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ABSTRACT

Renewed interest in hydrogen storage materials has resulted in the development of Ti-doped $NaAlH_4$. Different doping methods such as mechanical milling with powdered $TiCl_3$, or wet doping in solvents such as tetrahydrofuran (THF), yield enhanced kinetics. Still, the location and action of the Ti dopant is an open question. In order to address titanium substitution in the bulk, we present lattice parameter measurements of crushed single crystals which were exposed to Ti during growth. Rietveld refinements suggest that the titanium does not appear to enter the bulk by this method of exposure. Therefore, reaction products are investigated by x-ray diffraction of completely reacted samples of solvent-mixed versus mechanically milled $3\,NaAlH_4{+}TiCl_3$. Formation of $TiAl_3$ is observed in mechanically milled materials, but not solution mixed samples, where bonding to THF likely stabilizes Ti-based nanoclusters. The Ti in these clusters is activated by mechanical milling.

INTRODUCTION

Sodium alanate decomposes first to the hexa-hydride and then to sodium hydride, through the decomposition reactions: $NaAlH_4 \rightarrow \frac{1}{3}Na_3AlH_6 + \frac{2}{3}Al + H_2 \rightarrow NaH + Al + \frac{3}{2}H_2$. This decomposition was first shown to be kinetically enhanced and reversible by Bogdanovic and coworkers by the addition of Ti-dopant [1, 2]. The rate of these reactions is enhanced by several orders of magnitude by the addition of the dopant, which lowers the activation energy of the absorption and desorption processes [3]. However, the method by which the Ti-dopant works, either by bulk substitution in the alanate structure(s) or by lowering reaction barriers at the surface, is still not understood [4, 5].

There is a striking difference in hydrogen sorption rates when doping through different techniques. For example, mechanically milling Ti-halide dopants with $NaAlH_4$ powder results in rapid initial kinetics, while the same milling with TiH_2, or $TiAl_3$ as a dopant results in very slow initial kinetics. However, it has been shown that samples prepared through mechanical milling of $NaAlH_4$ and TiH_2 show hydrogen absorption rates that increase upon cycling from extremely poor, to rates comparable to doping with Ti-halides [6].

The location of dopant Ti in sodium alanate has become the leading question in the study of the enhanced kinetics in this complex-hydride system. In what compounds, if any, is the titanium located after the doping procedure, and how are these affecting the reaction kinetics?

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There is some evidence to suggest that Ti may substitute in the alanate structure resulting in lattice parameter changes upon doping through mechanical milling [7], however, the absence of a lattice parameter standard in these studies casts doubt on the validity of the results obtained. In addition, others have been unable to produce similar results [5]. There are, however, first-principles studies indicating that Ti may substitute in the bulk $NaAlH_4$ structure, if accompanied by a hydrogen vacancy [8]. The role of defect induced stability for the inclusion of Ti in the bulk structure of $NaAlH_4$ has not been fully addressed.

Doping with Ti nanoclusters has been demonstrated and results in faster absorption reaction kinetics than doping with Ti-halides [9, 10]. The Ti nanoclusters in the work of Fichtner, *et al.*, and Bogdanovic, *et al.*, were prepared in solutions of tetrahydrofuran (THF) and are due to the strong coordination of the oxygen in THF with the transition metal, resulting in 13 atom icosahedral clusters of Ti which form the core and have six THF ligands. Because $TiCl_3$ reacts with $NaAlH_4$ in THF solution, the products of this reaction are of interest.

Early sample preparation methods of solution-doped samples in toluene and ether did not require mechanical milling for activity [1, 2]. In this paper, we indicate the differences between some of the compounds formed in solvent-free production of active materials, and those prepared through $TiCl_3$ doping in THF. Samples prepared by doping in THF did not show hydrogen sorption activity unless mechanically milled. This information may help to indicate the nature of the compounds which are active by different doping procedures.

EXPERIMENTAL DETAILS

Single crystal samples of $NaAlH_4$ were grown by solvent evaporation from *Sigma Aldrich* 1 M solutions of $NaAlH_4$ in THF. For “Ti-exposed” single crystals, $TiCl_3$ was added to this solution at 4 at. %, before the solvent evaporation. The single crystals were subsequently crushed in a mortar and pestle, and *NIST* powdered silicon was added as lattice constant standard for x-ray diffraction refinements.

Powdered $NaAlH_4$ was prepared from a 1 M solution of *Sigma-Aldrich* $NaAlH_4$ in tetrahydrofuran (THF) by vacuum evaporation of the solvent [11]. Samples of $3\,NaAlH_4 + TiCl_3$ were prepared for comparison by solvent and solvent-free techniques. This ratio was chosen so that all of the alanate would be consumed leading to larger quantities of reaction products. A solvent-free sample was prepared by mechanical milling of $NaAlH_4$ powder and $TiCl_3$ powder in a SPEX mill as described elsewhere [4]. A solution-mixed sample was prepared in THF in an argon-filled dry box by the addition of 0.257 g of $TiCl_3$ to 5 cc of 1 M $NaAlH_4$ in THF, which was allowed to evaporate at room temperature in an argon dry box.

The Ti nanoclusters synthesized in the work of Fichtner, *et al.*, were prepared by reaction of $TiBr_4$ and $K[BEt_3H]$ in THF, were filtered and dried, and then mechanically milled with $NaAlH_4$. Due to the similarity of the reactions of $TiCl_3$ and $NaAlH_4$ in THF, solution-mixed samples of 4 at. % $TiCl_3$ and $NaAlH_4$ were prepared for hydrogen sorption experiments. Two samples were prepared, one which was dried before the sorption experiments, and one which was mechanically milled for 30 min after drying, and before the sorption experiments.

X-ray diffraction was performed using Cu-K_α radiation on a *Scintag* XDS-2000 using Bragg-Brentano geometry and airless sample holders. X-ray fluorescence spectra were collected on a KEVEX Omicron using 50 kV, 1 mA, 50 μm aperture and 100 sec collection time.

Hydrogen sorption experiments were performed on sample sizes of about 2 g, which were transferred to a sealed stainless-steel sample vessel and connected to a pressure, and temperature-controlled hydrogen manifold. All steps for sample preparation and transfer into the reactor vessel occurred inside an Ar glove box with oxygen levels below 3 ppm.

Magic angle spinning (MAS) nuclear magnetic resonance (NMR) measurements are described in detail in this proceedings in "Investigation of Ti-doped $NaAlH_4$ by Solid-State NMR," J.L. Herberg, and R.S. Maxwell.

RESULTS AND DISCUSSION

Rietveld refinement using powder x-ray diffraction of 4 at. % "Ti-exposed" single crystals was performed with SIMREF 2.6 [12]. Peak shapes of the x-ray data were fit using the pseudo-Voigt profile containing a mixture of Gaussian and Lorentzian shapes. The refinement is illustrated in Figure 1. The lattice constants from the fit to the "Ti-exposed" sample are $a = 5.0238$ Å and $c = 11.3506$ Å. The lattice constants from a pure $NaAlH_4$ crushed single crystal are $a = 5.0238$ Å and $c = 11.3504$ Å, indicating that there is no observable shift in the lattice constants due to the exposure of Ti *by this method.* The titanium does not appear to enter the bulk $NaAlH_4$ lattice. This may be because the crystal is grown slowly and the Ti is either rejected as an impurity, or is confined to some other compound, such as a Ti-Al, or Ti-H compound, and is not available for inclusion into the lattice.

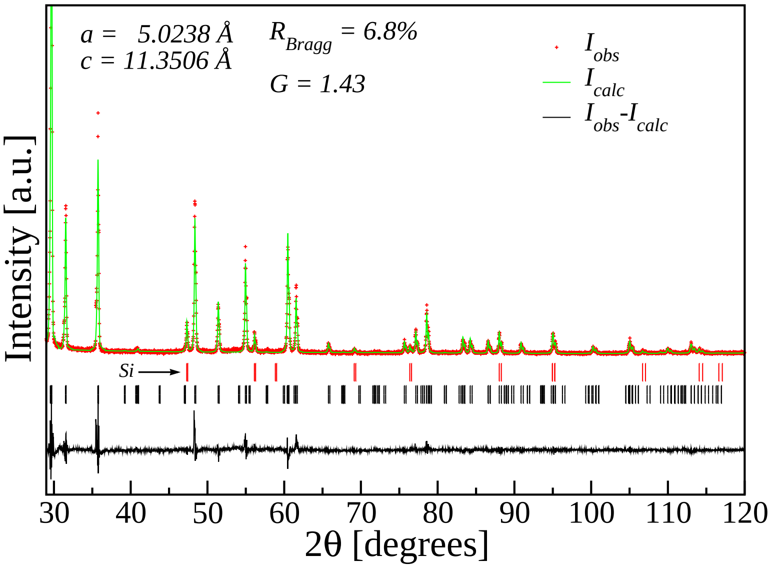

Figure 1: Rietveld refinement of "Ti-exposed" crushed single crystals. The lattice parameters show no change within 0.0002 Å, suggesting that no titanium is introduced into the lattice with this method of doping.

In addition to the negative result obtained above, the assumption that Ti is incorporated into bulk decomposition structures of the alanate, allowing them to remain "active" for absorption, is not supported for the last decomposition product, NaH. Preliminary annealing studies of NaH, mechanically milled with $TiCl_3$, bulk Ti metal, and other Ti compounds, show no lattice parameter changes in diffraction data. Lattice parameter changes observed upon mechanical mixing of TiF_3 and NaH are consistent with fluorine substitution in the NaH lattice, as the lattice parameter shifts linearly between bulk NaH and bulk NaF.

In order to determine the possible structures in which Ti may be residing, the dopant level was increased to a large enough value that all the available alanate is consumed, leaving only NaCl, and Ti-Al-H reaction products. Mechanically milled mixtures of $3\,NaAlH_4{+}TiCl_3$

show that $TiAl_3$ formation is likely [4]. However, the same dopant ratio applied in a solution of THF shows no indication of $TiAl_3$. X-ray diffraction in Figure 2a shows that no bulk Ti or $TiAl_3$ is formed in solution mixing of $NaAlH_4$ and $TiCl_3$. The only observed peaks in our experiments correspond to bulk Al, and NaCl. Because of the strong scattering of Ti with respect to the other elements in this sample, one would expect it to be visible in the x-ray spectrum. There is an indication of another phase in the x-ray spectrum between 15-40 degrees 2θ, shown as a very broad increase in the background intensity. This is probably due to a very fine particle size (nanometer) or amorphous phase.

The presence of Ti is clearly indicated in the x-ray fluorescence spectrum of the solution-mixed sample, shown in Figure 2b, despite the absence of any indication of bulk (hcp) Ti or $TiAl_3$. The Ti may form a $TiAl_xH_y$ compound, or a Ti-Al nano-particle colloid, as the presence of hydrogen is indicated by proton NMR in the solution mixed sample.

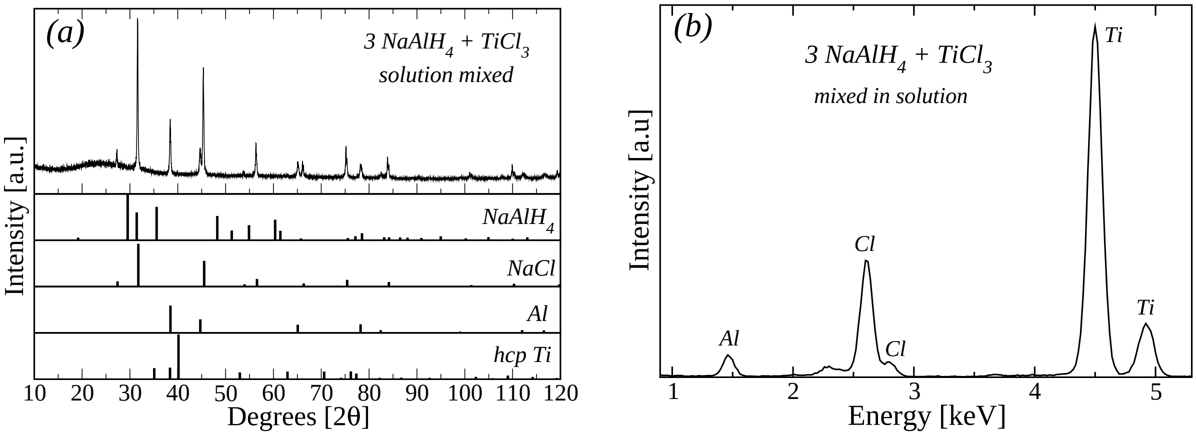

Figure 2: X-ray diffraction (a) and X-ray fluorescence (b) of THF solution mixed $3\,NaAlH_4 + TiCl_3$. Diffraction data shows no Ti-compounds, but the presence of Ti in the material is evidenced by the clear XRF signal, which, together with the XRD indicates the presence of Ti in either nano-particle or amorphous compounds.

The sorption kinetics of the 4 at. %-doped samples, solution-mixed in THF, indicate that mechanical milling of the samples was required for activity. The sample not milled after evaporating the THF was initially desorbed at 160 °C into a vacuum, releasing 53 % of its reversible hydrogen over a 1.5 hr period. A subsequent absorption showed no hydrogen uptake, over a 2 hr period, at pressures up to 82 bar at a temperature of about 95 °C. In contrast, the sample which was mechanically milled after drying desorbed about 73 % of its reversible hydrogen over a 1.5 hr period at 160 °C. A subsequent absorption of the milled sample at about 85 °C and 85 bar over 2 hrs indicated an absorption of over 90 % of the hydrogen which was initially desorbed.

The possible reactions occurring in the THF solvent include:

$$\mathrm{TiCl_3 + 3\,Na^+ + 3\,(AlH_4)^- \longrightarrow TiAl_3 + 3\,NaCl + 6\,H_2} \tag{1}$$

$$\mathrm{TiCl_3 + 3\,Na^+ + 3\,(AlH_4)^- \longrightarrow TiH_2 + 3\,NaCl + 3\,Al + 5\,H_2} \tag{2}$$

$$\mathrm{TiCl_3 + 3\,Na^+ + 3\,(AlH_4)^- \longrightarrow TiAl_xH_y + 3\,NaCl + (3-x)\,Al + \left(6 - \frac{y}{2}\right)\,H_2} \tag{3}$$

$$\mathrm{TiCl_3 + 3\,Na^+ + 3\,(AlH_4)^- \longrightarrow [Ti_{1-y}Al_y \cdot 0.5\,THF]_x + 3\,NaCl + (3-y)\,Al + 6\,H_2} \tag{4}$$

Compound	ΔG_f° [kJ/mol]
TiAl	-72
TiH_2	-86
$TiAl_3$	-136
$TiAl_xH_y$	—

Table 1: Formation energies for possible Ti-Al-H compounds.

The free energies of formation for some Ti-Al and Ti-H compounds are shown in Table 1. The difference in Gibbs' free energy for reactions (1) and (2) is about 50 kJ/mol, favoring reaction (1), or the formation of $TiAl_3$. X-ray diffraction data in Figure 2a clearly show bulk aluminum and no $TiAl_3$. We may suppose that the Ti resides in some unknown Ti-Al-H phase represented by reaction (3), or may have formed a colloid. Formation energies of Ti-Al compounds suggest that there may be Ti-Al colloids formed which require mechanical milling to remove the THF, allowing the sample to show activity.

^{27}Al MAS NMR of the solvent mixed sample of $3\,NaAlH_4+TiCl_3$ definitively shows that no $TiAl_3$ is present and indicates aluminum in bulk and possibly Al_2O_3. This is in contrast to the solvent-free mechanically milled sample, where NMR indicates that some aluminum is present in the form of $TiAl_3$, consistent with XRD measurements. This indicates a difference between the compounds formed in solvent-doped and mechanically milled samples. Proton NMR also indicates that hydrogen is present in the solvent-doped sample, but may be due to residual THF, suggesting that colloids may form as discussed above. However, a possible candidate for the Ti compound in the solvent-doped sample is TiH_2, although this would be unexpected considering the free energy of formation data in Table 1.

CONCLUSION

The formation reaction products in doped $NaAlH_4$ depend on the method of preparation. Mechanical milling and solution mixing result in different compounds. The formation of $TiAl_3$ is indicated in mechanical milling, but does not appear to form in solution mixed samples, as indicated by x-ray diffraction, and NMR. The resultant Ti is also not present in bulk crystals grown from solutions containing titanium. These results are consistent with the possibility that in solution doped samples in THF, the titanium either forms a Ti or Ti-Al colloid, which becomes an active component after mechanical milling, thus gaining the benefits of the Ti nano-particle formation from a simple procedure. Further studies are on-going to determine the effect of mechanical milling of solution-mixed samples, which may result in Ti-Al or Ti-Al-H as the active compounds.

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