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Characterization of the Local Titanium Environment in Doped Sodium Aluminum Hydride using X-ray Absorption Spectroscopy

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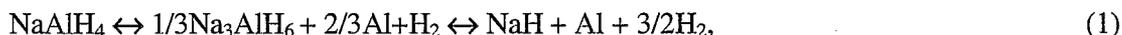
ABSTRACT

Ti *K*-edge x-ray absorption spectroscopy was used to explore the local titanium environment and valence in 2-4 mol% Ti-doped sodium alanate. An estimate of the oxidation state of the dopant, based upon known standards, revealed a zero-valent titanium atom. An analysis of the near-edge and extended fine structures indicates that the Ti does not enter substitutional or interstitial sites in the NaAlH₄ lattice. Rather, the Ti is located on/near the surface and is coordinated by 10.2±1 aluminum atoms with an interatomic distance of 2.82±0.01 Å, similar to that of TiAl₃. The Fourier transformed EXAFS spectra reveals a lack of long-range order around the Ti dopant indicating that the Ti forms nano-clusters of TiAl₃. The similarity of the spectra in the hydrided and dehydrided samples suggests that the local Ti environment is nearly invariant during hydrogen cycling.

INTRODUCTION

The demonstration of reversible hydrogen cycling in Ti-doped sodium aluminum hydride [1] has generated considerable interest in the sodium alanates. Since this discovery there has been a number of studies focused on improving the catalytic effects and understanding the role of the dopant in the sodium alanates. Despite this tremendous effort, the mechanism by which NaAlH₄ is activated in the presence of a small amount of a transition metal is still not well understood. In part, this is because the location and valence of the activating species is unknown.

The reversible decomposition of sodium aluminum hydride occurs through the following two-step reaction:



yielding a theoretical hydrogen capacity of 5.6 wt%. There are a number of possible mechanisms by which a metal dopant (e.g. Ti) might enhance the dehydriding kinetics of reaction 1, such as assisting the conversion of atomic hydrogen into molecular hydrogen at the surface. However, this situation is unlikely due to the strong thermodynamic driving force on the Ti to form a hydride in the presence of the desorbed hydrogen. Another proposed mechanism involves the substitution of the dopant into the lattice. X-ray diffraction studies of Ti and Zr-doped NaAlH₄ have revealed lattice distortions associated with doping NaAlH₄, suggesting a bulk substitution of Ti for Na [2, 3]. The enhanced kinetics is attributed to vacancy formation induced by the insertion of Ti³⁺ or Ti⁴⁺ into the lattice. Another possibility is that the hydrogen diffuses to the surface in an Al-H complex where it is dissociated by the catalyzing agent and releases H₂. This process leads to a significant coalescence of Al on the particle surface in the dehydrided state. Energy dispersive spectroscopy of Ti-doped NaAlH₄ has revealed Al segregation towards

regions of higher Ti concentration on the particle surface upon the initial dehydriding [4]. The formation of a Ti-Al alloy is also supported by x-ray diffraction studies [5, 6]. A number of recent investigations of Ti-doped NaAlH₄ using x-ray absorption spectroscopy have shown the Ti locally coordinated by Al atoms in the TiAl₃ configuration [7]. These experiments also show that the Ti is atomically dispersed in the Al, has no long-range order (i.e. amorphous) and is unaffected by hydrogen cycling [7, 8].

In this investigation, the properties of the Ti dopant in NaAlH₄ were studied using the Ti *K*-edge measured by x-ray absorption spectroscopy (XAS). The Ti valence was determined using the x-ray absorption near-edge structure (XANES) and the local environment was characterized by the extended x-ray absorption fine structure (EXAFS).

EXPERIMENTAL DETAILS

Ti-doped NaAlH₄ was prepared by mechanically milling 95 % pure NaAlH₄ (Alfa Chem. Co.) with TiCl₃ (Aldrich 99%) in a Fritsch Pulverisette 6 planetary mill. The powders (~1.2 g) were milled in a 250 mL tungsten carbide bowl using seven 15 mm diameter WC balls (~26 g each) for 1.5 h. The sample preparation and mechanical alloying was performed in an inert Ar atmosphere. Samples containing 2 mol % and 4 mol % TiCl₃ were prepared for this study. The Ti-doped materials were cycled four times through the two-steps of reaction 1 to ensure a homogenous Ti distribution. Standards of TiO, Ti₂O₃, TiO₂ (anatase + rutile), TiH₂ and Ti foil were studied as received from the manufacturer. The preparation of the TiH_{1.1}, Ti_{0.08}Al_{0.92}, Ti_{0.02}Al_{0.98}, FeTi and TiAl₃ compounds is described elsewhere [7]. All powders were sieved through 325 mesh (44 μm) and brushed onto Kapton tape, while the ductile alloys of Ti_{0.08}Al_{0.92}, Ti_{0.02}Al_{0.98} and FeTi were pressed into a thin pellet.

Ti *K*-edge spectra were collected at beamline X-19A at the National Synchrotron Radiation Light Source (NSLS) using a Si(111) double crystal monochromator. Spectra were recorded in fluorescence yield using a passivated implanted planar silicon detector for the reasonably concentrated samples and a 13-element Ge detector (Canberra) with an energy resolution of 240 eV for the diluted samples. Due to small Ti concentrations, the near-edge spectra were not corrected for "self-absorption". Additional experimental details are listed elsewhere [7]. All samples were kept at room temperature. Air sensitive samples were measured in a sealed sample holder with an Ar environment. All spectra were background subtracted and normalized to a 100 eV window, 100 eV above the edge onset.

RESULTS AND DISCUSSION

XANES

The Ti *K*-edges from a series of Ti standards are displayed in Fig. 1a. The edges from TiAl₃ and two Al samples with 2 mol% and 8 mol% Ti (Fig. 2b) are qualitatively identical. This is not surprising since Ti is immiscible in Al at room temperature and will nucleate the TiAl₃ phase even at low dopant levels [9]. The Ti *K*-edges from TiH₂ and TiH_{1.1} (Fig. 2c) are also very similar, suggesting that the structural environment around the Ti is essentially the same. The weak (less pronounced) oscillations above the edge in the substoichiometric compound (TiH_{1.1}) are indicative of a decrease in the local order with respect to TiH₂.

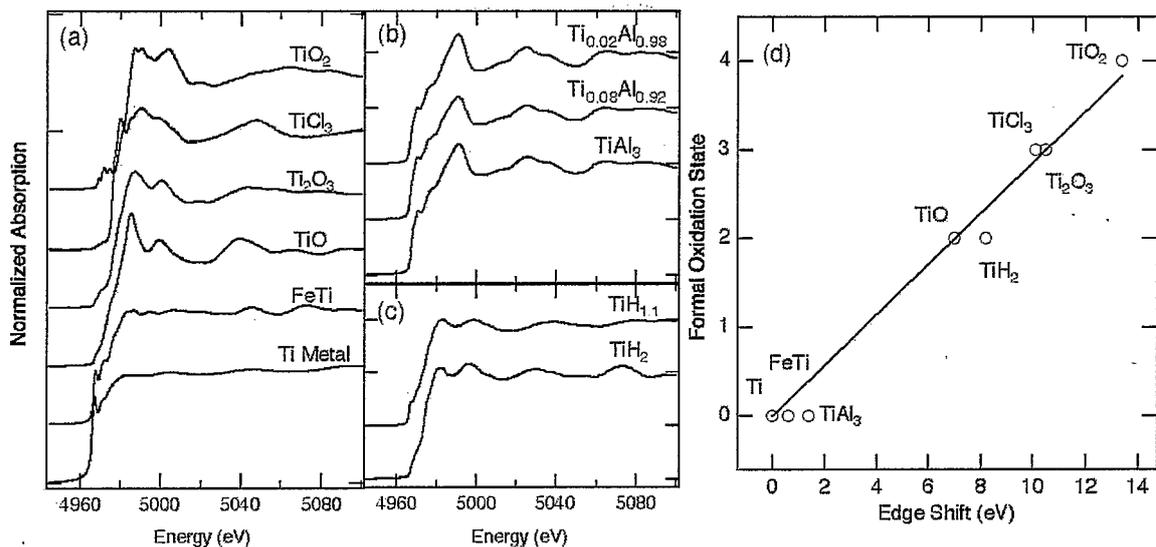


Figure 1. (a) Ti *K*-edges from Ti metal, FeTi, TiO, Ti₂O₃, TiCl₃, TiO₂, (b) TiAl₃, Ti_{0.08}Al_{0.92} and Ti_{0.02}Al_{0.98}, (c) TiH₂ and nonstoichiometric TiH_{1.1}. (d) Shift in the Ti *K*-edge onset energy with respect to the formal oxidation state in a series of Ti standards.

The most interesting features of Fig. 1 are the large chemical shifts in the Ti *K*-edge, relative to Ti metal. The shift of the Ti *K*-edge reflects changes in the binding energy of the Ti 1*s* electron. The largest observed shift is about 13 eV between Ti metal, containing neutral Ti atoms, and TiO₂, containing Ti⁴⁺. The increase in the 1*s* binding energy is due to the reduced screening of the nuclear charge as the outer electrons are pulled off the atom. A plot of the relationship between the edge onset and the Ti valence is shown in Fig. 1d. The onset of the *K*-edge was defined by the maximum of the first derivative. In cases where the peak in the first derivative was clearly split, such as TiH_{1.1}, the onset was chosen as the midpoint between the two peaks. There is a linear correlation between the oxidation state of the Ti ion, *n*, and the edge shift with respect to Ti metal, ΔE . This relationship can be expressed as: $n = c\Delta E$, with $c = 0.28 \pm 0.01$.

The edge onset energies were used to determine the Ti valence in the Ti-doped sodium alanates. The near-edge structure of the 2 and 4 mol% Ti-doped samples are shown in Fig. 2a. Figure 2b displays a plot of the Ti *K*-edge from the hydrided NaAlH₄ (2 mol% TiCl₃) and TiAl₃. In the hydrided and dehydrided compounds the Ti is essentially zero-valent (total charge transfer of half an electron, or less). Although the neutral character of the Ti valence is supported by other studies [1, 4-6, 10], this is the first direct evidence of zero-valent Ti at low dopant levels (2-4 mol%). The Ti *K*-edge of the mechanically milled material (no cycling) exhibits peaks at 4988 eV and 4998 eV (Fig. 2a). This structure may be indicative of a superposition of edges from Ti in multiple environments, the initial TiCl₃, TiH_{2-x}, and TiAl₃. The decomposition of NaAlH₄ during mechanical milling liberates Al and H₂, either of which may form a compound with Ti. Although TiAl₃ is more stable, the liberated H₂ is considerably more mobile and therefore more likely to react with Ti, forming TiH_{2-x}. It is likely that the formation of TiAl₃ predominately occurs during the first decomposition, where metallic Al is more abundant. Another interesting feature of Fig. 2a is the similarity of the hydrided and dehydrided spectra. This suggests that the local Ti

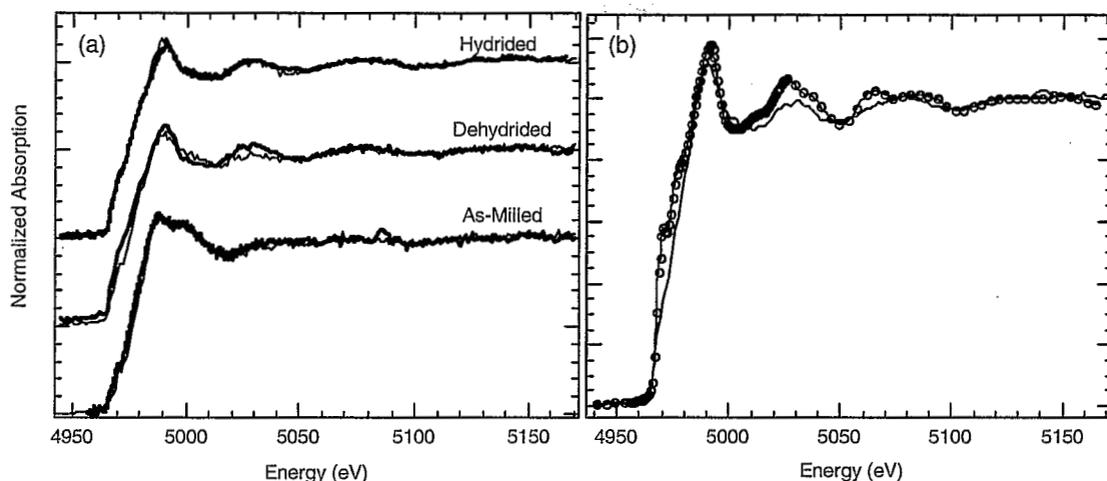


Figure 2. (a) Ti *K*-edges from sodium alanate doped with 2 mol% (—) and 4 mol% Ti (---). Edges are shown for the as-milled material (no cycling), the dehydried (NaH + Al) and the hydrided material (NaAlH₄) after four cycles. (b) Ti *K*-edges from TiAl₃ (---○) and fully hydrided NaAlH₄ with 2 mol% Ti (—).

environment is nearly invariant with hydrogen cycling (reaction 1).

EXAFS

Further insight into the local Ti environment was achieved through an analysis of the extended fine structure. Figure 2b qualitatively shows the similarity of the EXAFS oscillations from the doped alanate and TiAl₃. However, the oscillations are noticeably less pronounced in the doped alanate, signifying that the Ti may form a disordered TiAl₃ alloy. Figure 3 displays a plot of the k^2 -weighted EXAFS spectra from TiAl₃ and 2 mol% Ti-doped NaAlH₄. The standard procedures for experimental data reduction were used to obtain $k^n\chi(k)$ EXAFS spectra [11], which demonstrates good data quality up to $\sim 17 \text{ \AA}^{-1}$ and $\sim 12 \text{ \AA}^{-1}$ for TiAl₃ alloy and Ti-doped NaAlH₄, respectively. The $k^2\chi(k)$ EXAFS functions exhibit a clear similarity and are consistently in phase below 8 \AA^{-1} , indicating that the local environment of the Ti is chemically and structurally similar in the two samples.

The Fourier transform (FT) of the EXAFS signal from TiAl₃ is shown in Fig. 3b. The major peak at about 2.3 \AA is due to single scattering of the photoelectron by 12 Al nearest-neighbor atoms. $\text{FT}[k^2\chi(k)]$ does not account for a phase shift at the central and backscattering atoms and is therefore not a true pair distribution function. The more distant Ti-X (X = Ti, Al, and Ti) neighbors are evident at about 3.4, 4.4, and 5 \AA (uncorrected), though these are obscured by multiple-scattering contributions to the EXAFS signal. Contributions from Ti-Al pairs were isolated through a back Fourier transform to k space. The resulting data were then fit to two competing models and the structural parameters of the best model are summarized in Table I.

The FT of the EXAFS signal from Ti-doped NaAlH₄ (Figs. 3c) exhibits a single peak at about 2.3 \AA due to scattering from the first shell of Al neighbors. The corrected Ti-Al interatomic distance is $2.82 \pm 0.01 \text{ \AA}$ and the coordination number is 10.2 ± 1 (somewhat reduced, compared

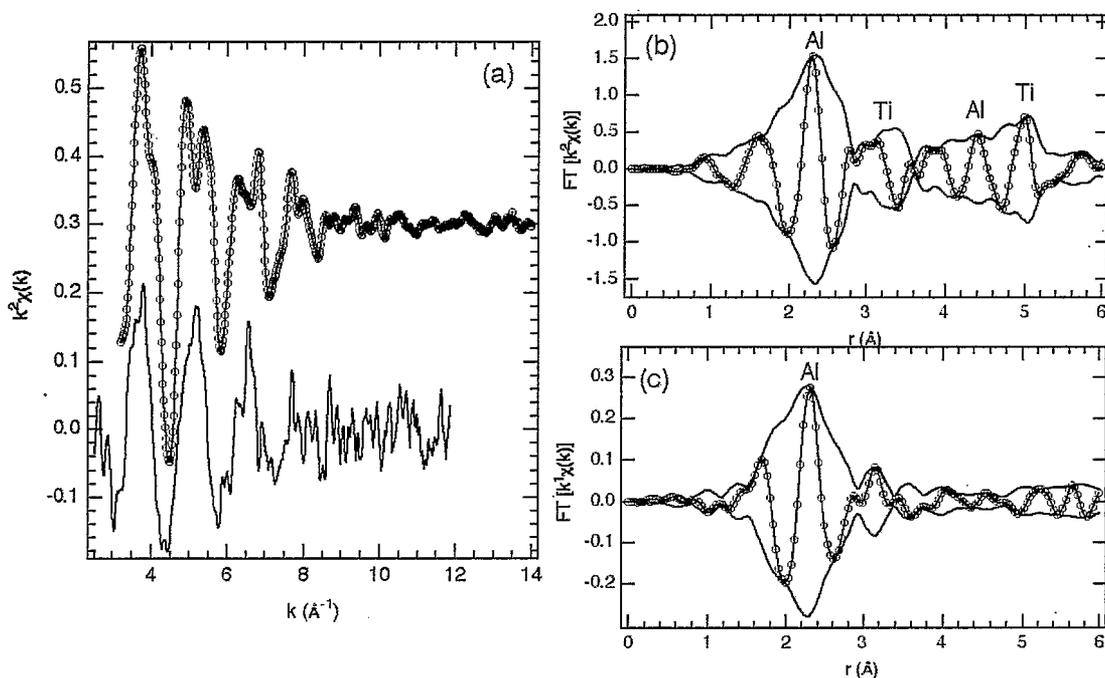


Figure 3. (a) k^2 -weighted EXAFS spectra for TiAl_3 (—o—) and 2 mol% Ti-doped NaAlH_4 (—). FT showing imaginary part (—o—) and magnitude (—) for (b) TiAl_3 and (c) 2 mol% Ti-doped NaAlH_4 .

to that in TiAl_3 alloy). The reduced coordination number may be attributed to Ti atoms located on the surface. All peaks beyond 2.3 Å are strongly suppressed indicating that the local Ti environment is disordered beyond the first Al shell. The weak peak at 3.2 Å may be assigned to a Ti-Ti shell with a coordination number of 2 or less. This is a significant reduction from the expected 4 or 6 titanium neighbors in TiAl_3 with tetragonal ($I4/mmm$) or cubic symmetry ($Pm-3m$), respectively. These results suggest that the titanium forms a Ti-Al nano-cluster consisting of only a few Ti core atoms that is located on or near the surface. The lack of long-range order and the absence of Ti-Ti neighbors is supported by other studies that demonstrate that Ti is

Table I. Local structure parameters including interatomic distance, R , and Debye-Waller factor, DW, of TiAl_3 and of 2 mol% Ti-activated NaAlH_4 (rehydrided). Best models (split shell for TiAl_3 corresponding to $I4/mmm$ structure and single shell model for Ti-doped sample) are provided.

Sample	EXAFS				Diffraction*	
	Atom	R , Å	DW / 10^{-3} , Å ²	N	R , Å	N
TiAl_3	Al ₁	2.74±0.02	3.7±0.6	3.8±0.4	2.715	4
	Al ₂	2.88±0.02	6.7±1.0	7.6±1.0	2.879	8
$\text{NaAlH}_4 + 2\% \text{ Ti}$	Al	2.82±0.01	17.7±3.1	10.2±1	-	-

* Tetragonal (space group $I4/mmm$), $a=3.840$, $c=8.5786$ Å

atomically dispersed in this system [8,12]. This also explains why long-range order experimental techniques, such as XRD, fail to identify and characterize Ti-containing phase(s) in the doped alanates.

CONCLUSIONS

The near-edge structure of the Ti *K*-edge clearly demonstrates that the Ti is zerovalent in doped sodium aluminum hydride. An analysis of the extended fine structure shows that the Ti is coordinated by a single shell of approximately 10 Al atoms. The lack of long-range order and reduced coordination numbers indicate that the Ti is atomically dispersed and forms a Ti-Al cluster on or near the surface. There is no evidence of a bulk lattice substitution. The Ti *K*-edges and EXAFS are similar in the hydrided and dehydrided states at ambient temperature and pressure, suggesting that the atomic and electronic environments around Ti are likely invariant during hydrogen cycling.

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