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Tritium Aging Effects in Hydride Materials - Studies at the Savannah River Site

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Introduction

The Savannah River Site (SRS) is a U.S. Department of Energy owned facility involved in part in hydrogen isotope separation operations. Metal hydrides figure prominently in those processes [1-4]. The primary hydrogen isotope of interest to SRS is tritium. Tritium decay is known to induce aging affects in metal hydrides [5-10] which are thought to arise primarily because of structural changes in the hydride caused by the deposition and migration of ^3He, the tritium decay product. In general, the changes induced by aging (lowering of plateau pressure, increased inhomogeneity, decreased capacity) are deleterious and the desire is to avoid them if possible.

One metal hydride material used at SRS is 50 weight percent palladium supported on kieselguhr (Pd/k). Kieselguhr is a diatomaceous earth (primarily silicon dioxide based) commonly used as a catalyst support. Depositing Pd on the kieselguhr was expected to spread it out producing a higher surface to volume ratio, which would promote ^3He release and mitigate aging effects. In order to experimentally investigate this proposition, the research facility at SRS, the Savannah River Technology Center (SRTC), placed three samples of different Pd/k types into a long-term study of tritium aging effects.

The second major hydride material employed in SRS processes is $LaNi_{(5-x)}Al_{(x)}$ (typically called LANA or LANAx), where x can be 0.03-1.0. This material shows more severe aging effects than palladium or Pd/k. Plateau pressure decreases occur early, and plateau sloping and heel ingrowth become severe, with older samples showing up to 50% capacity loss due to heel formation. SRTC has had several samples in a long-term aging study which started in 1987 and continues to this day. Some earlier studies have already been published [10,11].

In addition to studies on actual process materials, SRTC is involved in developing and testing new alloys via collaboration with several different groups. SRTC typically conducts the tritium studies and some `cold' work using protium or deuterium, while our collaborators typically prepare new alloys and study their `cold' hydrogen properties in more detail. As an example of this kind of work, we have examined the aging properties of several $Pd_{(1-x)}M_{(x)}$ alloys, where M = Ni, Co, and Cr and x = 0.05 and 0.1. In general, these materials showed more severe aging effects than pure Pd, but less than the LANA materials.

Experimental

SRTC's facility for studying metal tritide chemistry is equipped with two linked all-metal manifolds enclosed in an air-hood and operated through gloveports. System pressures are limited to less than 182 psia, although actual operating pressures are usually lower. Tritium is supplied from a $LaNi_{4.5}Al_{0.5}$ bed. Pressure is measured with 10,000 torr MKS Baratron pressure sensors that have been calibrated to NIST traceable standards.

The three Pd/k samples used represented three different synthetic methods. The first was prepared by Pd deposition from a $PdCl_2$ solution combined with thermal decomposition at 3-400 ^oC (PDK1). The second sample was derived from the first by 1100 ^oC heat treatment (PDK2). The third sample was prepared by thermal decomposition of deposited $(NH_3)_4Pd(NO_3)_2$ at 300-350 ^oC (PDK3)[12]. The LANA samples placed into the aging study were of several base compositions, with x= 0.3, 0.75, 0.8. All were prepared as custom Hy-Stor alloys by Ergenics, Inc. The Pd alloys were prepared by LANL.

Results and Discussion

Table 1 presents results on Pd/k ^3He release determined by sampling the overpressure at the end of the storage period and analyzing with mass spectrometry. Gas phase ^3He in excess of that born in the overpressure has been released from the solid. Typical bulk hydride material comes as (or becomes due to decrepitation) fine powder. This material form has been observed to release approximately 5% of the ^3He produced in the bulk by T decay. In contrast to expectations, the as-received and process Pd/k samples do not show the expected enhanced ^3He release that can be observed in improved Pd/k. The enhanced release rate of improved Pd/k suggests we could expect to see less severe aging effects in that material, and this is observed.

Figure 1 presents 120 ^oC isotherms for all the Pd/k samples, which graphically show the lesser aging of improved Pd/k. Also of note is the fact that the process Pd/k shows the largest amount of plateau pressure depression and sloping. This can probably be traced to the morphological effects of heat treatments (sintering). The order of increasing heat treatment severity is PDK2 > PDK1 > PDK3, which correlates with the increasing evidence of aging (larger particles release less ^3He, resulting in more plateau depression and sloping). Morphological effects have been noted elsewhere in similar materials [13].

Figure 2 presents tritium isotherms for virgin and aged LANA.75. LANA materials clearly show much more severe aging effects when compared to Pd and Pd/k. Whereas 2-3 years of tritium aging in Pd/k produced a small heel of ~0.05 T/Pd units, a similar amount of exposure in LANA.75 produces a heel of ~0.25 T/M units. In addition, the plateau sloping observed in Pd/k was minimal and restricted to the early part of the isotherm. But in LANA.75, the slope is severe and in fact extends over the entire isotherm. Prior work [10,11] has show some of this damage can be repaired or `healed' by repeated absorption-desorption cycling, but significant aging still exists even after 20 cycles.

Plateau pressure and flatness, and overall hydrogen capacity represent the primary engineering parameters of interest when applying metal hydrides. Changes in these parameters need to be anticipated in order to predict material lifetimes in specific applications. The SRTC work is aimed at developing an understanding of these factors. In addition, we are involved in a continuing search for better materials that show a more desirable balance of properties and cost. In that light we have recently been examining several Pd alloys.

Figure 3 shows some representative results for a $Pd_{.91}Ni_{.09}$ alloy. After aging for 11 months, the expected heel has begun to develop and plateau pressure decreases are observed. Of note however is the greater extent of heel ingrowth. While Pd itself will develop a 0.05 T/M heel, the alloy has developed a larger heel of ~0.09, almost twice that of pure Pd. Studies with other alloy compositions show that the extent of heel development is a function of composition. In addition, the thermodynamic parameters that characterize the isotherms are also compositionally dependent.

Summary

The Savannah River Technology Center is actively involved in studying the aging effects induced by radiolytic tritium decay in a variety of materials. This presentation has focused on our work in the arena of metal hydride materials. We have briefly illustrated the major effects one can observe upon aging metal tritides. We have also illustrated that both the chemical composition and the morphological form of the hydride material can be expected to exert an influence on the material's aging behavior.

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Figure and Table Captions

Table 1. Percent of ^{3}He detected (as a percent of the total ^{3}He generated during the aging period by radiolytic T decay in both gas and solid phases) in the gas over aged Pd/k samples. Note that the sample age is the cumulative age. In other words, PDK1 was sampled at 2.3 years and again at 5.8 years. PDK1 and PDK2 show typical release percentages for powder material. PDK3 is unusually high.

Figure 1. 120 ^{o}C desorption isotherms from aged and virgin Pd/k samples, illustrating the decreasing plateau pressures and increased plateau sloping observed in aged samples. (Note: Aged isotherms forced to T/Pd=0.05) Symbols: Square - As Received, Circle - Process Material, Triangle - Improved, Diamond - Process Material (this sample was virgin material, but was studied in 1995 (PDK4)). Lines Solid - 1998 data, Dashed - 1995 data.

Figure 2. 80 ^{o}C desorption isotherms from aged and virgin LANA.75. Dates on Figure are the month and year data was recorded. Virgin material studies began in 5/87.

Figure 3. Tritium desorption isotherms for virgin and aged $Pd_{.91}Ni_{.09}$. All aged samples had 338 days of storage with a full load of tritium. A slight healing can be observed by comparing the two 35 ^{o}C isotherms.

Table 1. ^{3}He Detected in Gas Phase (as % of total) at Different Sample Ages (years) over Pd/k

Sample	Age	% ^{3}He in gas
PDK1	2.3	10
PDK1	5.8	8
PDK2	2.3	4
PDK2	5.1	5
PDK3	2.2	24
PDK3	5.8	26