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Local metal and deuterium ordering in the deuterated ZrTiNi C14 Laves phase

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Abstract

Local structure of the hexagonal C14 Laves phase in an annealed approximately equiatomic ZrTiNi alloy was studied before and after deuteration using neutron total scattering. Rietveld refinements of the $P6_3/mmc$ AB_2 model demonstrate that the A-sites are shared by Zr and Ti, whereas the two non-equivalent B-sites are occupied by a mixture of Ti and Ni. Reverse Monte Carlo refinements using a joint fit of the neutron total scattering data in real and reciprocal spaces revealed significant short-range ordering of Ti and Ni on the B-sites. The refined Ti–Ni nearest-neighbor distances are appreciably shorter than the corresponding Ti–Ti and Ni–Ni distances. Nevertheless, the differences in the effective sizes of chemically distinct tetrahedral interstices (i.e. $[Zr_2Ti_2]$, $[Zr_2TiNi]$, $[Zr_2Ni_2]$, etc.), which are important for hydrogen absorption, remain rather small. Rietveld refinements of the structure of the deuterated sample $TiZrNiD_{2.14}$ confirmed that deuterium occupies various $[A_2B_2]$ tetrahedral interstices. RMC refinements suggested a strong preferential occupation of deuterium in the $[Zr_2Ti_2]$ and $[Zr_2TiNi]$ tetrahedra whereas the $[Zr_2Ni_2]$ sites remained nearly empty. These results support earlier models which predicted preferential occupancy by hydrogen in sites coordinated by metals that form the most stable binary hydrides. The deuterium atoms in the $[Zr_2TiNi]$ tetrahedra are displaced toward Ni. X-ray absorption near-edge structure measured for Ti, Zr, and Ni K-edges demonstrated that deuteration is accompanied by the reduction in the density of unoccupied electronic states (just above the Fermi level) associated with Ti and Zr.
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Keywords: Hydrogen storage; Laves phases; Neutron diffraction

1. Introduction

Innovation in battery technology is required to realize vehicle electrification goals [1]. Nickel–metal hydride (NiMH) batteries, which store hydrogen in a solid hydride phase, are currently used in most hybrid vehicles and provide reliable and safe performance [2]. With the development of new electrodes, NiMH batteries may become competitive with the energy densities of lithium-ion batteries. Materials considered for advanced negative electrodes are based on multi-component Laves- or body-centered-cubic (bcc)-type crystal structures and store hydrogen reversibly by filling interstitial tetrahedral sites [2]. Optimization of their performance is critically dependent on precise understanding of crystal chemistry and the energetics of populating these interstitial positions.

Laves phases AB_2 commonly crystallize with either cubic C15 ($MgCu_2$-type, space group $Fd\bar{3}m$) or hexagonal C14 ($MgZn_2$ type, $P6_3/mmc$) structures [3], which represent 3C and 2H polytypes, respectively, of tetrahedral closed-packed Frank–Kasper structures having a common slab composed of triangular and Kagomé layers. Laves phases absorb hydrogen in the tetrahedrally coordinated interstices; both structural types feature a total of 17 interstices per AB_2 formula [4,5]. The interstices are only partially populated and the number of absorbed hydrogen atoms rarely exceeds 5 (maximum 7) per AB_2 formula unit [5]. Both C15 and C14 (Fig. 1) binary Laves phases contain three chemically distinct types of tetrahedral sites available

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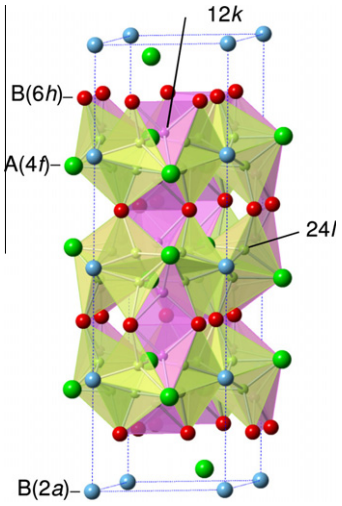

Fig. 1. A schematic drawing of the C14 structure. Metal A and B sites are indicated. The two $[A_2B_2]$ tetrahedral sites 24*l* and 12*k* that are preferentially occupied by hydrogen are indicated using polyhedra of different color. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

for hydrogen: $[B_4]$ (×1), $[AB_3]$ (×4), and $[A_2B_2]$ (×12). Most studies of hydrogenated Laves phases converge on the preference of hydrogen to occupy larger $[A_2B_2]$ sites followed by occupancy of $[AB_3]$ interstices, whereas the smallest $[B_4]$ tetrahedra typically remain empty [5]. The distances between the centers of face-sharing tetrahedra (<1.5 Å) are believed to be too short for hydrogen atoms to populate both neighboring sites; these restrictions constrain possible hydrogen distributions. Earlier theoretical calculations [6] suggested that H–H distances shorter than 2.1 Å are unfavorable because of H–H electrostatic repulsion (the so-called Switendick criterion). More recent experimental studies using nuclear magnetic resonance reported violations of this criterion in some hydrides, since H–H distances of ≈1.5 Å have been observed [7,8]; in Laves phases, these distances would correspond to H occupancy in nearest edge-sharing $[A_2B_2]$ interstices.

Commercial Laves-phase alloys designed for negative electrodes in NiMH batteries are typically multi-component systems with several species mixed on both A (Zr, Ti) and B (Ti, V, Cr, Mn, Ni) sites [2]. Rietveld refinements of the structures of several ternary Laves structures did not detect long-range order for the metal atoms, whereas analyses of deuterated samples confirmed a preference for D to occupy the $[A_2B_2]$ interstices [9]. However, average-structure refinements provide no information on the distribution of hydrogen over chemically distinct tetrahedra (e.g. $[A_2B'_2]$, $[A_2B''_2]$ or $[A_2B'B'']$ in the $A(B', B'')_2$ phase) or on the local distortions associated with hydrogen occupancy; yet, such detailed knowledge is critical for optimizing alloy compositions. Measurements of X-ray/neutron total scattering enable simultaneous determination of local and average atomic structures and therefore, in principle, can address this problem. Recently, applications of neutron total scattering to local-structure determination in several metal hydrides have been reported [10–12], providing important, hitherto inaccessible, information on local hydrogen occupancies. Previous total scattering studies of hydrogenated Laves phases have been limited to C15-type $ZrCr_2D_4$, which features a single chemical type of $[A_2B_2]$ tetrahedra (i.e. $[Zr_2Cr_2]$) preferentially occupied by deuterium [12]. In the present study we combined determination of the average structure with analyses of a real-space pair-distribution function (PDF) obtained from the total neutron scattering to determine local structure in a Zr–Ti–Ni C14 Laves phase. This ternary system was selected because it yields approximately single-phase C14 samples near the equiatomic ZrTiNi composition, contains transition B-site metals (i.e. Ti and Ni) that exhibit different hydrogen affinities as well as dissimilar neutron scattering lengths ($b_{Ti} = -3.37$ fm, $b_{Ni} = 10.3$ fm), and displays appreciable hydrogen absorption at elevated temperatures/pressure with slow desorption at ambient conditions. This combination of characteristics was expected to facilitate detection of short-range metal and hydrogen ordering, if present.

2. Experimental

2.1. Sample preparation and initial characterization

An alloy ingot of nominal composition 38.7 Ti:33.3 Ni:28.0 Zr (at.%), hereafter referred to as ZrTiNi, was prepared by arc melting pure Ti, Zr and Ni on a water-cooled copper hearth under a high-purity argon atmosphere. The ingot was melted three times to ensure sample homogeneity. The as-cast alloy was vacuum-sealed in a quartz tube (7×10^{-6} Pa) filled with a helium gas. The sealed sample was annealed at 1073 K for 120 h. The overall composition of the annealed alloy was determined using inductively coupled plasma (ICP) measurements (Table 1). Imaging of the sample using back-scattered electrons in a scanning electron microscope (SEM) revealed the presence of primary (matrix) and secondary (inclusions) phases. Energy-dispersive X-ray spectroscopy (EDS) measurements, calibrated using the results of the ICP analyses, demonstrated that both phases exhibit similar elemental compositions (Table 1). EDS confirmed homogeneous distributions of constituent elements within the primary and secondary

Table 1
Results of compositional measurements (at.%) for the annealed ZrTiNi alloy. The EDS measurements were calibrated using the total composition determined from the ICP analyses. Numbers in parentheses refer to a single standard deviation in the measured concentrations. The concentrations and their standard deviations reported for the primary and secondary phases were obtained from the EDS measurements at 20 distinct locations within each phase.

Composition	Zr	Ti	Ni
Total (ICP)	27.9(1)	38.3(1)	33.7(1)
Total (EDS)	27.80(7)	38.33(7)	33.66(9)
Primary phase	27.79(6)	38.30(5)	33.91(7)
Secondary phase	26.6(2)	41.7(2)	31.76(5)