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Tritium Aging Effects in some Pd - Cr, Ni, and Co Alloys

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Introduction

Tritium aging effects on metal tritides used for hydrogen storage and isotope separation have been of ongoing interest to a variety of researchers [1-11]. Most studies have focused on single element materials, but some Pd-based alloys have been examined (1, 2, 4, 8, 9). The Savannah River Site contains the US Dept. of Energy's Tritium Facility whose mission is tritium purification and processing. As part of a general approach towards understanding the science of tritium processing, the Savannah River National Laboratory has maintained an active research program into the properties of metal hydride materials, which includes both tritium decay effects [2, 3, 8, 9-12] and development and characterization of potential alternative materials [13-15]. As a part of this program we have studied tritium aging effects in select Pd—X alloys (X= Co, Cr, Ni).

The ^{3}He produced by ^{3}H (or T) decay in the solid hydrided material is primarily retained in numerous bubbles that form in the material relatively early in the aging process [refs to bubbles]. These bubbles induce a lattice strain that causes an expansion of the metal lattice, which in turn alters the desorption properties of hydrogen isotopes, although Gupta and Gupta have explored an electronic component of that as well [16]. Typically, plateau pressures are lowered as ^{3}He in the bulk increases (some ^{3}He is lost to the gas phase). It is this change in plateau pressure that often presents an issue for tritium processing.

At the same time a 'heel' develops where a fraction of the hydrogen isotopes cannot be desorbed at the chosen temperature, but instead can only be driven out by increasing the temperature. This heel readily exchanges with freshly loaded hydrogen isotopes; a fact that is exploited in determining the amount of hydrogen contained in the heel. In Pd and Pd alloys, the heel encompasses approximately 0.05 or so Q/M units (Q = H + D + T) of the capacity (typically maximum capacities of Pd are about 0.67 Q/M units) [2, 3, 5, 6]. In La-Ni-Al alloys however, the heel can reach ~1/3rd of the total capacity (usually ~0.75 Q/M) [9].

As the tritium decay progresses the created He agglomerates into bubbles. In very old metal tritides, the network of bubbles can interconnect with each other and to the surface via cracks, creating an unhindered path to the external gas phase. When this occurs, He release can be quite rapid and is called 'breakout'. It is thought this can be assisted by cycling, especially during the desorption part of the process where the metal hydride's expanded lattice contracts back to the dehydrided state. In fact this can happen before breakout occurs, and part of the decay-induced effects will be reversed, or 'healed'. So far, we have not observed this process to produce a complete return to the virgin state however. As well, the healing effect has been avoided in previous studies by keeping the isotherm temperatures low. Heating the materials to elevated temperatures can drive out 3He from the bulk thereby healing (at least partially) the tritium decay damage.

Further, while Pd and Pd alloys typically exhibit P-c (pressure-composition) isotherms with nearly ideal characteristics, the aging induces a change in this behavior. Typical Pd isotherms show very flat plateaus with reasonably sharp transitions from the sloping P vs c curves of the pure alpha and beta phase regions. However, tritium aging often induces a pronounced slope to the plateau, especially in the

lower half of the Q/M region of the plateau. In alloys such an effect is typically attributed to compositional inhomogeneity or even complete phase separation. The sloping plateaux generically indicate a heterogeneity not originally present in the virgin materials.

In this paper additional tritium aging studies on some Pd-X alloys, where X = Co, Cr, and Ni, are presented. Most of the results are derived from approximately 1 year of static T-aging with the exception of one Pd-Ni sample that saw an additional ~3 years of static aging.

Experimental

Alloys of nominally 5 and 9 atomic% were melt spun by Los Alamos National Lab and formed into foils which were supplied for these studies. The alloy foils were cut into small squares (~150 pieces, ~3x12.5 mm) for loading into sample cell through Cajon 4-VCR gland.

Virgin material Isotherms for Co and Ni alloys were previously published [12] and included are full details on sample preparation and experimental protocols. The same processes were used for Pd-Cr alloys. Each sample cell was attached to an S-shaped stand-off tube mounted on a double all metal valve equipped with 4-VCR connections. Samples were loaded with tritium (typically 99%+ isotopic purity) after determining virgin isotherms and aged statically. i.e. without any temperature cycling, at room temperature.

Table 1 presents a summary of the alloys studied. Shown is their designation, nominal composition, the sample weight used in the study, and the number of days of static T-aging accumulated. The PdNi1 sample shows two values for the days aged as it was examined after both aging periods.

The tritium manifold used for isotherm determination was an all metal Sieverts apparatus installed in a floor-to-ceiling air hood in the Tritium Facility. Because the composition affects the plateau pressure at a given temperature, isotherm determinations were carried out at different temperatures for some of the alloys.

Heel content is determined by a successive dilution method. The nearly empty sample is rapidly loaded with an alternative isotope and not allowed to reach equilibrium, thereby keeping the loss of the original heel isotope to the gas phase to a minimum. Then the sample cell is closed and the remaining gas evacuated, whereupon the sample cell is reopened and heated to drive out a large part of the hydrogen isotopes adsorbed. A sample is taken of this gas and analyzed for isotopic composition. The remaining isotope content is driven out and evacuated, whereupon the process is repeated (usually 3-4 times is sufficient). Once the original isotope has been diluted down sufficiently, the sum of that isotope removed in all the steps defines the heel size.

Sample PdNi1 was disassembled after the second set of isotherms were collected and removed for additional studies. It was found that the foil pieces had apparently broken down into small pieces, giving the sample the appearance of a powder. SEM images of the aged material are shown in Figure 1. The material seems to have fractured smoothly along crystal faces, some of which show striations. Some of the sample was transferred to Sandia National Laboratory and used in further studies

(Robinson, this conference). For this sample, the He/M ratio was estimated by computing the amount of He formed and allowing for some loss to the gas phase. These calculations were guided by mass spectral analysis of the He content of the sample's overpressure taken at the time studies on the aged material were initiated. The ^{3}He content of PdNi1 was estimated as 0.031 and 0.116 after the first and second aging period, respectively.

Results and Discussion

Figures 2 to 6 present tritium isotherms from the virgin and aged samples described in Table 1. Typical tritium aging effects are observed, namely plateau pressure lowering, heel growth, and increased sloping of the plateau, especially in the lower T/M regions. Of note however is the appearance of healing in Figures x, y, and z which occur after only a few cycles. These materials show a strong propensity to 'heal' tritium decay-induced damage, and are not stable with cycling at even the low temperatures used in these studies. Figure 7 presents a virgin material's 273K tritium desorption isotherm obtained after a single loading absorption step, which compares favorably to those of Figure 1(d) in Ura, et al [17], once the isotope effect and scale differences are considered. This material was not tritium aged.

Conclusions

In conclusion, the Pd-X (X = Co, Cr, Ni) alloys examined show typical tritium aging effects: plateau pressure depression, developing plateau slope, and heel formation, but seem to be very sensitive to cycling. "Healing", or increased plateau pressures, were observed after just a 2-3 cycles at working temperatures.

Based on the Pd-9wt%Cr sample's 273K T_2 desorption isotherm and its comparison to the protium isotherms of Ura, et al[17], a strong isotope effect exists in this Pd alloy. In addition the Pd-5%Ni sample was shown to have broken down into smaller particles due to tritium aging.

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Table 1. Sample Identification, composition, and days aged

IDENTIFIER	COMPOSITION (weight)	COMPOSITION (atomic)	Sample Wt.	Days Aged
PdCo1	2.8 wt% Co	4.8 at% Co	3.80	309
PdCo2	5.2 wt% Co	8.8 at% Co	3.18	328
PdCr1	2.5 wt% Cr	4.8 at% Cr	3.00	346
PdCr2	4.6 wt% Cr	8.8 at% Cr	3.17	(*)
PdNi1	2.8 wt% Ni	4.8 at% Ni**	3.42	321, 924
PdNi2	5.2 wt% Ni	8.8 at% Ni	3.30	338

(*) PdCr2 was not aged due to high plateau pressures and slow kinetics at working temperatures

(**) PdNi1 was extracted from the test cell and studied with additional techniques [ref to Robinson].

Figure 1. SEM photographs of the tritium-aged Pd-5 at% Ni (PdNi1) alloy 'foil'. (a) 60X magnification, particles are 100-200 microns across, (b) 75X, (c) 200X, and (d) 500X.

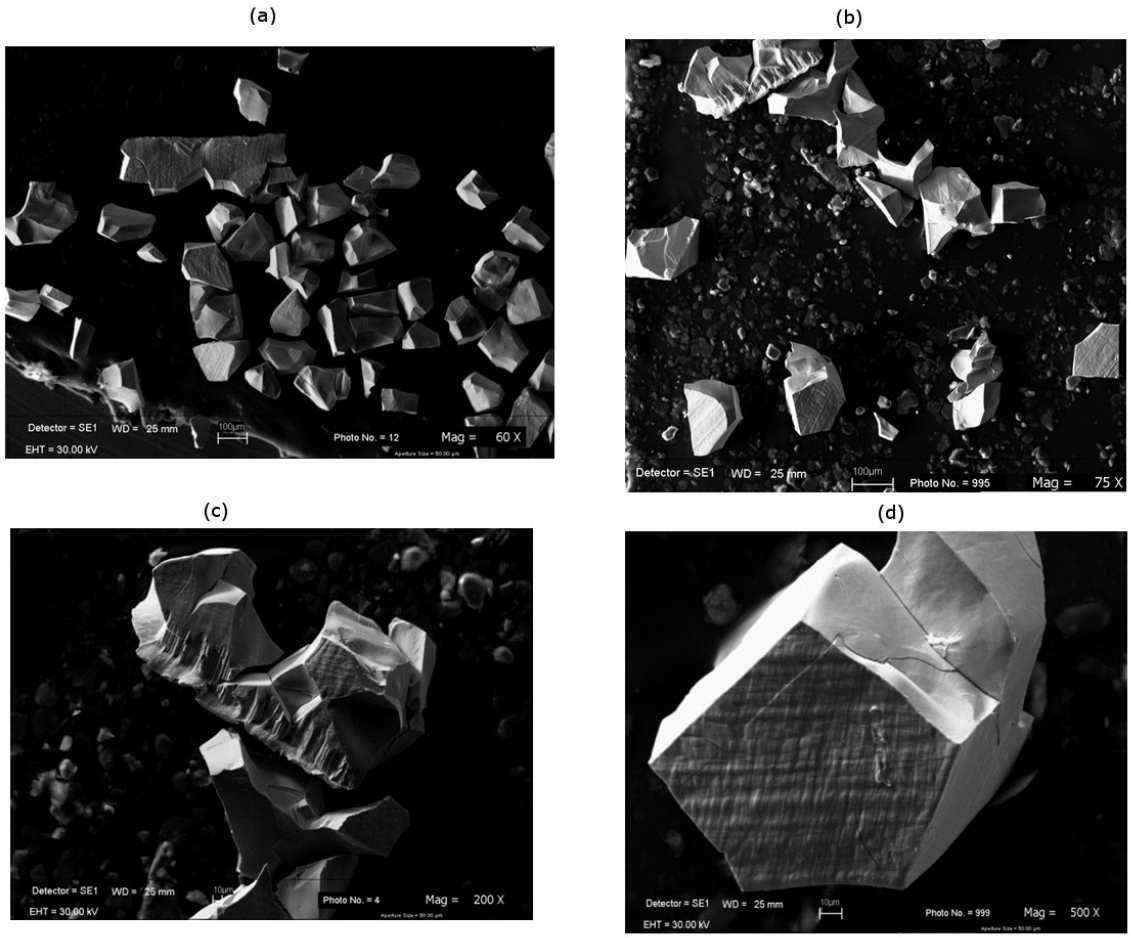

Figure 2. T_2 Desorption Isotherms from virgin (V) and 309–day aged (A) PdCo1

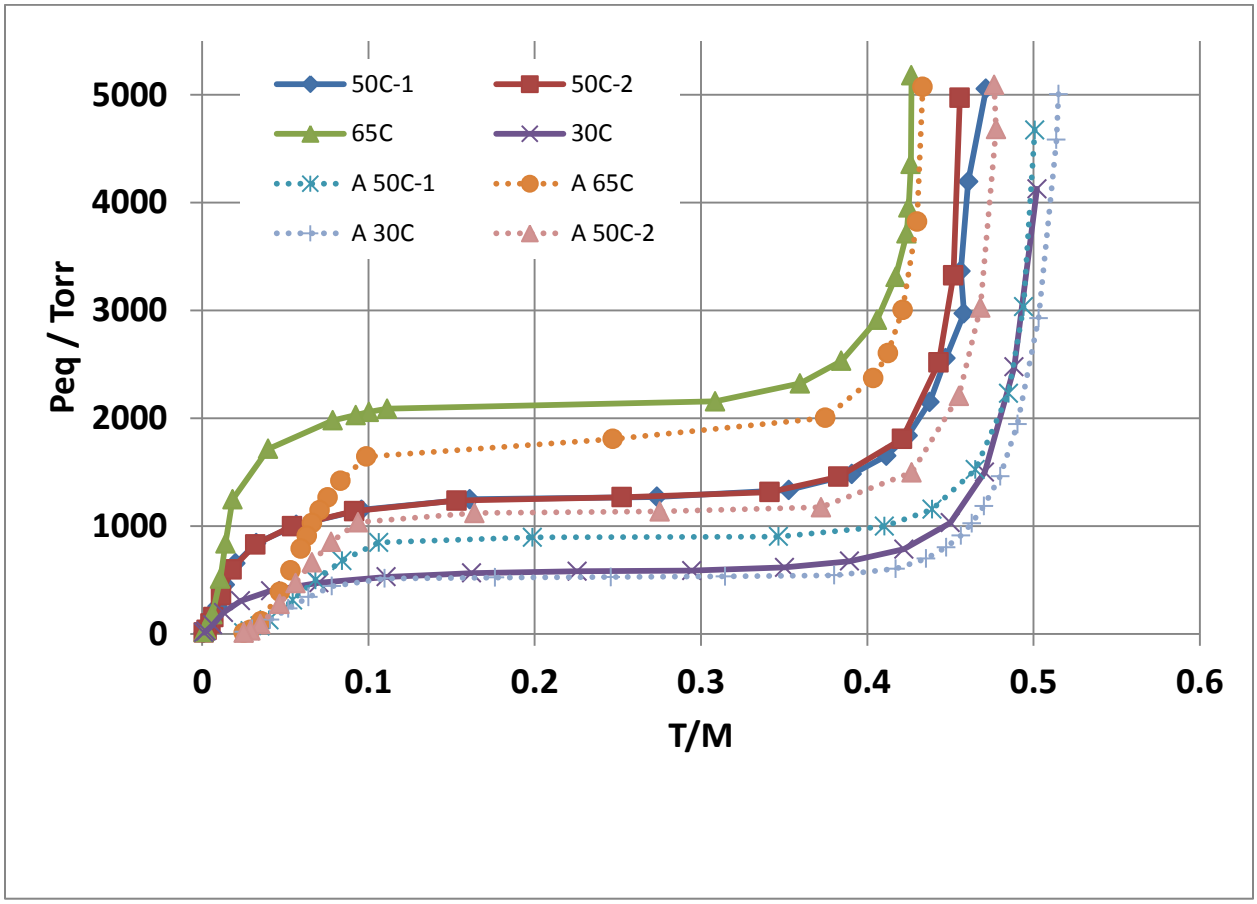

Figure 3. T_2 Desorption Isotherms from virgin (V) and 328–day aged (A) PdCo2

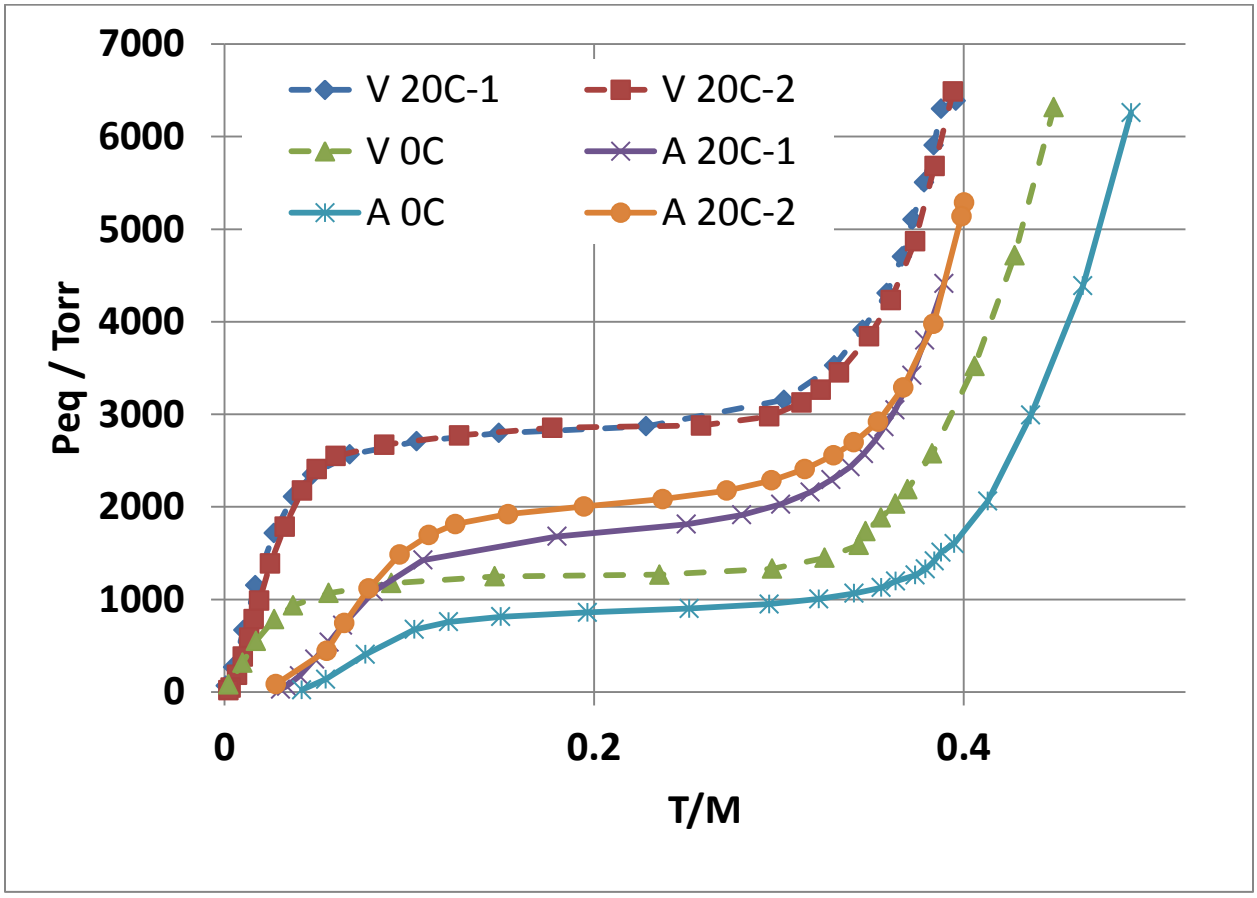

Figure 4. T_2 Desorption Isotherms from virgin (V) and 237–day aged (A) PdCr1

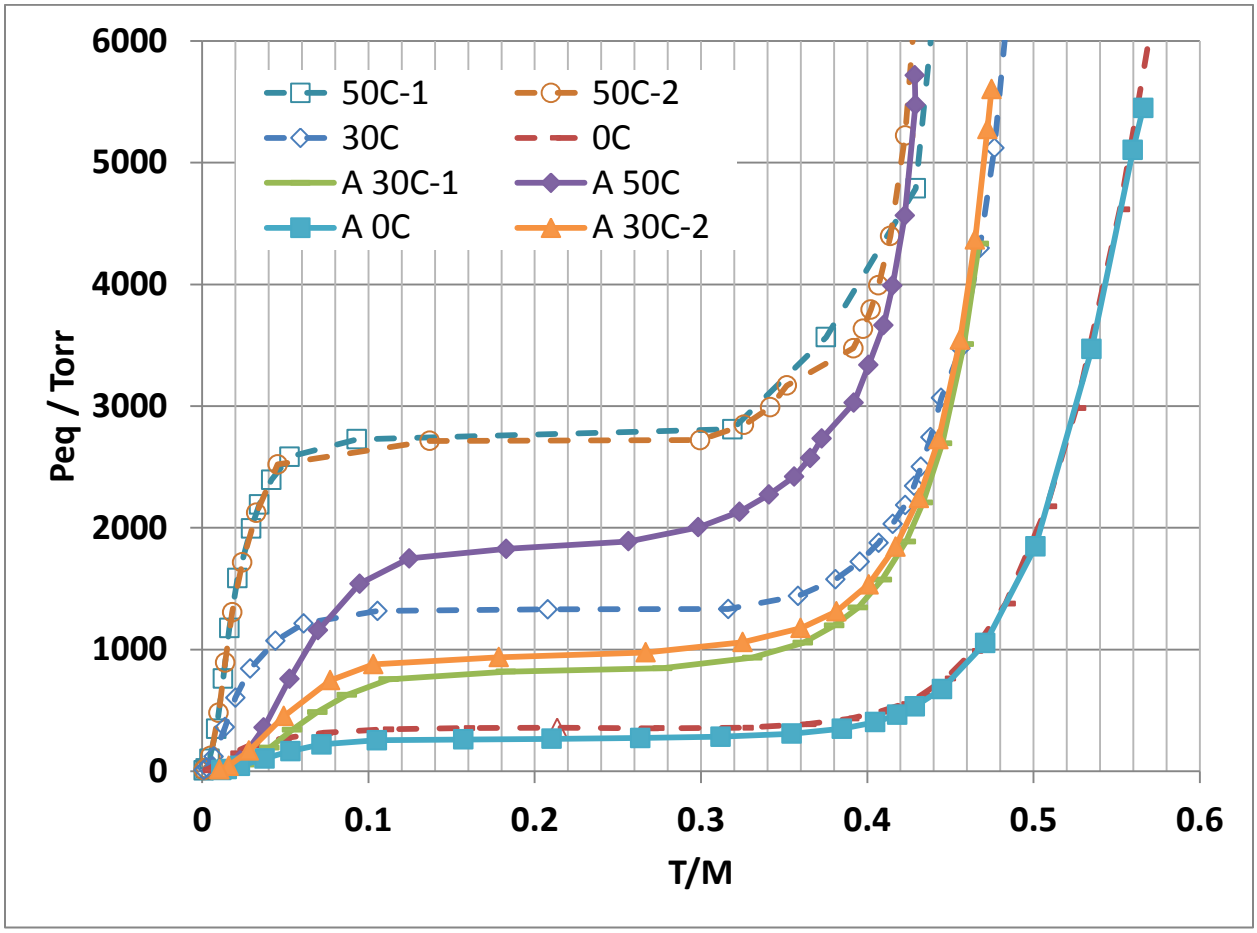

Figure 5. T_2 Desorption Isotherms from virgin (V) and –day aged (1A &2A) PdNi1

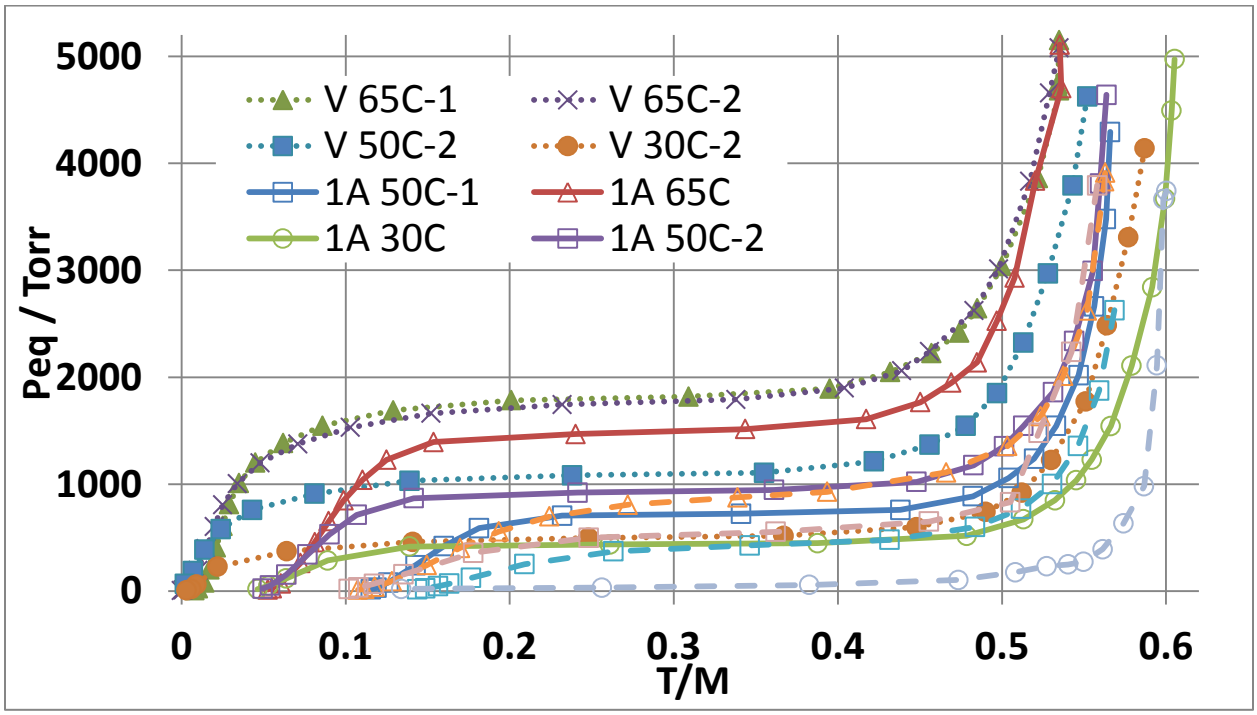

Figure 6. T_2 Desorption Isotherms from virgin (V) and –day aged (A) PdNi2

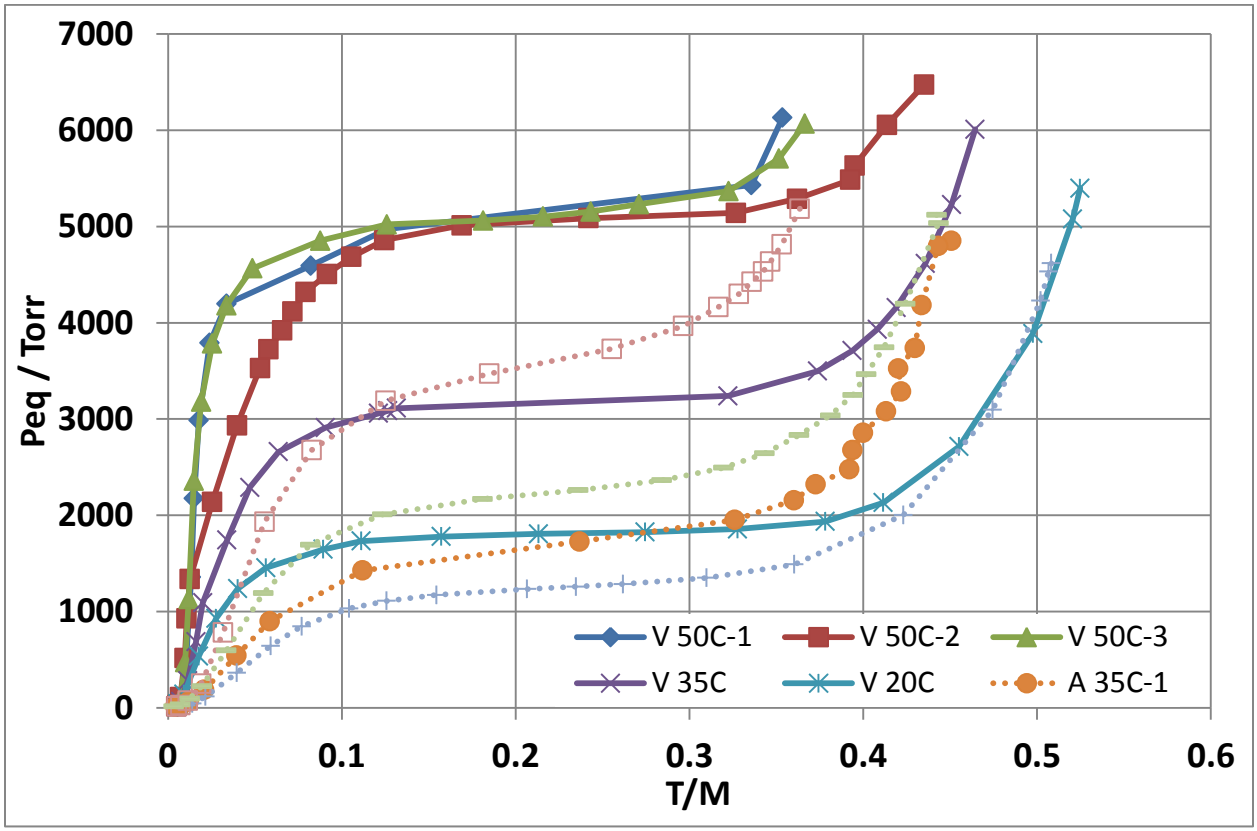

Figure 7. 273K T_2 Desorption Isotherm from virgin PdCr2 (loaded in 1 step – rightmost point)