HYDROGEN ABSORPTION IN THE Zr-AI SYSTEM

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Summary

A series of Zr–Al alloys has been prepared and the reaction with hydrogen studied by microbalance thermogravimetric analysis and differential thermal analysis. Their geometric and electronic structures have been studied by X-ray powder diffraction, X-ray photoelectron spectroscopy (XPS) and ion scattering spectroscopy (ISS). General tendencies related to increasing overall aluminium content in the alloys transcend any structural differences of different phases for the initiation of hydriding and for hydrogen solubility. The phenomena can be explained by the negative charge transfer from zirconium to aluminium resulting in a greater repulsion for hydrogen atoms by aluminium, and by the surface enrichment of zirconium though segregation observed in XPS and ISS analyses.

1. Introduction

The reactions of hydrogen with some M_5X_3 phase compounds of the transition metals and p elements, such as rare earth silicides and zirconium aluminides, have recently been investigated. The properties of these compounds as potential hydrogen storage materials and some basic generalizations for prediction of the interstitial site preference for hydrogen occupancy of these compounds have been established [1–4]. In general, however, the reactions of hydrogen with alloys of transition metals and the p elements have been relatively unknown, and the characteristics and properties of the products therefore have not been well defined [5]. Therefore, from the standpoint of both understanding further the properties of these materials and proving or completing the supposed generalizations, further studies in this field are warranted, especially on some systems which have not been studied systematically.

The Zr-Al alloy system appears to be an ideal system for a systematic study of the reaction of hydrogen with alloys of a transition metal with one of the p elements. The system contains a series of compounds with similar compositions but different structures and provides an opportunity to establish the importance of local geometric considerations relative to longer range geometric and electronic factors implicit in the crystal structures. This work expands the investigation of the hydriding behaviour of M_5X_3 compounds to the whole Zr-Al system. Although some Zr-Al alloys are known to absorb hydrogen under appropriate conditions [4,6], the whole system has not been thoroughly investigated. In the periodic table, aluminium is on the border between the transition metals and the p elements, and is an extreme case of a relatively electropositive metallic element acting as a p element. However zirconium is a typical transition metal which is electropositive and can form stable binary hydrides. Therefore, the studies of this system should give a significant insight into the boundary between transition elements and p elements. Aluminium is one of the lightest metals and could provide favourable weight and volume efficiencies for hydrogen storage if it could be activated for reversible hydrogen absorption by alloying with small amounts of zirconium.

The Zr-Al phase diagram was established by McPherson and Hansen [7] from metallographic and limited thermal studies, and later partially corrected by Potzschke and Schubert [8]. Besides the solid solutions of zirconium and aluminium there are 11 intermetallics in the diagram (an oxygen-stabilized phase, $Zr_5Al_3O_x$, is included), and their preparations and crystal structures have been described in detail by Potzschke and Schubert [8]. In these intermetallics, Zr_5Al_3 , Zr_3Al_2 and Zr_5Al_4 are known to absorb considerable amounts of hydrogen [6]. Other zirconium-rich alloys are supposed to absorb hydrogen, but the relevant experimental data have not been reported.

2. Experimental details

The Zr-Al alloys were prepared by arc-melting stoichiometric mixtures of ingot zirconium (Aldrich Chemical Company Inc., 99%) and aluminium (Koch-Light Laboratories Ltd., 99.999%) in a small argon arc furnace. All the samples were melted three times to make them homogeneous. The loss of weight during melting was less than 1%. These samples are described as being in the "as-cast condition". A group of arc-melt samples were wrapped in tantalum foils, vacuum sealed in silica tubes, and then set in a kanthal furnace for annealing. A Hägg-Guinier focusing camera with Cu K α X-radiation was used for powder diffraction analysis. The measurement data were interpreted, indexed and refined using a versatile powder indexing program POWD [9]. The treatment conditions and the structures of the Zr-Al alloys used in the studies are listed in Table 1. The convention used is that overall compositions are expressed per 100 metal atoms, *e.g.* Zr₇₅Al₂₅, and specific phases identified from diffraction data are represented by empirical formulae, *e.g.* Zr₅Al₃.

The hydrogen sorption of the Zr-Al alloys was measured quantitatively in a thermogravimetric analysis (TGA) microbalance system as described previously [1-4].

The differential thermal analysis (DTA) was carried out in a Shimadzu Thermal Analysis Instruments 30 Series. The sample and the reference (pure alumina) were heated in hydrogen with a flow rate of 35 ml min⁻¹ at a constant heating rate of 5° C min⁻¹. The system was calibrated by the measurement of the

TABLE 1

Treatments and structures (X-ray powder analysis) for the Zr-Al alloys

Composition	Treatment	Phases present	Structure	Lattice parameter
Zr ₇₅ Al ₂₅	As-cast	$Zr_2Al + trace of \alpha-Al$	·	
Zr ₇₅ Al ₂₅	Annealed 850 °C, 2 w	$Zr_3Al + trace of$ α -Al + Zr_2Al	$Cu_3Au(L1_2)$ Cubic <i>Pm3m</i>	a = 4.380(2) Å $V = 84.04 \text{ Å}^3$
Zr ₆₇ Al ₃₃	As-cast	Zr_5Al_3		
Zr ₆₇ Al ₃₃	Annealed at 950 °C, 100 h	Zr ₂ Al	$Ni_2In(B8_2)$ Hexagonal $P6_3/mmc$	a = 4.889(7) Å c = 5.925(6) Å $V = 122.70 \text{ Å}^3$
Zr ₆₆ Al ₃₄	As-cast	Zr ₅ Al ₃	W ₅ Si ₃ (D8 _m) Tetragonal 14/mcm	a = 11.036(7) Å c = 5.388(3) Å $V = 656.33 \text{ Å}^3$
$Zr_{63}Al_{27}$	As-cast	$Zr_{3}Al_{3} + Zr_{3}Al_{3}$	- ,	
$Zr_{63}Al_{37}$	Annealed at 900 °C, 100 h	$Zr_{3}Al_{2} + Zr_{2}Al +$ trace of D8 + 7r Al		
$Zr_{60}Al_{40}$	As-cast	Zr_3Al_2	Tetragonal P4 ₂ /mnm	a = 7.630(0) Å c = 6.990(7) Å $V = 406.98 \text{ Å}^3$
$\operatorname{Zr}_{60}\operatorname{Al}_{40}$	Annealed at 950 °C, 100 h	Zr_3Al_2 + trace of $D8_8$		
Zr ₅₇ Al ₄₃	As-cast	Zr_5Al_4 + trace of Zr_3Al_2		
Zr ₅₇ Al ₄₃	Annealed at 950 °C, 100 h	Zr_4Al_3 + trace of $D8_8$	Hexagonal Põ	c = 5.430(4) Å c = 5.386(3) Å $V = 137.56 \text{ Å}^3$
Zr ₅₆ Al ₄₄	As-cast	Zr ₅ Al ₄	Ti₅Ga₄-type Hexagonal P6₁/mcm	a = 8.437(0) Å c = 5.800(3) Å $V = 357.57 \text{ Å}^3$
$Zr_{56}Al_{44}$	Annealed at 950 °C, 100 h	Zr_4Al_3 + trace of $D8_8$ + Zr_2Al_3	2 - 37	
$Zr_{50}Al_{50}$	As-cast	$Zr_2Al_3 + Zr_5Al_4$		
$Zr_{50}Al_{50}$	Annealed at 950 °C, 100 h	$Zr_2Al_3 + Zr_4Al_3 +$ trace of $D8_8$		
$Zr_{40}Al_{60}$	As-cast	Zr_2Al_3 + trace of $ZrAl_2$	Orthorhombic Fdd2	a = 9.598(8) Å b = 13.905(2) Å c = 5.572(5) Å $V = 743.78 \text{ Å}^3$
Zr ₃₃ Al ₆₇	As-cast	$ZrAl_2$ + trace of $ZrAl_3$	$MgZn_2(C14)$ Hexagonal $P6_2/mmc$	a = 5.281(0) Å c = 8.743(9) Å $V = 211.19 \text{ Å}^3$
Zr ₂₅ Al ₇₅	As-cast	ZrAl ₃	DO_{23} Tetragonal 14/mmm	a = 4.009(3) Å c = 17.281(5) Å $V = 277.79 \text{ Å}^3$

heat of fusion of pure indium. The method is a dynamic technique and required the estimation of the hydride composition of the sample. As there was no appreciable variation of lattice parameter with hydrogen content, this was estimated from the microbalance data and was the major source of uncertainty.

A versatile Leybold-Heraeus LHS-10 Surface Analysis System was used for X-ray photoelectron spectroscopy (XPS) and ion scattering spectroscopy (ISS) analysis which necessitated that the as-cast Zr-Al alloys were ground and polished to disc shapes suitable for insertion. The hydrided samples were powders which were pressed into a flat nickel cup after which the top layers were carefully removed to expose fresh surface before examination. The vacuum in the main chamber was less than 5×10^{-8} Torr during operation. All samples were cleaned by argon ion bombardment prior to analysis and the XPS spectra were obtained using Mg K α radiation with a power of 350 W. The ISS spectra were obtained with He⁺ ions generated from Helium at a pressure of 6×10^{-5} Torr with primary energy of 1000 eV at a constant scattering angle $\theta = 117^{\circ}$. The energy scale was calibrated using the Au $4f_{7/2}$ peak. Pure zirconium and aluminium samples were used to establish a sensitivity scale for the calculation of the surface composition. The XPS calculations utilized the measurement of the peak area and for ISS the measurement of the peak height was utilized. The peak area method is more accurate but both of them are satisfactory for giving relative concentrations.

3. Results

3.1. TGA microbalance hydriding experiments and structural analyses

Considerable differences in initiation and absorption behaviour for hydriding in the Zr-Al system have been exhibited in TGA microbalance hydriding experiments (see Table 2).

A general tendency for the initiation behaviour transcending any structural differences of the various phases studied can be related to aluminium content in Zr–Al alloys (see Table 2). It is difficult to initiate hydrogen absorption in pure zirconium but initiation is made easier by adding aluminium; however, the addition of excessive aluminium to the alloys increases the initiation difficulties. An optimum aluminium content with respect to initiation exists around $Zr_{63}Al_{37}$ (Zr_5Al_3) for as-cast samples. For alloys with aluminium contents above $Zr_{60}Al_{40}$ (Zr_3Al_2), both an increase in temperature and higher pressures have to be used to initiate hydriding (see Table 2).

Two types of initiation behaviour in Zr-Al alloys can be distinguished. The alloy $Zr_{63}Al_{37}$ (Zr₅Al₃) is most easily initiated and exhibits an onset of an accelerating absorption of hydrogen after being heated in hydrogen to a relatively low temperature (100-200 °C). The hydriding reactions are very rapid processes taking only several seconds in every case. The zirconium-rich alloy Zr₇₅Al₂₅ (Zr₃Al) represents another type of initiation behaviour. Under certain pressures and temperatures this alloy starts to absorb hydrogen, but the rate of hydriding is quite slow and maintenance at high temperature is necessary for the hydriding to continue (at least two or three cycles from 260 °C to 420 °C at 0.85 atm were

TABLE 2

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Sample		P_{H_2}	Hydriding		$\pm H^a$	Hydride		
Composition	Treatment		Initiation	Cycling		Composition	Gravimetric	Volumetric
$Z_{r_{55}} A_{15}$ $Z_{r_{75}} A_{125}$ $Z_{r_{75}} A_{125}$ $Z_{r_{67}} A_{135}$ $Z_{r_{67}} A_{135}$ $Z_{r_{67}} A_{135}$ $Z_{r_{67}} A_{135}$ $Z_{r_{67}} A_{135}$ $Z_{r_{67}} A_{145}$ $Z_{r_{57}} A_{145}$	As-cast As-cast Annealed As-cast As-cast As-cast Annealed As-cast Annealed As-cast Annealed As-cast As	0.85 atm 0.85 atm 8 atm 8 atm 8 atm 8 atm 8 atm 8 atm 8 atm	700 °C 2 cycles 260-420 °C 2 cycles 260-420 °C 2 550 °C 2 cycles 180-400 °C 150 °C 120 °C 350 °C 350 °C 350 °C 350 °C 350 °C Max. 440 °C Max. 440 °C Max. 410 °C Max. 410 °C Max. 410 °C Max. 410 °C Max. 410 °C Max. 410 °C	6 cycles 400-700 °C 5 cycles 260-420 °C 4 cycles 260-420 °C 6 cycles 30-220 °C 6 cycles 180-400 °C 6 cycles 180-360 °C 7 cycles 180-350 °C 7 cycles 160-350 °C 6 cycles 240-440 °C	40.0 9.0 7.9 22.3 9.2 9.2 7.4 6.9 6.9 6.9 6.9 6.9 6.9 6.1 6.1 6.1 6.1 12.2 9.4 9.4 7.4 7.4 7.4 7.4 7.4 7.4 7.4 7.4 7.4 7	$\begin{array}{c} Zr_{100}H_{200}\\ Zr_{75}Al_{25}H_{11}\\ Zr_{75}Al_{25}H_{12}\\ Zr_{67}Al_{33}H_{88}\\ Zr_{67}Al_{33}H_{81}\\ Zr_{67}Al_{37}H_{74}\\ Zr_{65}Al_{37}H_{74}\\ Zr_{65}Al_{37}H_{74}\\ Zr_{65}Al_{37}H_{74}\\ Zr_{57}Al_{37}H_{74}\\ Zr_{57}Al_{37}H_{74}\\ Zr_{57}Al_{37}H_{74}\\ Zr_{57}Al_{37}H_{11}\\ Zr_{57}Al_{37}H_{11}\\ Zr_{57}Al_{31}H_{11}\\ Zr_{57}Al_{51}H_{11}\\ Zr_{57}Al_{51}H_{11}$	$\begin{array}{c} ZrH_{2,0}\\ ZrY_{2,0}\\ Zr_{2}AlH_{3,5}\\ Zr_{3}AlH_{2,6}\\ Zr_{5}Al_{3}H_{6,5}\\ Zr_{5}Al_{3}H_{6,5}\\ Zr_{5}Al_{3}H_{6,5}\\ Zr_{5}Al_{4}H_{6}\\ Zr_{5}Al_{4}H_{6}\\ Zr_{4}Al_{3}H_{6}\\ Zr_{4}Al_{3}H_{6}\\ Zr_{4}Al_{3}H_{6}\\ Zr_{4}Al_{3}H_{6}\\ Zr_{4}Al_{3}H_{6}\\ ZrAl_{3}H_{6}\\ Zr$	ZrH _{1.8} Zr ₂ AlH ^{3,4} Zr ₃ AlH ^{4,7} Zr ₅ Al ₃ H _{6,7} Zr ₅ Al ₃ H _{5,6} Zr ₅ Al ₃ H _{5,6} Zr ₅ Al ₃ H _{2,6} Zr ₅ Al ₃ H _{2,7} Zr ₅ Al ₄ H ⁵ Zr ₅ Al ₄ H ⁶ Zr ₄ Al ₃ H _{0,8}
^b The hydride is	based on the h	ydriding of the	major component phase	in the alloy.				

necessary). If the temperature drops, absorption also stops. The other Zr-Al alloys show behaviour more or less between these two types.

The existence of a second phase or the presence of impurities can strongly affect the ease of initiation of hydriding. This is a characteristic of the alloys around Zr_5Al_4 . Thus pure Zr_5Al_4 ($Zr_{56}Al_{44}$) shows no hydrogen reversability under the maximum experimental conditions (8 atm, 410 °C), although a hydride with low hydrogen content, $Zr_5Al_4H_{2.4}$, is formed under these conditions. However, slight deviation of the composition dramatically changes the alloy's initiation and hydrogen absorption properties. The more zirconium-rich composition $Zr_{57}Al_{43}$, containing only a trace of Zr_3Al_2 in a matrix of Zr_5Al_4 , can be initiated at 3 atm and shows a much higher hydrogen absorption capability and reversibility (see Table 2). However, adding more aluminium to the alloy ($Zr_{50}Al_{50}$, a mixture of Zr_5Al_4 and Zr_2Al_3) also improves the initiation of Zr_5Al_4 (see Table 2).

The absorption behaviours of Zr–Al alloys are not primarily a function of the structure of a phase so much as of the composition of the phase. The critical composition for hydrogen absorption is $Zr_{50}Al_{50}$ (33 wt.% Al). The alloys with compositions of $Zr_{40}Al_{60}$, $Zr_{33}Al_{67}$ and $Zr_{25}Al_{75}$, which have aluminium contents over one atom for one corresponding zirconium atom, generally do not absorb hydrogen (see Table 2). For the alloys which do react with hydrogen under the experimental conditions, the reaction properties of the alloys can be classified using the shapes of their *C*–*T* curves and the structures of the hydrides (see Fig. 1 and Table 3).

The high temperature phase Zr_5Al_3 is different from the other phases studied and shows a detectable α - β phase change for reversible hydriding. A monoclinic hydride of Zr_5Al_3 with six to seven hydrogen atoms forms directly on reaction with hydrogen with no obvious intermediate stages [4]. More than two hydrogen atoms can rapidly desorb when the hydride is heated to 220 °C (see Fig 1). Further X-ray powder diffraction analysis of the hydride $Zr_5Al_3H_{3.9}$, resulting from heating to 200 °C in vacuum, showed an expanded body-centred tetragonal cell 4% larger than the host cell (see Table 3). If this phase is regarded as an α -phase hydride, then the monoclinic phase is the β -phase hydride. The characteristics of this α - β phase change are that of a relatively continuous process rather than a one-step process at a defined temperature. Therefore, although the hydriding of Zr_5Al_3 is considered as an example of a system with detectable α - β phase change, the high hydrogen content in the α -phase and the continuous desorption features make it a borderline case compared with systems with clearly defined α - β phase changes, such as the rare earth silicide hydrides [1-3].

All other alloys, $Zr_{75}Al_{25}$, $Zr_{67}Al_{33}$, $Zr_{60}Al_{40}$, $Zr_{57}Al_{43}$, $Zr_{56}Al_{44}$ and $Zr_{50}Al_{50}$ in the Zr-Al system give no indication of any phase change in their hydriding (see Fig 1 and Table 3). The alloys show very similar hydrogen absorption features whether as-cast or annealed although the structures of the samples are different.

The annealed alloy of composition $Zr_{67}Al_{33}$ exhibits a phase change on hydriding from a hexagonal Zr_2Al phase to an orthorhombic structure with a volume 14% larger than the host hexagonal structure (see Fig 1 and Table 3). The orthorhombic cell is an alternative of the expanded hexagonal cells with the angle



Fig. 1. The absorption capacity $N_{\rm H}$ (expressed as hydrogen atoms per 100 constituent alloy atoms) vs. the temperature for hydriding of Zr-Al alloy. The curve for $Zr_{75}Al_{25}$ (Zr₃Al) for the annealed sample; the curve for the as-cast sample agrees closely and is therefore not drawn. $Zr_{60}Al_{40}$ (Zr₃Al₂) is similar and only the curve of the as-cast sample is drawn. Although the curve for the alloy Zr₅₀Al₅₀ when as-cast is similar to the curve for the annealed alloy and is not drawn, the activation pressure for the as-cast alloy is higher, at 8 atm instead of 3 atm.

TABLE 3

Hydride	$a(\mathbf{A})$	b (Å)	$c(\mathbf{\dot{A}})$	β (°)	Volume (Å ³)	Structure
Zr ₂ AlH _{2.8}	8.689	5.358	6.006	_	279.6	Orthorhombic P
$Zr_5Al_3H_{3.9}$	11.056	_	5.585		682.7	Tetragonal I
Zr ₅ Al ₃ H _{6.5}	11.062	11.062	5.868	90.53	718.1	Monoclinic I
	12.474	11.062	5.868	117.53		Monoclinic C
$Zr_3Al_2H_{2.8}$	7.591	_	7.221	_	416.1	Tetragonal P
$Zr_4Al_3H_{2.9}$	5.490	_	5.559	_	145.1	Hexagonal P
$\operatorname{Zr}_{5}\operatorname{Al}_{4}\operatorname{H}_{6,0}^{2}$	8.605	—	5.909	—	378.9	Hexagonal P

X-ray powder analysis results for the hydrides of the Zr-Al alloys

between two *a* axes being less than 120° caused by the axis along the short diagonal increasing in length by more than the axis along the long diagonal. Although the structure of the hydride is different from the host alloy, there is no evidence of any phase change in the C-T curve for the hydriding process (see Fig. 1).

3.2. Thermodynamic data measurements

The thermodynamic data for the hydriding process measured by DTA and TGA, together with data from the literature [10, 11], are listed in Table 4 for the alloys Zr_3Al , Zr_5Al_3 and Zr_3Al_2 . For those alloys for which the pressure was higher than atmospheric pressure or long heating times were needed to activate the alloys, the DTA technique could not be used and the data for these alloys were not determined.

TABLE 4

Thermodynamic data for the hydriding of the Zr-Al alloys

Hydriding ^ª	$\Delta H(\mathrm{kJ}(\mathrm{mol}\mathrm{H}_2)^{-1})$	$\Delta S \left(J \operatorname{K}^{-1} (\operatorname{mol} H_2)^{-1} \right)$	Remark
Zr-ZrH ₂	169.5		Ref. 10
Zr ₃ Al-Zr ₃ AlH ₃₉	121	_	DTA
Zr _s Al ₃ -Zr _s Al ₃ H ₄	118	_	DTA
$Zr_{3}Al_{2}-Zr_{3}Al_{2}H_{2}$	69		DTA
$Zr_{5}Al_{3}H_{r}(\alpha-\beta)$	67	176	TGA
$\mathbf{Zr}_{3}\mathbf{Al}_{1.9} - \mathbf{Zr}_{3}\mathbf{Al}_{1.9}\mathbf{H}_{x}$	66.9	7.4	Ref. 11

^aThe final compositions of the hydrides in the DTA analyses are estimates only based on the temperature at which the absorption reaction was complete, and are established from the corresponding hydrogen contents measured from the microbalance analyses.

TABLE 5

Observed binding energies of the Zr-Al alloys in the XPS studies

Composition	In situ preparation	$Zr 3d_{5/2}(eV)$	$Zr 3d_{3/2}(\mathrm{eV})$	Al 2p(eV)
Zr	Ar bombardment	178.8	181.1	
Zr ₃ Al	Ar bombardment	178.8	181.2	70.6-72.3
Zr ₅ Al ₃	Ar bombardment	178.8	181.1	70.9-73.2
Zr _s Al ₃	None	183.2(178.8 ^a)	185.6	73.9-76.4
Zr _s Al ₃	Ar bombardment + 250 °C, 45 min vacuum	179.4	181.4	_
$Zr_{5}Al_{4}$	Ar bombardment	178.9	181.1	70.4-72.7
ZrAl	Ar bombardment	178.9	181.3	71.9
ZrAl ₂	Ar bombardment	179.0	181.3	72.0
ZrAl	Ar bombardment	179.0	181.1	72.3
Al	Ar bombardment	_	_	72.8
Zr ₅ Al ₃ H _{6.5}	None	$182.4(178.3^{a})$	184.6	73.8-75.0

^aSatellite line.

The experimental results for hydriding of Zr_5Al_3 and Zr_3Al_2 gave larger than expected experimental deviations by about 10% owing to uncertainty in estimating the hydride compositions. The thermodynamic data obtained from these DTA measurements can be considered to give only an approximate value of the enthalpy change for the hydriding reaction. For Zr_3Al the speed of absorption was quite slow and the reaction lasted over a period representing a significant temperature range, so that the value obtained from the experiment cannot be related to a single temperature.

The enthalpy change for hydriding of Zr_5Al_3 obtained from DTA shown in Table 3 corresponds to the reaction of the alloy with hydrogen to produce the α -phase solid solution. The thermodynamic data for the α - β phase change of the hydriding of Zr_5Al_3 were obtained from C-T plots obtained at different pressures. A Vant' Hoff plot of the α - β isotherms was derived from which the enthalpy and entropy of the α - β phase change were calculated.

3.3. XPS and ISS analyses

The binding energies of the zirconium 3d core level and aluminium 2p core level for Zr-Al alloys and one of the hydrides, $Zr_5Al_3H_{6.5}$, were determined by XPS (see Table 5 and Fig. 2). The zirconium 3d core level spectra were the most prominent peaks for the element, and all the Zr-Al alloys measured (even with zirconium contents as low as that in ZrAl₃) gave sufficiently strong signals to allow determination of the zirconium 3d binding energy. As shown in Fig. 2, the measurements of the binding energies for the zirconium $3d_{5/2}$ spectra do not show any significant change with the increasing aluminium content in the alloys, although a slight shift of 0.2 eV more positive may be inferred. However, for aluminium the binding energies determined from the 2p spectra of the alloys rich in aluminium (ZrAl₃, ZrAl₂ and ZrAl) showed significant shifts of 0.5–0.9 eV more negative than metallic aluminium. The decrease in the binding energy is more marked for



Fig. 2. Binding energies of the zirconium $3d_{5/2}$ core level (full circles) and the aluminium 2p core level (open circles) vs. composition in the Zr-Al alloys.

higher aluminium content $(ZrAl_3)$ than for more zirconium-rich alloys (see Fig. 2). However, when the contents of aluminium in the alloys are less than 50 at.% $(Zr_5Al_4, Zr_5Al_3 \text{ and } Zr_3Al)$, the 2p peaks become broad and split, and the accurate positions are not able to be distinguished satisfactorily regardless of the effort used to decrease the background noise and increase the signal-to-noise ratio of the peaks (see Table 5)

The XPS spectra of the hydride $Zr_5Al_3H_{6.5}$ were studied for comparison with the spectra of the host alloy Zr_5Al_3 under different conditions (see Table 5). For the zirconium 3d core level spectra, both hydriding and oxidation shift the peaks to more positive values, indicating an increase in oxidation state of zirconium to $Zr^{\delta+}$. However, there are differences in extent for hydriding and oxidation. Slight oxidation of the surface by heating *in vacuo* strongly affects the features of the peaks, making the intensity of the $3d_{5/2}$ level lower than that of the $3d_{3/2}$ level, but causes only a small change in binding energy position, indicating a probable overlap of two doublet peaks. Surfaces having a normal oxide layer, *i.e.* before cleaning by argon bombardment, show the strongest chemical shift of 4.4 eV from 178.8 to 183.2 eV for the $3d_{5/2}$ level. The hydriding has a very similar effect as oxidation on binding energy, although the shift is smaller (from 178.8 to 182.4 eV for the $3d_{5/2}$ level). The strong chemical shifts caused by oxidation and hydriding also produce low binding energy satellite peaks with intensities approximately one-



Fig. 3. The relative concentrations of zirconium and aluminium measured by XPS (open circles) and ISS (full circles) vs. composition in the Zr-Al alloys. The zirconium enrichment is expressed in terms of the observed Zr/Al atomic ratio divided by the expected Zr/Al atomic ratio in the alloys.

third of the main $3d_{5/2}$ peak and at about the position expected for metallic zirconium. For the spectra of the aluminium 2p core level, although the accurate positions of the peaks cannot be easily distinguished from the background noise, the outline of the spectra still show the same tendency as the zirconium 3d spectra, namely that oxidation strongly, and hydriding to a lesser extent, shifts the binding energy of aluminium 2p to more positive positions.

The relative concentrations of the constituents in the top layers of the Zr-Al alloys were measured by XPS and the surface layers by ISS. For ISS analysis, the zirconium peak was affected by retained argon after bombardment and probably by other unknown factors and was not symmetrical. The zirconium peaks overlapped the aluminium peak and the individual peak area therefore could not be measured directly for zirconium and aluminium. The relative concentrations in the top surface layer had to be calculated by measuring the peak height and correcting by comparison with the spectra of the pure elements. The analyses that result from both XPS and ISS are shown for comparison in Fig. 3. The observed atomic ratio of Zr-Al, and the zirconium enrichment expressed in terms of the observed atomic ratio of Zr-Al divided by the expected atomic ratio of Zr-Al (matrix atomic ratio), are plotted relative to alloy composition. The results from both XPS and ISS show the same tendencies of enhanced surface Zr-Al ratio and zirconium enrichment. The differences in the degree measured by the two techniques are a reflection of the different penetration depths; the ISS technique indicates higher Zr-Al ratios and greater zirconium enrichment than does the more penetrating XPS technique. The curves also show that although the observed surface atomic ratio of Zr-Al decreases with increasing concentration of aluminium in the matrix, the relative enrichment of zirconium on the surface increases. This relative enrichment of zirconium is the greatest on the surface as measured by ISS in the aluminium-rich region (see Fig. 3).

4. Discussion

4.1. Initiation in the Zr-Al system

The necessity for some preliminary treatment before hydriding occurs is a frequently encountered phenomenon. The reasons for any induction period before reaction include removal of protective surface layers and surface rearrangement including segregation to allow easy dissociative chemisorption of hydrogen.

The two types of initiation behaviour in Zr-Al alloys identified with the change in aluminium content illustrate two different initiation processes for hydriding. For the most easily initiated alloy $Zr_{63}Al_{37}$ (Zr_5Al_3), it appears that the energy barrier for hydrogen dissociation is very low or effectively zero, and the initiation process (*i.e.* the heating to 100–200 °C) mainly plays the role of a cleaner removing a poisoning surface as proposed by Schlapbach *et al.*[12]. The initial hydriding raises the temperature and as a result of expansion of the metallic lattice the surface layer cracks and the reaction then speeds up; as hydriding disintegrates the host metal, fresh surface is produced and the reaction is further accelerated.

However, for the second type of initiation behaviour represented by the

zirconium-rich alloy $Zr_{75}Al_{25}$ (Zr_3Al) a continuous heating process is needed to supply energy for either removing a stable protective surface layer or for overcoming the high energy barrier for either the dissociative chemisorption or for the diffusion step of the reaction. The experimental results do not give sufficient detail to decide this.

The segregation observed on the alloy surfaces from XPS and ISS analysis can be related to the initiation process. Surface segregation occurs for many hydrogen storage systems [12]. In the well known hydrogen storage alloy LaNi, it is suggested that in the surface, lanthanum diffuses to the surface and metallic nickel clusters are formed which catalyse the hydrogen absorption. Using XPS analysis, a large lanthanum enrichment up to the concentration ratio La:Ni = 1:1has been found [12]. Similar segregation occurs in the Zr-Al system and zirconium enrichment has been found in all compositions of the Zr-Al alloys (see Fig. 3). Following the reasoning of Schlapbach et al. [12], this phenomenon would arise from the surface energy of zirconium being lower than that of aluminium, and this effect could be further enhanced by the strong chemisorption of oxygen on zirconium. Because the zirconium diffuses to the surface, the surface layers of the alloy could decompose and bond with oxygen, thus leaving the fresh unprotected subsurface of the alloy; the dissociative chemisorption could easily occur on this metallic subsurface. However, the segregation has to be within limits to improve the initiation property. A pure zirconium surface is not desirable because of the known difficulties of hydriding zirconium and insufficient segregation, such as in Zr₂Al, may not decompose the structure on the surface layer and make it too difficult for hydrogen to penetrate. When excessive amounts of aluminium are added to the alloy, along with very strong segregation in the surface layer, such as in ZrAl₂, the exposed subsurface of the alloy may even be aluminium enriched, which could result in a much higher energy barrier for dissociation as hydrogen does not chemisorb on the major component aluminium [13]. For the easier initiation behaviour of the alloys formed with several phases, segregation is also important; it is possible that the polyphase system creates some active sites which might be caused by segregation along the grains.

4.2. Hydrogen solubilities in the Zr-Al system

Hydrogen solubilities in Zr-Al alloys have been determined in the TGA microbalance experiment and are illustrated in Table 1 and Fig. 1.Some features of the solubility and its relationship with composition and structure can be elucidated from the results.

The hydrogen solubility of Zr-Al alloys generally decreases with increasing aluminium content in the alloy. The relationship between hydrogen solubility at room temperature and aluminium content can be illustrated in Fig. 4. Despite the differences in treatment or structure, the hydrogen solubilities *vs* aluminium content lie on a straight line with little scatter, which shows that the hydrogen solubility decreases proportionally with increasing aluminium atom ratio content. The slope of the line is about 3.4H/Al and for one aluminium atom added in the alloy there will be 3.4 hydrogen atoms loss of solubility of the hydride expressed as $M_{100}H_x$.



Fig. 4. Relationship between the hydrogen solubility and aluminium content in the Zr-Al alloys.

A reference line (the broken line) is also drawn on the figure assuming that in the alloys aluminium acts only as an inert diluent and there is no effect of one on the other for hydrogen absorption; *i.e.* the zirconium absorbs two hydrogen atoms per metal atom whereas the added aluminium does not absorb any hydrogen. The slope of this line is therefore calculated as 2H/Al. The results confirm that there is a considerable interaction between zirconium and aluminium in all compounds of Zr-Al alloys which decrease the hydrogen solubility in the alloys at the rate of about 1.4H/Al.

Although the Zr/Al ratio is dominant in determining solubility there are some differences in hydrogen solubility for different crystal structures with similar compositions and there is deviation from the proportional relations (see Fig. 4). Any structure effect seems to be present for individual cases only and does not have general application. For example, the compositions $Zr_{75}Al_{25}$ and $Zr_{50}Al_{50}$ show no dependence of hydriding behaviour on the structures of the phases present either before or after heat treatment. For the composition $Zr_{67}Al_{33}$ the hydrogen activation and desorption behaviours of samples containing the $Zr_{5}Al_{3}$ phase are quite different from those of the samples containing the $Zr_{2}Al$ phase, although the total absorptions are very similar. The composition $Zr_{57}Al_{43}$ shows significant differences of behaviour, depending upon whether the $Zr_{5}Al_{4}$ or the $Zr_{4}Al_{3}$ phase is present. Factors affecting activation are not as easily surmised as those affecting total hydrogen solubility.

The lack of any strong dependence on crystal structure in the Zr-Al system is not surprising. The site geometries available in all the alloys while not identical are similar, *i.e.* tetrahedral and octahedral sites with varying degrees of distortion are found formed from: 4Zr, 6Zr, 3Zr + 1Al, 4Zr + 2Al, 2Zr + 2Al, *etc.* The exact geometry of an interstice varies with the overall structure and the ratios of the types of sites (*e.g.* ratio of 4Zr sites to 2Zr + 2Al sites) are dependent on composition. The effect different sites have on the macroscopic absorption behaviour depends upon the stability of hydrogen at particular sites. The absorption energy for a site can be expected to become more positive as the number of aluminium atoms forming the site increases. This type of approach has been used by Jacob and Shaltiel [14] to estimate the enthalpy of absorption on various types of sites and to explain semi-phenomenologically the hydrogen absorption capacity of some transition metal alloys. A procedure using a modified version of Jacob's model to account for aluminium-hydrogen interactions developed by Clark and Wu is described fully elsewhere [15]. The application of the model is based on the electronic charge redistribution identified in the XPS measurements. An upper limit on the enthalpy is indicated at which hydrogen on a site becomes unstable and the possible stable sites are estimated by using Westlake's geometric criteria [16].

In the Zr-Al system, the enthalpy for the hydriding has been measured to be quite high (see Table 4), and hydrides obtained in the TGA system are all stable in a vacuum of 10^{-4} Torr at room temperature. This confirms that the Zr-Al alloys generally have a strong affinity for hydrogen and this has been exploited to getter hydrogen at low pressures [6].

4.3. Electronic structures in the Zr-Al hydriding system

When adding aluminium to zirconium, although the binding energies of the zirconium 3d level do not show much change, the binding energy of the aluminium 2p level is significantly changed, giving a negative shift of nearly 1 eV by the time half of the aluminium is substituted by zirconium (see Table 4 and Fig. 2). This indicates a charge distribution in the alloy which gives a slightly positive metallic $Zr^{\delta+}$ state for zirconium and a relatively strongly negative $Al^{\delta-}$ state for aluminium is consistent with the electronegativity difference between zirconium and aluminium and provides some explanation of the properties of hydrogen absorption of Zr-Al alloys related to their aluminium contents.

For the binding energies of hydrides measured from XPS, as shown in Table 5, the $3d_{5/2}$ core level' is at 182.4 eV (3.6 eV above the metal) with a satellite at a low binding energy of 178.3 eV (0.5 eV below the metal). These results show that the charge redistribution in the hydride of Zr_5Al_3 has a similar but weaker effect to that resulting from oxidation, and suggests that the electron transfer is from metal to hydrogen in the hydride. These observed results are very similar to the $3d_{5/2}$ core level spectra of LaH₃ measured by Schlapbach *et al.* [17] and Schlapbach and Scherrer [18], in which the $3d_{5/2}$ level is at 838.7 eV or 2.9 eV above the metal (835.8 eV) with a low energy satellite at 835.0 eV or 0.8 eV below the metal. They have explained this effect by a shake-down process related to the screening of the 3d core hole formed by the photoemission [18], and distinguished the main peak, corresponding to the final state with poorly screened 3d holes, and the satellite representing the well screened final state [17].

However, the reliability of the measured data from the XPS analysis has to be considered. For the alloy samples, the surfaces were primarily cleaned by argon bombardment *in situ* in the XPS and ISS studies. There is a possibility that the lighter atoms such as aluminium in the Zr-Al alloys are more easily removed from the surface in the argon bombardment and this may affect the final results. Any error introduced by this preparation method is quite difficult to estimate and therefore is not included in the calculation. For the hydride $Zr_5Al_3H_{6.5}$, which was necessarily in the form of pressed powder (because the alloy was reduced to powder during hydriding), the shift of the binding energy (3.6 eV for the $3d_{5/2}$ spectra) measured by XPS is comparable with the shift in LaH₃ [17]; it is still larger than most of the transition metal hydrides (0–2 eV [18]), and not too far from the shift for oxide (4.4 eV). The additional measurements of the oxygen 1s spectra show a constant high intensity for the oxygen peak, and suggest that the oxygen was substantially adsorbed on the surface of the hydride powder. Although the relatively larger probing depth of the XPS technique makes it less sensitive to surface contamination [19], the possible effect of the adsorbed oxygen on the bonding energy cannot be totally discounted.

To explain the phenomenon that the hydrogen solubility in general decreases proportionally with increasing aluminium atom percentage in the Zr-Al system, two approaches can be used. The first approach is based on binding energy changes in the Zr-Al alloys. Significant electron charge shifts have been found in all Zr-Al alloys investigated. The XPS measurements suggest that in Zr-Al alloys electron density is shifted from zirconium to aluminium, making the oxidation state of aluminium more negative, i.e. more like a non-metal element in the alloys. The relatively slight positive charge obtained for the zirconium would not affect greatly its bonding with hydrogen, whereas the negative charge obtained for aluminium will have a significant effect. Other XPS studies [1, 20] also show a shift in electron density from the metal to hydrogen, in agreement with the observation in this work. In the present system therefore the hydrogen and aluminium each has an increased negative charge and mutual repulsion can be expected. Therefore, in the hydriding of Zr-Al alloys, the aluminium would play a role as atom-blocking interstitial sites to hydrogen absorption as suggested by Rudman et al. [21]. From this picture, the interaction between aluminium and zirconium will result in a greater repulsion for hydrogen atoms than would be expected of a model in which the aluminium that does not absorb hydrogen simply substitutes for the hydrogen-absorbing zirconium in the alloy. The degree of electron charge shift will then more or less decide the extent of hydrogen content for the alloys.

The second approach is based on the concept of the band structure of the hydride as applied by Switendick [22]. While it may be more correct for describing the nature of the bonding at the moment it is not possible to deal with the complicated alloy hydride system quantitatively. Addition of hydrogen into the host metal lattice modifies the d or f electronic energy states of the metal. The electrons, both from metal and hydrogen, fill the energy states in increasing order from lowest energy state to highest until all electrons are accommodated. There are two requirements for forming a stable hydride with a high hydrogen solubility: there must be enough empty (above the Fermi energy E_f) d or f energy states available and their energies must be sufficiently low. However, if a metal alloys with a relatively electronegative component, there will be a charge transfer of the valence electrons which will raise the Fermi energy and the average energy per electron. Therefore the hydrogen in the alloy will be destabilized and the solubility of hydrogen in the alloy will decrease. However, there is a fundamental difference between

alloying with transition metals and with p elements. For alloying with transition elements, following upon the net charge transfer from relatively positive metal to negative metal, the d-d or d-f hybridization of the valence electrons could result in an opposite d electron transfer from the fuller to the emptier states as suggested by Watson and Bennett [23, 24]. This could happen when alloying with transition elements containing a large population of valence d electrons, such as iron, cobalt and nickel [25]. For instance in LaNis, following upon the electron charge transfer from lanthanum to nickel, the d-f hybridization of the alloy's valence electrons results in a d electron transfer from fuller to emptier states. Such empty states near the Fermi level allow more hydrogen electrons to be accommodated at the cost of stability [23, 24]. For alloying with p elements there is a similar charge transfer, for example in Zr-Al alloys. This charge transfer can be observed from the binding energy change in the XPS analysis (see Table 5); but as there are no d level valence electrons in p elements, we can assume there is no extra empty d band introduced by alloying with them. Therefore, increasing the component of the p element causes a loss of stability without compensation of an extra amount of hydrogen absorption. This qualitative explanation is not only applicable to Zr-Al alloy hydride, but may also be used to explain the general features of other transition p element hydride systems, namely the low hydrogen solubility and low equilibrium pressure for hydrogen absorption.

5. Conclusions

In the Zr-Al system the initial hydriding is made easier by adding aluminium into zirconium, but the addition of excessive aluminium to the alloy makes activation more difficult. This phenomenon can be related to the segregation observed on the alloy surface found from XPS and ISS analysis. In the Zr-Al system, zirconium enrichment has been found in all compositions of the Zr-Al alloys. A proper degree of segregation improves the initiation behaviour.

The hydrogen solubility in Zr-Al alloys generally decreases with increasing aluminium content in the alloy. When the aluminium addition is over 50 at.%, the alloys no longer absorb hydrogen under experimental conditions up to 410 °C and 8 atm. Despite the differences in solubility owing to different treatments or structures, a straight line can be drawn which shows the hydrogen solubility to decrease proportionally with increasing aluminium content expressed as an atomic ratio. The extra repulsion between hydrogen and aluminium caused by the electron shift from zirconium to aluminium in an overall aluminium content is suggested to explain the phenomenon. The solubilities of several Zr-Al alloys, exhibiting large deviations from the proportionality, do not appear to be determined by the long-range overall structure, and are expected to be determined by short-range neighbouring effects.

The alloys capable of absorbing hydrogen all react with hydrogen reversibly. The enthalpies of hydriding have been measured to be quite high with low equilibrium pressures. The Zr-Al alloys generally have a strong affinity for hydrogen in hydriding. Only the high temperature phase alloy Zr_5Al_3 presents a rapid $\beta - \alpha$

phase change on hydriding in which a monoclinic β -phase hydride of Zr₅Al₃H_{6.5} loses two hydrogen atoms from 30 to 220 °C at 0.85 atm to form a tetragonal α -phase hydride. The thermodynamics of the reaction are determined as $\Delta H = 67$ kJ (mol H₂)⁻¹ and $\Delta S = 176$ J K⁻¹ (mol H₂)⁻¹.

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