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Frequency-domain hydriding and dehydriding kinetics of $LaNi_5H_x$

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Abstract

The kinetics of hydrogen absorption and desorption by $LaNi_5$ have been studied at several values of the hydrogen-to-metal ratio near the absorption and desorption plateaux. The dependence of the hydrogen-to-metal ratio on frequency rather than time was measured, using small sinusoidal perturbations of the hydrogen gas pressure. In contrast to the usual complex behaviour in the time domain (mixed order kinetics, rate dependent on pressure) the hydride responded linearly and the results are well described by the frequency dependences of two concurrent and one consecutive first-order reaction steps. Relaxation times (proportional to the reciprocal of reaction rate constant) ranging from a few seconds to nearly 300 s were determined for the three reaction steps, depending on the hydrogen content. In the linear regime of these experiments, the kinetics of absorption and desorption are generally considerably slower near the desorption plateau than near the absorption plateau. Some candidate physical reaction steps are discussed and it is conjectured that the three relaxation times are due to chemi(de)sorption (consecutive) and diffusion parallel and perpendicular to the *c* axis (concurrent) in a surface phase, probably α-$LaNi_5H_x$, through which all the atomic flux of H enters and leaves the metal hydride.

1. Introduction

While many studies of metal-hydride kinetics have been published, there is little agreement on reaction mechanisms and even on rate constants (*e.g.* refs. 1, 2 and references cited therein). This is due partly to the difficulty of relating experimental kinetic data to hydride microstructure and, apparently, partly to the intrinsic complexity of the reaction mechanism. Furthermore, the hydriding reaction is strongly exothermic ($\Delta H \approx -40$ kJ (mol $H_2)^{-1}$), so an experiment in which the reaction is driven to completion liberates considerable heat. Typically, the reactant metal is in finely divided form, so the thermal resistance to the surroundings is large. Isothermal conditions cannot be routinely maintained without adopting special precautions such as using a multiple-cell sample container of high thermal conductivity. The diffusion of H_2 through the powder to the metal surface also affects the kinetics of most samples. It is usually necessary to construct a phenomenological model of the macroscopic hydriding reaction, taking account of heat flow, metal geometry, *etc.* [3]. Non-integral reaction orders are often found, and little light has so far been shed on the microscopic reaction mechanism.

In 1987 Gray and Young [4] reported the first results of a technique for measuring the kinetic parameters of the metal–hydrogen and other solid–gas reactions in the frequency domain. This technique arose as a response to the problems caused by large excursions in the amount of hydride. It was reasoned that perturbing the hydriding reaction by only a small amount relative to a previously-established static condition would ameliorate the problems caused by heat and gas flow, but would introduce the new difficulty of reliably detecting the signals from small changes in hydride content. Repeating the perturbation would allow the signal to be averaged, and applying a sinusoidal modulation to, say, the hydrogen concentration would allow continuous signal averaging and bring all the advantages of analysis in the frequency domain. By applying a small sinusoidal modulation of the hydrogen gas pressure at selected points on the absorption plateau Gray and Young found that in the linear regime in which their experiments were conducted, the hydriding and dehydriding of $LaNi_5H_x$ could be described by two competing rate-limiting steps, each with first-order kinetics.

The purposes of this paper are to introduce and discuss the frequency-domain technique for measuring hydride kinetics more fully than was possible within the format of ref. 4, to present new experimental data, including a determination of the actual locus of the hydride during kinetic measurements and kinetic data taken on the desorption plateau of $LaNi_5H_x$, and to offer an extended discussion of all the results obtained so far.

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2. The frequency-domain technique

Consider a reversible reaction which at $t=0$ is established in a static initial state, ideally but not necessarily an equilibrium state. An instantaneous change is then applied to the parameter α which is suitably related to the degree of completion of the reaction, *e.g.* a product concentration:

$$\alpha'(t)=\Delta\alpha\cdot U(t)\cdot F(t) \tag{1}$$

where $\alpha'(t)=\alpha(t)-\alpha_0$. Equation (1) represents the shift of the reaction from the initial state α_0 to a new (quasi)equilibrium at $\alpha_0+\Delta\alpha$. $U(t)$ is the unit step function and $F(t)$ contains the time dependence characteristic of the particular reaction mechanism. Suppose that the reversible first-order reaction

$$A \underset{k_{\text{rev}}}{\overset{k_{\text{for}}}{\rightleftharpoons}} X$$

is displaced from its initial state by suddenly increasing the concentration of A by an amount $\Delta[A]$. The rate law for the product is

$$[\dot{X}]'+(k_{\text{for}}+k_{\text{rev}})[X]'=k_{\text{for}}\Delta[A]U(t) \tag{2}$$

with solution

$$[X]'=[X](t)-[X]_0=\frac{k_{\text{for}}}{k_{\text{for}}+k_{\text{rev}}}\Delta[A][1-\exp(-t/\tau)]$$

where

$$\tau=\frac{1}{k_{\text{for}}+k_{\text{rev}}}$$

$$[X]_0=\frac{k_{\text{for}}}{k_{\text{for}}+k_{\text{rev}}}[A]_0$$

The change in $[X]$ is proportional to $\Delta[A]$, so this reaction responds linearly to a perturbation and a transfer function can be defined in the time domain:

$$G(t)=\frac{[X]'(t)}{\Delta[A]U(t)}=\frac{k_{\text{for}}}{k_{\text{for}}+k_{\text{rev}}}[1-\exp(-t/\tau)]$$

Laplace transforming eqn. (2) gives a transfer function in the frequency domain

$$g(s)=\frac{[X]'(s)}{\Delta[A]u(S)}=\frac{k_{\text{for}}}{k_{\text{for}}+k_{\text{rev}}}\cdot\frac{1}{1+s\tau} \tag{3}$$

where $u(s)=\mathscr{L}[U(t)]=1/s$ and $s=\sigma+i\omega$. Similar results are obtained when the method of detailed balance is applied microscopically to an ensemble of atoms able to hop between two states separated by an energy barrier, with transition probabilities replacing the rate constants used here.

Reactions which are macroscopically not first-order will respond non-linearly to a perturbation, but can be "linearised" by making the perturbation sufficiently small. Expanding a general rate law for a reaction about its steady-state position,

$$\dot{\alpha}'(t)=-k_1\alpha'-k_2(\alpha')^2-k_3(\alpha')^3-\dots$$

and restricting the reaction to the vicinity of the established steady state, $\alpha'=0$, leads immediately to a first-order rate law and a transfer function of the form of eqn. (3).

This result has the disadvantage of obscuring the true order of the reaction, which has no "signature" in the frequency domain. In recompense, the frequency-domain technique has two important advantages in distinguishing the steps in a complicated reaction mechanism; first, no order need be assumed for a particular step, and second, the convoluted response of consecutive steps is simply a product of their transfer functions in the frequency domain.

3. Linearity, reversibility, equilibrium and hysteresis

To sensibly measure frequency responses the studied system must be linear, *i.e.* a suitably small sinusoidal perturbation of the chosen experimental parameter must evoke a sinusoidal response. Since most metal hydrides exhibit pressure hysteresis, which is usually taken to be synonymous with irreversibility and non-linearity, it is appropriate to consider these concepts before discussing the experimental results.

At some arbitrarily low frequency the pressure perturbation may be regarded as quasistatic and the linear response will also be reversible, implying that the system evolves through a continuum of equilibrium states. Thus reversibility is a necessary but insufficient condition for linearity. A metastable system can also be reversible for excursions within a local energy minimum and, if the energy barriers between adjacent energy minima are high, will exhibit equilibrium properties on finite time scales. Thus the distinction between stable and metastable equilibrium is fundamentally one of time scale.

Reversibility and equilibrium are macroscopic concepts; microscopic processes are intrinsically reversible. Transitions between the microscopic states of a system occur reversibly because the fundamental equations describing the system (Schrödinger's and Maxwell's equations) are invariant under time reversal; the motion of one H atom from one site to another must be reversible in that the reverse motion can occur by the same path. Thus the distinction between reversible and irreversible behaviour is ultimately one of the distance scale on which we observe the system.

Two fundamentally different models of pressure hysteresis have been in favour at various times in the last

50 years (see ref. 5 for a review of hysteresis). In the first, H–H correlations in a hydrided metal could in principle lead to the α–β bistability. This model is analogous to the macroscopic spin-up/spin-down bistability and thus hysteresis caused by spin–spin interactions in ferromagnets. The absorption and desorption plateaux would then be regarded as mixed states by which the "forbidden" region between the pure α (dilute hydride) and pure β (concentrated hydride) equilibrium states could be traversed by some mechanism such as the nucleation and growth of β in α. In the likely event that the states between pure α and pure β are local energy minima separated by energy barriers, the system would respond linearly to a sufficiently small perturbation and would not spontaneously move from α towards β or *vice versa*, appearing experimentally to be in equilibrium until a larger perturbation forced it into an adjacent minimum.

In the second picture, the concept of energy loss and therefore hysteresis, irreversibility and disequilibrium, through defect production associated with α–β hydride interconversion is invoked. The α–β interconversion is viewed as intrinsically irreversible, on the implicit assumption that the hopping of individual H atoms causes defects. Defect creation requires energy, so, once again, the system would not spontaneously evolve from α to β or *vice versa*, giving the experimental appearance of quasistasis, but presumably maintaining its hysteretic response on an arbitrarily fine scale. Recent work [6] has shown that the main effect of defects in $LaNi_5H_x$ is in fact to *reduce* hysteresis.

In either picture the pure α and β hydrides absorb and desorb reversibly, so the vertical portions of the hysteresis loop would be reversible but possibly nonlinear.

Starting at a point on the absorption plateau and applying a small sinusoidal pressure perturbation, it was found [4] that the response of the hydrogen-to-metal ratio, $\delta(H/M)/\delta P$, is linear and of order 10^{-3} kPa^{-1}. In contrast, the reciprocal of the slope of the absorption plateau is of order 10^{-2} kPa^{-1}. There are two conceptually different mechanisms by which this effect could be observed on the absorption plateau when a steady rise in pressure is followed by a small pressure drop. In the first, the hydride jerks between local metastable states, analogous to the way in which the domain walls in a ferromagnet stretch around and snap past pinning centres. On a sufficiently small scale the plateau would be seen to consist of reversible vertical sections in which the hydride would be constrained to a local energy minimum, and irreversible horizontal sections in which conversion of α to β hydride occurred. In the second possibility, the scale of pressure change is large enough that the plateau appears smooth. A quasistatic pressure decrease would cause the α and β hydrides to desorb reversibly until the β hydride became unstable against conversion to α, approaching the desorption plateau.

An experiment aimed at distinguishing these possibilities is reported below.

4. Experimental details

The apparatus used to apply the frequency-domain technique to a metal hydride is described in ref. 7. Briefly, a Sartorius 4406 microbalance was modified to make available the analogue weight signal, which was measured by a fast digital voltmeter linked to a computer. The hydrided metal was allowed to settle at a selected value of H/M for several days. Then the H_2 gas pressure was sinusoidally modulated by a small amount, and the consequent change in the hydrogen-to-metal ratio of the hydride was monitored by weighing the metal hydride. Figure 1 shows a typical result for $LaNi_5$ at 30 °C. The equilibrium H_2 pressure was approximately 180 kPa, corresponding to $H/M = 0.74$ on the desorption plateau. The pressure modulation depth was 0.88 kPa RMS, giving a weight response of 5.8 μg RMS on a sample able to absorb 58 mg of H at $H/M = 1$, *i.e.* a RMS change in H/M of only 100 ppm. The H concentration responds to the modulation very linearly in this regime (*c.f.* large hysteresis loops for major concentration excursions); the reaction is reversible, but the response is phase lagged by 63° at the depicted frequency of 8.33 mHz. By accumulating and measuring many sinusoidal cycles, and controlling the laboratory and sample temperatures to ± 0.1 °C and ± 0.005 °C respectively, weight sinusoids smaller than 50 ng RMS were measured in this way.

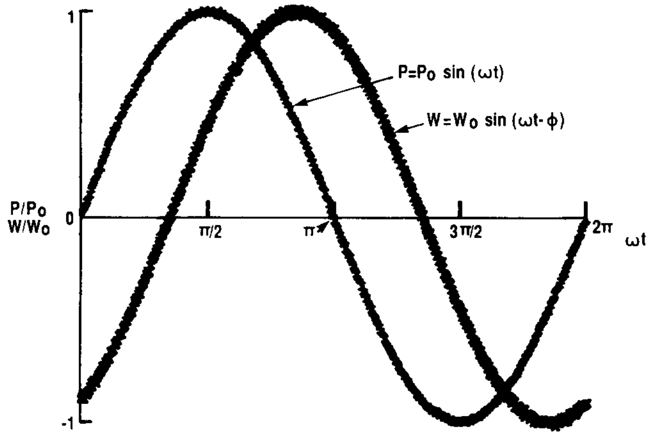

Fig. 1. Linear, phase-lagged sinusoidal response of $LaNi_5H_x$ hydrogen content to a sinusoidal modulation of the hydrogen pressure. RMS pressure perturbation 0.88 kPa, frequency = 8.33 mHz, RMS weight change = 5.8 μg, corresponding to a 100 ppm change in H/M.

Kinetic measurements were made on hydrogen-cycled samples of $LaNi_5$ (Research Chemicals alloy number 1241), at frequencies between 10 μHz and 40 mHz, for the following values of H/M at 30 °C: 0.18, 0.54, 0.84 on the absorption isotherm, and 0.74, 0.40 on the desorption isotherm. A further measurement was made at H/M = 0.17 on the desorption isotherm at a temperature of 70 °C, to test the speed of the measuring system.

An experiment using pressure ramps and a triangular pressure modulation waveform was also performed to determine the locus of (P, H/M) during the kinetic measurements.

5. Results

5.1. *Locus of (P, H/M)*

After settling on the absorption plateau at a base pressure around 300 kPa, a pressure ramp approximately 20 kPa high was applied over a period of several hours, taking extreme care that no accidental pressure decrease occurred until an intentional ramp down was started. As shown in Fig. 2, the transition from α–β hydride conversion on the plateau to linear desorption on the vertical portion of the isotherm occurs gradually in a pressure range of several kilopascals. Then the pressure was increased again, retracing the path followed during desorption until about 4 kPa below the absorption plateau, where irreversibility sets in. A subsequent ramp down in pressure again causes a linear response. This result confirms the sufficiency of linearity for reversibility.

No 'graininess" of the absorption plateau due to conversion of macroscopic volumes of α to β hydride was found within the pressure resolution of about 10 Pa; on the scale of this experiment the conversion process is continuous.

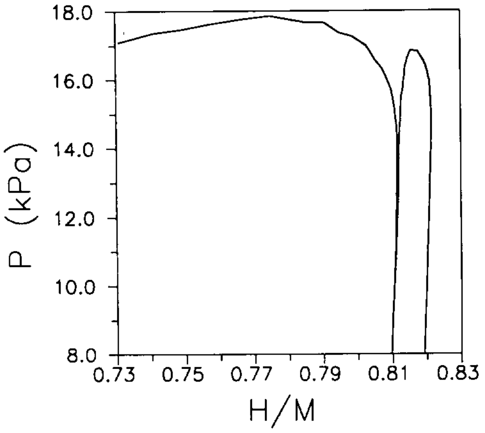

Fig. 2. Experimental locus of (H/M, P) during pressure ramp up followed by ramp down. H/M = 0.8 on the absorption plateau. Note transition region between $\alpha \rightarrow \beta$ hydride conversion on plateau and $\alpha + \beta$ desorption.

The crossover from irreversibility near the plateau to linearity a few kilopascals away was investigated by applying periodic triangular pressure modulation waveforms with amplitude less than 1.0 kPa, immediately following a 20 kPa ramp up from a base pressure on the absorption plateau. Figure 3 shows the result for an amplitude of 0.1 kPa peak-to-peak. The sample is evolving from irreversibility towards linearity, but would have taken many more cycles to settle than the 10 recorded. When this experiment was repeated with a triangular pressure waveform of amplitude 1.0 kPa, the locus of (P, H/M) was single-valued and co-linear with the vertical portion of the desorption isotherm shown in Fig. 2 after only 10 cycles.

It is clear from the above that, due to the execution of many sinusoidal pressure cycles, and the inevitable leakage of some hydrogen during long experiments, the frequency response data taken "on" the absorption plateau reflect the state of the hydride on the linear vertical portion of the desorption isotherm shown in Fig. 2. No complementary experiment was performed on the desorption plateau, but it is reasonable to assume that the kinetic data taken there reflect the state of the sample on the linear vertical portion of the absorption isotherm starting at the selected value of H/M.

5.2. *Kinetics*

The measurements made on (or, more correctly, near) the absorption plateau were previously reported in ref. 4, but are analysed in greater detail here. Figure 4 shows all the data obtained so far on both plateaux. The pressure signal was fitted to a sinusoid by the non-linear least-squares method, to determine its amplitude and frequency, and to establish a reference phase. The weight signal was force fitted by the same method to a sinusoid of the frequency so determined, giving am-

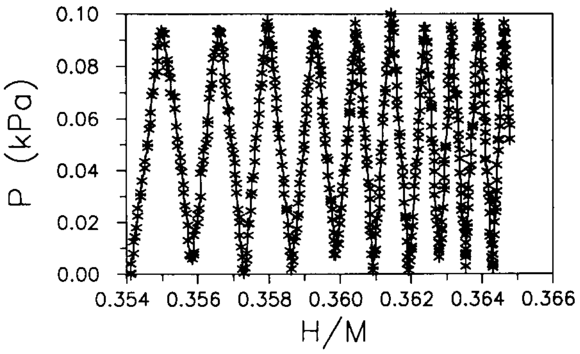

Fig. 3. Evolution towards linear response during 0.1 kPa pressure cycling following pressure ramp up. H/M = 0.36 on absorption plateau.

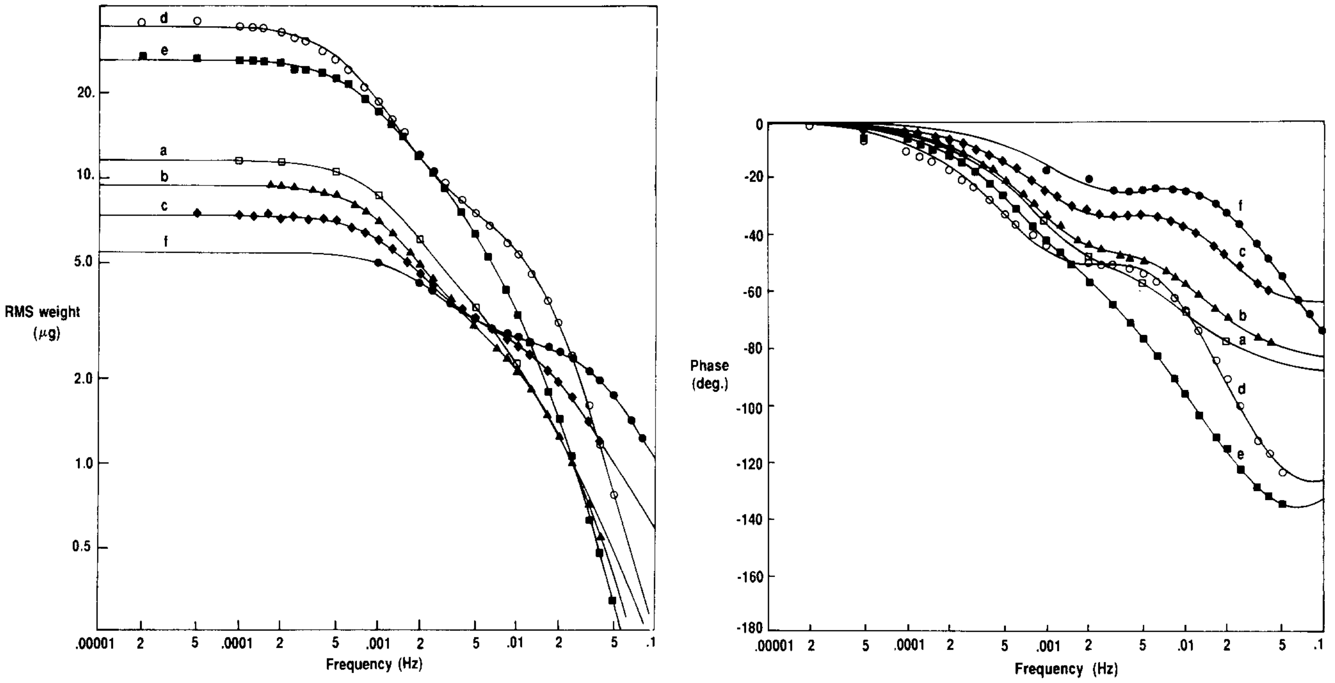

Fig. 4. Amplitude and phase dependence on sinusoidal modulation frequency for the following values of H/M: (a) 0.18; (b) 0.54; (c) 0.84; (d) 0.74; (e) 0.40; (f) 0.17; (a)–(c) on absorption isotherm; (d)–(f) on desorption isotherm; all data at $T=30$ °C except (f) which was at 70 °C.

plitude and phase relative to the pressure waveform. An allowance was also made for any drift in the weight signal during the measurement due to, for instance, the sample scavenging trace oxygen from the surroundings. The drift was significant in signals of order a few micrograms or less for measurements lasting many hours.

As recounted in ref. 4, the simplest function able to synthesize the dip in phase angle evident in most of the data around 3 mHz, with some claim to represent a real physical process, is the sum of two poles of the form of eqn. (3). This corresponds to two competing first-order kinetic processes which provide alternative paths for the same reaction step. The conclusion of Section 2, that linearity implies first-order kinetics, is thus confirmed.

A two-pole transfer function does not adequately describe the data taken on the desorption plateau. The data are well fitted by a transfer function of the form

$$\frac{\delta(\text{weight})}{\delta(\text{pressure})} \alpha g(\omega) = \left[\frac{A}{1+i\omega\tau_A} + \frac{1}{1+i\omega\tau_B}\right] \frac{C}{1+i\omega\tau_C} g_{\text{sys}}(\omega) \qquad (4)$$

τ_A and τ_B are the relaxation times of two competing, first-order rate-limiting reaction steps. τ_C is a faster, sequential first-order step. g_{sys} accounts for small phase and amplitude effects due to the microbalance, pipework and pressure sensor, manifested as an upturn in the phase angle at the highest frequencies. To test the appropriateness of eqn. (4), it was resolved into amplitude and phase functions, which were fitted separately to the measured amplitude and phase responses. Table 1 shows the values of the fitted parameters, from which the solid lines in Fig. 4 were drawn. Values obtained by fitting amplitude and phase data are listed together for comparison. With few exceptions they agree well, the differences giving an indication of their reliability. The values obtained from phase data are probably more reliable since one less parameter is fitted to the same

TABLE 1. Parameters obtained by fitting eqn. (4) to experimental data. "Ampl. Phase" indicate fit to amplitude or phase of $g(\omega)$. "abs.", "des." indicate data taken on the absorption or desorption plateau. All measurements at $T=30$ °C, except H/M = 0.17 des., which was at $T=70$ °C

H/M		A	τ_A (s)	τ_B (s)	τ_C (s)	C (μg)
0.18	Ampl.	4.19	149	22.0	1.61	2.20
abs.	Phase	4.01	165	24.0	1.05	
0.54	Ampl.	3.65	150	14.0	3.89	2.01
abs.	Phase	3.63	163	16.3	0.92	
0.84	Ampl.	1.98	125	8.94	0.01	2.45
abs.	Phase	2.04	126	8.25	0.44	
0.74	Ampl.	4.83	262	11.5	7.22	5.80
des.	Phase	4.87	267	12.4	5.91	
0.40	Ampl.	3.40	204	41.8	7.22	5.85
des.	Phase	3.22	210	45.6	6.88	
0.17	Ampl.	1.17	80.9	3.71	1.18	2.49
des.	Phase	1.22	86.5	3.64	1.28	

number of data points, and the phase angle is a more rapidly varying function of frequency than is the amplitude.

Pole C was not necessary to obtain a good fit to the data taken on the absorption plateau: the degree of fit was just a good without it, and the values obtained for τ_C correspond to angular frequencies beyond the range of the measurements. Thus the conclusion of ref. 4, that on the absorption plateau the rate-limiting reaction step consists of two competing first-order processes, needs no qualification here. The data taken at H/M = 0.74 and 0.40 on the desorption plateau, however, could not be fitted without pole C. Presumably the corresponding physical mechanism also operates near the absorption plateau with a pole frequency beyond the range of these measurements. The A- and B-pathways are also faster on the absorption plateau.

From Table 1 we see that the B pathway, the faster alternative, gets faster at high values of H/M on both plateaux. The relative atomic fluxes through the A and B pathways, given by the parameter A, behave differently; the B pathway is more popular at high H/M on the absorption plateau and *vice versa* on the desorption plateau.

6. Discussion

It is initially surprising that the data in Fig. 4 are so well fitted by eqn. (4), taking no account of distributed activation energies. Typically the absorption plateau is considerably sloped on a free energy (ln P) scale, the desorption plateau less so. This implies a distribution of site free energies, the highest being occupied last. Such a model has been proposed in ref. 8. To see why this does not cause a smearing of the frequency response, consider an ensemble of interstitial H sites with free energy G. For another ensemble with free energy $G' = G + \delta G$, the relative plateau pressure and relaxation time are

$$\frac{P'}{P} = \exp\left(\frac{\delta G}{kT}\right)$$

$$\frac{\tau'}{\tau} = \exp\left(\frac{-\delta G}{kT}\right)$$

where a constant activated energy, G^*, is assumed. The spread of relaxation times should therefore be similar to the spread of absorption pressures. In the sample studied here $P'/P \approx 1.2$ over the full absorption plateau, but the pressure range during sinusoidal cycling corresponds to $P'/P \leqslant 1.01$. A very small range of site energies is explored, causing a virtually undetectable smearing of the frequency response.

After ramping the pressure to the point at which kinetic measurements are to begin, the first few sinusoidal pressure cycles evidently cause the hydride to gradually settle into a state in which the H/M ratio responds linearly to small pressure changes, implying macroscopic reversibility and therefore equilibrium between the α and β hydrides. Conversely, macroscopic disequilibrium between α and β must occur on the plateaux. The development of linear response probably reflects a cyclic motion of the α–β hydride boundary, which, by a combination of defect creation and pinning, gradually settles into an energy minimum. The response to a small pressure change could then be of two types: displacement of the α–β boundary involving only elastic strain energy, or reversible absorption and desorption of the α and β hydrides without interconversion. Given that no graininess of the absorption plateau was detected, it is implausible that the α–β boundary responds elastically on the 1 kPa pressure scale of the kinetic measurements. We conclude that the mechanism observed is simultaneous, reversible absorption and desorption of the α and β hydrides, in agreement with previous work [9].

Only processes by which the sample gains or loses hydrogen were detected in these experiments. Since the H concentration in the β-hydride is much greater than in α, interconversion between α and β will cause absorption or desorption through the metal surface when the solubility range of either the α- or β-hydride is exceeded. The diffusion of H atoms through each hydride will then affect the kinetics of hydrogen gain and loss by the sample, but, since the β hydride grows from the α hydride, these diffusion processes must be sequential rather than parallel.

By the arguments above, the kinetic measurements reported here involve no α–β interconversion; the α and β hydrides absorb and desorb simultaneously so as to maintain a mutual equilibrium. However diffusion through the α and β hydrides cannot be associated respectively with the A and B poles in the frequency response. This conclusion is arrived at from a comparison of the contributions to the weight change due to the A and B pathways. If, say, the A pathway corresponded to diffusion of H through α hydride, its contribution to the change in sample weight relative to the B pathway would be determined by the fraction of α hydride, and so would be much greater near the start of the absorption plateau than at its end, and *vice versa* on the desorption plateau. Table 1 shows that the ratio of atom fluxes through the A and B pathways changes by a factor of about two between H/M = 0.18 and 0.84 on the absorption plateau whereas, according to the inverse lever rule, the ratio of the atomic fractions of α and β hydrides changes by a factor of 50 to 100, depending on the limiting compositions taken for the pure α and β phases.

If the A and B pathways were available in both the α and β hydrides, it is unreasonable that the relaxation times for pathway A in α and pathway A in β should be the same given their different microstructures, and two poles would occur in the frequency response for each hydride, *i.e.* four in all. This possibility was explored by including in eqn. (4) a frequency-independent term due to parallel poles at frequencies above the range of the data. The best fits to the data were with this term set to zero on average, indicating that there are no unobserved fast pathways parallel to A and B.

Alternatively, if the A and B pathways belonged only to the α (β) hydride, the amplitude of the weight signal at the lowest frequency ($C(A+1)$ in Table 1) would scale with the atomic fraction of α (β), whereas there is no such trend.

A conjecture consistent with the above is that both the A and B pathways could belong to a surface phase, possibly α hydride, of which a small fraction might always persist at the metal surface, supposing the β hydride to be unstable there. There is no evidence from neutron diffraction studies of $LaNi_5D_x$ to support this speculation. Kinetic measurements will be made in the pure α and β hydrides to find whether the frequency responses show evidence of two simultaneous processes when the author's ultramicrobalance, currently in development, becomes available.

Since $LaNi_5H_x$ is hexagonal, the A and B pathways could reflect different diffusion rates parallel and perpendicular to the c axis. The rather complicated variation of the relaxation times and relative atomic fluxes at different values of H/M during absorption and desorption would most likely reflect the local strain and defect concentration due to the 24% mismatch in the unit cell volumes of the α and β hydrides. It is clear from recent studies [6] of the process by which $LaNi_5$ is activated to absorb hydrogen that defects play a major role in H diffusion.

Pole C, being consecutive to poles A and B near the desorption plateau, and presumably near the absorption plateau too, probably belongs to a physical process at the metal surface. During desorption, equilibrium between chemisorbed H atoms in the metal surface and the H_2 gas is established at a lower free energy, indicated by the lower gas pressure, relative to absorption. If the same activated surface states must be transited to escape from chemisorbed states to physisorbed ones, or directly to free molecules, the activation free energy will be higher than during absorption. The relaxation times for absorption and desorption via a single activated state are related to the activation energy for absorption, G_A, by

$$\tau_{abs}=\tau_0 \exp\left(\frac{G_A}{kT}\right)$$

$$\tau_{des}=\tau_0 \exp\left(\frac{G_A+\Delta G}{kT}\right)$$

$$\Delta G=kT \ln\left(\frac{P_{abs}}{P_{des}}\right)$$

The ratio of P_{abs} to P_{des} under the conditions of the experiments reported here is about two, implying that the relaxation time for desorption should be greater than that for absorption by the same factor. From Table 1, pole C is around six times faster during absorption, but the above calculation takes no account of the different conditions during absorption and desorption, particularly the H vibration frequency, which is basically $1/\tau_0$ in the above equations, and any dependence of the activated energy on local strain etc. τ_c is rather constant on each plateau, which supports the idea that it belongs to a surface process relatively unaffected by changes occurring deeper in the crystals. The values of τ_A and τ_B are larger on the desorption plateau relative to absorption. This is to be expected since the α and β hydrides were also in equilibrium with the gas during this experiment, leading to a higher activation energy for diffusion during desorption by the mechanism just discussed, independent of which hydride they belong to.

The importance of entropy in determining the reaction rate can be seen by examining the data in Table 1 taken at 70 °C on the desorption plateau. This measurement was performed to test the speed of the apparatus and the adequacy of the model of the instrumental effects ($g_{sys}(\omega)$) in eqn. (4), in the expectation that poles A, B and C would be pushed to frequencies beyond the range of the apparatus. However Table 1 shows that τ_A has decreased by a factor of only three. τ_B has decreased by a larger factor, which cannot be reliably estimated since τ_B changes rapidly with H/M on the desorption plateau. As expected, the fast B pathway handles much more of the atomic flux at the higher temperature. For two temperatures, $T_2>T_1$, the ratio of relaxation times due to activation through the same activated state is

$$\frac{\tau_2}{\tau_1}=\left[\frac{\Omega^*}{\Omega_I}\cdot\frac{\tau_1}{\tau_0}\right]^{T_1/T_2-1}=\left[\exp\left(\frac{E_A}{kT}\right)\right]^{T_1/T_2-1} \qquad (5)$$

where Ω_I and Ω^* are the number of complexions in the initial and activated states respectively, and E_A is the activation potential energy. Taking $T_1=303$ K, $T_2=343$ K, $\tau_1=240$ s, $\tau_2=80$ s, $\tau_0=10^{-14}$ s, eqn. (5) gives $E_A\approx 0.25$ eV for pathway A, compared to $G_A\approx 1$ eV, the difference expressing the contribution of entropy through the availability of activated states. A similar value for E_A was reported in ref. 1, derived from an Arrhenius plot for excursions along the plateaux. There is no in-principle reason why the values should be similar, although the argument below shows it to be plausible.

Recent *in situ* X-ray diffraction measurements [10] have shown that, on the absorption plateau, $LaNi_5H_x$ absorbs further H into an intermediate superconcentrated α^* hydride which later expands to form the β hydride, apparently with no change in H content. A superdilute β^* hydride was observed during desorption, which later contracted to form the α hydride. In consequence, kinetic experiments by other than microstructural techniques actually observe the kinetics of α^*/β^* formation. Therefore, despite the different experimental conditions (reversible excursions near the plateaux compared to irreversible excursions along the plateaux), it is possible that the rate-limiting reaction steps observed in the present work are those that operate in general.

7. Conclusions

Perhaps the greatest difficulty encountered in interpreting a kinetics experiment is to identify the microscopic causes of the macroscopic effects observed. In general, evidence from a microscopic technique is needed to fill out the picture, and that is true here also. However, the frequency-domain technique does make the process a little simpler because the various steps of the reaction mechanism are "laid out" in the frequency domain, rather than convoluted in time.

The frequency-dependent absorption of H by $LaNi_5$ has been investigated. Measurements were made in the area enclosed by the pressure-composition hysteresis loop, adjacent to the absorption and desorption plateaux. At the modulation pressures used, the pressure-to-H/M transfer function is linear and therefore reversible, indicating that the α and β hydrides absorb and desorb H so as to maintain equilibrium with each other and the H_2 gas. In consequence of the linear response, the steps of the reaction have first-order kinetics. The transfer function is dominated by two parallel poles, with relaxation times τ_A and τ_B, and one faster sequential pole with relaxation time τ_c, τ_A and τ_B characterize alternative pathways, A and B, by which the flux of H atoms enters and leaves the sample. The reaction step characterized by τ_c affects all the H flux, and is therefore thought to be associated with a surface process such as chemi(de)sorption. The relative atomic fluxes through the A and B pathways change only slowly as the phase proportions of α and β change. It is therefore unlikely that pathway A is associated with the α hydride and B with β, or *vice versa*, as the flux through either would be zero at one end of each plateau. Pathways A and B cannot be feasibly ascribed to diffusion in both α and β because the different lattice dimensions imply different activation energies for diffusion, and four relaxation times rather than two. The most reasonable conclusion, which requires experimental verification, is that all three relaxation times belong to processes occurring in a surface phase, probably α-$LaNi_5H_x$, through which the entire flux of H atoms flows, and that β-$LaNi_5H_x$ is unable to form stably at the surface.

The kinetics are dominated by entropy, *i.e.* the availability of activated states for H diffusion, which could explain the variation of the relaxation times of the rate-limiting processes with the relative proportions of α and β hydride.

A more detailed study is underway to obtain data at more temperatures and to determine if the parallel diffusion pathways occur in the pure α and pure β hydrides.

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References

1 J. T. Koh, A. J. Goudy, P. Huang and G. Zhou, *J. Less-Common Met., 153* (1989) 89.
2 Y. Josephy and M. Ron, *J. Less-Common Met., 147* (1989) 227.
3 P. Dantzer and E. Orgaz, J. Less-Common Met., 147 (1989) 27.
4 E. M. Gray and T. L. Young, *J. Phys. C, 20* (1987) L187.
5 S. Quian and D. O. Northwood, *Int. J. Hydrogen Energy, 13* (1988) 25.
6 E. H. Kisi, C. E. Buckley and E. M. Gray, *J. Alloys Comp., 185* (1992) 369.
7 T. L. Young and E. M. Gray, *Int. J. Hydrogen Energy, 13* (1988) 351.
8 T. Mütschele and R. Kirchheim, *Scripta Metall., 21* (1987) 135.
9 B. S. Bowerman, C. A. Wulff, G. E. Biehl and T. B. Flanagan, *J. Less-Common Met., 73* (1980) 1.
10 E. H. Kisi, E. M. Gray and A. J. Chessor, *Phys. Rev. Lett.*, submitted for publication.