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Neutron diffraction study of atomic bonding properties in the hydrogen-absorbing $Zr(Al_xFe_{1-x})_2$ system

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Abstract

Powder neutron diffraction of $Zr(Al_xFe_{1-x})_2$ intermetallics (x=0–1) has been performed at room temperature in an attempt to study the variation of their bonding properties as a function of x. The Debye–Waller factors indicate a minimum of the bonding strength for both the Zr and the Fe/Al sites in the $Zr(Al_xFe_{1-x})_2$ compounds at x=0.2. A similar minimum has also been observed by other experimental techniques, and it corresponds to the maximum hydrogen absorption in the above intermetallic system.

Keywords: Laves phase; Crystal structure; Debye–Waller factor

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1. Introduction

The purpose of the present research is to study the Zr and Fe/A1 atomic bonding strengths across the $Zr(Al_xFe_{1-x})_2$ series by high-resolution neutron diffraction. The Laves phase $Zr(Al_xFe_{1-x})_2$ compounds exhibit an interesting hydrogen-absorbing behavior. $ZrFe_2$ and $ZrAl_2$ do not practically absorb hydrogen while there is a maximum in the hydrogen capacity of the Zr $(Al_xFe_{1-x})_2$ system at intermediate x values [1]. The hydride stability increases at the same time monotonically with x. We shall refer to such systems as ‘‘anomalous’’ (a term coined by Gachneidner [2] in the present context) with regard to their hydrogen sorption properties. The maximum hydrogen absorption capacity of the $Zr(Al_xFe_{1-x})_2$ system at x=0.2 was found to coincide with the minimum bonding strength of the Fe atoms as determined by Mössbauer spectroscopy [3] and nuclear resonant photon scattering (NRPS) [4]. No information about the variation of the Zr cohesion across the above series has been reported so far. The results regarding the atomic stiffness in the Fe/Al substitutional sites may be compared with the Fe bonding strength derived from NRPS [4] and Mössbauer measurements [3].

2. Experimental details

The $Zr(Al_xFe_{1-x})_2$ (x = 0, 0.083, 0.2, 0.5 and 1) compounds were prepared in an arc furnace under argon atmosphere by melting the weighted fractions of the pure (99.9% or better) metals on a water-cooled copper hearth. The quality of the samples was checked by X-ray diffraction and by preliminary neutron diffraction experiments at the Nuclear Research Center-Negev (NRCN). Good, single-phased samples, weighing 10–15 grams, were utilized for neutron diffraction measurements at the DN5 diffractometer of the Siloe reactor, Centre d’Etudes Nucléaires, Grenoble. Each investigated compound was crushed to powder and introduced into a cylindric sample holder accommodating about 2 cm^3 of material. One very weak line in the $ZrAl_2$ diffractogram did not vanish despite long thermal treatments applied to the $ZrAl_2$ sample. We attribute this line to the presence of small quantities of Zr_2Al_5· A neutron wavelength of 1.341 Å was used as a compromise between a good angular resolution and a wide angular scan. The diffracted neutron beam from each sample was recorded for about 5 h by a BF_3 multidetector system, accumulating simultaneously 800 points within the 2θ range of 80°.

3. Results and analysis

The normal width or the diffraction lines enables the use

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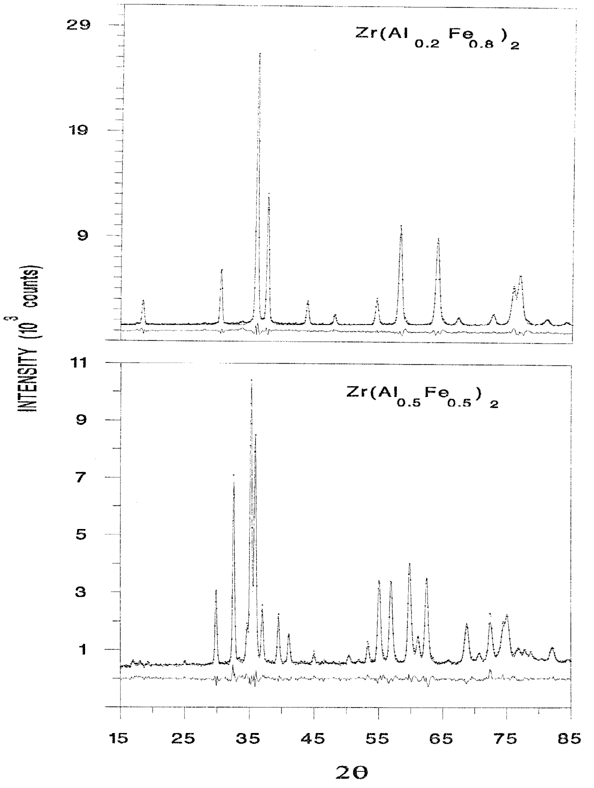

Fig. 1. The observed (points) and calculated (line) powder neutron diffraction patterns of the cubic $Zr(Al_{0.2}Fe_{0.8})_2$ and the hexagonal $Zr(Al_{0.5}Fe_{0.5})_2$ compounds. The difference between the two patterns is shown in the lower part of each diagram.

of the modified Rietveld profile analysis [5], for which the FULLPROF program [6] was utilized. Fig. 1 presents typical diffraction patterns of cubic ($x \leq 0.2$) and hexagonal ($x > 0.25$) Laves phase structures, respectively. The good agreement between the observed and the calculated patterns confirms the high quality of the samples. Isotropic displacement factors, B, were derived from the profile refinements (Table 1) by utilizing the angular dependence, e^{-2W}, of the nuclear diffraction peaks, where $W = B(\sin\theta/\lambda)^2$. For completeness, all the other derived structural parameters are presented in Table 1. They are in good agreement with data published previously by other investigators, e.g. [1,7,8].

Each crystallographic site is characterized by a single B value. For simplicity, one B value was assigned to the (Fe, Al) atoms even when these atoms occupy more than one site. The Debye temperatures, θ_D, of the Zr and the (Fe, Al) atoms were derived from the B factors by assuming the Debye approximation [9]:

$$B = \frac{3h^2}{2mk\theta_D}\left[1 + 4\left(\frac{T}{\theta_D}\right)^2 \int_0^{\frac{\theta_D}{T}} \frac{x}{e^x - 1}\,dx\right]$$

The above equation was solved for θ_D by numeric methods. This is the first time, to the best of our knowledge, that the Zr bonding properties of the $Zr(Al_xFe_{1-x})_2$ have been monitored as a function of x. The variation of the Zr and (Fe, Al) Debye temperatures (Fig. 2) clearly indicates a decreased bonding strength at $x = 0.2$ for both sites. Such a feature has been previously observed for the Fe atoms by Mössbauer spectroscopy [3] and NRPS [4]. The present results support further the notion of the rule of the reverse capacity [4] in the $Zr(Al_xFe_{1-x})_2$ and other similar systems. This rule states that softening of the metal lattice may result in increase of the hydrogen absorption capacity in certain intermetallic compounds and vice versa. On the other hand, bulk measurements of the heats of formation [10] of the $Zr(Al_xFe_{1-x})_2$ did not show any special features in the vicinity of $x = 0.2$, and increased

Table 1
Refined crystallographic data for the intermetallic compounds $Zr(Al_xFe_{1-x})_2$ at room temperature

x	0	0.083	0.2	0.5	1
Space group	Fd3m (227)	Fd3m (227)	Fd3m (227)	$P6_3$/mmc (194)	$P6_3$/mmc (194)
Structure type	C15	C15	C15	C14	C14
Lattice constants (Å)	7.0721(4)	7.0899(4)	7.1271(4)	5.1446(7) 8.3636(7)	5.281(1) 8.742(1)
Zr position	8a (1/8, 1/8, 1/8)			4f (1/3, 2/3, z)	
Zr coordinates				$z = 0.0621(3)$	$z = 0.0653(3)$
Zr occupation	1				
B_{zr} (Å^2)	0.46(6)	0.49(6)	0.92(5)	0.72(6)	0.54(8)
θ_D (Zr)	290(10)	279(11)	202(6)	230(9)	266(13)
(Al, Fe) position	16d (1/2, 1/2, 1/2)			2a (0, 0, 0), 6h (y, 2y, 1/4)	
(Al, Fe) coordinates				$y = 0.831$	$y = 0.828(1)$
(Al, Fe) occupation	1			Random occupation	
$B_{Al, Fe}$ (Å^2)	0.44(4)	0.41(4)	0.60(3)	0.65(5)	0.82(8)
θ_D (Al, Fe)	378(13)	403(15)	342(9)	362(11)	401(16)
M_{Fe} (μ_B)	1.72(6) (1.60, 630 K[a])	1.69(6) (1.46, 540 K[a])	–[b] (1.12, 340 K[a])	–	–
Reliability Factor (%)	2.85	2.33	3.50	3.28	5.1
Magnetic R-factor	3.97	3.13	–	–	–

[a] These values for the iron magnetic moments and magnetic transition temperatures, respectively, are derived from bulk magnetic measurements (Ref. [7])

[b] A better agreement of the neutron results is obtained for a non-magnetic phase. We attribute this to the proximity of the magnetic transition temperature to the room temperature at which the neutron measurements were carried out.

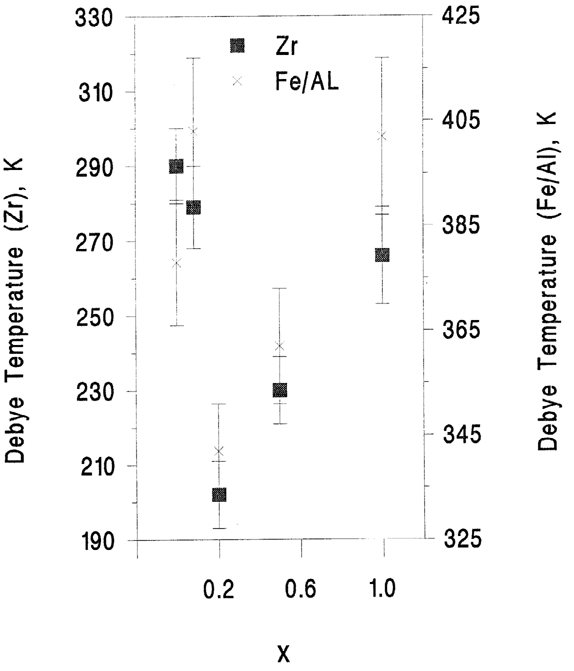

Fig. 2. The Debye temperatures at the Zr and the Fe/Al sites in the $Zr(Al_xFe_{1-x})_2$ system as a function of x.

monotonically with x. The elastic constants [11] showed some characteristic behavior around $x=0.2$, but its nature is not completely understood. Kinetic hydrogenation results [12] of $Zr(Al_xFe_{1-x})_2$, $x=0.2$, 0.5 indicated a significant increase of the activation energy for the hydriding process with the increase of the Al content. It is of interest to investigate further these anomalous systems as an understanding of their distinct hydriding behavior may have implications in two different and important directions: 1. It may indicate ways for protecting metal alloys against hydrogen corrosion. 2. It may indicate ways for enhancement of the hydrogen absorption in certain intermetallics.

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