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The Structures of Hydride Phases in the Ti$_3$Al/H System

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Abstract

The structures of hydride phases in the Ti$_3$Al/H system have been examined by neutron diffraction. The reason for our interest in this system is a recent report that a titanium aluminide, or its hydride, may play a possible role as dopant or catalysts in the formation of certain alkali metal aluminum hydrides that may render these complex hydrides useful as hydrogen storage materials.
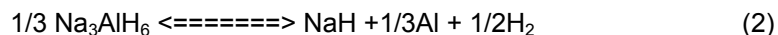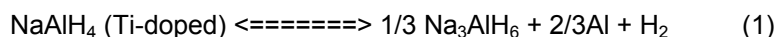
Introduction

While complex hydrides of the light elements, e.g. LiAlH$_4$, NaAlH$_4$, Na$_3$AlH$_6$, are attractive hydrogen storage materials based on their high hydrogen contents, the problems of formation from the elements and the reversible recovery of hydrogen have in the past prevented any serious consideration of these materials as candidates for practical hydrogen storage. The attention has instead been focused for the last 30 years or so on the metallic hydrides and a number of alloys suitable for storing hydrogen have been developed. While many factors such as hydrogen capacity (H/M), reversibility, thermodynamic stability, cyclic stability, activation, kinetics of absorption and desorption, volume changes, hysteresis, etc., need to be considered in developing a storage alloy, the hydrogen capacity is of prime importance in a vehicular application. The hydrogen contents of a few metal hydrides are listed in Table I and are compared to other materials. In addition to other drawbacks, the metal hydrides with high hydrogen contents, e.g. LiH, TiH$_2$, VH$_2$, MgH$_2$ and Mg$_2$NiH$_4$, are too stable and require unacceptably high temperatures to recover hydrogen. TiFeH$_2$ and LaNi$_5$H$_{67}$ do not require high temperature for hydrogen recovery, but the available content is below 2 percent. Despite extensive research efforts in the past, it has not been possible to improve appreciably on this figure. This appears to be due to several inherent properties of metal hydrides. The hydrogen capacity, H/M, depends on the electronic structure of the metal or alloy, the number of sites in the structure and the availability of these sites in view of the minimum required distance between hydrogen atoms is 0.210 nm [1] and, of course, the value of M.

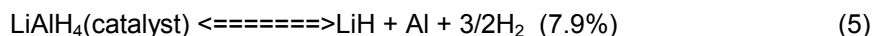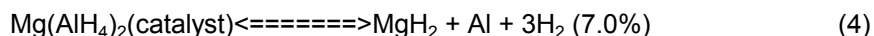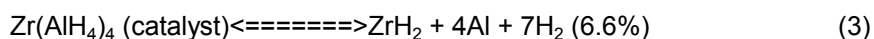### TABLE I
Hydrogen Contents of Selected Materials

Material	Weight percent H	Density (g/ml)
Liquid H$_2$	100	0.071
Water	11.2	1.00
LiH	12.7	0.80
VH$_2$	4.0	4.5
TiH$_2$	4.0	3.8
MgH$_2$	7.6	1.4
Mg$_2$NiH$_4$	3.8	2.6
LaNi$_5$H$_6$	1.5	8.25
FeTiH$_2$	1.9	5.5

Recently, Bogdanovic and Schwicardi undertook a bold, new direction into hydrogen storage materials through their investigation into Ti-doped complex hydrides of the light elements (LiAlH$_4$,

NaAlH$_4$, Na$_3$AlH$_6$) [2]. Their results suggest these compounds may indeed be potential novel reversible hydrogen storage materials when combined with certain catalysts [2] as illustrated in reactions (1) and (2)

$$NaAlH_4 \text{ (Ti-doped) } <=======> 1/3 \; Na_3AlH_6 + 2/3Al + H_2 \qquad (1)$$

$$1/3 \; Na_3AlH_6 <=======> NaH + 1/3Al + 1/2H_2 \qquad (2)$$

Reaction (1) yields 3.7 wt% hydrogen and 5.6 percent is available if the reaction proceeds through (2). The hydrogen in NaH is very tightly bound and is not recoverable in a practical storage material. Bogdanovic and Schwicardi made PVC measurements. From hydrogen dissociation measurements at 484 and 353K, the two plateau pressures corresponding to reactions (1) and (2) were extrapolated to lower temperatures by Van't Hoff plots. It was estimated that the dissociation pressure of the first plateau is 1 bar below room temperature and that the second plateau pressure reaches 1 bar between 373 and 423K [2]. These values put these materials in the categories of low and medium temperature reversible hydrides, respectively [3]. Similar reactions may be suggested for other alanates having even higher hydrogen contents:

$$Zr(AlH_4)_4 \text{ (catalyst)} <=======> ZrH_2 + 4Al + 7H_2 \; (6.6\%) \qquad (3)$$

$$Mg(AlH_4)_2 \text{(catalyst)} <=======> MgH_2 + Al + 3H_2 \; (7.0\%) \qquad (4)$$

$$LiAlH_4 \text{(catalyst) } <=======> LiH + Al + 3/2H_2 \; (7.9\%) \qquad (5)$$

The mechanism by which the dopant or catalyst works is not known, but the suggestion has been made that a titanium aluminide (or its hydride) may be involved [2].

Four titanium aluminide phases have been identified as stable at room temperature: Ti$_3$Al, TiAl, TiAl$_2$ and TiAl$_3$. Ti$_3$Al and TiAl both have large compositional existence ranges, 22 to 39 and 48 to 69.5 atomic percent Al, respectively, while TiAl$_2$ has a very narrow existence range, 65 to 68 percent Al and TiAl$_3$ is a line compound [4]. Our focus in this study is the Ti$_3$Al phase that has the hexagonal D019 structure. Based on hydrogen absorption data and x-ray studies, Rudman et al [5] reported two ternary hydride phases in the Ti$_3$Al/H system below 473K, a bcc phase for $0.4 < x < 0.5$ and a fcc phase for $x > 1$, where x refers to the hydrogen to metal ratio (H/M). The fcc phase was said to be metastable and disproportionated to give TiH$_2$ on heating above 473K. The fcc phase has been observed by others, but the existence of the bcc phase has been questioned [6]. The structure of a new hydride phase with $x = 0.25$, i.e. Ti$_3$AlH, was recently determined by neutron diffraction measurements to be of the cubic (perovskite-like) E21 type [7]. The Al atoms in this structure occupy the corners of the cube, while the Ti atoms are in the face-centered positions (cf. AgCu$_3$) and hydrogen is located at the center of the cube surrounded by a perfect octahedron of Ti atoms. We report here the structure of the metastable fcc phase and its disproportionation. X-ray and neutron diffraction techniques were used for structure analysis. Because of the much more favorable ratio of coherent to incoherent cross-section of deuterium as compared to that of hydrogen, the deuteride rather than the hydride was used in our investigation.

Experimental

Ti$_3$Al was prepared by a reactive sintering technique in which well mixed elemental powders (45 micrometers or less) of Al and Ti in the appropriate stoichiometric ratio were heated in an evacuated and sealed stainless steel container to a temperature sufficiently high to initiate the exothermic reaction between Al and Ti [8]. The sample was heated under high isostatic pressure at a rate of about 50K/min; the final temperature was 1220K, the pressure 2040 bar and the hold time one hour. After cooling to ambient temperature the steel can was removed and x-ray and neutron diffraction patterns were recorded. All samples were vacuum annealed at 1200K until

they were substantially one-phase materials, although a trace of TiAl was generally present. The samples were prepared for deuterium absorption by degassing at 725K. Next, deuterium was introduced into the system at a pressure of 9.2 bars and the temperature quickly reduced to below 473K. This temperature was then maintained while the absorption took place. The amount of deuterium absorbed was calculated from the pressure drop and the known volume of the system. The neutron diffraction patterns of the deuterium free samples were made in air. The deuterated sample, pulverized during the absorption process, was further ground to a fine powder under an argon atmosphere and transferred to a 5 mm vanadium cylinder and sealed. The powder patterns were recorded using neutron wavelengths of 0.15380 or 0.1825 nm.
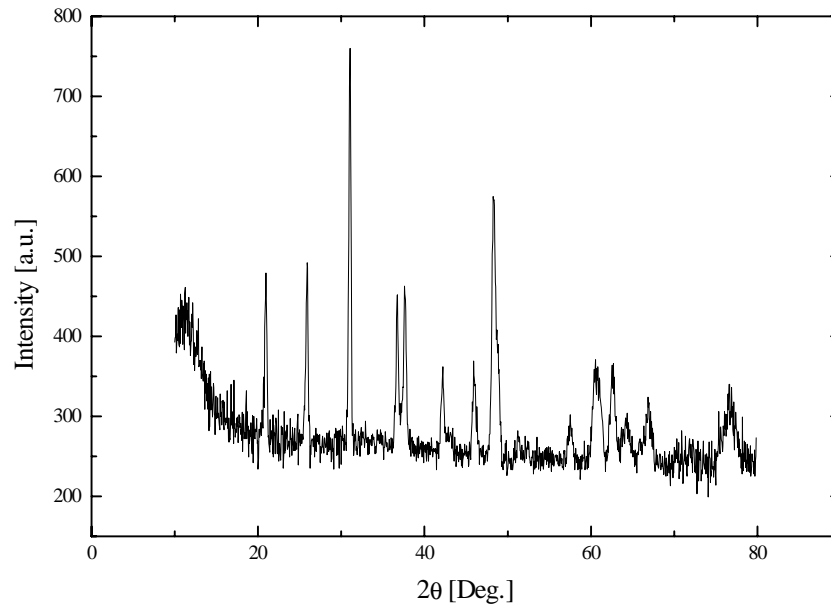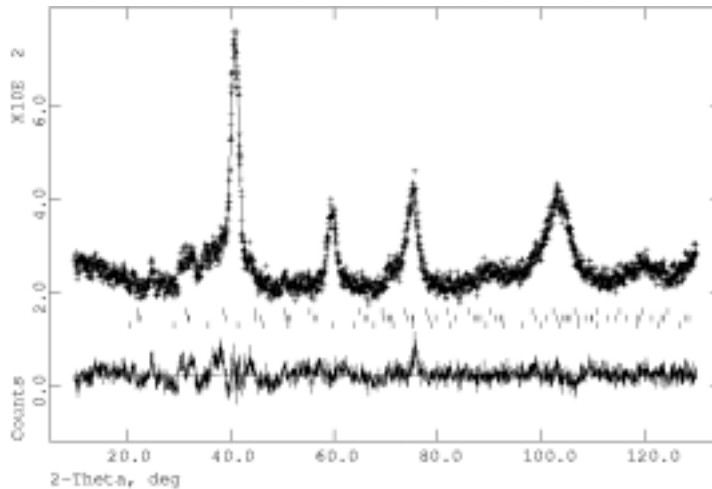

Figure 1 - Neutron diffraction diagram of the Ti$_3$Al sample, prepared by reactive sintering.

Results

X-ray diffraction patterns of filings of the as-prepared Ti$_3$Al sample showed only the Ti$_3$Al phase. The neutron diffraction pattern of the bulk (a 6 cm machined, cylindrical piece), however, revealed clearly the presence of a fair amount of TiAl as well (Figure 1). The amount of TiAl was substantially reduced following a three-day vacuum anneal at 1200K (Figure 2) and TiAl was barely discernable after an additional anneal for one week. The neutron diffraction data were analyzed using the General Structure Analysis System (GSAS) [9]. The computer program is based on the Rietveld method [10] and is capable of extracting structural information and analysis from diffraction data obtained on multiphase systems. The neutron diffraction data obtained on a deuterium free sample, prepared by the reactive sintering technique after the second anneal, was refined and the results are summarized in Table II. The result of the refinement on a deuterided sample of nominal composition Ti$_3$AlD$_{2.9}$ is also tabulated. Diffraction patterns generated from the refinements are compared to the experimentally recorded patterns in Figures 2 and 3.
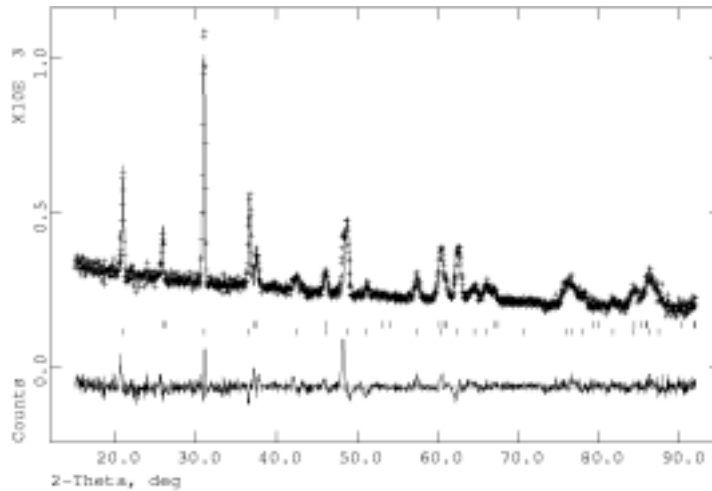
Figure 2 - Neutron diffraction diagram of Ti₃Al following three days of vacuum annealing.

Figure 3 - Neutron diffraction diagram of partially disproportionated Ti₃AlD₅.₉ (nominal composition).

Discussion

There is good agreement between the calculated and observed neutron diffraction patterns for the annealed, deuterium-free Ti₃Al samples. The decrease of the TiAl phase in the reactive sintering sample after a three day vacuum anneal is clearly seen by comparing Figures 1 and 2. By scanning the strongest TiAl peak in the neutron diffraction pattern, we estimated approximately 1-2 % TiAl in the sample following an additional week of vacuum anneal. The additional intensity in the observed pattern of the 100, 101, and 201 reflections of the reactive sintering sample may be due to preferred orientations, although the additional intensity near the 201 reflection appears to be different and may be due to a reaction intermediary. It should be noted that the intensity near the 201 peak decreased significantly during the annealing process. The refinement data for the sample (Figure 2) indicated that, in addition to a weight fraction of 91% Ti₃Al and 9% TiAl, the composition of the Ti₃Al phase was slightly titanium rich, i.e. Ti had substituted for Al on some of the Al sites. The calculated Al site occupation is 0.86 Al and 0.14 Ti. The cell parameters for the Ti₃Al phase are 0.58072 nm for (a) and 0.46582 nm for (c). The R-factor is 0.0643 (R_{wp}).
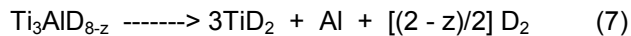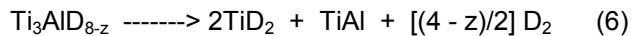
Schwartz et al. recently prepared Ti_3AlH by exposing stoichiometric Ti_3Al to hydrogen gas at 0.1MPa pressure and a temperature of 873K [7]. It is interesting to note that the resulting cubic hydride structure, in which Al occupy the corners, Ti the face-centered positions and hydrogen the center of the cube, is slightly Al-deficient and the untransformed Ti_3Al phase is Al-rich [7]. This may indicate a slow disproportionation process that ultimately leads to TiH_2 as the final product.

The higher hydride of Ti_3Al may be prepared at lower temperatures and higher hydrogen pressures [5]. This hydride, however, is metastable and disproportionates to give TiH_2 as the final product. Rudman et al [5] reported absorption isotherms from 323K to 473K and hydrogen pressures to 70 bars. Disproportionation was clearly indicated for the 473K isotherm. X-ray patterns of the metastable phase were in agreement with an fcc metal lattice [5]. Our own data is in agreement with this. Our neutron diffraction data place the hydrogen atoms in tetrahedral sites and the maximum ideal composition is thus Ti_3AlH_8. The lower and higher hydrides have the same structure of the metallic lattice, but hydrogen occupies different sites in the two structures, octahedral sites in the former and tetrahedral sites in the latter. We studied the disproportionation reaction by exposing the reactive sintering sample to 9.2 bar deuterium pressure over a two-day period. The sample temperature was held at 345K. The final nominal composition was $Ti_3AlD_{5..9}$. The neutron diffraction pattern of this sample is shown in Figure 4 and the results of the refinement of the diffraction data are listed in Table II.

TABLE II
Results of Neutron Diffraction Structure Analysis

Sample	Phases	Cell parameters(nm)	Fraction(wt.%)	R_w
Ti_3Al	Ti_3Al	a = 0.58072	91	0.0643
(D free)		c = 0.46582		
	TiAl	a = 0.40145	9	
		c = 0.40772		
$Ti_3AlD_{5.9}$	$Ti_3Al_{0.25}Ti_{0.75}D_{7.2}$	a = 0.43977	87	0.0669
	TiAl	a = 0.40145	6	
		c = 0.40772		
	Ti_3AlD	a = 0.40879	7	

The refinement of the pattern revealed several interesting features. First, a small amount of the Ti_3AlD phase is present. This is probably due to loss of deuterium from the sample during the handling, which involved temporary exposure to vacuum when going into the argon filled glove box. Second, the M/D ratio of the major phase is 7.2 and not 5.9 as the nominal composition indicated. Finally, titanium atoms have substituted for aluminum on aluminum sites in the lattice; in fact, we find titanium atoms in approximately 3/4 of the aluminum sites. This means that the phase is richer in titanium than the composition $Ti_3AlD_{7.2}$ indicates. The more accurate formulation of the phase would be $Ti_3Al_{0.25}Ti_{0.75}D_{7.2}$. If the substitution were to be carried out to completion, i.e. until all the aluminum sites were occupied by titanium, the result would be TiD_2. Our view is that Ti_3AlD_8 is metastable and nonstoichiometric with respect to deuterium content (D<8) and will dissociate at a rate that depends on the temperature. The disproportionation, if carried out to completion, is suggested to occur as in equation (6) or (7):

$$Ti_3AlD_{8-z} \text{ -------> } 2TiD_2 + TiAl + [(4 - z)/2] D_2 \quad (6)$$

$$Ti_3AlD_{8-z} \text{ -------> } 3TiD_2 + Al + [(2 - z)/2] D_2 \quad (7)$$

In the intermediary stages we would expect the precipitation of TiAl or Al from Ti_3AlD_{8-z} leading to enrichment in titanium and increase in D/M of the hydride phase as aluminum is removed from the structure. We believe the value of the lattice parameter supports this view. The value for our sample, 0.43977 nm, is less than that of TiD_2 (0.446 nm [4]), reflecting the presence of some aluminum on titanium sites in the TiD_2 lattice (atomic radius of Al is slightly smaller than that of Ti

and the D/M ratio is also less). The presence of Al on Ti sites in TiD_2 is similar to having Ti on Al sites in the Ti_3AlD_{8-z} structure. Assuming a disproportion reaction, as in (6) or (7), this should lead to an increase in the TiAl fraction of the sample or the presence of elemental aluminum. Under the conditions of deuterium absorption in our studies, the TiAl phase would not be expected to absorb appreciable amounts of deuterium and nor would elemental Al. While there is some increase in the TiAl fraction when compared to the deuterium free sample (from an estimated 1-2 percent to 6.2 percent), the increase is far from enough to account for the expected increase based on mass balance estimates. We believe the reason for this is that TiAl (or Al) formed at these low temperatures and reaction conditions is amorphous or nanocrystalline and is, therefore, not easily detected in the neutron diffraction pattern. There is, in fact, some indication of very broad, underlying intensity in the pattern suggesting that this might be the case, but further studies are needed to clarify this question.

Considering the reaction conditions, i.e. the temperature and hydrogen pressure, of reactions (1) and (2) used by Bogdanovic' and Schwicardi [2] and the disproportionation behavior described above, it is likely that the catalytic effects reported are due to titanium and not to titanium aluminide/hydride.

Conclusions

Ti_3Al reacts with hydrogen under appropriate conditions of temperature and pressure to form a hydride of composition Ti_3AlH_{8-z}. The hydride is metastable and disproportionates at relatively low temperatures. The final products of the disproportionation reaction are TiH_2 and amorphous TiAl or elemental Al. At intermediate stages the disproportionation produces an enrichment of titanium in the phase resulting from substitution of titanium on aluminum sites. The hydrogen content, H/M, simultaneously increases as the hydrogen sites become energetically more favorable due to the greater attraction of titanium for hydrogen as compared to that of aluminum.

Acknowledgement

References

[1]   Switendick, A. C. (1979), Z. Phys. Chem. NF **117**, 89.
[2]   Bogdanovic, B. and Schwicardi, M. (1997), J. Alloys and Compounds, **253-254**, 1.
[3]   Buchner, H., Energiespeicherung in Metallhydriden, Springer-Verlag, Wien, 1982.
[4]   Murray, J. L. (1987) Al-Ti (Aluminum-Titanium), in Binary Phase Diagrams of Titanium, ASM, 225.
[5]   Rudman, P. S., Reilly, J. J., and Wiswall (1978), R. H., J. Less-Common Met., **58**, 231.
[6]   Xiao, H. Z., Robertson, I. M., and Birnbaum, H. K., (1996), J. Mat. Res., **11** (9), 2186.
[7]   Schwartz, D. S., Yelon, W. B., Berliner, R. B., Lederich, R. J., and Sastry, S. M., (1991), Acta Metal. Mater., 39, no. 11, 2799.
[8]   Maeland, A. J., and Narasimhan, D. (1989), in High Temperature Ordered Intermetallics Alloys, Liu, C. T., A.I. Taub, N.S. Stoloff, N. S. and C.C. Koch, eds., Materials Research Society, **133**, Pittsburg, PA , p.723.
[9]   Larson, A. C., and Von Dreele, R. B., GSAS General Structure Analysis System, LANCE, MS-H805, Los Alamos National Laboratory, Los Alamos, NM 87545.
[10] Rietveld, H. M. (1969), J. Appl. Cryst., **2**, 65.