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.

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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.

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 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 for 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) at 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 ^{3}He 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
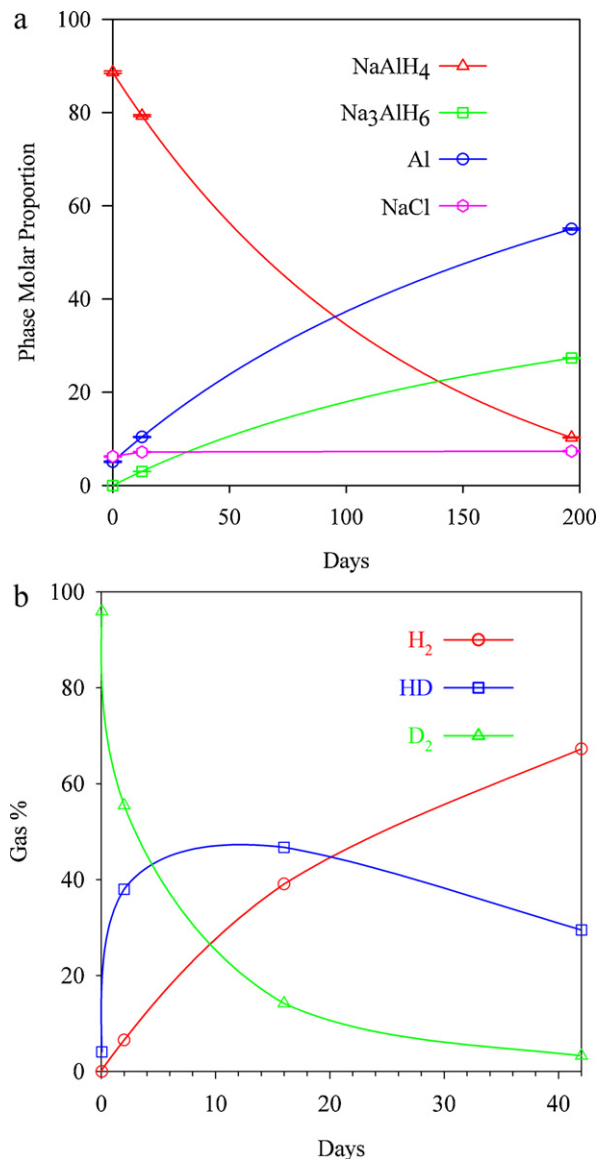
Fig. 1. (a) Long term room temperature disproportionation of PM $NaAlH_4 + 0.02TiCl_3$ measured up to 196 days, showing an exponential decay in $NaAlH_4$ phase proportion. (b) Room temperature HD scrambling of PM only $NaAlH_4 + 0.1TiCl_3$ measured up to 42 days against a starting pressure of 1 bar D_2.

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.

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