[a]	C (T/M)[b]	s (T/M^{-1})[b]
40	0.67	0.79	0.59	1.64
80	0.67	0.80	0.61	1.50
115	0.64	1.10	0.61	2.00

[a]"Virgin" sample.
[b]After 202 days of tritium aging.

Table 2. Thermodynamic parameters for the β–α phase transition in "virgin" and tritium aged LANA.75 tritide as a function of tritide composition (T/M).

T / M	ΔH (kJ/mol·T)[a]	ΔS (J/mol·T/K)[a]	ΔH (kJ/mol·T)[b]	ΔS (J/mol·T/K)[b]
0.14	21.1	57.5	22.8	57.1
0.30	21.6	59.7	23.4	60.1
0.46	21.7	60.4	24.1	63.1

[a]"Virgin" sample.
[b]After 202 days of tritium aging.