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Functionality of the nanoscopic crystalline Al/amorphous $Al_{50}Ti_{50}$ surface embedded composite observed in the $NaAlH_4 + xTiCl_3$ system after milling

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ABSTRACT

The $NaAlH_4 + xTiCl_3$ ($x < 0.1$) system has been studied by a combination of X-ray synchrotron and neutron diffraction, and isotopic H_2/D_2 scrambling after the completion of the milling process, and the first thermal release of hydrogen (H). An in situ X-ray synchrotron diffraction study of the isochronal release of hydrogen from planetary milled (PM) $NaAlH_4 + 0.1TiCl_3$ shows that crystalline (c-) $Al_{1-x}Ti_x$ phases do not form until almost all H is released from the sample, demonstrating that the surface embedded nanoscopic crystalline Al/amorphous (a-) $Al_{50}Ti_{50}$ composite facilitates the release of H during the very first thermal desorption. Planetary milled (PM) $NaAlH_4 + xTiCl_3$ is observed to disproportionate at room temperature, with no $NaAlH_4$ remaining after ca. 200 days. A complete lack of ambient hydrogen release from PM $NaAlH_4 + 0.1Al$ (80 nm) measured over 200 days suggests that the nanoscopic a-$Al_{50}Ti_{50}$ phase is entirely responsible for the hydrogen release during thermal desorption of milled $NaAlH_4 + xTiCl_3$. Isotopic H/D exchange has been observed by combined neutron and X-ray synchrotron diffraction on a PM $NaAlD_4 + 0.04TiCl_3$ sample, after exposing the milled sample to 20 bar H_2 at 50 °C for ca. 6 days. Under these pressure/temperature (P/T) conditions, disproportionation of $NaAlD_4$ is avoided, and ca. 32% of D atoms are exchanged with H atoms. Asymmetrically broadened reflections in the synchrotron data show peak splitting into two unit cell types, one expanded with H, the other remaining close to pure D based unit cell dimensions. The 2-phase model when fitted to the neutron data demonstrates that ca. 56% of D atoms in ca. 58% of all unit cells are exchanged with H, yielding a $NaAl(H_{0.56}D_{0.44})_4$ composition for the expanded unit cells. HD scrambling (1 bar mixture of H_2 and D_2 at 23 °C) performed on desorbed H empty PM $NaAlH_4 + 0.1TiCl_3$ shows classic $H_2 + D_2 \leftrightarrow 2HD$ equilibrium mixing, demonstrating that nanoscopic Ti containing $Al_{1-x}Ti_x$ surface embedded phases perform a H_2 dissociation/recombination function that unadulterated $NaAlH_4$ cannot.

1. Introduction

The transition metal enhanced $NaAlH_4$ system currently remains as the prototypical example of obtaining hydrogen reversibility and rapid absorption/desorption hydrogenation kinetics in the complex hydride family. The early transition metals such as Sc [1], Ti [2] and rare earths such as Ce [1,2] have proven to be the most efficient additives for the $NaAlH_4$ system. Understanding the location and functionality of the transition metal (TM)/rare earth (RE) containing phases is paramount to basic understanding and potentially further engineering other classes of complex hydrides such as the borohydride family [3,4]. Large quantities of hydrogen can be contained in phases such as $LiBH_4$ and $Mg(BH_4)_2$, containing 18.5 and 14.9 wt.% H, respectively, but these compounds are greatly hindered as practical hydrogen storage materials by high thermal and kinetic stabilities, and no suitable destabilizing catalysts have been found to date. A common theme among the addition of metal enhancing species to $NaAlH_4$ is the formation of nanoscopic $Al_{1-x}TM_x$ [5–7] or $Al_{1-x}RE_x$ [2] phases that are embedded on the surface of $NaAlH_4$ powder grains [8].

In [8], the location of Ti was determined after the completion of the $NaAlH_4 + xTiCl_3$ milling process at short times of ca.

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1 h. It was observed by combinatorial X-ray synchrotron diffraction and transmission electron microscopy (TEM) measurements that Ti was located in a nanoscopic composite of Al nanocrystals immersed in an amorphous $Al_{50}Ti_{50}$ matrix. This nano composite is embedded on the surface of moderately defected (uncorrelated) single crystals of $NaAlH_4$. From the study in [5], it is known that nanoscopic crystalline (c-) $Al_{1-x}Ti_x$ phases can be formed from the nano Al/a-$Al_{50}Ti_{50}$ composite by extended planetary milling (>10 h) producing c-$Al_{80}Ti_{20}$, isothermal vacuum annealing (at 150 °C) producing c-$Al_{88}Ti_{12}$, isochronal annealing (2 °C/min) producing c-$Al_{86}Ti_{14}$, or from hydrogen (H) cycling (150 bar at 150 °C) yielding c-$Al_{85}Ti_{15}$. This suggests that at some stage during the very first thermal desorption of hydrogen from milled $NaAlH_4 + xTiCl_3$, the amorphous $Al_{50}Ti_{50}$ in the nanoscopic Al/a-$Al_{50}Ti_{50}$ composite must be depleted/transformed to a crystalline $Al_{1-x}Ti_x$ structure. The matching of size ranges from dark field measurements for the nanoscopic Al crystals (2–20 nm) in the Al/a-$Al_{50}Ti_{50}$ composite in PM $NaAlH_4 + 0.1TiCl_3$ compared to the size range of c-$Al_{85}Ti_{15}$ nanocrystals (4–25 nm) in H cycled $NaAlH_4 + 0.1TiCl_3$ from the study in [5] indicates that Ti atoms are sourced from the a-$Al_{50}Ti_{50}$ matrix, where they locally diffuse into the Al nanocrystals. This process occurs within the nanoscopic Al/a-$Al_{50}Ti_{50}$ composite on the $NaAlH_4$ powder grain surface during the very first thermally induced release of H.

It is the aim of this study to determine the temperature that Al nanocrystals are converted to c-$Al_{1-x}Ti_x$ structures, and in doing so demonstrate the temperature range over which the amorphous $Al_{50}Ti_{50}$ may be considered functional in terms of H release. We also utilise isotopic H_2/D_2 scrambling in combination with neutron diffraction to demonstrate that the surface embedded nano Al/$Al_{50}Ti_{50}$ composite is not only capable of molecular H_2 dissociation/recombination, but also promotes bulk diffusion of H within the $NaAlH_4$ structure.

2. Experimental procedure

$NaAlH_4$ was purchased from Albermarle Corporation (LOT NO.#: 22470404-01). All halide precursors were purchased from Sigma–Aldrich Chemicals Inc. (>99.99% purity). 80 nm Al (99.9% purity) was obtained from Nanostructured & Amorphous Materials Inc. $NaAlD_4$ was synthesised in accordance with previously reported wet synthesis of $NaAlH_4$ [9]. At all times, all powders have been handled under inert Ar or N_2 atmosphere in a dry glove box, with <1 ppm O_2 and H_2O. Milled $NaAlH_4$ powders (pure and with $TiCl_3$ and Al additive) were prepared in 1 g quantities in a Fritsch P7 planetary mill, with ball to powder ratio (bpr) of 20:1, at 750 rpm for a period of 1 h, under glove box atmosphere. Milled powders were taken directly to the beamline after milling for diffraction measurements. HD scrambling studies were performed with a dual focussing high resolution VG Model 70 SE Mass Spectrometer. The instrument was focussed on 4 amu (D_2). Samples were introduced through a stainless steel inlet. Initially with the inlet at a working temperature of 180 °C, a mixture of H_2 and D_2 could be slowly and reproducibly hybridised. As such, the inlet was cooled and head gas samples were prevented from remaining in the inlet for too long a period. Samples were connected from glassware with a double ended 20 gauge needle through a pair of septa. Accelerating voltage was 8000 V. Resolution was set to 800, yielding excellent sensitivity at low AMU. Detection efficiency for H_2 was ca. 7% less than HD. Detection efficiency for HD was ca. 7% less than D_2. HD measurements were performed typically up to 7 days at ambient temperature. Powder X-ray diffraction data were recorded at the Swiss–Norwegian Beamline (SNBL) at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. Samples were contained in rotating 0.8 mm boron–silica glass capillaries. High resolution data ($\Delta d/d \sim 2 \times 10^{-4}$) was typically collected at 295 K between 5 and 35° 2θ, in steps of 0.003–0.030°, depending on the sample broadening. A wavelength of 0.4998 Å was obtained from a channel cut Si (1 1 1) monochromator. Medium resolution ($\Delta d/d \sim 3 \times 10^{-3}$) in situ annealing data were collected on a 2-D image plate (MAR345) over the 2θ range 3–34° with step size 0.015° and exposure time of 30 s. A wavelength of 0.7111 Å was used. Powder neutron diffraction data was collected using the PUS diffractometer at the JEEP II reactor at Kjeller, Norway [10]. Monochromated neutrons with $\lambda = 1.5550$ Å were obtained from a Ge (5 1 1) focussing monochromator. The detector unit consists of two banks of seven position-sensitive ^3He detectors, each covering 20° in 2θ (binned in 0.05° steps). Data was collected in the 2θ range 10–130°. The as synthesised $NaAlD_4$ and the isotopically D/H exchanged $NaAl(D_{1-x}H_x)_4 + 0.04TiCl_3$ powders were measured in a sealed cyclindrical vanadium sample holder of 5 mm diameter, which was rotated at room temperature. Neutron diffraction patterns were modelled with the Rietveld diffraction analysis software RIETICA [11]. A mixed H/D model in space group $I4_1/a$ was refined for the isotopically D/H exchanged $NaAlD(H)_4$ structure type. A Voigt profile function was used to separate size and strain contributions to the diffraction line shape. The strong background induced from the presence of H atoms in the structure was modelled with a type I Chebyshev polynomial. X-ray synchrotron diffraction patterns were analysed by the Rietveld method, using RIETICA. Diffraction lineshape profiles were fitted with a full Voigt function, with the instrumental shape determined by a NIST LaB_6 660a lineshape standard, further annealed to 1800 °C.

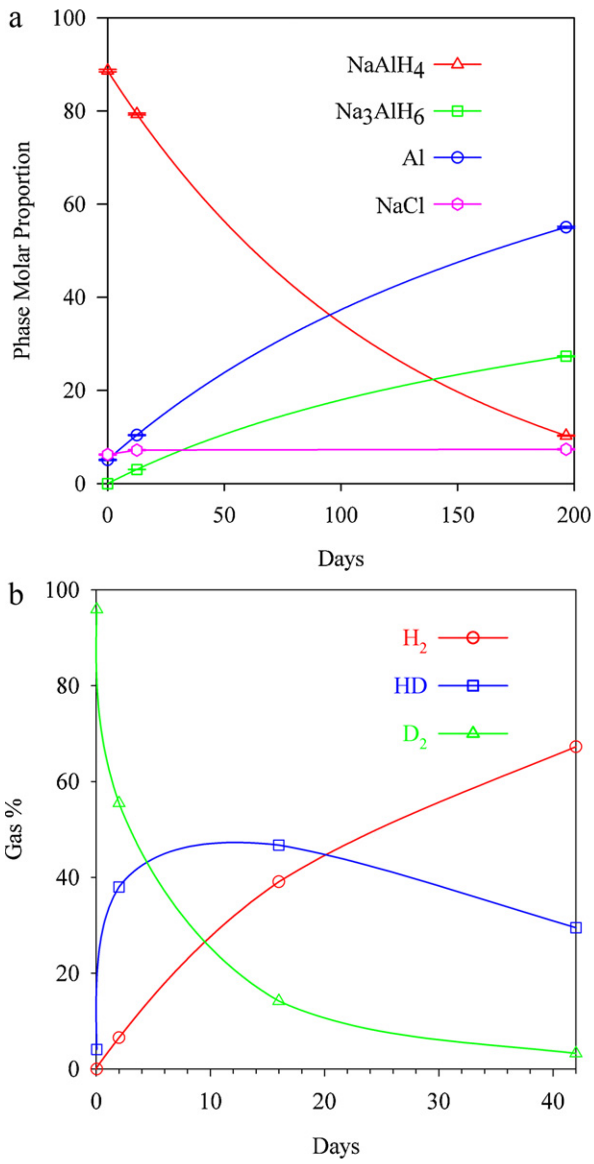

Fig. 1. (a) Long term room temperature disproportionation of PM $NaAlH_4 + 0.02TiCl_3$ measured up to 196 days, showing an exponential decay in $NaAlH_4$ phase proportion. (b) Room temperature HD scrambling of PM only $NaAlH_4 + 0.1TiCl_3$ measured up to 42 days against a starting pressure of 1 bar D_2.

3. Results and discussion

In typical 1 h PM $NaAlH_4 + xTiCl_3$ samples, the conditions on the powder surface after milling are sufficient to allow room temperature desorption of hydrogen from the sample, demonstrated in Fig. 1(a). There is almost complete exponential decay of $NaAlH_4$ into Na_3AlH_6 and Al after 196 days of storage in an inert atmosphere glove box. It is clear that significant amounts of H are released from the powder bulk where no Ti containing phases are present. This indicates that under ambient conditions, the surface embedded Ti

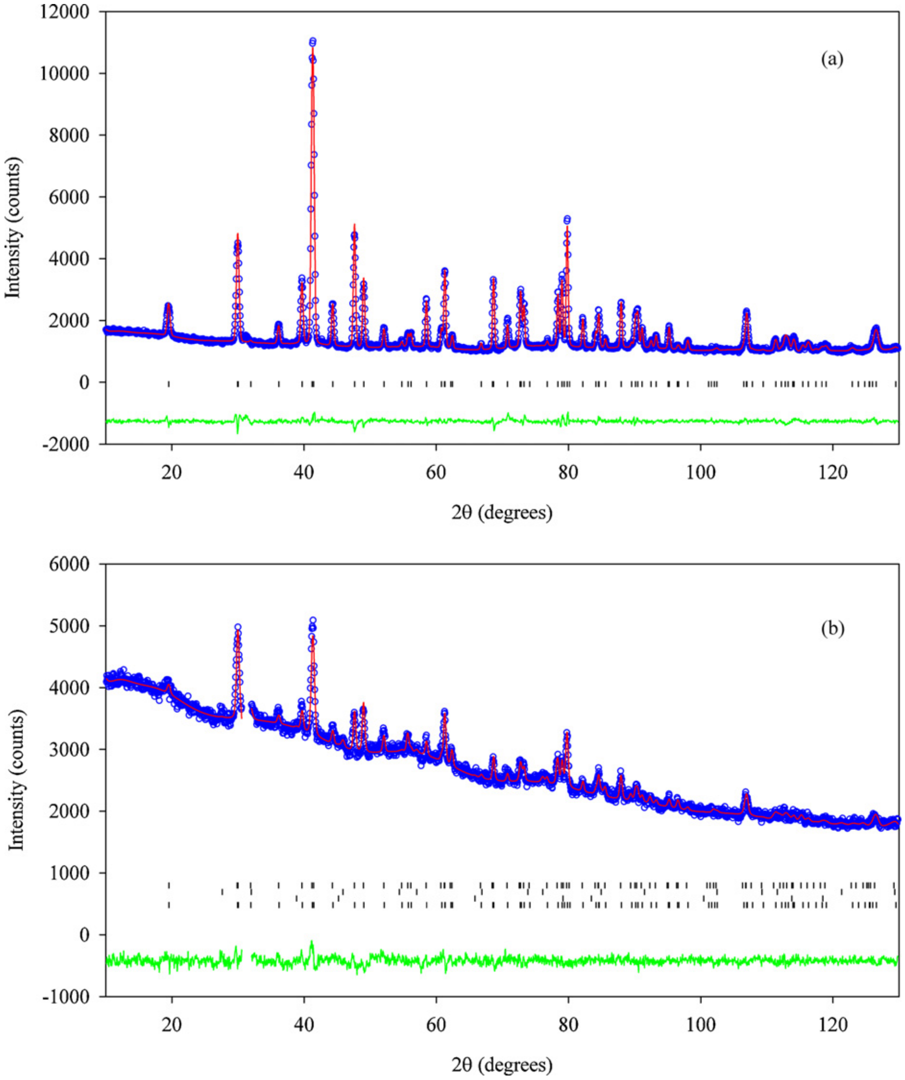

Fig. 2. (a) Neutron diffraction pattern of as synthesised pure $NaAlD_4$. Data are represented by open circles, the calculated Rietveld fit by the solid line. The difference profile between the data and the calculated pattern is below. Reflection markers for $NaAlD_4$ are given by the vertical bars. (b) Neutron diffraction pattern of PM $NaAlD_4 + 0.04TiCl_3$ after soaking under 20 bar H_2 at 50 °C for ca. 6 days. Reflection markers from top to bottom represent the H expanded phase $NaAl(H_{0.56}D_{0.44})_4$, NaCl, Al and the remaining unexpanded $NaAlD_4$ phase.

rich nano Al/a-$Al_{50}Ti_{50}$ composite performs a molecular H_2 recombination function that unadulterated $NaAlH_4$ cannot, and facilitates the release of H bound in the $NaAlH_4$ bulk. It is not yet clear if after 196 days, H will begin to be released from Na_3AlH_6.

We have utilised isotopic HD scrambling experiments to confirm that the surface embedded Ti rich nano Al/a-$Al_{50}Ti_{50}$ composite works in reverse, and also dissociates molecular H_2 and allows atomic H back into the $NaAlH_4$ structure by allowing H transport across the near surface $NaAlH_4$/a-$Al_{50}Ti_{50}$ interface. By near surface, we refer to the $NaAlH_4$/a-$Al_{50}Ti_{50}$ interface, which is on average 10 nm below the outer powder grain surface [8]. It is at this interfacial monolayer where Ti atoms may protrude into the $NaAlH_4$ unit cell, and very locally distort Al–H bonds immediately in the vicinity of the interface. Fig. 1(b) shows a HD scrambling experiment on PM $NaAlH_4 + 0.1TiCl_3$, conducted at room temperature under a starting D_2 pressure of 1 bar for 42 days. The starting pressure of 1 bar is above the predicted plateau pressure of ca. 0.5 bar at room temperature, based on an average extrapolation of all known pressure–composition–temperature (PCT) data for Ti enhanced $NaAlH_4$ [12–15]. Based on equivalent plateau pressures between $TiCl_3$ enhanced $NaAlH_4$ and $NaAlD_4$ at 130 °C in [12], we assume also that at low temperature, the hydride/deuteride plateau pressures are equivalent to each other. As such, we then expect that disproportionation of $NaAlH_4$ is avoided under 1 bar D_2 gas pressure. In Fig. 1(b), a clear exponential rise in HD fraction is observed over the first 14 days, after which, the HD fraction can be observed to artefactually decrease as the finite supply of D_2 is consumed. Even after nearly all D_2 is consumed after 42 days, the H_2 fraction does not appear to have plateaued, indicating that some $NaAlH_4$ decomposition may have occurred to release H. As no isotherms exist for the PCT diagram at room temperature, we must rely on the extrapolation of the van't Hoff function and the assumption of no isotope affect at low temperature. Clearly, the starting pressure of 1 bar D_2 is close to the predicted plateau pressure for $NaAlH_4$ at ca. 0.5 bar, indicating that HD scrambling should be performed at higher pressure to observe H/D exchange in $NaAlH_4$.

Such an experiment has been conducted at 50 °C and 20 bar of D_2 on milled $NaAlH_4 + 0.04TiCl_3$ [16]. At 50 °C, the predicted plateau pressure is ca. 1.7 bar, which is well below the 20 bar starting pressure, again suggesting that $NaAlH_4$ disproportionation will be avoided (and again assuming no significant isotope effect at low

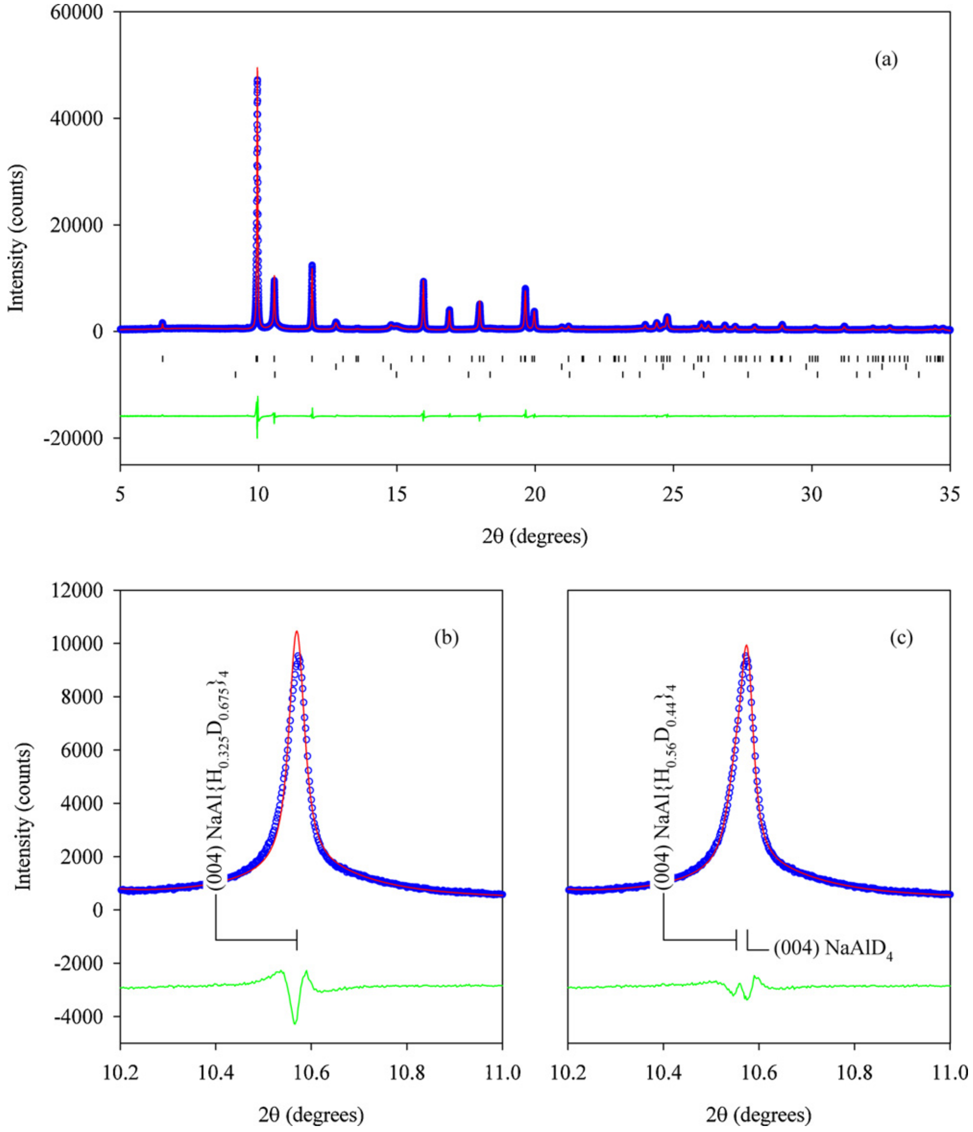

Fig. 3. (a) High resolution X-ray synchrotron diffraction pattern of PM $NaAlD_4$ + $0.04TiCl_3$ after soaking under 20 bar H_2 at 50 °C for ca. 6 days. A single phase calculated fit is shown to demonstrate the artefactual positional misfit. (b) Single phase $NaAl(H_{0.325}D_{0.625})_4$ model showing artefactual positional misfit for the (004) reflection. (c) A 2-phase model fit to the (0 0 4) doublet with misfit removed. The model contains 58% H expanded $NaAl(H_{0.56}D_{0.44})_4$ unit cells, and 42% pure $NaAlD_4$ unit cells.

temperature). In [16], a steep decay in D_2/HD ratio can be observed over an initial period of ca. 33 h, after which the ratio plateaus. In total, 1.3 of the 4 formula units of H of $NaAlH_4$ are estimated to have exchanged with D, on the basis of 2.13×10^{-2} mol of D atoms recovered at 180 °C after annealing the pre-evacuated sample at the end of the HD scrambling period. It is inferred that bulk exchange of H with D in the $NaAlH_4$ phase has occurred, without decomposition.

With knowledge of the surface structure from our previous study [8], it is possible to further investigate the nature of this apparently exchanged D. As $Al_{50}Ti_{50}$ is known to absorb hydrogen, the H(D) absorption properties of the surface become relevant. A comprehensive study of the H absorption properties of amorphous and crystalline $Al_{1-x}Ti_x$ alloys demonstrates that a-$Al_{50}Ti_{50}$ and a-$Al_{60}Ti_{40}$ absorb significant quantities of H at room temperature, up to $Al_{60}Ti_{40}H_{21}$ and $Al_{50}Ti_{50}H_{36}$, under 50 bar H_2 pressure [17]. As 96% of the exchanged D was recovered on annealing to 180 °C in [16], only a small fraction of D could possibly be absorbed by the surface embedded a-$Al_{50}Ti_{50}$ phase. This is consistent with the analysis that to store the recovered 2.13×10^{-2} mol of D atoms, 40 times as much H(D) would need to be stored in the a-$Al_{50}Ti_{50}$ phase than is observed experimentally for bulk micron-sized powders [17]. Further, TDS analysis demonstrates an extremely high hydrogen release temperature of >800 K for both a-$Al_{50}Ti_{50}H_{36}$ and a-$Al_{60}Ti_{40}H_{21}$ [17], indicating it is highly unlikely that H(D) proceeds through the 5–10 nm thick surface embedded a-$Al_{50}Ti_{50}$ phase. Rather, atomic H is likely to diffuse along/around the surface of the nanoscopic a-$Al_{50}Ti_{50}$ phase.

In order to study the distribution of exchanged bulk H observed in [16], we have emulated the experiment in reverse, by studying a deuteride, PM $NaAlD_4$ + $0.04TiCl_3$, under hydrogen gas, H_2, at 20 bar and 50 °C. We have observed the pre and post exchanged samples by neutron and X-ray synchrotron diffraction. As D and H have opposite sign and differing magnitude neutron scattering lengths, and as H also has a large incoherent scattering cross section, the exchange of D with H in the deuterated bulk will show strong reflection intensity reductions and a strong background increase in a neutron diffraction pattern. Diffraction can also confirm that $NaAlH_4$ decomposition has been avoided during the H/D exchange, or alternatively verify the presence of H in any Na_3AlD_6 produced. Fig. 2(a and b) shows the dramatic changes in neutron

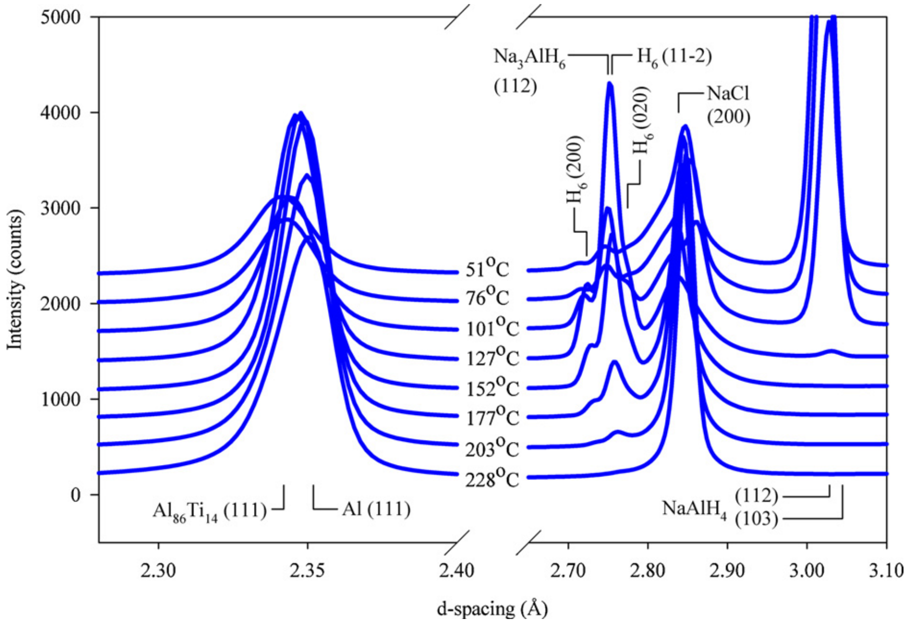

Fig. 4. In situ isochronal (2 °C/min) annealing data in the hydrogen release temperature range 51–228 °C from PM $NaAlH_4 + 0.1TiCl_3$, across the most interesting range of *d*-spacing from 2.28 to 3.10 Å.

diffraction patterns before and after soaking a $NaAlD_4 + 0.04TiCl_3$ sample under 20 bar H_2 gas at 50 °C for ca. 6 days. Maximum Bragg reflected intensity of the $NaAlD_4$ phase is reduced to ca. 13% of the starting magnitude, and the incoherent background structure is more than doubled. A minor instrumental reflection is observed at 31.18° in the pure $NaAlD_4$ sample, which is excluded from the refinement in Fig. 2(b). The reflection markers from top to bottom in Fig. 2(b) represent the H expanded $NaAlD_4$ phase, NaCl, Al and the remaining unexpanded $NaAlD_4$ phase. No $Na_3Al\{D_{1-x}H_x\}_6$ or Na_3AlD_6 phase is evident, demonstrating that H is exchanged only with the $NaAlD_4$ phase, and no disproportionation occurs, which is consistent with the equilibrium plateau pressure for the $NaAl\{D_{1-x}H_x\}_4$ phase being well below 20 bar at 50 °C. Initially, a single phase mixed $NaAl\{D_{1-x}H_x\}_4$ model was fitted to the neutron data, with the best fit yielding ca. 32.5% occupancy of H, in excellent agreement with [16], where 1.3 out of the 4 formula units of H were exchanged with D. Although a statistically satisfactory fit to the neutron data was obtained with the single phase model, one experimental reflection remains almost completely underfitted by the calculated model (2 0 0) (at $2\theta = 36.18°$). High resolution X-ray synchrotron data of the D/H exchanged sample provided the information necessary to produce calculated intensity in the (2 0 0) reflection. Fig. 3(a) shows the X-ray synchrotron diffraction pattern of the D/H exchanged sample with a single phase model fitted. Positional misfit is apparent everywhere in the difference profile, and on close inspection, strong leading edge, high *d*-spacing asymmetry is evident on every reflection, indicating the presence of two tetrahydride phases. Rietveld fitting of the synchrotron data utilised the following methodology: (i) a single phase model was fitted, with unit cell dimensions intermediate between the pure $NaAlH_4$ and pure $NaAlD_4$ unit cells, with $a = 5.0148$ Å and $c = 11.3247$ Å and $\chi^2 = 3.122$. This model contributes zero intensity to the (2 0 0) doublet in the neutron data; (ii) a 2-phase model was fitted, with the remaining un-exchanged $NaAlD_4$ unit cell constrained at pure $NaAlD_4$ dimensions, with $a = 5.0084$ Å and $c = 11.3034$ Å, and a mixed H/D cell with $a = 5.0138$ Å and $c = 11.3257$ Å, yielding a $\chi^2 = 2.504$. When this model is applied to the neutron data, the (2 0 0) doublet intensity is ca. (3/4) fitted, and the number of expanded unit cells determined by quantitative phase analysis (QPA) is slightly overestimated at ca. 73%; (iii) a 2-phase model was fitted, with both the exchanged and un-exchanged unit cell dimensions refined, yielding $a = 5.0095$ Å and $c = 11.3106$ Å for the pure $NaAlD_4$ cell, and $a = 5.0163$ Å and $c = 11.3351$ Å for the mixed H/D unit cell, with final $\chi^2 = 2.059$. This model yields an excellent fit to the (2 0 0) doublet in the neutron data, with the final number of affected unit cells in the sample standing at ca. 58%, yielding a final mixed H/D unit cell of composition $NaAl(H_{0.56}D_{0.44})_4$. This final 2-phase model also demonstrates that the mixed H/D cell mechanically dilates the un-exchanged $NaAlD_4$ cells prismatically by ca. 1%. Fig. 3(b) shows the (0 0 4) reflection for the single phase model, and Fig. 3(c) the final 2-phase model, with the artefactual positional misfit removed. Lineshape analysis indicates the mosaic of the exchanged H/D unit cells is ca. 100 nm compared to ca. 250 nm for the un-exchanged cells, demonstrating that large regions of each powder grain have experienced exchange and allowed long ranged H/D diffusion to occur within the $NaAlD_4$ structure on a depth scale of 100 nm from the surface. Although the $NaAl(H_{0.56}D_{0.44})_4$ composition represents an average measurement, the mixed H:D ratio suggests H and D can be mixed in individual AlD_4 units. A significant fraction of the powder remains un-exchanged, with 42% of all unit cells remaining as pure $NaAlD_4$, which is likely because the system has reached an equilibrium distribution.

Commensurate with the observation that milled pure $NaAlH_4$ samples have produced spectral features in infra red and NMR data [18,19] indicating perturbed Al–H bonds, we have also studied a milled only pure $NaAlH_4$ sample (no additive) with HD scrambling. We observe a 10% rise in HD fraction over 7 days for $NaAlH_4$ under a 1 bar H_2/D_2 mixture, considerably less HD than that observed for $TiCl_3$ enhanced $NaAlH_4$. We have not measured this sample by diffraction, and cannot ascertain that bulk H/D exchange has occurred, however, it is clear that the pure $NaAlH_4$ surface after milling is amenable to molecular dissociation/recombination of H_2. The non-zero strain component in the pure milled $NaAlH_4$ diffraction lineshape, combined with the single crystalline nature of the powder grains strongly suggests that the strain component is of a non-correlated nature, as no grain boundary network exists. It is thus likely that the grain is moderately defected with either free edge or screw dislocations. The termination of free edge/screws on the powder grain surface may serve as dissociation/recombination sites for molecular H_2, by virtue of the extra energy stored as line tension in the dislocation cores. After the first thermal desorption and subsequent first absorption of hydrogen (with typical H cycling conducted up to 150 °C and 150 bar), the $NaAlH_4$ lineshape is considerably sharper, indicating that all the free microstructure has been annealed out. As such, the uncorrelated microstructure may provide a minor role during the first low temperature release of hydrogen before the $NaAlH_4$ phase is completely decomposed, however, in subsequent H cycles it is of no real significance. To eliminate the potential role of nanoscopic Al in dissociation/recombination of molecular H_2/and or bulk release of H, a $NaAlH_4 + 0.1Al$ (80 nm) sample was milled and stored in the glove box at ambient temperature, and followed over 1.5 years, to test if Al destabilized $NaAlH_4$. After 1.5 years, the diffraction patterns are identical, with only $NaAlH_4$ and Al present, with no indication of Na_3AlH_6. While we might expect a reduced effect for the larger 80 nm Al compared to the 20 nm Al in the surface embedded nano Al/a-$Al_{50}Ti_{50}$ composite, no bulk H is released at all, and it is a safe assumption that the a-$Al_{50}Ti_{50}$ phase is directly responsible for the ambient release of bulk H.

Considering the large amount of D/H exchange observed, and the obvious H_2 molecular dissociation/recombination properties at 23–50 °C, knowledge of the crystallisation temperature of the surface embedded nanoscopic a-$Al_{50}Ti_{50}$ phase is desirable from the point of view that H does not appear to be stored in it, nor travel through the a-$Al_{50}Ti_{50}$ bulk. Fig. 4 shows isochronal annealing of a PM only $NaAlH_4 + 0.1TiCl_3$ sample, over the temperature range 51–228 °C. Most of the H from $NaAlH_4$ is desorbed by 127 °C, and most of the H from Na_3AlH_6 by 203 °C. Crystalline $Al_{1-x}Ti_x$ is observed to start forming at 177 °C, with a strong asymmetry on Al (1 1 1) evident by 203 °C. As most of the H has been released from the sample by 203 °C, it is clear that the a-$Al_{50}Ti_{50}$ matrix allows molecular H_2 recombination for almost the entire release of H from the sample, from both the $NaAlH_4$ and Na_3AlH_6 phases. The formation of crystalline $Al_{1-x}Ti_x$ phases from the a-$Al_{50}Ti_{50}$ matrix is not a crystallisation of the amorphous matrix itself, which is expected to crystallise in a single phase state at ca. 660 °C for $Al_{50}Ti_{50}$ [20]. Rather, the formation of ca. 4–25 nm $Al_{85}Ti_{15}$ crystallites observed in H cycled $NaAlH_4 + xTiCl_3$ [5] is consistent with local diffusion of Ti atoms from the a-$Al_{50}Ti_{50}$ matrix into the 2–20 nm pure Al crystallites. The growth of c-$Al_{1-x}Ti_x$ appears to be limited, with very close matching of the size ranges, Al 2–20 nm: $Al_{1-x}Ti_x$ 4–25 nm, and similar dislocation density in the 2–20 nm Al and 4–25 nm $Al_{1-x}Ti_x$ [5].

The annealing data from Fig. 4 also highlight another experimental difficulty for conducting HD scrambling experiments on the $TiCl_3$ enhanced $NaAlH_4$ system. It is stated in [16] that “H/D exchange is much faster than rehydrogenation of decomposed alanate”. This statement alludes to the origins of the kinetic rate limiting feature for hydrogen absorption in the $NaAlH_4 + xTiCl_3$ system, and implicitly assumes that molecular H_2 dissociation/recombination is not rate limiting, which appears consistent with the rate study in [12] indicating diffusion of AlH_x entities are the rate limiting step. There exist several problems with the HD interpretation from [16]: (i) the D_2/HD decay at 50 °C and 20 bar observed in [16] occurs due to the presence of an a-$Al_{50}Ti_{50}$ phase on the $NaAlH_4$ surface. Comparing the absorption rate to milled data is difficult as after the first thermal desorption to remove H, c-$Al_{88}Ti_{12} \leftrightarrow$ c-$Al_{86}Ti_{14}$ forms [5] (as in Fig. 4) from the nanoscopic Al/$Al_{50}Ti_{50}$ composite, and the rate of HD scrambling may not be the same on these crystalline surfaces as the a-$Al_{50}Ti_{50}$ surface; (ii) the rate of HD scrambling is highly likely pressure/temperature (P/T) and mol% $TiCl_3$ dependent, and (iii) conducting HD scrambling at 50 °C and 20 bar are sufficient P/T conditions to hydride a H empty $NaAlH_4 + xTiCl_3$ sample, and as such two processes (H/D exchange and direct un-exchanged surface HD scrambling) are contributing to the final HD scrambling rate. Such features demonstrate that to obtain the true exchange independent HD surface scrambling rate, it is necessary to conduct HD scrambling at P/T conditions at which the sample will not hydride (i.e., at pressures below the equilibrium plateau pressure), and after at least one thermal desorption has occurred to create crystalline $Al_{1-x}Ti_x$ phase from the Al/a-$Al_{50}Ti_{50}$ composite, so that H absorption rate and HD scrambling rate are referenced to the same c-$Al_{1-x}Ti_x$ phase. As the surface embedded c-$Al_{1-x}Ti_x$ phase does not change composition after ca. 2 H cycles [5], HD scrambling can be performed on twice hydrogen cycled H empty samples, from room temperature upwards at moderate H_2/D_2 pressures to obtain the H/D exchange independent temperature dependent surface only HD scrambling rate. Fig. 5 shows HD scrambling conducted on an isothermally desorbed PM $NaAlH_4 + 0.1TiCl_3$ sample, for a 1 bar mixture of H_2/D_2 at room temperature, conducted over 7 days. Classic equilibrium $H_2 + D_2 \leftrightarrow 2HD$ mixing is observed, demonstrating that c-$Al_{1-x}Ti_x$ ($x < 0.25$) phases formed during H cycling perform a classic H_2 dissociation/recombination function.

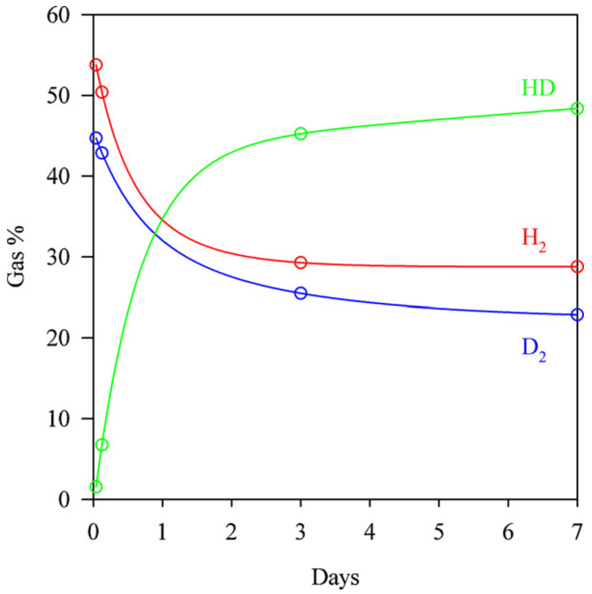

Fig. 5. HD scrambling of a starting 1 bar mixture of H_2 and D_2 on dehydrided PM $NaAlH_4 + 0.1TiCl_3$. A 1.19:2.00:0.95 mixture of H_2:HD:D_2 is obtained after 7 days (normalised to HD), showing near classic equilibrium mixing according to $H_2 + D_2 \leftrightarrow 2HD$.

4. Concluding remarks

The nanoscopic Al/a-$Al_{50}Ti_{50}$ composite embedded on the surface of single crystalline $NaAlH_4$ powder grains allows the release of H from $NaAlH_4$ and subsequent molecular H_2 formation at ambient temperature over ca. 200 days. Isotopic H/D exchange observed over 6 days for PM $NaAlD_4 + 0.04TiCl_3$ under 20 bar H_2 at 50 °C indicates that the surface embedded nano Al/a-$Al_{50}Ti_{50}$ composite performs a molecular H_2 dissociation/recombination function, and facilitates bulk exchange of D with H. After the D/H exchange period, 58% of all unit cells are expanded by H to form the composition $NaAl(H_{0.56}D_{0.44})_4$. The mosaic of ca. 100 nm for $NaAl(H_{0.56}D_{0.44})_4$ indicates that long ranged diffusion of H/D is possible within the $NaAlD_4$ structure at 50 °C and 20 bar. Isochronal annealing of PM only $NaAlH_4 + 0.1TiCl_3$ shows that almost all H is released before crystalline $Al_{86}Ti_{14}$ is observed, demonstrating that the nano Al/a-$Al_{50}Ti_{50}$ composite performs the H release function during the first thermal desorption. A lack of hydrogen release from $NaAlH_4 + 0.1Al$ (80 nm) over 1.5 years strongly suggests that a-$Al_{50}Ti_{50}$ is the phase that is functionally responsible for H release during the very first thermal desorption of milled $NaAlH_4 + xTiCl_3$. Ambient HD scrambling on post thermal desorbed PM $NaAlH_4 + 0.1TiCl_3$ shows near classic 1:2:1 equilibrium mixing according to $H_2 + D_2 \leftrightarrow 2HD$, indicating that both a-$Al_{50}Ti_{50}$ and c-$Al_{86}Ti_{14}$ perform a classic molecular H_2 dissociation/recombination function that unadulterated $NaAlH_4$ cannot. The $Al_{1-x}Ti_x$ phases also provide a thermally stable sink for Ti, which subsequently provides a stable monolayer of $Al_{1-x}Ti_x$ phase at the near surface $NaAlH_4/Al_{1-x}Ti_x$ interface.

Our study serves as a model for $TiCl_3$ addition to $NaAlH_4$ from 2 points of view: (i) the addition of $TiCl_3$ to $NaAlH_4$ results in Ti containing phases embedded on the $NaAlH_4$ surface that are nanoscopic in dimension, and that are efficient at molecular dissociation/recombination of H_2, and (ii) the dispersion of these nanoscopic Ti containing phases on the $NaAlH_4$ surface implies that the interfacial area between $Al_{1-x}Ti_x$ phases and $NaAlH_4$ is only small, but greatly efficient at releasing hydrogen from the $NaAlH_4$ bulk, even at great distances from the surface where Ti is embedded. The surface location of Ti also highlights the importance of reducing the size of the $NaAlH_4$ bulk to reduce bulk limiting AlH_4 diffusion distances. Understanding of the near surface $Al_{1-x}Ti_x/NaAlH_4$ interface in promoting rate limited hydrogen release from the $NaAlH_4$ bulk is of utmost importance. The surface embedding of well distributed and isolated nanoscopic $Al_{1-x}Ti_x$ phases suggests that AlH_4 tetrahedra can only be perturbed in very limited numbers locally at the near surface $Al_{1-x}Ti_x/NaAlH_4$ interface, initiating a hydrogen release reaction which propagates into the $NaAlH_4$ bulk. Local charge imbalance of AlH_4^- units and Ti coordination in the $Al_{1-x}Ti_x/NaAlH_4$ interface is crucial to understanding how this reaction propagates from the surface into the bulk. High resolution TEM is the obvious tool to provide direct space images of this interface, however, electron beam induced evaporation of Na and H which destroys the interface precludes such an observation [21]. Density functional theory models of Ti substitution in the $NaAlH_4$ surface (slab models) may be relevant in this regard [22], and provide at least a simplistic picture of how Ti atoms may be locally coordinated by H in the $Al_{1-x}Ti_x/NaAlH_4$ interface.

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