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Abstract

This paper seeks to explore some of the effects of passivating a $LaNi_{4.25}Al_{0.75}$ sample by air oxidation under controlled conditions. Passivation of this metal hydride alloy seems to have two distinct regimes. The first occurs with air oxidation at 80°C and 20°C. It is characterized by complete reversibility upon hydrogen readsorption, although said readsorption is hindered substantially at room temperature, requiring the material to be heated to produce the reactivation. The second regime is illustrated by 130°C air oxidation and is characterized by irreversible loss of hydrogen absorption capacity. This passivation does not hinder hydrogen readsorption into the remaining hydride material.

Introduction

La-Ni-Al alloys, i.e. $LaNi_{5-x}Al_x$ where $x < 1.0$, have been used at the Savannah River Site for several years in tritium storage applications. Tritium decay in the hydride induces property changes, and eventually the material must be replaced with fresh material to be useable in current processes. The old material must then be disposed of properly. However, the hydrogen loading and unloading cycles produce a decrepitated material of high surface area. Such material is considered pyrophoric, and simple disposal of untreated but still filled hydride beds is not an acceptable waste disposal practice. The hydride material must be passivated before any such action can be undertaken.

Likewise, leaks and maintenance breaks of process lines can accidentally expose the hydride material to air, which can partially or fully passivate the material. An additional complication in these scenarios is the fact that rarely is a process bed totally empty of hydrogen isotopes. That hydrogen can react with oxygen to form water, releasing heat which warms the bed above room temperature. Leaks or line breaks can also occur while the bed is already at elevated temperatures due to standard processing conditions.

La-Ni-Al alloy reaction with oxygen has been studied previously. Perhaps the most relevant report in relation to the objectives of this study is that of Goodell [1]. In that study, stoichiometric and off-stoichiometric $LaNi_5$ and $LaNi_{4.7}Al_{0.3}$ were cycled in hydrogen to activate the material, and subsequently cycled in a hydrogen/0.1% oxygen mix. The reversible hydrogen capacity of the material was followed using fixed cycling times at 25 and 85°C. Goodell found that such cyclic exposure for short-term cycling (~30 or less cycles) produced a reduced rate of hydrogen absorption that produced an apparent reduction in cyclic capacity which was subsequently slowly restored. The recovery was helped by increased temperature. However, long-term cycling (up to ~300 cycles) produced some irreversible damage. Goodell also noted that aluminum substitution increased the material's resistance to these effects, and that the formation of water via hydrogen oxidation moderated alloy oxidation.

Oxidation of La-Ni alloy surfaces has been the subject of many studies, with the first being that by Siegmann, Schlapbach, and Brundle [2] (see also references in Goodell [1]). Those authors found that air-exposed $LaNi_5$ had a La enriched surface, and this La was oxidized. They also showed that in the native surface, this oxide was actually a hydroxide, and that it could be converted to oxide by specific treatments. This area has remained an actively researched one, especially in relation to the use of the hydride materials in Ni-MH batteries [3-5]. Geng, Han, and Northwood [6] explicitly studied the capacity decrease upon air oxidation of a $LaNi_{4.7}Al_{0.3}$ material, finding that over the span of 60 days, the capacity dropped from H/M~1 to H/M~0.8, at which point the capacity loss seemed to stop. Presumably, the hydride they used was initially nearly pristine. Activation processes most likely convert the hydroxide to oxide, but rehydrogenation and air exposures would potentially reconvert at least some back to hydroxide. As well, the activation process could foster the formation of Ni metal clusters on the surface. Prior studies of these and similar systems have concluded that such Ni metal particulates form on the surface and serve as hydrogen dissocation sites during the hydrogen absorption process, although whether these clusters are oxidized or not seems to be a function of pretreatment [7-10].

Wallace, et al, reported that $LaNi_5$ and related compounds could be oxidized extensively to form highly active catalysts [11]. The extent of oxidation was quite large and typically carried out at higher temperatures than the studies reported here, i.e. 350^oC in Wallace [11]. Other groups also reported that in catalytic studies with oxygen-containing gases, the hydride material would also be oxidized similarly [12-14]. Goncharuk and Endrzheevskaya [15] reported observing a 23% weight gain from air exposure of $LaNi_5$ beginning at ~200-250^oC in TGA experiments (note that Figures 1 and 2 in [15] appear to have been switched in the English translation of the article at least). Kleperis, et al [16] reported a 3.14% weight gain in similar experiments using nominally pure Ar, accompanied by structural and XRD spectra changes. The data suggested that trace oxygen was the culprit.

This paper explores some of the effects of passivating $LaNi_{4.25}Al_{0.75}$ under slightly different conditions than those used by Goodell and others. Experiments have been conducted with room air at 20, 80, and 130 ^oC and it has been found that different results are obtained at different temperatures.

Experimental

A single 5.404 g. sample of $LaNi_{4.25}Al_{0.75}$ was exposed to room air at several progressively increasing temperatures and its subsequent hydrogen absorption capacity studied. The sample was placed in a stainless steel sample holder equipped with a thermocouple well and attached to a stainless steel Sieverts' apparatus constructed primarily out of Cajon VCR parts. An oil-free Boc Edwards GVSP30 scroll pump typically produced a base pressure of <10 millitorr. All volumes were calibrated by He expansion from a NIST-traceable calibrated volume. Sample heating was accomplished by placing the sample cell is a covered Glas-Col beaker heater and using a Barnant Temperature Controller (PID) to adjust sample temperature which was measured with a type K thermocouple inserted into the thermocouple well. The sample cell was constructed from two ½-inch stainless steel pipe caps welded together and fitted with a Cajon 4VCR welded fitting in the circular end. The thermocouple well was formed from a 1/8-inch tube pinch-welded at one end and inserted into the cell via a hole drilled in the pipe cap end. The well was then welded into place. Air humidity, while nominally being controlled to ~50% by building ventilation controls, was in fact quite variable and this represents a potentially significant source of variation in results, although prior study on $LaNi_{4.75}Al_{0.25}$ has suggested otherwise [17].

The sample was passivated by air exposure under differing conditions, and then reactivated by hydrogen exposure. Sixteen different passivation/reactivation cycles were conducted on the sample. Initially air was introduced to the sample while it was at room temperature (nominally 20^{o}C). It was observed that the rate of reaction, as indicated by the pressure drop in the closed manifold, decreased quickly, so the approach was developed wherein the sample was allowed to react for 5-15 minutes, evacuated, and then re-exposed with fresh air until such time as the pressure drop was minimal. Typically 3 to 4 cycles were sufficient to reach this end state, but some variations in the protocol occurred during protocol development. For the 80 and 130^{o}C passivations, after ~two cycles at room temperature, the sample was heated to 80 or 130^{o}C during the final air exposure. The amount of available O_2 consumed in each step and for each full passivation cycle was computed based on pressure drop, and are tabulated in Table 1, along with the nominal temperature during the final step of each cycle. The final steps typically extended for multiple hours, usually overnight, but in one case it was extended over a weekend and produced complete O_2 consumption from the gas in the manifold.

Samples were always baked for several hours (usually overnight) under active vacuum at 80^{o}C prior to any passivation or reactivation steps. Rate-of-rise measurements were used to indicate the hydride material was desorbed. After passivating, the sample was evacuated to the base pressure, and hydrogen was introduced at ~5000-7000 torr with the sample at room temperature in order to assess the extent and impact of the passivation. In cases where hydrogen absorption was inhibited, the sample was heated to 80^{o}C, whereupon it readily absorbed hydrogen in all cases. Partial 80^{o}C hydrogen desorption isotherms in the beta phase region were then determined, in some cases in replicate which are designated below as a hyphenated number appended to the cycle number, i.e. 16-3.

Results and Discussion

The material used in our study is quite old and presumably had undergone the initial capacity loss noted by Geng, Han, and Northwood [6], leaving a La oxide/hydroxide-rich surface. The maximal loading obtained in this study was H/M~0.75.

In these studies, total O_2 uptake during 130^{o}C oxidations was 0.069 g., which would translate to a ~1.3% weight gain, which is less than half that obtained by Kleperis, et al

[16]. This indicates that further oxidation of the sample should be possible, which is consistent with the continuing capability to absorb hydrogen, albeit at a reduced total amount. The nominal O_2 uptake during the room temperature steps was neglected in this calculation because the studies at 20 and 80^oC indicated that it was fully reversible, while that at 130^oC was not.

Room temperature and 80^oC passivation almost totally prevented normal rapid hydrogen uptake observed in activated samples. If the sample was allowed to sit with hydrogen over it for long periods of time, slow absorption was detected, and leaving it thusly overnight produced extensive H_2 absorption. Hydrogen absorption was rapidly accomplished by heating to 80^oC. With room temperature and 80^oC passivation, no significant capacity loss was noted in the sample, and only experimental error was noted (random ordering on the H/M axis of sequentially obtained isotherm fragments), see Figures 1 and 2. Both Figures contain a virgin 77^oC H_2 desorption isotherm from this sample for comparison. The 77^oC isotherm is slightly offset due to the equilibrium temperature difference. Cycle 7-1 was a lower pressure single point hydrogen absorption determination and is not shown. These results are consistent with those of Goodell [1] for his short-term exposures.

Much more extensive oxygen consumption was noted when the sample was heated to 130^oC during the latter exposures for varying time periods. In one case, when left heating over a weekend, 101% available O_2 consumption was measured. Upon subsequent hydrogen exposure at room temperature, hydrogen uptake was rapid, producing noticeable temperature spikes in the sample. Hydrogen absorption capacity was observed to systematically decrease with the number of treatments so applied (except in one case), and these decreases were not reversible. Isotherm fragments were reproducible as evidenced by the cycle 16 replicates (see Figure 3 for details). This also is consistent with the capacity decrease noted by Goodell [1] for his long-term exposures.

Cycle 16-4 was a full desorption isotherm determination. It is compared to the virgin material 77^oC isotherm in Figure 4. This method of presenting the data emphasizes the capacity loss. At 6000 torr for example, the capacity has decreased from H/M of ~0.78 to ~0.65 which is a ~17% decrease.

It is reasonable to assume the remaining non-oxidized hydride material would nominally load to the same level as before, so a scaled isotherm was computed by forcing the highest loading points of the oxidized material's isotherm to overlay the virgin material beta-phase curve. This scaled isotherm is shown in Figure 4 as well. This method of plotting emphasizes that the beta phase and plateau region isotherm have not significantly changed. However, that may not be true in the alpha-phase region. This region is expanded in Figure 5, where an additional cycle of data (16-5) scaled identically to the 16-4 data, and consisting of both absorption and desorption data, is also plotted. The apparent offset between the virgin and 16-4 data (scaled and unscaled) is probably due to cumulative error in the isotherm determination process. That error is minimized by the procedure used to obtain cycle 16-5 data where full loading was not obtained. In that situation the desorption data overlays the absorption data almost exactly, and seems to be heading back to the (0,0) point (lowest equilibrium pressure determined in 16-5 was 0.7 torr).

The 16-5 data does not seem to reproduce the virgin curve shape in this region. This may be due to some experimental error, or it may be due to some effect of included oxide particles in the hydride material. In related work with internally oxidized Pd alloys [18], such shifts in apparent H/M axis intercepts of the alpha phase isotherms are noted as well. This work needs to be reproduced and studied further before any final conclusions are drawn.

Clearly two types of 'oxidation' are occurring in the sample. That at 80°C and below which is nondestructive to the sample and fully reversible, and that at 130°C which is destructive to the sample and irreversible. The oxidation might be expected to lead to primarily La oxide or hydroxide and free Ni metal. (Prior work has suggested that very little of the Al is oxidized [5]. This is understandable since the free energy of formation of La_2O_3 is about 20 kcal/mole more negative than for the formation of Al_2O_3 [19].) That Ni would then serve as hydrogen dissociation sites which would facilitate the observed rapid H_2 uptake. The virgin La-Ni-Al material used here was well activated and had rapid H_2 uptake. Likewise, the 130°C passivated sample had rapid H_2 uptake, as did the reactivated sample after 20 and 80°C passivations. While the protocols used in the 130°C experiments include two brief air exposures at room temperature first, it is unclear from these results if any of the oxide formed at the lower temperatures remained after the 130°C heating.

It is also unclear whether the slightly greater O_2 consumption obtained by the 80°C treatments (compared to 20°C treatments, see Table 1) produced any of the severe oxidation experienced at 130°C. The reactivation results do not indicate any systematic pattern such as seen in the 130°C results. Upon closer examination, it can be observed (see Figures 1 and 2) that the 80°C passivation treatments produce desorption isotherms that all lie to the left (lower H capacity) of those arising from room temperature passivations. The shift is not large, and run-to-run variation within each set appears random, unlike the nearly systematic decrease with 130°C passivations. However, the slight offset to lower H/M values in the 80°C data might indicate some destructive oxidation had taken place in one or more cycles. This also seems consistent with Goodell's results [1] where he noted more rapid onset of capacity decrease when he raised the experimental temperature from 25 to 55 and 85 °C.

An additional unexplained aspect is seen in cycle 14, where no loss of hydrogen capacity was noted on reactivation even though passivation was conducted for ~17 hours at 130°C, and produced similar O_2 consumption. As noted above, one possible important variable may have been water content of the air. Sufficient time was provided for oxidation to expect some loss in capacity. Clearly, more studies would be beneficial in working out these anomalies.

With the lower temperature passivations, an attempt to detect water desorption was made. In a few cases, the manifold was emptied and then the hydrogen from the sample cell was allowed to flow back into the manifold and an attached 25cc sample bottle. Subsequently the sample bottle was transported to a mass spectrometer for analysis, but no water above background was detected in these cases. Real time mass spectroscopy might produce a different picture.

Conclusions

Passivation of this metal hydride alloy seems to have two distinct regimes. The first occurs with air oxidation at 80°C and 20°C. It is characterized by complete reversibility upon hydrogen readsorption, although said readsorption is hindered substantially at room temperature, and the material had to be heated to produce the reactivation. The second regime is illustrated by 130°C air oxidation and is characterized by irreversible loss of hydrogen absorption capacity. This passivation does not hinder hydrogen readsorption into the remaining hydride material however. The 130°C air oxidation seems to occur at a lower temperature than previously recognized. Unexplained aspects of this process remain and further research may be beneficial.

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Figures

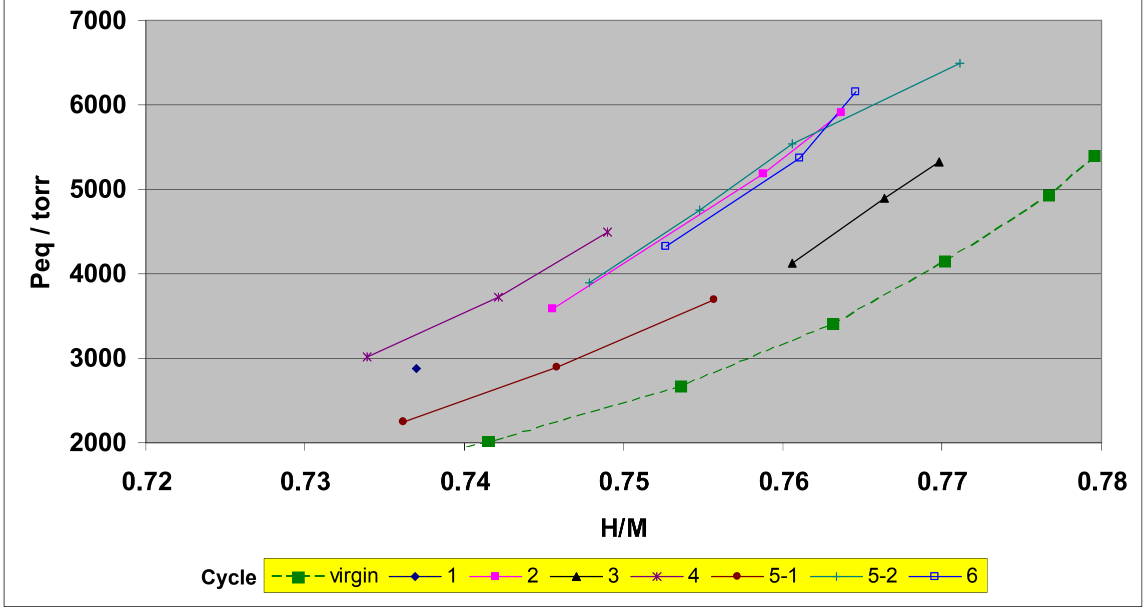

Figure 1. 80°C H_2 Desorption Isotherms after 20°C Passivation/Reactivation (virgin at 77°C)

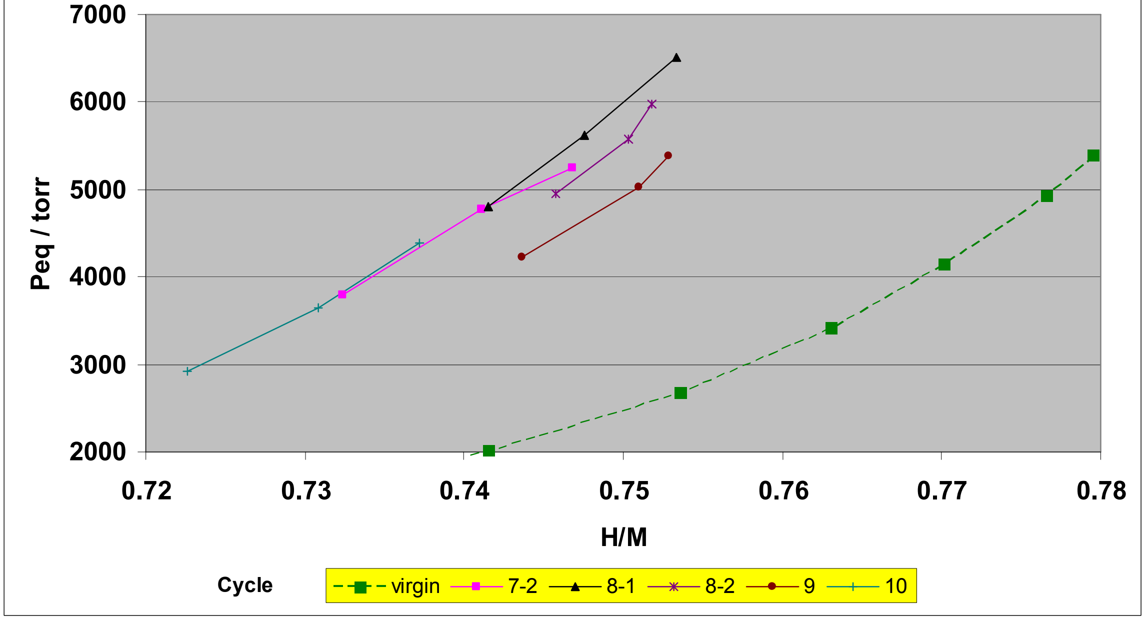

Figure 2. 80°C H_2 Desorption Isotherms after 80°C Passivation/Reactivation (virgin at 77°C)

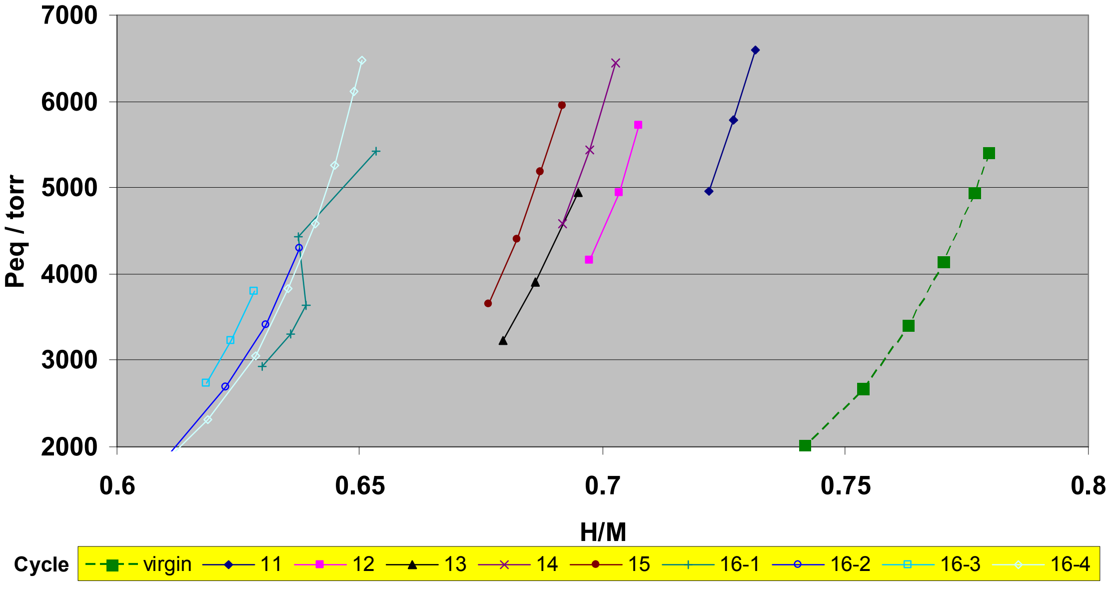

Figure 3. 80°C H_2 Desorption Isotherms after 130°C Passivation/Reactivation (virgin at 77°C)

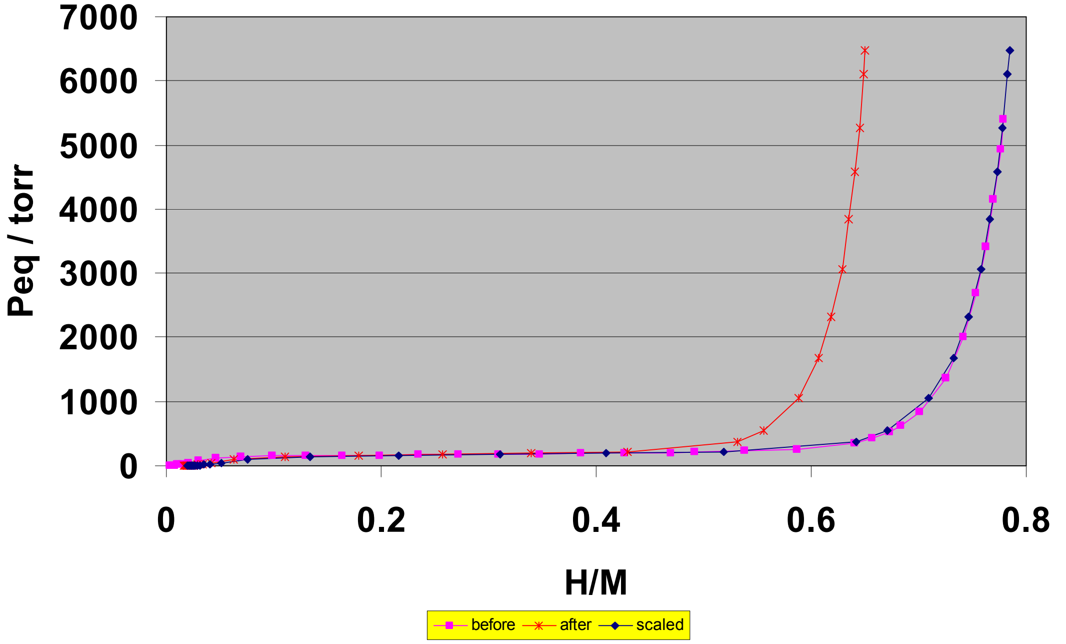

Figure 4. Comparison of Scaled and Unscaled 80°C H_2 Desorption Isotherms after 16 Passivation/Reactivation Cycles and Virgin 77°C Isotherm

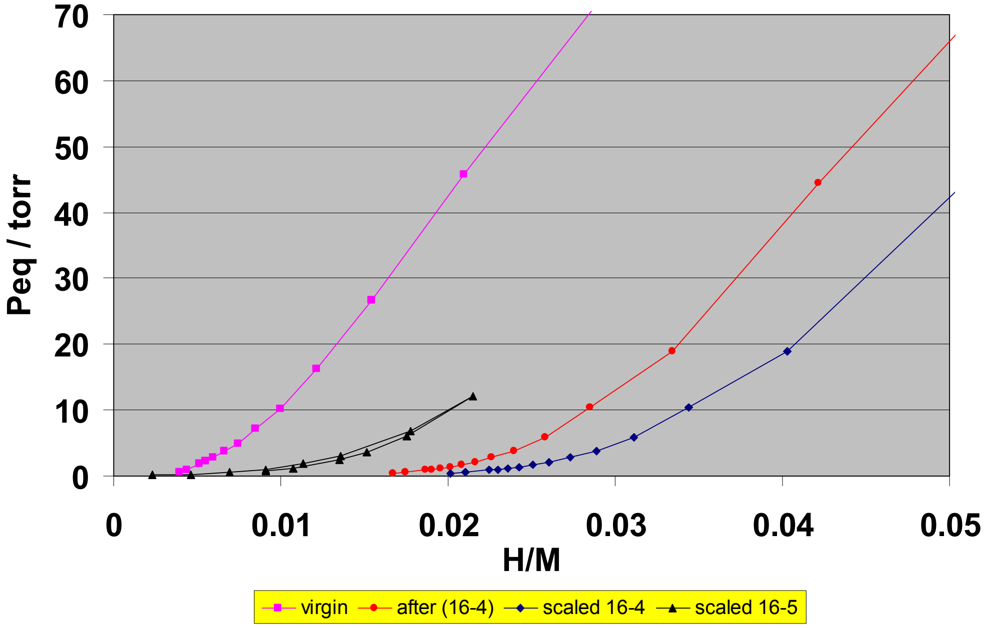

Figure 5. Comparison of Scaled and Unscaled 80°C H_2 Isotherms after 16 Passivation/Reactivation Cycles and Virgin 77°C Isotherm

Table 1. Passivation Steps Performed on $LaNi_{4.25}Al_{0.75}$ Sample

Cycle	Nom. T	%O2 consumed per step	Total % O2 consumed
1	20	15.957 1.455 0.471	5.960
2	20	12.164 2.966 0.754 0.691 0.770 0.248	2.906
3	20	6.356 3.053 1.282 0.686 0.750	2.430
4	20	8.340 1.670 0.970 0.882 0.691	2.510
5	20	8.608 0.791 0.182 0.268	2.468
6	80	8.591 13.514 3.265	8.434
7	80	8.698 2.405 34.189	15.112
8	80	9.024 1.826 30.870	13.914
9	80	10.861 2.316 28.930	14.042
10	80	9.698 1.619 27.704 16.933	13.984
11	130	9.755 40.892 66.986	39.174
12	130	7.541 1.698 70.140	26.431
13	130	7.035 1.405 78.224	28.856
14	130	6.778 62.889	34.894
15	130	8.064 1.710 71.966	27.249
16	130	8.934 3.135 101.096	37.712