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by

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AGING EFFECTS IN PALLADIUM AND $LaNi_{4.25}Al_{0.75}$ TRITIDES

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ABSTRACT

Palladium and $LaNi_{5-x}Al_x$ (x=0.30, 0.75, 0.85), which form reversible hydrides, are used for tritium processing and storage in the Savannah River Site (SRS) tritium facilities. As part of a program to develop technology based on the use of reversible metal hydrides for tritium processing and storage, the effects of aging on the thermodynamic behavior of palladium and $LaNi_{4.25}Al_{0.75}$ tritides are under investigation. During aging, the ^3He tritium decay product remains in the tritide lattice and changes the thermodynamics of the tritium-metal tritide system. Aging effects in 755-day-aged palladium and 1423-day-aged $LaNi_{4.25}Al_{0.75}$ tritides will be reported. Changes in the thermodynamics were determined by measuring tritium desorption isotherms on aging samples. In palladium, aging decreases the desorption isotherm plateau pressure and changes the α-phase portion of the isotherm. Aging-induced changes in desorption isotherms are more drastic in $LaNi_{4.25}Al_{0.75}$. Among the changes noted are: (1) decreased isotherm plateau pressure, (2) increased isotherm plateau slope, and (3) appearance of deep-trapped tritium, removable only by exchange with deuterium. Various processes occurring in the tritide lattice which might be responsible for the observed aging effects in palladium and $LaNi_{4.25}Al_{0.75}$ tritides will be discussed.

INTRODUCTION

Metals and intermetallic compounds which react to form reversible hydrides offer several advantages for storing and processing tritium. Some advantages are:

- Low pressure, high density storage.
- Rapid delivery of high purity ^3He-free tritium.
- Reduction in the number of pumps needed.
- More compact equipment allowing easier placement of equipment in glove boxes for secondary containment.

Other publications describe these advantages in greater detail, and describe some of the production-scale applications of metal hydrides at SRS[1-3].

Metal hydrides used for tritium processing accumulate decay ^3He in the metal hydride lattice. This ^3He induces structural changes in the metal lattice which in turn influence the absorption-desorption characteristics of the metal hydride. It is for this reason that we have been investigating aging effects in these materials. Thus far, only slight changes in the absorption-desorption thermodynamics of palladium have been observed. In a previous publication, Walters and Lee[4] reported decreases in desorption pressures only on the lower portion of the plateau. In this paper, we report further changes in the isotherm plateau (α-β phase coexistence region), as well as changes in the α phase portion of the isotherm.

Aging effects in $LaNi_{4.25}Al_{0.75}$ tritides were recently reported by Nobile *et al.*[5] and Walters *et al.*[6] for aging times up to 861 days. In these publications, changes in the desorption isotherms were reported, and can be summarized as follows:

- Decreased isotherm plateau pressure, which decreases with increased aging.
- Increased isotherm plateau slope, which also increases with aging.
- Appearance of deep-trapped tritium, removable only by isotopic exchange with deuterium. The amount of deep-trapped tritium increases with aging.

The previous publications have also presented results which indicate that the aging effects are partially reversible by absorption-desorption cycling and brief heating of aged samples to 350 °C. Data has since been collected for palladium and $LaNi_{4.25}Al_{0.75}$ for aging times up to 755 and 1423 days, respectively. This paper presents the most recent data collected, and discusses some of the processes which might be responsible for the observed aging effects.

EXPERIMENTAL

Materials

Palladium powder (Engelhard, Edison, NJ), prepared by precipitation from solution, and having particles in the range 0.3 to 1 µm (determined by scanning electron microscopy) was used. The particles tend to agglomerate into larger clusters. Neutron scattering determined the grain size to be in the range 0.03 to 0.07 µm. The specific surface area, measured by the BET method, was 1.15 m^2/g.

La-Ni-Al alloy having the nominal composition $LaNi_{4.25}Al_{0.75}$ (Ergenics, Ringwood, NJ), was prepared in 32 kg batches by vacuum melting of the lanthanum and nickel components with subsequent addition of aluminum to the melt. After allowing to solidify as an ingot, the material was annealed in argon for 18 h at 1100 °C. An X-ray diffraction technique determined the material to be of the composition $LaNi_{4.25}Al_{0.75}$.

Tritium used for sample loading and desorption isotherm measurements was supplied from a $LaNi_{4.25}Al_{0.75}$ storage bed. Mass spectrometry analysis of tritium desorbed from the storage bed indicates that the gas is 97.7% tritium, 1.5% deuterium, 0.7% protium, 0% ^3He, and 0-0.1%Ar.

Sample Tritium Loading

Palladium and $LaNi_{4.25}Al_{0.75}$ samples (5.0 ± 0.2 g) were placed in the stainless steel cell shown in Fig. 1. The samples were evacuated, activated with deuterium, and thermally cycled between 30 and 150 °C at least five times to complete the particle decrepitation process. Samples were evacuated overnight to a pressure less than 5 Pa. Tritium was then quantitatively loaded from a calibrated volume onto the sample, which was initially at room temperature. Loadings of 0.60 T/M (tritium to metal ratio) for palladium, and 0.60-0.65 T/M for $LaNi_{4.25}Al_{0.75}$ were achieved. The loaded samples were placed into dormant storage at room temperature. Desorption isotherms were measured at intervals ranging from 10 to 1100 days. After desorption isotherms were measured, samples were reloaded and placed back into dormant storage.

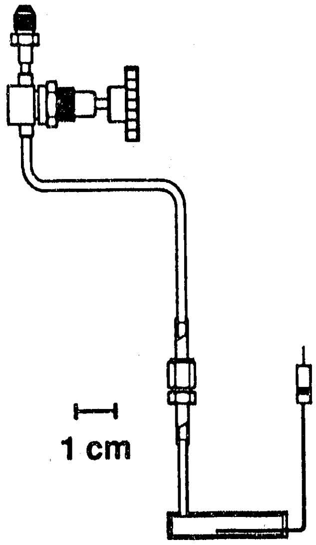

Fig. 1. Sample Container

Desorption pressure-composition (P-C) isotherms

Desorption P-C isotherms at 80 °C were measured on aged palladium, and on unaged and aged $LaNi_{4.25}Al_{0.75}$. The tritium desorption isotherm for unaged palladium was taken from data published by Lässer and Klatt[7]. Isotherms were measured on a previously-described tritium gas manifold[8]. The manifold is equipped with calibrated volumes and MKS Instruments type HA Baratron 0-1333 kPa capacitance manometers. During isotherm measurements, the sample cell was wrapped with heat tape and a temperature controller maintained it at the desired temperature to within 0.5 °C.

RESULTS

Palladium

Fig. 2 shows 80 °C desorption isotherms for palladium aged up to 755 days. Aging decreases the desorption pressure and shifts the a-phase portion of the isotherm toward higher T/M values. The lower portion of the plateau is affected to a greater extent than the upper plateau. Fig. 3 shows the plateau pressures at 0.15 and 0.45 T/M vs. time. Initially there is a large drop in desorption pressure of the lower plateau after aging for just 10 days. After this initial pressure decrease, the pressure decreased at a slower rate up to 393 days, and

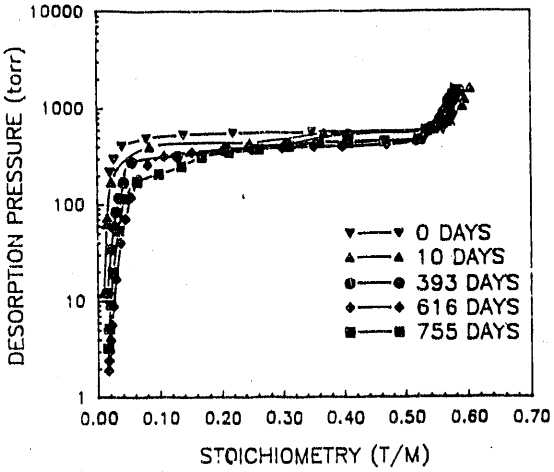

Fig. 2. Desorption Isotherms at 80 °C for Aged and Unaged Palladium.

then slightly increased between 393 and 616 days. A pressure decrease then occurred after 616 days. After an initial slight decrease between 0 and 10 days, the desorption pressure of the upper plateau remained fairly constant up to 393 days, and then decreased between 393 and 616 days. Between 616 and 755 days, the pressure of the upper plateau increased.

There are also significant changes in the α-phase portion of the isotherm. There is a shift in the α-phase solubility curve toward higher T/M values. Fig. 4 shows an enlarged view of the α-phase region for 3 isotherms. For the 616- and 755-day-aged samples there is some deep-trapped tritium which does not completely desorb from the material, as it does on the isotherm after 10 days aging. The deep-trapped tritium consists of about 0.02 T/M. For the 616- and 755-day-aged samples, the isotherm was continued at a higher temperature (150 °C) at the completion of the 80 °C isotherm. The 150 °C isotherms are also shown in Fig. 4. At this temperature, all of the deep-trapped tritium desorbed from the material.

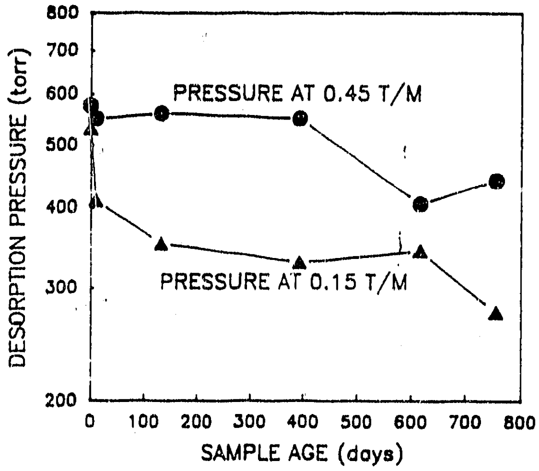

Fig. 3. Desorption Pressure vs. Aged Time for Aged and Unaged Palladium at T/M of 0.15 and 0.45.

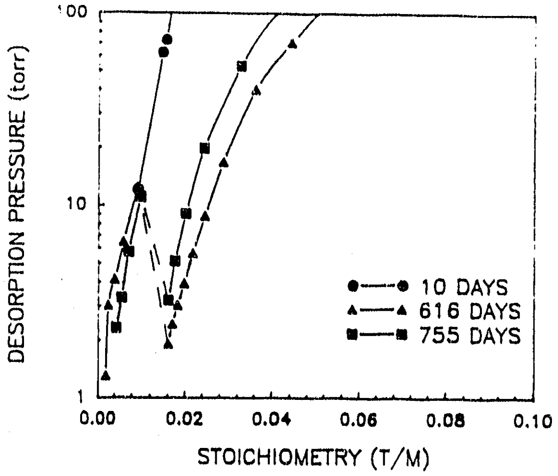

Fig. 4. Desorption Isotherms in the α-Phase Region for Palladium at 80 and 150 °C.

$LaNi_{4.25}Al_{0.75}$

Isotherms were collected for $LaNi_{4.25}Al_{0.75}$ for aging times as long as 1432 days. Fig. 5 shows 80 °C desorption isotherms for $LaNi_{4.25}Al_{0.75}$ for aging times up to 1273 days. The additional data collected at 1432 days will be discussed below. The trends mentioned in the introduction, which were reported previously, are continuing. Fig. 6 shows the unaged isotherm, the 861-, 1273-, and 1423-day-aged isotherms. Also shown are isotherms at 150 °C, which are continuations of the 80 °C isotherms. Somewhat unexpectedly, the desorption pressures for the sample aged for 1423 days are higher than those of the sample aged

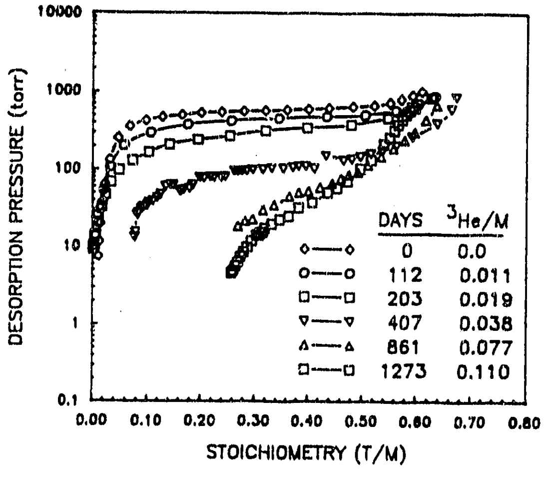

Fig. 5. $LaNi_{4.25}Al_{0.75}$ Desorption Isotherms for Aged Times up to 1273 days.

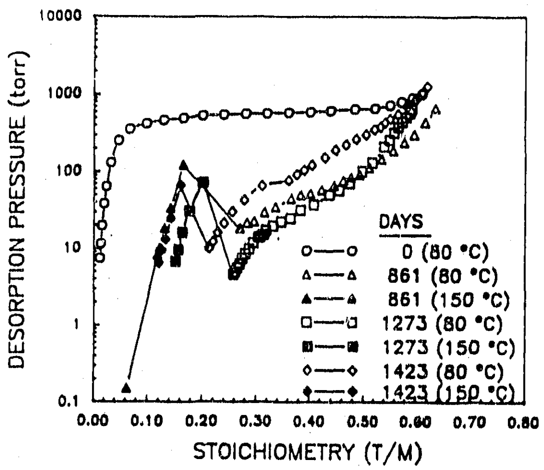

Fig. 6. $LaNi_{4.25}Al_{0.75}$ Desorption Isotherms for Aged Times up to 1423 days.

An explanation for this apparent anomaly is provided later. Some deep-trapped tritium was desorbed at 150 °C; however, at completion of the 150 °C isotherm, some deep-trapped tritium remained in the sample. The amount of deep-trapped tritium in the 1273-day-aged sample is greater than that of the 861-day-aged material. However, unexpectedly, the deep-trapped tritium in the 1423-day-aged sample is less than that of the 1273-day-aged sample. Fig. 7 shows desorption pressure, isotherm slope, and deep-trapped tritium vs. time for $LaNi_{4.25}Al_{0.75}$. With the exception of the data at 1423 days, the trends previously reported are continuing.

DISCUSSION

Palladium

The changes observed in the palladium desorption isotherms as a function of time are evidently due to lattice structural changes induced by ^{3}He deposition. Previous ^{3}He release measurements[9,10] have indicated that the majority of ^{3}He is retained in the lattice. Thomas and Mintz[11], who attempted to characterize the effects of ^{3}He from tritium decay in palladium foils, observed a uniform distribution of small defects exhibiting strain contrast after 20 days while fully loaded with tritium. This indicates that damage to the lattice from ^{3}He occurs almost immediately, and is consistent with our observation of significant changes in the plateau at early times (10 days). The initial large desorption pressure change is likely due to the early dislocation-induced strain in the lattice observed by Thomas and Mintz. A strained lattice such as this is likely to have vacancies, dislocations, and self-interstitials, such as described by Lasser *et al.*[12]. The lattice with these defects probably contains a range of tritium sites of configuration different than in the undamaged lattice. Thomas and Mintz[11] observed 1.5-2.0 nm ^{3}He bubbles in their samples after 66 days. This result suggests that formation of dislocations and strain gives way to ^{3}He bubble formation, as a way of accommodating lat

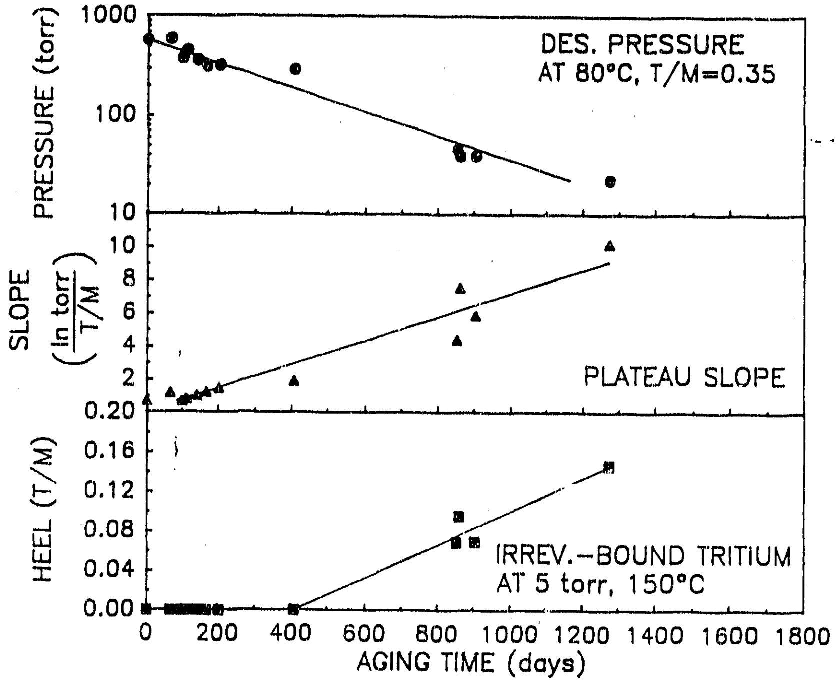

Fig. 7. Desorption Pressure, Isotherm Slope and Deep-Trapped Tritium for Aged $LaNi_{4.25}Al_{0.75}$.

tice ^3He. This picture is consistent with the formation of vacancies and eventually bubbles, which is the basis of the self trapping mechanism described by Wilson *et al.*[13]. Helium in bubbles is probably less effective in causing local dislocations and lattice damage, and thus this explains the slower pressure decrease at longer times (10 to 133 days) with our samples. The mechanisms responsible for the desorption isotherms changes at greater than 400 days are not known, but appear to be more erratic in nature, suggesting more chaotic processes are operative, such as bubble coalescence, loop punching, etc. The reasons for the observed greater changes in the lower part of the plateau are unclear, but it is possible that the lower plateau represents sites which are closer to defects or high strain areas, whereas tritium far from defects would not experience large changes in site energies. The upper plateau possibly is comprised of tritium sites which are far from defects and high strain areas.

$LaNi_{4.25}Al_{0.75}$

Results reported above indicate that aging effects are more pronounced with $LaNi_{4.25}Al_{0.75}$ than with palladium. In addition to the decrease in desorption pressure being more drastic in $LaNi_{4.25}Al_{0.75}$, the desorption isotherm plateau becomes sloped with aging, and deep-trapped tritium is formed which cannot be removed by heating under vacuum, but can only be removed by isotopic exchange with deuterium.

There are differences between the nature of these materials which we believe are partially responsible for the observed differences in aging effects. $LaNi_{4.25}Al_{0.75}$ is an intermetallic compound, whereas palladium is a pure metal. Intermetallic compounds have a unit cell comprised of a specific ordering of elements in the compound. $LaNi_{4.25}Al_{0.75}$ has a hexagonal close packed structure, the same as $LaNi_5$. Aluminum atoms added to the material substitute with nickel atoms and afford tailoring of the equilibrium hydrogen pressure by changing lattice parameters. Nevertheless, any damage or disordering of the unit cell will significantly modify or destroy the compound's ability to react with hydrogen. Since palladium is a pure metal, rearrangement of atoms in its lattice should not affect hydrogen absorbing sites as significantly as with $LaNi_{4.25}Al_{0.75}$.

Similar to palladium, $LaNi_{4.25}Al_{0.75}$ experiences lattice damage from ^3He buildup in the lattice. Transmission electron microscopy examination of aged $LaNi_{4.25}Al_{0.75}$ samples by other investigators in our laboratory have shown the existence of lattice damage, dislocations and ^3He bubbles. It is believed that ^3He causes the formation of self-interstitials and vacancies, similar to those described by Lasser *et al.*[12] for tantalum tritide. The formation of vacancies and self-interstitials can be represented by the following reaction:

$$LaNi_{4.25}Al_{0.75} \rightarrow La_{1-x}Ni_{4.25-y}Al_{0.75-z} + xLa_{SIA} + yNi_{SIA} + zAl_{SIA}$$

where La_{SIA}, Ni_{SIA}, and Al_{SIA} represent La, Ni, and Al self interstitial atoms. The damaged lattice now consists of a substoichiometric structure having the formula $La_{1-x}Ni_{4.25-y}Al_{0.75-z}$. This substoichiometric structure now may have open La coordination sites, which can possibly more strongly bind to tritium, hence making a more stable tritide (elemental La forms a very stable hydride), which would explain the lower desorption pressure. In such a lattice, one would realistically expect formation of a distribution of sites (i. e., variations of localized values of y and z) of different energies, which would explain the isotherm slope. Large localized values of y and z would probably form very stable sites, which are those in which the deep-trapped tritium presumably resides. Deep-trapped tritium could also result from reaction of tritium with La_{SIA}.

An apparent anomaly in the aging results was mentioned above. Desorption pressures of 1423-day-aged $LaNi_{4.25}Al_{0.75}$ were higher than those of the 1273-day-aged sample. Some additional information on the history of the sample provides some insight into the reason for this apparent anomaly. The desorption isotherm for the 1273-day-aged sample was measured after the sample was held in dormant storage for about 1100 days. After the isotherm measurement at 1273 days, the sample was placed back into storage for about 150 days, after which the isotherm at 1423 days was measured. We have previously reported that absorption-desorption cycling partially reverses aging effects in $LaNi_{4.25}Al_{0.75}$. Fig. 8 shows the effect of absorption-desorption cycling on the desorption isotherm. After 20 cycles, the desorption pressure of the aged isotherm has substantially increased. We believe that the isotherm 1273-day isotherm measurement and subsequent reloading of the sample (which is equivalent to 1 cycle) caused the observed increase in desorption pressure.

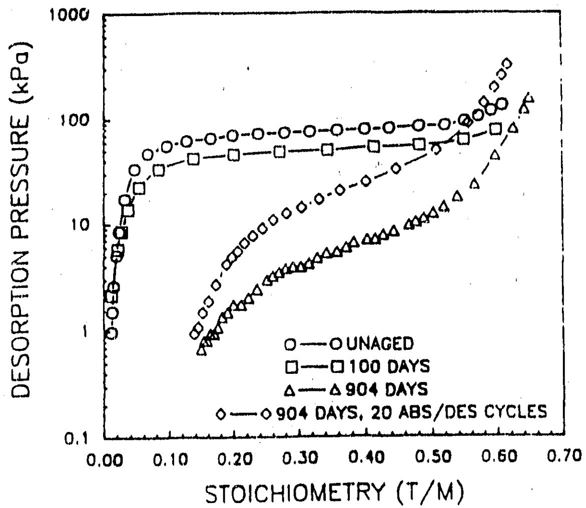

Fig. 8. Partial Reversal of Aging Effects in $LaNi_{4.25}Al_{0.75}$.

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