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Tritium aging effects in palladium on kieselguhr

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Abstract

Fifty wt% Pd on kieselguhr (Pd/k) is used in hydrogen isotope separation processes at the Savannah River Site. Long-term aging studies on this material were undertaken in June 1992. P-c-T data showing the aging effect of tritium loading for long periods will be presented and discussed covering from June 1992 to March 1998. Lowering of plateau pressures and increasing indications of inhomogeneities have been observed in both tritium and deuterium absorption isotherms at 0°C, and desorption isotherms at 80 and 120°C.

Keywords: Tritium; Palladium; Kieselguhr; Silica; Aging; Hydride

1. Introduction

The Savannah River Site (SRS) is a US 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 the ^{3}He 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 particular metal hydride material used at SRS is 50 wt% 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 ^{3}He 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.

One Pd/k sample was taken from actual process material. This material had originally been prepared by thermally treating $PdCl_2$-saturated kieselguhr, but the as-prepared material was found to have a high chloride content. This material had to be further heat-treated for several hours at 1100°C to reduce the Cl content. This material then became the base process material. A sample of the as-received material was also placed into the study. A third sample was taken from a Pd/k prepared by thermally decomposing $(NH_3)_4Pd(NO_3)_2$ absorbed on kieselguhr. This material was called 'improved' Pd/k because the process was a non-chloride one, and thus chloride corrosion problems could be avoided.

Select virgin samples were investigated by H_2, D_2, and T_2 isotherm determination and then loaded to T/Pd ratios of ~0.65. Those samples were then placed in storage at room temperature for 2–3 years, at which time they were reinvestigated in order to determine aging effects. Subsequently, they were reloaded and again stored for 2–3 years. In brief, the virgin material behavior is very similar to that of bulk palladium powder. However the different Pd/k samples do exhibit different aging characteristics. This paper presents the results obtained by investigations conducted on samples aged for ~2 and ~5 years.

2. Experimental

SRTC has two facilities for studying metal hydride chemistry. One is equipped with several stainless steel gas-handling manifolds for isotherm determination with non-radioactive hydrogen isotopes. The second facility is designed to handle tritium, and has two linked manifolds

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for radioactive work 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 $LaNi_{4.5}Al_{.5}$ bed. Both facilities use Nupro valves and Cajon metal-to-metal connections.

Stainless steel sample holders used in this study are horizontal beds approximately 9 cm long and 2 cm in diameter [9]. These have either a dual thermocouple welded into the vessel such that the thermocouple tip is located in the sample, or a thermocouple well similarly placed. Two Nupro valves are mounted on a vertical tube located on one side of the bed and are used to connect to the manifolds via Cajon VCR-4 type connections.

Pressures are normally measured with 10 000-torr MKS Baratron pressure sensors that have been calibrated in the SRS Standards Laboratory to NIST traceable standards. Sample sizes and designations are: 'as-received' (labeled PDK1), 7.3 g 55 wt% Pd/k; 'process' (labeled PDK2), 7.3 g 51 wt% Pd/k; 'improved' (labeled PDK3), 3.5 g 55 wt% Pd/k; process (labeled PDK4), 53.1 wt% Pd/k (used for additional virgin material studies). The primary Pd/k samples (PDK1, 2, and 3) were originally loaded and studied in mid-1992. Properties were redetermined in mid-1995 and again in mid-1997 (PDK2) and early to mid-1998 (PDK1 and 3).

As received Pd/k was prepared by saturating kieselguhr with $PdCl_2$ and then heat treating in the presence of ammonia and hydrogen at 300–400°C for as many cycles as required to obtain the desired weight percent Pd. The number of cycles can vary from as few as eight to as many as 30 for 55 wt% Pd material. Process Pd/k was as received Pd/k heated in air at 1100°C for 2 h. Improved Pd/k is kieselguhr loaded with $(NH_3)_4Pd(NO_3)_2$ and heat treated in air at 200–300°C to decompose the nitrate for as many cycles as required to obtain the desired wt% Pd.

3. Results and discussion

Fig. 1 shows tritium desorption isotherms acquired at 80°C with the three Pd/k samples and a pure Pd powder. Differences are very minor, with a slight plateau pressure elevation noted for the Pd/k samples as opposed to Pd powder. The process Pd/k sample seems to have a 'heel' in that the terminal T/Pd value obtained is not zero. In aged samples, a heel is an expected phenomenon and isotope exchanges are conducted to analytically determine its size. Unfortunately, such a determination was not conducted on the virgin materials. In aged samples, heels are determined and isotherms are adjusted to the determined values.

Table 1 presents results on ^3He release. The release data is 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. In contrast to expecta-

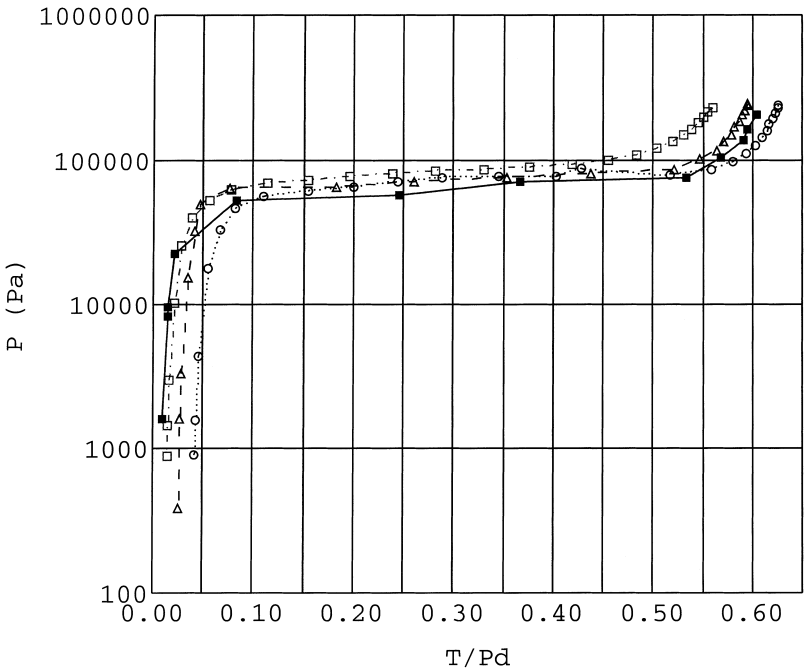

Fig. 1. Comparative 80°C tritium desorption isotherms for virgin Pd powder and Pd/k samples, illustrating the general agreement of virgin Pd/k with Pd powder. Symbols: (■) Pd powder, (□) as-received Pd/k, (○) process material Pd/k, (△) improved Pd/k.

Table 1
^{3}He detected in gas phase (as % of total)

Sample	PDK1	PDK2	PDK3
Age at sampling (years)	2.3	2.3	2.2
% of total generated	10	4	24
Age at sampling (years)	5.8	5.1	5.8
% of total generated	8	5	26

tions, the as-received and process Pd/k samples do not show the expected enhanced ^{3}He 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. The process Pd/k behaves most similarly to bulk Pd powder, and its tritium isotherms are shown in Fig. 2 (desorption isotherms are shown for 80 and 120°C, absorption isotherms are shown at 0°C). As can be seen, there is a progressive depression of the plateau pressures with sample age and an increase in plateau sloping in the lower T/Pd regions. The major capacity decrease of about 0.05 T/Pd units is observed to occur during the first aging period, with only minor changes noted from the second period in agreement with the literature [5]. The difference in fact was within experimental error, and thus all aged desorption isotherms are forced to a terminal T/Pd value of 0.05. Virgin material isotherms at 0 and 120°C on this figure were obtained with PDK4. The virgin 80°C data represents three sequential isotherms and illustrate good experimental reproducibility.

Fig. 3 presents 120°C isotherms for all the Pd/k samples, which graphically show the expected 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. The order of increasing heat treatment severity is process>as-received> improved, which correlates with the increasing evidence of aging (more heat implies more depression and sloping and less He release). Some duplicate runs were conducted but they did not show much variation, leading us to conclude that aging effect 'healing' observed in other hydride materials [9] was not significant in our experiments. Clearly some morphological effect is active in these samples, as has been noted elsewhere in similar materials [11].

We have also taken the step of comparing our results with those of other researchers. Lasser [6] has published Pd–T isotherm data, which we reproduce in Fig. 4. Overlaid on this data is the SRS data obtained at similar temperatures on several samples. The range spanned by the 80°C SRS data represents sample type and aging effects, and the virgin as-received Pd/k agrees well with Lasser's

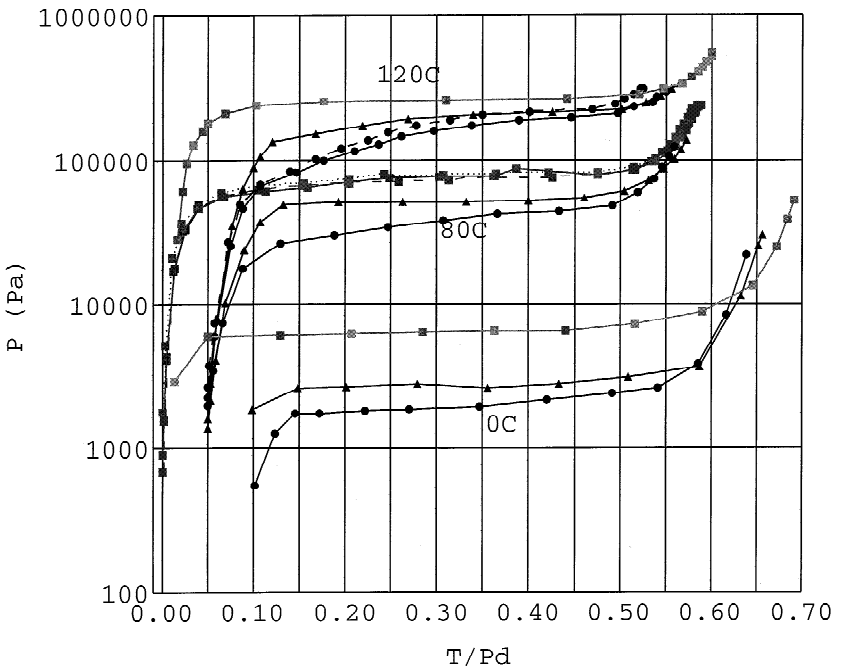

Fig. 2. Process Pd/k (PDK2) tritium 80 and 120°C desorption, and 0°C absorption isotherms for virgin and aged sample. The 120°C virgin isotherm is from sample PDK4, and was actually acquired in 1995. The three 80°C virgin material isotherms illustrate good reproducibility (solid, dashed, and dotted lines). Symbols: (■) virgin materials (1992), (▲) 1995 data, (●) 1998 data.

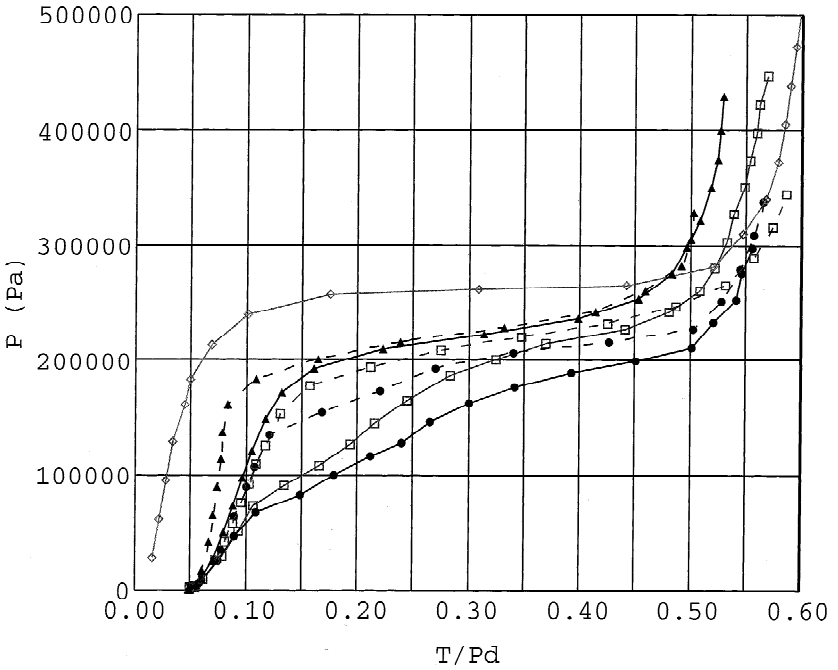

Fig. 3. Desorption isotherms (°C) from aged and virgin Pd/k samples, illustrating the decreasing plateau pressures and increased plateau sloping observed in aged samples. Note: aged isotherms forced to T/Pd=0.05. Symbols: (□) as-received, (●) process material, (▲) improved, (◊) process material. Lines: (—) 1998 data, (- - -) 1995 data, (◊) this sample was virgin material, but was studied in 1995 (PDK4).

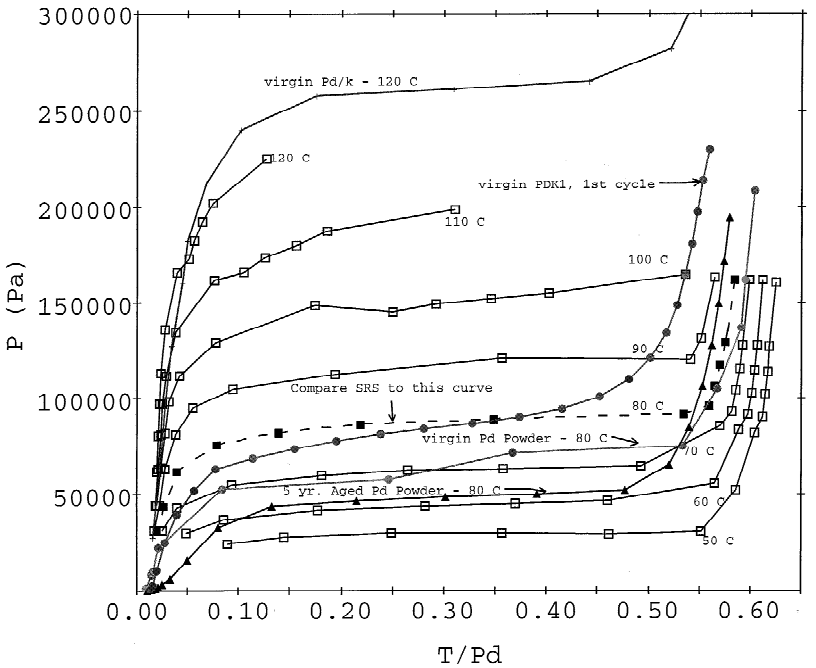

Fig. 4. Palladium–tritium desorption isotherms. Comparison of SRS data for virgin Pd/k and virgin and aged Pd powder to that of Lasser [6]. (Lasser's data from his ref. 5.55, converted to torr). Also shown is an isotherm from Pd powder that had been aged for 5 years. Symbols: (□) Lasser, (+) virgin process material (PDK4), (●) virgin as-received Pd/k, (△) virgin Pd powder, (▲) Pd powder aged 5 years.

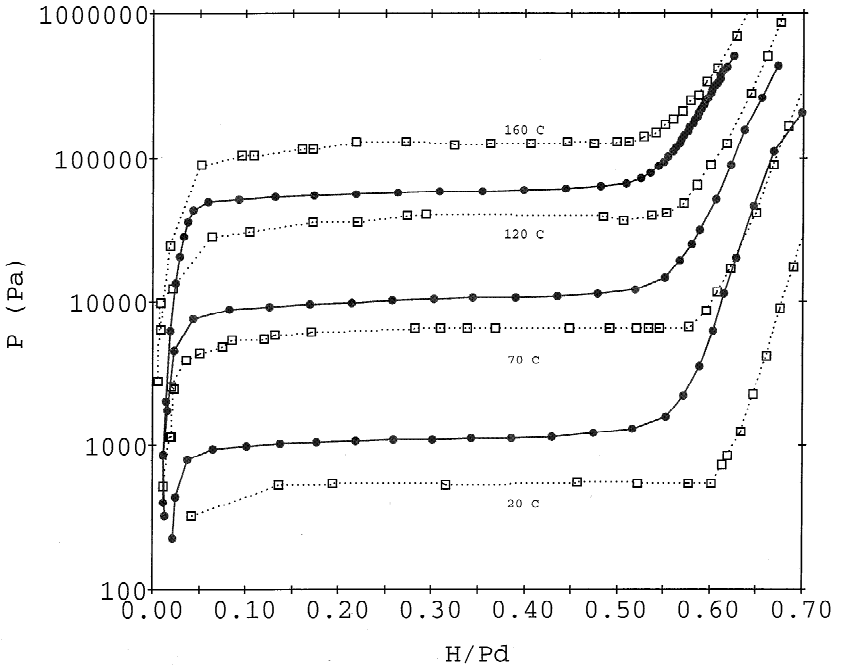

Fig. 5. Palladium–hydrogen desorption isotherms. Comparison of SRS data for virgin improved Pd/k to that of Wicke and Brodowsky [12] for Pd. (Note: Wicke and Brodowsky's Fig. 3.4 was scanned and digitized to get the data. Higher temperature (>160°C) curves not shown). Symbols: (□) Wicke, (●) virgin improved Pd/k.

data. Additionally, we have used van't Hoff parameters [6] to calculate expected plateau pressures and find that our data agree reasonably well. We have also compared to data published by Wicke [12] as shown in Fig. 5. In this case the SRS data also agree well with the published data. It should be noted that these comparisons further illustrate the fact that virgin Pd/k behaves essentially as bulk Pd powder.

4. Summary

In conclusion, we have shown that virgin Pd/k behaves essentially as Pd powder. Furthermore, as tritium decays inside the materials, aging effects are produced that correlate with those observed in aging Pd–T systems. We have also illustrated the apparent inverse correlation of aging effect magnitude and initial heat treatment. Future work will hopefully illuminate this effect more fully.

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