Stability of the hydrogen absorption and desorption plateaux in $LaNi_5$–H Part 5: H capacity

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Abstract

A systematic study was made by gravimetry, carefully preserving the system mass zero, of the positions of the $\alpha/\alpha+\beta$ and $\alpha+\beta/\beta$ phase boundaries and the plateau lengths in $LaNi_5$–H, while absorption–desorption cycling under various conditions of temperature and pressure. Our findings include: (i) in agreement with previous studies, the initial capacity of the virgin intermetallic is in excess of $H/M = 1.1$; (ii) however, the initial desorption plateau is shorter than the initial absorption plateau by nearly 0.1 in H/M, owing to the trapping of H, possibly in lattice defects; (iii) absorption–desorption cycling at any temperature in impure hydrogen shortens the plateaux (capacity degradation), greatly exacerbated by elevated temperature; (iv) however, the total H capacity remains relatively constant, with an exchange of H between 'reversible' sites and trap sites, manifest as the drift in the $\alpha/\alpha+\beta$ phase boundary noted above. The reality of the H trapping owing to activation has been proved by independent techniques, such as deep-inelastic neutron scattering. It is unlikely that this H is initially trapped in the form of LaH_x, although this and other La–Ni hydrides do form during extended cycling at elevated temperatures. © 1999 Published by Elsevier Science S.A. All rights reserved.

1. Introduction

Previous papers in this series [1–4] have dealt chiefly with the factors which determine the hydrogen pressures at which the absorption and desorption plateaux, that is, the roughly horizontal portions of the pressure–composition isotherms, occur. Here we turn our attention to the positions of the pure-phase regions, that is, the roughly vertical portions of the pressure–composition isotherms, whose separation defines the recoverable hydrogen capacity (RHC).

Many studies have been made of the effects of extended absorption–desorption cycling on the RHC of $LaNi_5$ [5–15]. The common basis for all this work was fundamentally the expectation that, while $LaNi_5H_6$ might be the initial product of hydrogenation, its instability relative to LaH_2 would dictate that decomposition to form the latter and elemental Ni would ultimately take place [16]. In a seminal paper by Cohen et al. [5], it was reported that the loss of RHC was greatly accelerated by elevated temperatures, as occur in thermal absorption–desorption cycling. The de-

pendence of the rate of loss of RHC on the maximum temperature of the thermal cycle was consistent with an activated process, and in fact matches closely the expected activation energy for diffusion of Ni in $LaNi_5$ [17]. Annealing experiments [5] demonstrated that the $LaNi_5$ could be recovered, apparently by the recombination of LaH_2 and Ni.

Later work addressed the issues of gas impurities and the effects of cycling conditions, but the problem was essentially framed in [5]: $LaNi_5H_6$ is intrinsically unstable and decomposes at elevated temperatures. An aging experiment under extreme conditions (180°C and 136 bar H_2 pressure) provided support for this picture [18].

One study superficially at odds with the tenor of the foregoing is that of Dantzer [9]. After careful preparation of a sample of high quality, charging of the hydrogenator with gas of purity 99.9999% and activation, 1000 cycles were executed by thermal cycling between 25 and 80°C. No loss of RHC owing to (post-activation) cycling was detected. Examination of the cycled sample with XPS and EXAFS revealed no significant change in either the electronic state of Ni or the average local environment [19]. This outcome may be viewed as a consequence of the relatively low desorption temperature used, at which Ni diffusion would be relatively slow: extrapolating the data

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in [5] (Fig. 4) around 50 000 cycles with a maximum temperature of 80°C would be required to induce a 50% loss of RHC.

Later studies have produced results less easy to accommodate in the above picture. For instance, in [13] it was reported that 1000 isothermal cycles at 80°C significantly reduced the RHC, although no X-ray diffraction lines belonging to Ni or stable La-hydrides were found. In [12,15] it was reported that isothermal cycling in relatively impure gas hastened the loss of RHC at elevated temperatures, but that: (i) annealing at 700–900 K partially recovered it; and (ii) the loss of RHC after 3300 cycles at 20°C in 99.99999% pure gas was minimal. The more rapid degradation owing to (supposedly) isothermal cycling was remarked on but not explained in [5].

A common difficulty with most of the studies mentioned is that, despite severe loss of RHC, it was unusual to observe diffraction peaks from LaH_2 or FCC Ni in the degraded material. In [5] this was explained as a consequence of the microscopic scale of events, leading to particle sizes (really coherently diffracting domain sizes) too small to generate sharp diffraction peaks.

A more plausible explanation was put forward in [11], based on the increasing stability of the La–Ni-hydrides as the Ni content decreases. This was that amorphous hydrides, beginning with $La_2Ni_7H_{8-10}$, first formed, eventually decomposing to the stable binary hydride(s). Again, the Ni precipitates were supposed to be too small to observe by diffraction.

Our investigation of the RHC of $LaNi_5$ originated in the observations during several cycling studies in our laboratory that: (i) the hydrogen absorbed during the first ever absorption by virgin metal was not fully recovered in the first desorption; and (ii) the hysteresis loop would not close perfectly, i.e. the pure α-phase region would shift slightly between absorption and desorption, accompanied by a commensurate translation of the pure α-phase region in every successive absorption isotherm to a slightly higher value of the hydrogen-to-metal atomic ratio, H/M. These observations were made by high-resolution gravimetry, in which the zero of hydrogen concentration can be maintained as an absolute measure, as long as the sample absorbs or adsorbs no other atoms. For this reason it was initially suspected that a small leak into the sample chamber must exist, allowing the accretion of oxygen. Finally, having eliminated the possibility of leaks by thorough testing of the apparatus, we made careful study of RHC during nominally isothermal cycling at 100°C, maintaining the zero of H/M, to clarify these matters. The results form the basis of this report.

2. Experimental details

The study was carried out mostly, but not exclusively, with a gravimetric hydrogenator based on a Sartorius high-pressure microbalance with 1 μg resolution. This instrument is computer controlled and operates in isochoral mode, using weight measurements to determine the H concentration, subject to the caveat mentioned about extraneous ab- or adsorbants. The chief difference between this technique and the more common manometric isochoral technique, is that the H concentration can be determined absolutely, starting from the activation of a virgin sample, as long as the balance tare is maintained. In contrast, manometric and volumetric techniques are relative and rely on the accumulation of changes in H/M. Hence their absolute accuracy degrades with the total number of gas aliquots introduced to and removed from the sample. A potentially important difference factor was the amount of gas to which the sample was exposed, which was large in comparison to a manometric hydrogenator, by virtue of the approx. 400 cc dead volume of the microbalance head. Hence the sample, weighing a gram or two, would getter a large amount of impurity from the gas introduced in each step along an absorption isotherm, tending to exacerbate impurity effects.

A single sample of $LaNi_{4.92}$ (NUCOR Research Chemicals alloy No. 1241) was absorption–desorption cycled in the microbalance more than 50 times at 100°C, starting from the virgin state. The tare of the microbalance was carefully maintained over several months to ensure that the sample weight was absolutely determined. Hydrogen of purity 99.999% was used for all the measurements.

3. Results

Fig. 1 shows the absorption and desorption isotherms recorded during cycles 1, 6 and 16, with α-phase portions highlighted by the use of a logarithmic pressure scale. These data confirm explicitly what is visible in many other data sets in which the activation cycle is included, namely, that there is an immediate reduction in RHC by an amount approaching 0.1 in H/M consequent on the activation. The essential point, however, is that the initial loss in RHC owes not to a reduction in the total H capacity, but to the growth of a 'trapping' region at low pressure. This effect is apparent in the data of Nomura et al. (Fig. 1 of [20]). However, the fact that the second absorption isotherm was plotted relative to zero H/M, rather than where the first desorption isotherm finished, masks the reality.

Fig. 1 also demonstrates that the region at the lowest values of pressure and H/M grows with cycling, further decreasing the RHC. Considering the entire hysteresis loop, however, the maximum H/M attained in the pure β phase is much less affected. The rate of loss of RHC was much greater at 100°C than at room temperature.

4. Discussion

While it is obvious that the sample is gettering the impure gas in the hydrogenator, whose total volume was
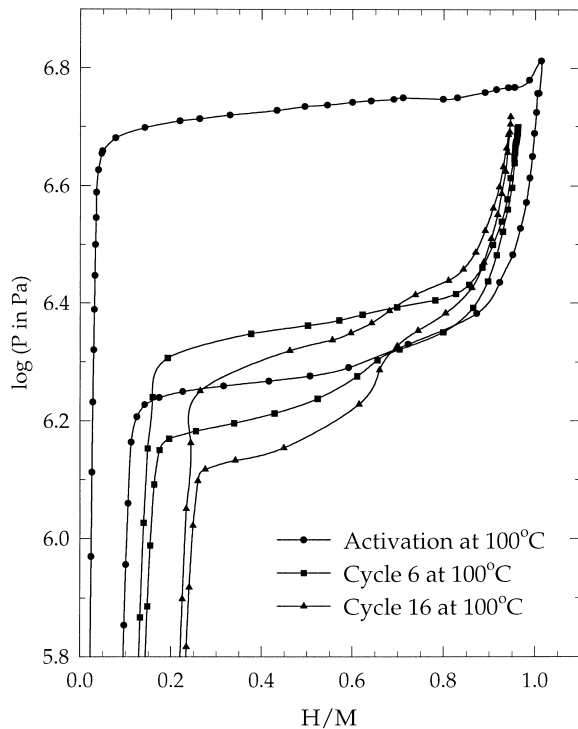
Fig. 1. Absorption–desorption isotherms for LaNi$_5$–H at 100°C. The cycle number is indicated for each pair of isotherms, starting from the activation of the virgin sample. Notice the trapping region generated by the single absorption, the growth of this region with cycling, and the rather small reduction of the total H capacity relative to the increase in the amount of trapped H.

around 500 cc for this study, the trapping region at low H/M is not an artefact owing to the accretion of impurities, because there is no commensurate increase in the total weight of the sample in the pure β phase. Nor is an accidental compensation between (say) oxygen absorption and loss of H capacity credible: if the trapping region were to apparently widen by 0.1 in H/M, as observed between cycles 2 and 16, owing to O accretion, a nonsensical loss of H capacity (1.6 in H/M) would be required to maintain the total sample weight constant in the pure β phase.

The data in Fig. 1 demonstrate, with a single sample in a continuous sequence of measurements under the same experimental conditions with a constant zero of H/M, that at least the initial 'degradation' of LaNi$_5$ owing to cycling in slightly impure gas is in fact a conversion of H in 'reversible' sites to sites which are best described as traps, in that the hydrogen is difficult to remove. H trapping in nominally desorbed LaNi$_5$ has been authenticated by a totally independent technique, deep-inelastic neutron scattering, in a sample previously hydrogenated only into the pure α phase [21] and following activation [22].

It is instructive to consider the possibility that stable La-hydrides are the repository of trapped hydrogen in the light of these data. Suppose that an effective disproportionation occurs according to

$$LaNi_5H_m \rightarrow xLaH_y + (1-x)LaNi_5H_m + 5xNi$$
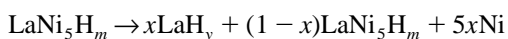
where $m/6$ is the maximum H/M attained at some reference pressure in the pure β phase. The stable La-hydride is manifest as a trapping region of width $xy/6$ in H/M, measured at some suitably low pressure in the pure α phase region, and the total H/M is reduced from $m/6$ by an amount $z/6$, because $y<6$ for the La-hydride. The stoichiometry constants must be then related by

$$z = x(m - y) \qquad (1)$$

For the intermetallic used in this study, the total H capacity near room temperature in the first (activation) cycle is $m \approx 6.8$ [23], in agreement with many other estimates, or $m \approx 6.0$ at 100°C.

Suppose that the width of the trapping region increases by 0.1 in H/M because the highest binary hydride, LaH$_3$, is formed. Eq. (1) shows that the total H content in the succeeding absorption–desorption cycle must consequently be reduced by nearly 0.1 in H/M. Our measurements show that this does not happen even between cycles 1 and 6, so activation must reduce the RHC by some other mechanism than the formation of LaH$_x$. Now suppose that the further extension of the trapping region to $H/M \approx 0.2$ is nevertheless due to the formation of LaH$_3$. Again, the total H capacity should be reduced by an amount much larger than what we observed. As before, the accretion of O can be discounted as a major factor, on the grounds that there is no reduction in RHC commensurate with any detectable mass gain owing to oxidation.

A similar difficulty was reported in the case of extensively cycled LmNi$_{4.85}$Sn$_{0.15}$ (Lm=La-rich Mischmetal) [24], in that the H/Lm ratio in the trapping region exceeded 3. The authors interpreted this as evidence of Lm–Ni–H decomposition products, although only weak LmH$_2$ and Ni diffraction peaks were detected.

The central issue is the amount of hydrogen sequestered per La atom, an amount close to 6 being necessary to explain the relative constancy of the total H content of our sample despite loss of RHC. The best candidate is La$_2$Ni$_7$H$_{\approx 9}$, with 4–5 H/La. In [11] it was reported that 1820 nominally isothermal cycles at room temperature in hydrogen of 99.999% purity caused a loss of 35% of the initial RHC (post-activation, presumably) and increased the saturation magnetisation to about 8 emu/g, or about one-seventh of the saturation magnetisation of FCC Ni at room temperature. Supposing that 35% of the LaNi$_5$H$_6$ decomposed to La$_2$Ni$_7$H$_{\approx 9}$, about one-seventh of the Ni atoms would be available to agglomerate as Ni precipitates. Presuming that the La$_2$Ni$_7$H$_{\approx 9}$ is (a) amorphous, and (b) non-magnetic, there is very good agreement between these results. The Ni precipitates must be extremely fine: recent high-quality neutron diffraction patterns [25], recorded after 75 cycles at 100°C, show no sign of broad peaks from precipitated Ni, despite its high coherent scattering length and a loss of RHC post-activation of about 30%.

The foregoing does not explain the immediate loss of RHC owing to the very first absorption of H by the virgin

intermetallic. It seems that a different mechanism to the decomposition is responsible, as it is unreasonable that very much the same trapping of H occurs under widely varying conditions, whereas the rate of loss of RHC during subsequent cycling varies drastically according to the conditions of temperature, pressure and (it appears) gas impurity. In our experience the initial trapping is insensitive to all these environmental parameters. Rather, this trapping should depend on an intrinsic property of the LaNi$_5$ microstructure, such as the existence of a high density of dislocations.

A correlation between dislocation density (indicated by peak breadth) and H detrapping (indicated by H$_2$ partial pressure) has been observed while annealing cycled but nominally desorbed LaNi$_5$ [26] during a temperature ramp from 100 to 850°C. Hydrogen was evolved quite rapidly at around 200°C, followed by an acceleration in the annealing rate. Most hydrogen evolution ceased near 500°C, where the annealing rate rapidly increased again, until complete annealing was achieved above 700°C. It therefore seems likely that the dislocations and H trapping are interdependent.

As demonstrated explicitly by neutron diffraction [23], activation induces strains characteristic of a high density of edge dislocations of the type $\frac{a}{3}\langle\bar{2}110\rangle\{0\bar{1}10\}$, which were estimated to exist at density 4.8×10^{12} cm^{-2} in desorbed LaNi$_5$ after a few isothermal cycles [27]. H binds readily to a vacancy [28], and these exist in dislocation cores, facilitating climb. Converting the above density to length of core per unit cell gives only 0.04 Å per unit cell, parallel to the *c*-axis, or about 1 dislocation per 100 unit cells. It has been estimated [29] that about one H atom may be trapped for every atomic plane intersected by a dislocation. In the present case (2 planes per cell perpendicular to the *c*-axis) this translates to about 1 H per 50 unit cells, far less than the average of about 1 H trapped per 2 unit cells owing to activation. Furthermore, dislocations are continually created at the partially coherent α–β interface as each particle transforms, so this kind of trap would probably be unstable, with trapped H atoms swept along by the moving dislocations [30].

On the other hand, it has been found that a substantial fraction of the H capacity of nanocrystalline materials resides in grain boundaries [31]. The size of the coherently diffracting domains in LaNi$_5$, which probably correspond to the volumes enclosed by grain boundaries, is quite small after activation, 300 Å being a typical estimate from the (roughly) isotropic particle-size broadening of the diffraction peaks [27]. It therefore seems more likely that, owing to the enormous total area of grain boundaries, and their rather stable dimensions, H would be trapped there, rather than in isolated dislocations. Although grain boundaries may essentially consist of dislocations, they probably contribute to the diffraction pattern in rather amorphous fashion, and would not be counted in the estimates of dislocation density made in that way [27]. Hence it is possible that H retained by the sample after the activation cycle really is trapped in dislocations, dominated by those in grain boundaries.

The role of the γ phase, LaN$_5$H$_{\approx3}$, remains uncertain. It was proposed [4] that the loss of RHC could be explained if the ultimate hydride phase became γ rather than β after hydrogenation at elevated temperatures. There is no evidence to date that this is so, although a continuous transformation between the β and γ phases has been observed [32], causing the apparent width in H/M of the β phase to increase, just as observed in extensively cycled LaNi$_{47}$Al$_{03}$–H [33] and extensively substituted battery materials [34]. The appearance of the γ phase in LaNi$_5$–H follows the same treatments that cause loss of RHC, but no connection between these two consequences is established.

The role played by impurities in loss of RHC remains unclear. Impurities hasten the loss of RHC at elevated temperatures [15]. Given that cycling in extreme purity gas at room temperature has a much smaller effect, it is presumably the impurities that caused the rapid loss of RHC we observed there, although the temperature rise in the sample was uncontrolled and may have been influential. Cohen et al. [5] found that isothermal cycling (variable pressure) at 20°C caused loss of RHC much faster than temperature-swing cycling, perhaps because of the continual introduction of fresh impurity-loaded gas and temperature rises in the sample interior during absorption. Certainly, we have demonstrated that impurities cannot directly cause the magnitude of RHC loss commonly observed by removing La from the intermetallic. The effect must be an indirect but more influential one, for instance by pinning dislocations or otherwise affecting the evolution of the microstructure during cycling.

In Part 2 of this series [2], we reported gravimetric measurements in the same equipment used for the present study, incorporating very large changes in H/M, which significantly reduced the RHC. Suspecting an effect on RHC of high interface velocity, we built a Cu sample cell in which the sample was a disk of thickness 1 mm, with a naked thermocouple 0.3 mm thick to monitor the interior temperature of the sample. The cell was immersed in a hydrostatic bath. The thermal properties of the cell were sufficiently good that the sample could be hydrided to $H/M=1$ in 20 s at 30°C with a 7°C temperature rise in its centre. We were unable to resolve any effect of the hydriding rate on RHC, and so conclude that the effects reported in [2] were caused by the temperature rise in the sample during very rapid absorption of 99.999%-pure hydrogen in the microbalance, where the heat-sinking of the sample via the surrounding gas is poor. Hence, the interior sample temperature could be elevated well above the nominal experimental temperature for a significant portion of the total duration of the experiment, accelerating the degradation mechanism. This also explains the otherwise inconsistent absence of a cumulative effect during desorption, i.e. the hysteresis loop should not have closed

if an irreversible modification of the microstructure occurred owing to high interface velocities: the loop closed because the sample temperature dropped rather than rose during desorption. The very significant degradation was observed in the present data after relatively few cycles at 100°C was no doubt hastened in the same way.

5. Conclusions

Factors leading to the loss of reversible H storage capacity in LaNi$_5$ were investigated by nominally isothermal absorption–desorption cycling at 100°C. Activation causes an immediate loss of nearly 0.1 in H/M capacity. This, and the subsequent loss of reversible capacity owing to cycling, is much more consistent with the conversion of 'reversible' H sites to trap sites than with the production of LaH$_x$, which cannot sequester sufficient H atoms per La atom to explain the relatively small reduction in total (reversible+trapped) H capacity. LaH$_x$ and other hydrides, of which La$_2$Ni$_7$–H$_{8-10}$ is the most likely candidate, do eventually form during extended cycling at temperatures sufficiently elevated for Ni atoms to diffuse readily.

Acknowledgements

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