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Letter

Hydrogen sorption properties of intermetallic TbNiAl and crystal structure of $TbNiAlD_{1.1}$

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Abstract

Hydrogenation (deuteration) of intermetallic TbNiAl with ZrNiAl type crystal structure has been studied by differential thermal analysis and X-ray and neutron powder diffraction. The compound absorbs up to 1.4 hydrogen (deuterium) atoms per formula unit at room temperature and atmospheric pressure, and desorbs hydrogen under vacuum in a multistep reaction at about 105°C, 160°C and 320°C, and deuterium at about 190°C and 450°C. Hydrogenation (deuteration) leads to an orthorhombic distortion of the hexagonal host structure; $TbNiAlH_{1.4}$: $a(\sim c_{hex})=3.7209(7)$; $b\ (\sim a_{hex}\sqrt{3})=12.353(2)$ Å; $c\ (\sim a_{hex})=7.636(1)$ Å; $TbNiAlD_{1.1}$: $a=3.70187(8)$; $b=12.4011(3)$; $c=7.6075(2)$ Å; space group Amm2. Three sorts of deuterium sites exist of which two have aluminium in their co-ordination polyhedra: trigonal bi-pyramidal $[Tb_3Ni_2]$ (88% occupancy) and two tetrahedral $[Tb_2NiAl]$ (67% and 10% occupancy). The metal–deuterium bond distances are Tb–D=2.18–2.42 Å, Ni–D=1.50–1.90 Å, and Al–D=1.64–1.85 Å. The deuterium–deuterium contact distances are all greater than 1.98 Å.

Keywords: Metal hydride; Hydrogen sorption; Structure refinement; Neutron diffraction

1. Introduction

Equiatomic RENiAl compounds crystallizing with the hexagonal ZrNiAl structure type are known for nearly all rare earth (RE) elements [1]. Their hydrogen sorption properties were recently studied for RE=Y, Gd, Tb, Dy, Er and Lu, with a particular emphasis on the influence of hydrogenation on the magnetic properties [2]. The compounds were found to absorb hydrogen at ambient temperature and atmospheric pressure to concentrations of up to 1.2–1.6 atoms per formula unit. Their structure underwent an orthorhombic distortion and their magnetic ordering temperatures decreased strongly upon hydrogenation. In this paper we present more detailed results on the hydrogen sorption properties of the terbium member and on the crystal structure of its deuteride $TbNiAlD_{1.1}$.

2. Experimental details

A sample of equiatomic composition TbNiAl was prepared from a mixture of elemental terbium (purity 99.8%), nickel (99.9%) and aluminium (99.9%) by arc melting in an argon atmosphere. The ingots were remelted several times to increase their homogeneity, but were not annealed. X-ray powder diffraction (Philips PW 1012/10 and Huber Guinier diffractometers, CuKα radiation) confirmed the formation of a ternary phase with hexagonal

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ZrNiAl type structure and refined cell parameters a=6.999(1) and c=3.879(2) Å, and traces of an unidentified impurity phase. After activation under vacuum at 300°C during about one hour, parts of the sample were hydrogenated (deuterated) at room-temperature and ambient pressure (hydrogen purity greater than 99.99%, deuterium isotope purity 99.8%) to a maximum concentration of H(D)/TbNiAl=1.40(±0.05) as measured volumetrically by monitoring pressure changes in a calibrated volume. The reaction started after a short incubation period and was completed within 60 min. Samples having lower hydrogen (deuterium) contents were obtained by step-to-step desorption from the saturated hydride (deuteride) in vacuum. After complete desorption, further hydrogenation (deuteration) proceeded immediately after gas admission into the reaction chamber. The thermal stability of the samples was studied by Hydrogen Differential Thermal Analysis (HDTA) at a constant heating rate of 5°C min^{-1}. Results on the hydride are represented in Fig. 1. Further details of the technique used can be consulted in [3].

The crystal structure analysis was performed on a deuteride sample of composition $\mathrm{TbNiAlD_{1.1}}$ by neutron powder diffraction on the High Resolution Neutron Powder Diffractometer [4] at the High Flux Beam Reactor at Brookhaven National Laboratory (focusing Ge(511) monochromator; λ=1.8857 Å; $2\theta_{\mathrm{max}}$=155°; $\Delta 2\theta$=0.05°; T=20°C; sample mass 7 g; cylindrical vanadium container of 9 mm inner diameter). The General Structure Analysis System [5], FullProf program [6] and Crystal Structure Determination software [7] were used for the structure refinements. Nuclear scattering lengths of Tb, Ni, Al and D were taken from [8]. The structure was described in orthorhombic space group Amm2 (No. 38) by placing the metal atoms on positions as derived from the hexagonal ZrNiAl structure type (space group P$\bar{6}$2m), and deuterium on various interstitial sites. Refinement results are presented in Table 1, and a comparison between the observed, calculated and difference neutron diffraction patterns is shown in Fig. 2.

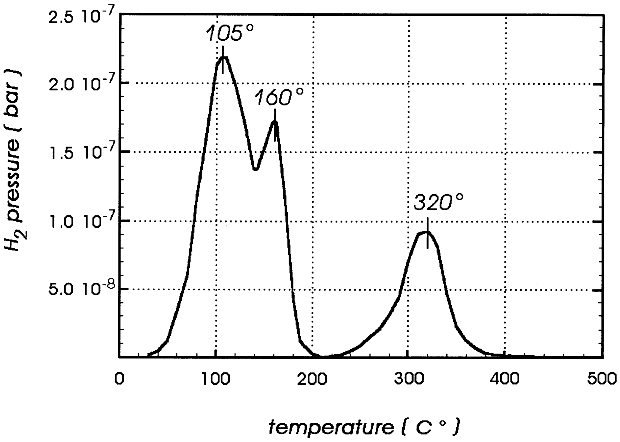

Fig. 1. HDTA traces of vacuum desorption for $\mathrm{TbNiAlH_{1.4}}$.

Table 1
Structure refinement results on neutron powder diffraction data for $\mathrm{TbNiAlD_{1.1}}$ (T=20°C; estimated standard deviations in parentheses)

Atom	Site	x	y	z	Site occupancies	U_{iso} ($\times 10^{-2}$ Å^2)
Tb1	4e	1/2	0.2092(4)	0.031(2)	1	1.4(1)
Tb2	2b	1/2	0	0.639(2)	1	1.5(2)
Ni1	4d	0	0.3319(3)	0.261(2)	1	1.71(9)
Ni2	2b	1/2	0	0.236(2)	1	2.3(1)
Al1	4d	0	0.1181(8)	0.323(2)	1	1.3(2)
Al2	2a	0	0	0.0000(–)	1	2.7(4)
D1	4e	1/2	0.3343(5)	0.251(2)	0.877(8)	2.8(1)
D2	4d	0	0.3821(6)	0.067(2)	0.674(9)	2.8(1)
D3	4d	0	0.2414(10)	0.402(3)	0.10(1)	2.8(1)

Space group Amm2 (No. 38); cell parameters: a=3.70187(8); b=12.4011(3); c=7.6075(2) Å; V=349.24(1) Å^3; Z=6; R_{p}=0.041; R_{wp}=0.054; χ^2=1.38; temperature factors of D1, D2 and D3 constrained to be equal.

3. Results and discussion

3.1. Lattice expansion and thermal stability

Hydrogenation (deuteration) of hexagonal TbNiAl leads to a lattice contraction along c_{hex} and a rather strong orthorhombic lattice distortion ($\mathrm{TbNiAlH_{1.4}}$: a ($\sim c_{\mathrm{hex}}$)=3.7209(7); b ($\sim a_{\mathrm{hex}}\sqrt{3}$)=12.353(2); c ($\sim a_{\mathrm{hex}}$)=7.636(1) Å; $\Delta a/c_{\mathrm{hex}}$=−4.1%, $\Delta c/a_{\mathrm{hex}}$=9.1%; orthorhombic distortion b/c=0.934$\sqrt{3}$; total volume expansion $\Delta V/V$=6.6%). The volume increment (2.6 Å^3/H atom) is close to that observed in other metal hydride structures [9]. Partial desorption from the saturated deuteride results in a compound of composition $\mathrm{TbNiAlD_{1.1}}$ with cell parameters a=3.70187(8), b=12.4011(3), c=7.6075(2) Å. As expected, its orthorhombic lattice distortion (b/c=0.941$\sqrt{3}$) and volume expansion ($\Delta V/V$=6.1%) are smaller than for the more saturated hydride. Further desorption leads to a deuteride of composition $\mathrm{TbNiAlD_{0.85}}$ (a=3.8038(1); b=12.4468(4); c=7.2647(4) Å) which has a still smaller orthorhombic lattice distortion (b/c=0.989$\sqrt{3}$) and volume expansion ($\Delta V/V$=4.5%).

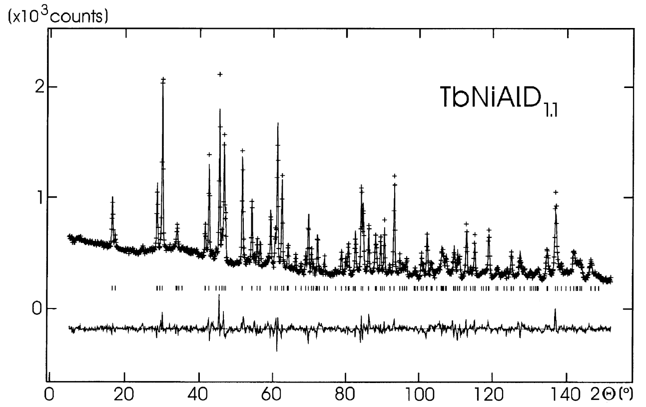

Fig. 2. Observed (+), calculated (line at top) and difference (line at bottom) neutron diffraction patterns of $\mathrm{TbNiAlD_{1.1}}$.

Desorption from the hydride occurs in several steps and starts under vacuum slightly above room temperature (Fig. 1). Three well resolved HDTA peaks occur, whose intensity decreases with increasing temperature. The first and most pronounced peak occurs at 105°C, while the others occur at 160°C and 320°C. Desorption is completed at 400°C with a recovery of hexagonal cell parameters (a=7.001(1) and c=3.880(1) Å) close to those of the intermetallic compound. When hydrogen desorption is interrupted at 220°C, i.e. at the point where the second desorption effect is completed, a lower hydride with H/TbNiAl=0.4 is obtained. Its lattice has hexagonal symmetry (a=7.034(1), c=3.897(1) Å) and shows an nearly isotropic lattice expansion by about 0.5% ($\Delta V/V$=1.5%, volume increment 2.0 Å^3/H atom) as compared to intermetallic TbNiAl.

The HDTA desorption traces of the deuterides TbNiAlD$_{1.1}$ and TbNiAlD$_{0.85}$ (not shown here) differ from that of the hydride mainly with respect to the higher onset temperatures (>90°C), the occurrence of two resolved peaks (instead of three) which are shifted to higher temperatures (>190°C and 450°C, respectively), and the higher temperature (>500°C) at which desorption is completed. All this suggests that the deuteride is thermally more stable than the hydride.

3.2. Crystal structure of the deuteride TbNiAlD$_{1.1}$

The structure of TbNiAlD$_{1.1}$ is shown in Fig. 3. It contains three partially occupied deuterium sites of which one (D1) has trigonal bi-pyramidal co-ordination [Tb$_3$Ni$_2$] with an occupancy of 88%, and two (D2, D3) have tetrahedral co-ordinations [Tb$_2$NiAl] with occupancies of 67% (D2) and 10% (D3). A fourth, tetrahedrally coordinated, site [Tb$_2$Al$_2$] near $x,y,z=\frac{1}{2}$, 0.13, 0.44 was initially considered to be partially filled, but later found to be empty. Notice that two of the occupied sites (D2, D3) have aluminium in their co-ordination sphere, and that none of these sites is co-ordinated by Ni2 and Al2.

The metal–deuterium bond distances are Tb–D=2.18–2.42 Å; Ni–D=1.55–1.85 Å; Al–D=1.64–1.85 Å (Table 2). They fit well into the expected range for ternary metal hydride structures [9] and are consistent with those in another ternary deuteride of the Tb–Ni–Al system, i.e. Tb$_3$Ni$_6$Al$_2$D$_{6.7}$ (Tb–D=2.18–2.23 Å; Ni–D=1.60–1.69 Å; Al–D=1.88 Å [10]). As to the unusually short Al–D distance of 1.64 Å (binary AlD$_3$: Al–D=1.72 Å [11]) it is presumably biased by the low deuterium occupancy of the site involved (D3, 10%). All deuterium–deuterium contact distances are greater than 1.98 Å.

Other known ternary metal deuterides with ZrNiAl type (or derivative) metal substructure are hexagonal ZrNiAlD$_{0.57}$ [12] and Zr$_6$FeAl$_2$D$_{10}$ [13]. Both contain aluminium as a p-element which is thought to ‘block’ hydrogen insertion into the metal interstices [14]. The deuterium atoms in these structures indeed appear to avoid aluminium as they occupy only trigonal bi-pyramidal sites [Zr$_3$Ni$_2$] (ZrNiAlD$_{0.57}$) or [Zr$_3$Fe$_2$] (Zr$_6$FeAl$_2$D$_{10}$), and tetrahedral sites [Zr$_3$Fe] and [Zr$_4$] (Zr$_6$FeAl$_2$D$_{10}$). This is no longer true in the presently studied TbNiAlD$_{1.1}$, in which deuterium occupies two types of tetrahedral sites [Tb$_2$NiAl] which are partially co-ordinated by aluminium.

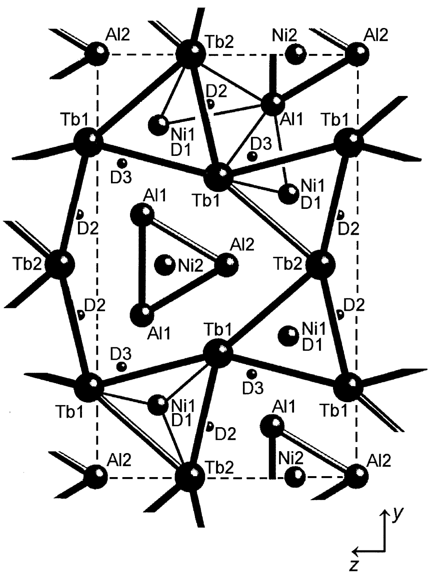

Fig. 3. Structure of orthorhombic TbNiAlD$_{1.1}$ viewed along [100]; atom layers at $x=0$ contain Ni1, Al1, Al2, D2, D3, and at $x=\frac{1}{2}$ Tb1, Tb2, Ni2, D1; the sites Ni1 and D1 overlap; thick lines: trigonal metal prisms, thin lines: co-ordination polyhedra of deuterium sites.

Table 2

Metal–deuterium bond distances and deuterium–deuterium contact distances (Å) in TbNiAlD$_{1.1}$

Tb1–D1	2.281(8)
–D1	2.20(1)
–2D3	2.18(1)
Tb2–2D1	2.224(8)
–4D2	2.421(6)
Ni1–2D1	1.8530(4)
–D2	1.604(9)
Al1–D2	1.86(1)
–D3	1.64(1)
D1–Tb1	2.281(8)
–Tb1	2.20(1)
–Tb2	2.224(8)
–2Ni1	1.8530(4)
–2D2	2.393(7)
D2–2Tb2	2.421(6)
–Ni1	1.604(9)
–Al1	1.86(1)
–2D1	2.393(7)
–D3	1.98(1)
D3–2Tb1	2.18(1)
–Ni1	1.55(1)
–Al1	1.64(1)
–D2	1.98(1)

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