

Thermodynamic characterization of the Zr–Mn–H system Part 2. Reaction of H₂ with two-phase alloys

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Abstract

The reactions of H₂(g) with the two-phase alloys (a) α -Zr + ZrMn_{2+x} and (b) α -Mn + ZrMn_{2+x} have been investigated. The homogeneity range of the Laves phase ZrMn_{2+x} intermetallic compound has been determined from the dependence of its hydrogen absorption behavior upon x and found to lie within the limits $x = -0.3 \pm 0.1$ and 1.0 ± 0.1 . Normally H₂(g) does not react with α -Zr below about 773 K, but it has been found that when it exists within the two-phase mixture, it reacts readily with hydrogen at room temperature. For alloys in the zirconium-rich two-phase field the hydrogen first reacts to form ZrH_{~2} and then it reacts with the ZrMn_{2+x} phase. The former reaction leads to equilibrium pressures which are too small to measure, but the latter leads to measurable pressures. Results for alloys within the manganese-rich two-phase field, $x \geq 1.0$, are also reported. Calorimetric determinations of the enthalpies of reaction with hydrogen for several zirconium-rich alloys within the two-phase fields are reported for both the zirconium-rich and ZrMn_{2+x} phases.

1. Introduction

The main purpose of this research is the examination of the hydrogen absorption characteristics of a series of Zr–Mn alloys which lie within two-phase fields on either side of the Laves phase C-14 intermetallic compound ZrMn_{2+x}. These two-phase fields are composed of α -Zr + ZrMn_{2+x} and α -Mn + ZrMn_{2+x}, where x will be determined in this research from the variation in pressure with x . The X-ray diffraction results given in Part 1 [1] and some other research suggest that x is close to -0.3 for the former and 1.0 for the latter; other results from the literature also suggest that there is a wide range of homogeneity, but they propose somewhat different limits [2, 3]. The published phase diagram for Zr–Mn [4] suggests that the zirconium-rich phase is almost pure zirconium whereas the manganese-rich phase contains some zirconium, but this is uncertain.

There have been many investigations of the Laves phase (C-14) ZrMn_{2+x} compounds [2–11] which have concentrated on alloys in the Laves phase C-14 homogeneous range. These compounds are of importance because they

show promise as hydrogen storage systems and because ZrMn_2 is the parent compound for many others which have more desirable properties for particular applications, *e.g.* $\text{ZrMn}_{1+x}\text{Fe}_{1+y}$ [3]. A published phase diagram [4] shows ZrMn_2 to be a line compound. Workers characterizing hydrogen absorption in these systems [2, 7], however, have shown that there is a homogeneity range especially on the manganese-rich side. A preliminary phase diagram has been published by Nishimiya [12] showing a wide range of homogeneity for the ZrMn_{2+x} C-14 Laves phase.

Nishimiya [12] has examined the X-ray patterns and hydrogen contents of two alloys in the zirconium-rich two-phase field, but generally the investigations of hydrogen absorption by alloys have been intentionally limited to single-phase alloys, because otherwise the interpretation of the results would be unnecessarily complex. In this research, however, the hydrogen absorption behavior of some alloys which lie within the two-phase fields will be examined in order to demonstrate the usefulness of such characterizations for the determination of phase boundaries. The alloys in the two-phase field $\alpha\text{-Zr} + \text{ZrMn}_{2+x}$ studied by Nishimiya were $\text{ZrMn}_{1.38}$ and $\text{ZrMn}_{0.78}$. He found from X-ray powder diffraction patterns that these zirconium-rich alloys have a slightly expanded $\alpha\text{-Zr}$ phase together with a Laves C-14-type ZrMn_{2+x} phase; the former's expansion indicates a solid solution of manganese in $\alpha\text{-Zr}$. Upon hydriding at 623 K using only moderately high hydrogen pressures, the zirconium-rich phase forms a hydride phase but the ZrMn_{2+x} phase does not because its plateau pressure is too high. The X-ray diffraction lines of the zirconium-rich hydride phase corresponded to pure zirconium dihydride and he postulated, therefore, that when the hydride forms at 623 K, the Mn atoms, which were in solid solution within the zirconium-rich phase, migrate out of the zirconium phase. If this is true, it is of considerable interest. In this research we will attempt to determine whether or not this is indeed the case by using reaction calorimetry, which is a different method from the X-ray diffraction one used by Nishimiya.

One purpose of this research is to measure p_f (or p_d) as a function of x , where these are the plateau pressures for hydride formation or decomposition respectively for the Laves phase C-14 ZrMn_{2+x} . In the homogeneity region of this C-14 Laves phase compound there will be a continuous change in these pressures or hydrogen chemical potentials with x , but in the adjacent two-phase regions the plateau pressures should be invariant with x . This will provide a method by which the range of homogeneity of the intermetallic compound can be obtained. This method was employed successfully by Buschow and van Mal [13] for the determination of the homogeneity limits of LaNi_{5+x} ; the X-ray determination of the lattice parameter dependence on x agreed with the results obtained using the chemical potential method. For this ZrMn_{2+x} system too we will compare the homogeneity limits determined by the plateau pressure method with those determined from X-ray diffraction [2].

Because of the facile reaction of hydrogen with the zirconium-rich phase, it was planned to carry out some reaction calorimetry on the zirconium-rich

two-phase field. In this technique the enthalpy of reaction with hydrogen is determined from the heat evolved when small increments of hydrogen are added to the hydrogen-containing sample. The purpose is to obtain the enthalpies of reaction with the zirconium-rich phase in order to determine whether or not the values reflect reaction with a pure or with a manganese-containing zirconium phase.

2. Experimental details

Two different all-metal apparatuses were employed which were capable of measuring hydrogen pressures to about 50 atm. The isotherms were determined volumetrically from pressure changes in known volumes.

A differential, twin-cell, heat leak calorimeter was employed for the measurements of the enthalpy with H_2 . This calorimeter has been described elsewhere [15] and has been successfully employed for several alloy- and pure metal-hydrogen systems [14, 16, 17].

2.1. Materials

The alloys were prepared by arc melting the pure components. The resulting buttons were annealed for 3 days at 1050 K *in vacuo*. They were then pulverized in a nitrogen atmosphere and re-annealed at 1050 K for 3 days or longer *in vacuo*.

Some of the alloys within the zirconium-rich two-phase field were examined by optical microscopy. The presence of the two phases is quite apparent in the polished sections. The Laves phase $ZrMn_{2+x}$ formed rectangular crystallites of about $20 \times 50 \mu m^2$ with the zirconium-rich phase located between the $ZrMn_{2+x}$ phase. A partially hydrided alloy in the zirconium-rich two-phase field was examined. The ZrH_2 phase was noted to have crumbled.

X-ray diffraction patterns were made of the hydrogen-free alloys. In the two-phase regions both phases were clearly present and, in agreement with the results of Nishimiya [12], in the zirconium-rich two-phase region the zirconium phase was slightly expanded as compared to pure α -Zr. Several zirconium-rich two-phase alloys were examined by scanning electron microscopy (SEM) and elemental analysis of the two phases disclosed that the zirconium-rich phase contained a small concentration of manganese; this is not indicated on the phase diagram, where a negligible solubility of manganese in the zirconium phase is shown [4]. Presumably our observed solubility pertains to the annealing temperature of 1050 K.

3. Results and discussion

3.1. Isotherms at 323 K

3.1.1. Alloys with $x \leq 0$

It was of interest to determine isotherms for alloys which are intentionally located within the two-phase field consisting of a zirconium-rich phase and

a C-14 Laves phase (ZrMn_{2+x}). Eight different contents were examined with compositions in the range from $x=0$ to -1.0 ; for several of these compositions more than one preparation of the alloy was made. For each sample two consecutive absorption isotherms were measured at 323 K: the first was carried out with the virgin (unactivated) alloy; after its completion the sample was evacuated for 1 h (573 K) and then a second absorption isotherm was determined. Sometimes these conditions were varied and these variations are noted (*e.g.* Fig. 1). It is of interest that these alloys do not require any activation treatment in order for relatively fast reaction with hydrogen to take place.

It can be seen from Figs. 1–3 that the first aliquots of hydrogen which are added during measurement of the isotherms for virgin samples lead to equilibrium hydrogen pressures which are too small for measurement with the existing pressure gauges. The intercept along the $n=\text{H}:\text{ZrMn}_{2+x}$ axis increases with the amount of negative deviation from the stoichiometric composition of $x=0$ (Figs. 1–3). This region of “zero” equilibrium hydrogen pressures results from the reaction of hydrogen with the zirconium-rich phase to form a very stable zirconium dihydride phase. In Fig. 1 the second absorption isotherm is shown following the usual evacuation at 573 K of the sample after the completion of the first isotherm. A third absorption isotherm is shown which was carried out after evacuation at 373 K. It can be seen that this isotherm commences from $n=0$ in contrast to the second isotherm. A fourth isotherm following evacuation at 373 K is not shown since this duplicates the third one.

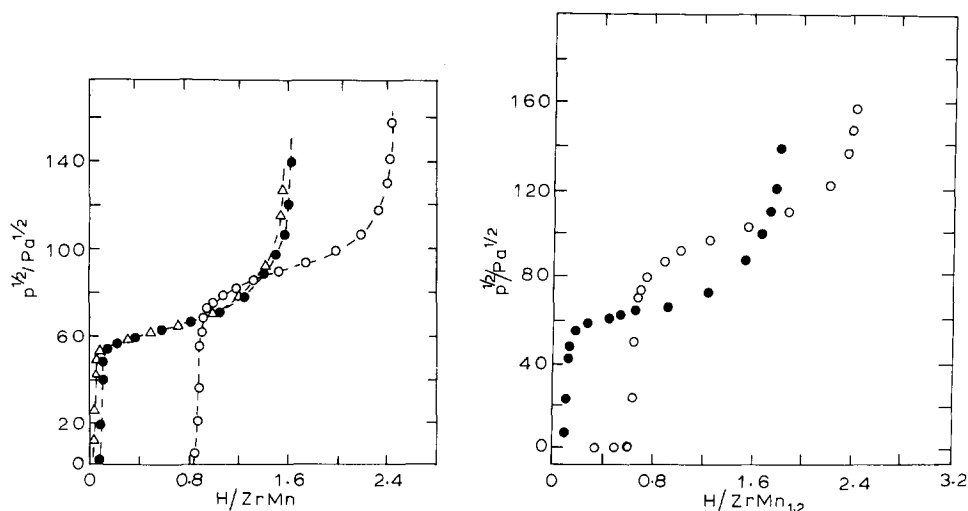


Fig. 1. Absorption isotherms for ZrMn at 323 K: \circ , first isotherm; \bullet , second isotherm after evacuation for 1 h at 573 K; Δ , third isotherm after evacuation for 1 h at 373 K.

Fig. 2. Absorption isotherms for $\text{ZrMn}_{1.2}$ at 323 K: \circ , first isotherm; \bullet , second isotherm after evacuation for 1 h at 573 K.

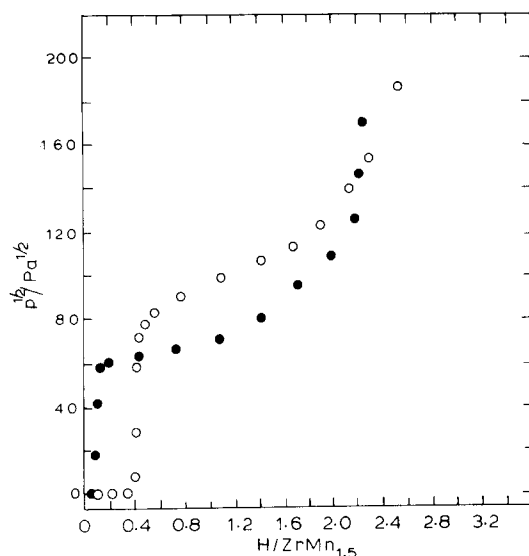


Fig. 3. Absorption isotherms for $\text{ZrMn}_{1.5}$ at 323 K: O, first isotherm, ●, second isotherm after evacuation for 1 h at 573 K.

The fact that the hydrogen reacts readily with the zirconium-rich phase at 323 K is of some interest, since $\text{H}_2(\text{g})$ will *not react with pure zirconium* under comparable conditions because an oxide film prevents access to the zirconium. Within the two-phase field the presence of the second phase, ZrMn_{2+x} , apparently acts as a protective shield for the zirconium phase against oxygen but allows hydrogen access to the inner zirconium-rich phases.

An alloy within the two-phase field with $x=0.4$ was initially hydrided and then dehydrided and annealed at various temperatures in order to determine the effect of annealing on the extent of the intercepts. After evacuation and annealing at 573 K for 1 or 12 h, the observed intercepts along the n axis are similar to those found after evacuation at 673 K for 1 h. Evacuation at 673 K for 12 h, however, resulted in a somewhat greater intercept. Evacuation at 873 K led to an intercept similar to that found for the virgin sample. Evacuation at 373 K, however, resulted in an almost zero intercept; this was also seen for $x=-1.0$ in Fig. 1. The extent of the intercept is unrelated to reaction with the ZrMn_{2+x} phase because the width of the plateau for the latter's reaction with hydrogen was found to be independent of the temperature of the evacuation. It seems that evacuation at $T \geq 673$ K removes significant amounts of hydrogen from the zirconium-rich dihydride phase.

The subsequent (second) absorption isotherms, following the initial hydriding and evacuation at 573 K, have lower p_f values than the initial ones for all the ZrMn_{2+x} compounds; this is seen in the isotherms for some alloys in the zirconium-rich two-phase field in Figs. 1–3. This has also been found for $\text{LaNi}_5\text{-H}$ [18], where it has been correlated with stored energy in the intermetallic resulting from the activation (cycle(s) of hydriding and

dehydrating) [19], and presumably it has the same origin for ZrMn_{2+x} . The difference between the two plateau pressures for virgin and activated ZrMn_{2+x} depends on the value of x . For $x = -1.0$ the difference between the two plateaux is small and constant with n . (This can be seen by shifting the plateau of the virgin sample to the left along the n axis in order to superimpose the steeply rising portions of the isotherms in Fig. 1.) For $x = -0.8$ the difference is larger but still relatively constant with n (Fig. 2). For $x = -0.25$ (not shown) the difference between the plateaux increases with n and for $x = 0$, the stoichiometric alloy (Fig. 4), the difference between the two isotherms is large and increases with n . When $x \leq -0.5$, the virgin plateau has a greater slope than the subsequent one (Figs. 1–3).

The degree of sloping of the absorption plateaux depends on x and whether or not the isotherm is measured with the virgin alloy or those which have already been cycled. The sloping is much greater for the first hydriding of the $x = 0$ alloy and this is also true for LaNi_5 .

The value of $\frac{1}{2}RT \ln[p_f(\text{vir})/p_f(\text{act})]$ (where "vir" and "act" refer to virgin and activated samples respectively) increases steadily with x ; at 50% conversion to the hydride phase this value is $0.7 \text{ kJ (mol H)}^{-1}$ for $x = -1.0$ and $1.0 \text{ kJ (mol H)}^{-1}$ for $x = 0$. This trend continues for the $x > 0$ alloys. Within the zirconium-rich two-phase field the extent of the plateau reaction associated with the ZrMn_{2+x} phase is comparable for all the two-phase alloys provided that their isotherms are compared on the basis of the fraction of

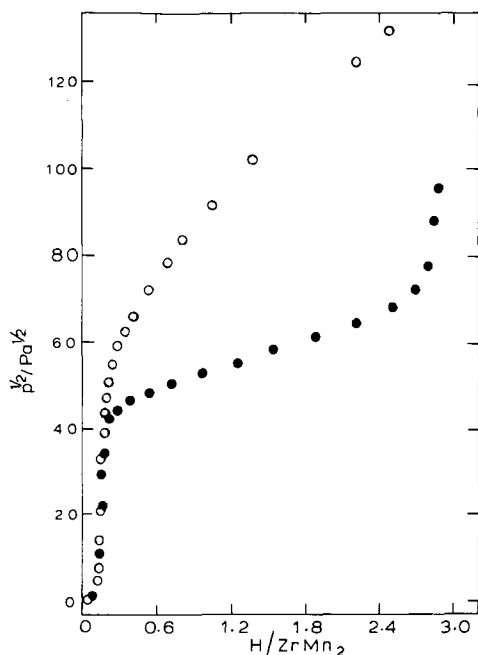


Fig. 4. Absorption isotherms for $\text{ZrMn}_{2.0}$ at 323 K: O, first isotherm; ●, second isotherm after evacuation for 1 h at 573 K.

ZrMn_{2+x} present. According to their hydrogen solubility behavior in the zirconium-rich two-phase field, the limiting composition of the ZrMn_{2+x} phase homogeneity region is slightly less than for the $x=0$ alloy as determined from the value of n where the initial increases in pressure in the dilute phase for the virgin sample and for the once-cycled sample coincide, *i.e.* approximately -0.3 ± 0.1 .

For ZrMn_2 it can be seen from Fig. 4 that the intersections along the n axis for the first (the initial) and second absorption isotherms are identical. There is no longer any strongly bound hydrogen such as found for the alloys with $x < -0.2$, *i.e.* the hydrogen is all removed by evacuation at 573 K for 1 h.

3.1.2. Alloys with $x > 0$

Isotherms for $x > 0$ show no indication of any initial region with immeasurably low hydrogen pressures (Figs. 5–7) characteristic of a zirconium-rich phase. Alloys with $x \geq 1.0$ have a manganese-rich phase which does not, however, absorb hydrogen at the pressures employed here. There is no tightly bound hydrogen in these alloys, as can be seen from the zero intercepts for both the initial and subsequent isotherms. It is curious that the sloping of the plateaux is smaller for the first hydriding compared to subsequent ones for these alloys with $x \geq 0$, since the opposite holds for alloys with $-0.5 \leq x \leq 0$. For the $x=2$ alloy (Fig. 7) it can be seen that annealing at 773 K after its

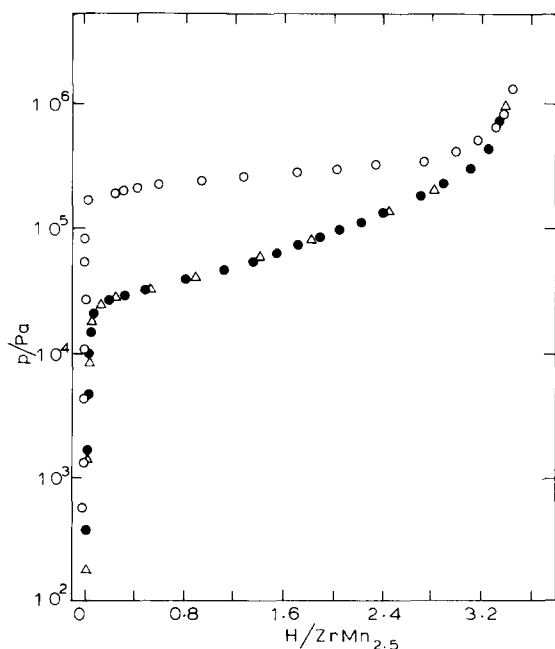


Fig. 5. Absorption isotherms for $\text{ZrMn}_{2.5}$ at 323 K: O, first isotherm, ●, second isotherm after evacuation for 1 h at 573 K; Δ, third isotherm after evacuation for 15 h at 323 K.

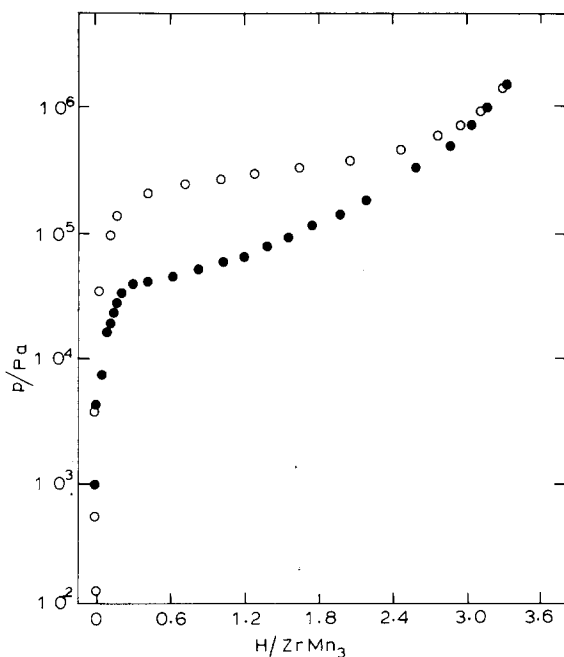


Fig. 6. Absorption isotherms for $\text{ZrMn}_{3.0}$ at 323 K: ○, first isotherm; ●, second isotherm after evacuation for 1 h at 573 K.

activation has little effect on its subsequent absorption isotherm even though there is a large difference between the first and second isotherms. This contrasts with LaNi_5 [18], where there are effects due to annealing of activated material commencing at 200 °C.

A plot of values of $\frac{1}{2}RT \ln p_f$ against values of x for the alloys is shown in Fig. 8 for the second absorption isotherm (323 K). It can be seen that there are changes in slope at approximately $x = -0.3$ and 2.0, indicating the range of homogeneity of the Laves phase intermetallic ZrMn_{2+x} . This agrees reasonably well with the homogeneity range found from X-ray diffraction [14]. It should again be noted that although these limits have been determined at 323 K, they refer to the annealing temperature of the alloy of 1050 K.

3.2. Calorimetric results for alloys within two-phase fields

Reaction calorimetric measurements and equilibrium pressure determinations were carried out over a wide range of hydrogen contents starting from $n=0$ for alloys with $x < -0.2$. Some results are shown in Figs. 9 and 10 for $x = -1.0$ and -0.6 respectively. It can be seen in Fig. 9 that, in keeping with earlier results, the equilibrium hydrogen pressures are too small to measure at low values of n but, nonetheless, the enthalpy for the reaction with the zirconium-rich phase can be measured, *i.e.*



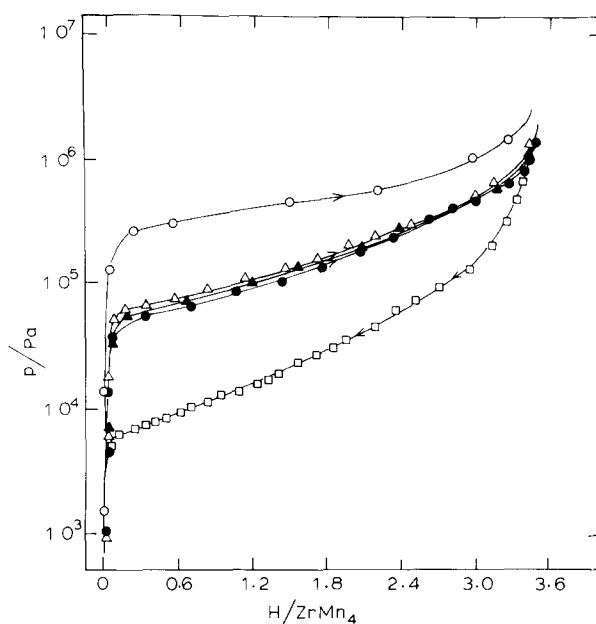


Fig. 7. Isotherms for $\text{ZrMn}_{4.0}$ at 323 K: \circ , first absorption isotherm; \bullet , second absorption isotherm after evacuation for 1 h at 573 K; \triangle , third absorption isotherm after evacuation and annealing at 773 K for 20 h; \square , desorption isotherm following third absorption isotherm, \blacktriangle , absorption isotherm following desorption isotherm.

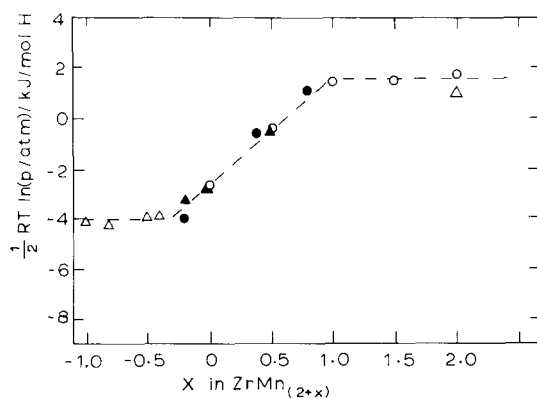


Fig. 8. Plot of $\frac{1}{2} RT \ln(p/\text{atm}) / \text{kJ/mol H}$ vs. x : \bullet , ref. 1; \triangle , \blacktriangle , \circ , different isotherms.

where "Zr" refers to the zirconium-rich phase which is not pure zirconium but contains some manganese in solid solution. According to the Zr-H phase diagram [20] at 323 K, as y increases, the first hydride phase which appears is the γ phase at $y=1.0$, next the δ phase at $y=1.5$ and finally hydrogen dissolves in the ϵ -phase at $y \geq 1.7$.

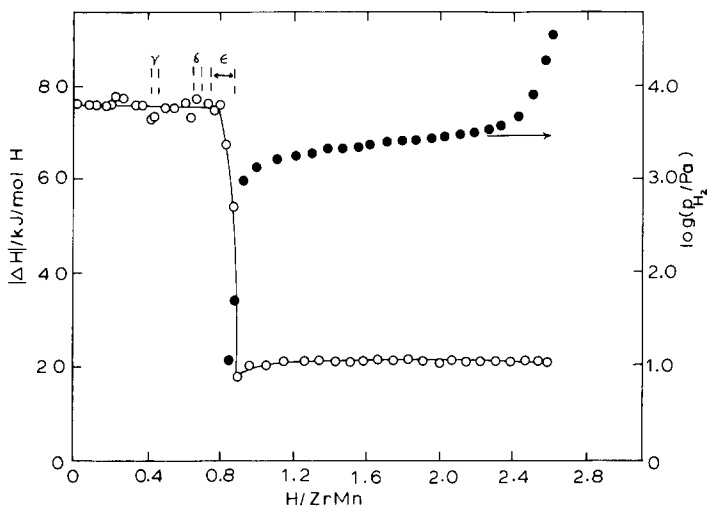


Fig. 9. Calorimetric titration of $\text{H}_2(\text{g})$ with ZrMn at 298 K. The alloy has not been previously activated. The labels on the calorimetric data indicate the approximate range of the pure zirconium–hydrogen phases.

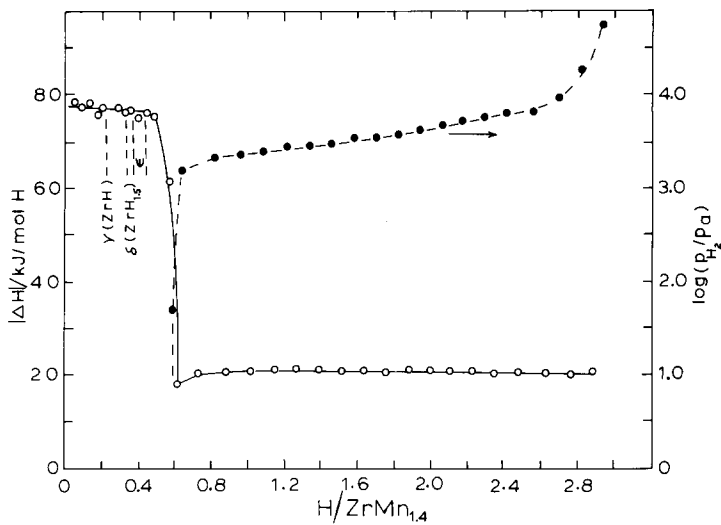


Fig. 10. Calorimetric titration of $\text{H}_2(\text{g})$ with $\text{ZrMn}_{1.4}$ at 298 K. The alloy has not been previously activated. The labels on the calorimetric data indicate the approximate range of the pure zirconium–hydrogen phases.

Nishimiya [12] found that the zirconium-rich phase has an expanded lattice compared to pure zirconium and similar results are obtained here, which indicates that the zirconium phase is not pure zirconium. The enthalpy

for reaction (1) within the two-phase field is $-77.0 \pm 1.0 \text{ kJ (mol H)}^{-1}$ at 298 K (Figs. 9 and 10) and there is a small decrease in exothermicity as the conversion to the hydride phase increases. The enthalpy measured here for reaction (1) is less exothermic than would be expected for pure zirconium. Turnbull [21] has presented a review of the enthalpies obtained for reaction (1) and has also determined values using solution calorimetry at 298 K. His are the most reliable ones for comparison with the present results. A series of enthalpies at different y values (ZrH_y) were determined and, from a relationship between ΔH and y given by Turnbull, we find $\Delta H_{\text{plat}} = -87.4 \text{ kJ (mol H)}^{-1}$ for $y = 1.63$, which is estimated to be the composition of the hydride phase formed at 323 K. The values found in the present study are less exothermic than this; the difference must be attributed to the presence of manganese in the zirconium phase, since it would be expected that alloying zirconium would reduce its enthalpy of reaction with hydrogen. For example, we have found that the reaction of H_2 with zirconium containing 2.5% Nb is less exothermic than with pure zirconium [22].

Two sets of calorimetric data for the absorption of H_2 by a $\text{ZrMn}_{1.2}$ alloy were obtained. The first set was for the virgin alloy. The second was for the same alloy sample after subjection to the following sequential treatment: (1) hydrided (323 K) and dehydrided; (2) hydrided at 773 K; (3) dehydrided at 1000 K. The object of this elaborate treatment before taking the calorimetric data was to test Nishimiya's [12] contention that hydriding at 773 K expels manganese from the zirconium-rich phase, resulting in a pure zirconium hydride phase. In the present experiments it was found that the enthalpies for reaction of $\text{H}_2(\text{g})$ with the zirconium-rich phase were only slightly more negative after the high temperature hydriding, *i.e.* $-79 \text{ vs. } -77 \text{ kJ (mol H)}^{-1}$; the enthalpy of reaction of H_2 with pure zirconium is $-87.4 \text{ kJ (mol H)}^{-1}$ [21]. The amount of manganese which has been expelled from the zirconium-rich phase is therefore seen to be relatively small.

As seen in Figs. 9 and 10, after the zirconium phase reacts completely, an abrupt decrease in exothermicity occurs, falling to a value of $-21.0 \text{ kJ (mol H)}^{-1}$ corresponding to hydriding of the ZrMn_{2+x} phase. Similar results for hydriding of the $\text{ZrMn}_{1.2}$ two-phase alloy yielded $-20.5 \text{ kJ (mol H)}^{-1}$ for hydriding of both the virgin material and the activated sample following the treatment described above, *i.e.* high pressure hydriding followed by evacuation at about 1000 K. Thus the average magnitude of all four of these calorimetric values was slightly greater than found for $x = -0.2$ [1], indicating that the limiting homogeneity range on the zirconium-rich side is about $x = -0.3$.

The calorimetric results obtained for the reaction of H_2 with alloys in the manganese-rich two-phase field are not as interesting and are not shown. Since the manganese-rich phase does not react with H_2 , the only reaction which occurs is that with the ZrMn_{2+x} phase. The calorimetrically measured enthalpies and equilibrium pressure data for $\text{ZrMn}_{3.5}$ were found to be almost identical to those for ZrMn_3 . This indicates that the limiting homogeneity range is $x = 1.0$ for the manganese-rich side of the C-14 Laves phase compound.

4. Conclusions

In this research a hydrogen titration technique has been employed to characterize the limits of the single-phase field of the C-14 Laves phase intermetallic compound in equilibrium with a zirconium-rich and a ZrMn_{2+x} phase. For the compositions in the two-phase alloy region gaseous hydrogen first reacts with the zirconium-rich phase (323 K), resulting in immeasurably low pressures characteristic of a zirconium hydride phase. For example, at 323 K the equilibrium hydrogen pressure for the α - δ plateau region of the Zr-H system is estimated to be 10^{-20} mbar [23] and the Zr(Mn) phase which exists here also has a very low pressure.

This is the first report of calorimetric measurements of enthalpies of reaction of hydrogen with intermetallic compounds in two-phase fields. This technique sequentially delineates the reaction of each phase with the gaseous hydrogen. The magnitude of the enthalpies, when coupled with information about the pure phases, yields information about the compositions of the coexisting phases. In the present case of the Zr-Mn system the zirconium-rich phase in the two-phase field must contain some manganese because the enthalpies for reaction (1) are less exothermic than would be expected for pure zirconium. In the case of the ZrMn_{2+x} phase the enthalpy is about $1.5 \text{ kJ (mol H)}^{-1}$ more exothermic than measured for $\text{ZrMn}_{1.8}$ and therefore the limiting stoichiometry of the C-14 Laves phase intermetallic compound is probably closer to $\text{ZrMn}_{1.7}$.

Acknowledgments

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