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Equilibrium, X-Ray, and ^{1}H-NMR Studies of the $ZrCr_2$-H System

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The pressure isotherms of the $ZrCr_2$–H system (20—200 °C, 10—700 Torr) and powder X-ray diffraction have shown the occurrence of two phases, cubic $ZrCr_2H_x$ ($x<1.0$) and hexagonal $ZrCr_2H_x$ ($2.5<x<3.5$). From the gradual change in the diffraction pattern with x, it has been concluded that samples with a low hydrogen concentration ($x<0.8$) contain another hexagonal phase. All these phases have Laves-type structures (C14 and C15). At 106 K, $ZrCr_2H_{2.66}$ has a much smaller second moment (7.2 G) of ^{1}H-NMR than the value calculated from the random-distribution model (77.9 G), which shows that the nearest sites can not be filled by hydrogen atoms at the same time. The system of $TiCr_2$–H has also been studied for comparison.

In 1961, Beck reported that the intermetallic compound $ZrCr_2$ absorbs hydrogen up to $ZrCr_2H_{3.42}$.¹⁾ More recently, Pebler and Gulbransen have studied the equilibria of the system and have established the formation of a solid solution of hydrogen in the hexagonal-metal phase.²⁾ They observed at lower temperature, a tendency for phase separation which may occur below 0 °C, but no new phase was detected by X-ray diffraction studies. The present paper will show evidence for the formation of three different phases on the hydrogenation of $ZrCr_2$ by the use of X-ray and dissociation-pressure measurements. The results of the study of the $TiCr_2$–H system will be mentioned only briefly, because more extended data have been published after the completion of this work.³⁾ It is, though, worthy of note that our samples of $TiCr_2$ were of the C14 type and not the C15 type used by Reilly in Ref. 3.

$ZrCr_2$ and $TiCr_2$ are the only intermetallic phases in Zr– and Ti–Cr systems, and both form Laves phases. The low-temperature form of $TiCr_2$ has the cubic $MgCu_2$ (C15) structure, and it is transformed into the hexagonal $MgZn_2$ (C14) structure at 1220 °C. About the polymorphic nature of the $ZrCr_2$ compound, the literature presents conflicting reports. For instance, Rostoker reported that the transformation from the low-temperature form with the $MgCu_2$ structure to the form with the $MgZn_2$ structure occurs at 990—994 °C.⁴⁾ However, according to Alisova *et al.*, the $MgZn_2$-type structure is the low-temperature form and the transition temperature is 1480±10 °C.⁵⁾ As will be discussed later, the $ZrCr_2$ used in this work contained both the cubic and hexagonal forms.

Experimental

Materials. The starting materials were electrolytic chromium (99.2%), sponge titanium (99.8%), and sponge zirconium (99.8%). Intermetallic compounds were prepared by non-consumable arc-melting in an atomsphere of argon, the buttons being inverted and remelted several times to ensure homogeneity. X-Ray diffraction analyses showed both samples to contain only the intermetallic phases. It was found by X-ray fluorescence analysis that the non-iron impurity did not exceed 0.05% in the $ZrCr_2$ sample; the results of the chemical analyses were: Zr, 46.83% (calcd. 46.73%); Fe, 0.091%. The hydrogen for the experiments was obtained by the thermal decomposition of titanium hydride, which had been prepared from sponge titanium and high-purithy hydrogen (99.9999%). The titanium hydride was stored in a vacuum and had never been taken out into the atmosphere before experiments.

Equilibrium Studies and Preparation of Hydrided Samples. The apparatus for the measurements of the dissociation pressure and for the preparation of hydrided samples was a vacuum line made of glass equipped with four gas reservoirs, a silica tube in which samples were laid, and another silica tube for the generation of hydrogen from titanium hydride. The vacuum of the system before the experiments was under 10^{-6} Torr. The pressure of hydrogen was measured with a mercury manometer. The hydrogen composition (x) was calculated from the changes in the quantity of hydrogen gas, as determined by the pressure measurements. Corrections for the volume change of the manometer and for the temperature of the heated part of the sample tube had been previously determined. The temperature of the sample was controlled within ±1 °C by the use of a thermostat and an oil bath. For the measurements of the dissociation pressures, several grams of the intermetallic compounds crushed into grains (10—20 mesh) with an Ellis mortar were used. The samples for X-ray and ^{1}H-NMR studies were prepared as follows: after preliminary hydrogenation, the intermetallic compound was powdered, dehydrided and hydrided again to give samples containing certain quantities of hydrogen. The samples were not crushed or powdered after the final preparation.

X-Ray and ^{1}H-NMR Studies. The X-ray studies were performed with a powder diffractometer using Ni-filtered Cu K_α radiation at an ambient temperature. Silicon was used as the internal standard. For the intensity measurements, samples were sprinkled on sample holders coated with adhesive agent. The least squares of the lattice parameters and the calculation of the reflection intensities were performed on a HITAC 8700/8800 computer at the Computer Centre of the University of Tokyo. The ^{1}H-NMR was measured with a Varian VF-16 wide-line spectrometer with a Varian variable-temperature accessory.

Results

The observed isotherms of the $ZrCr_2$–H and $TiCr_2$–H systems are shown in Fig. 1 and Fig. 2. The enthalpy and entropy changes of the reaction:

$$1/1.5\ ZrCr_2H_{1.0} + 1/2\ H_2 \longrightarrow 1/1.5\ ZrCr_2H_{2.5}$$

were calculated as $\Delta H = -11$ kcal/mol and $\Delta S = -26$ cal/K/mol (1 cal=4.184 J) from the temperature

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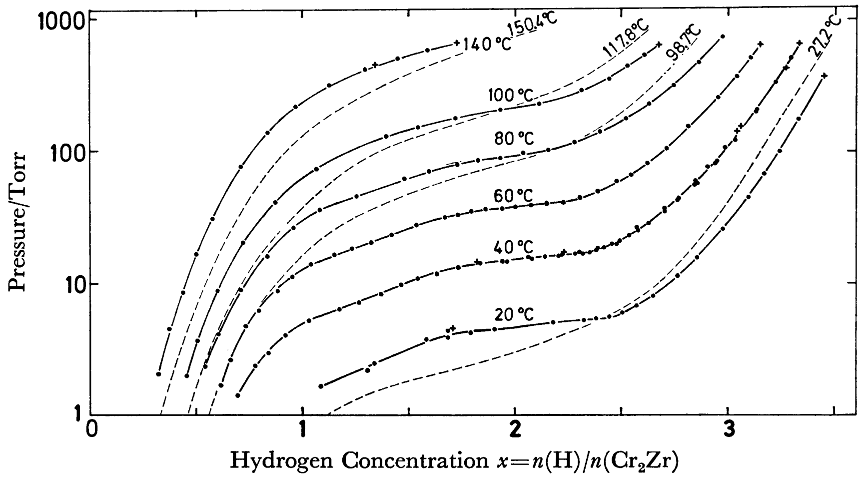

Fig. 1. Pressure-composition isotherms for the system of $ZrCr_2$-H.
+ Dehydriding; ● hydring.

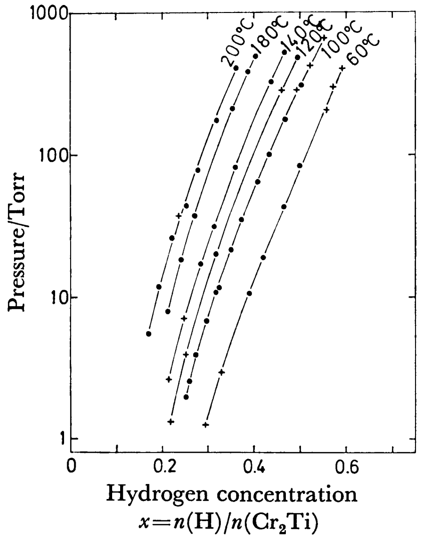

Fig. 2. Pressure-composition isotherms for the system of $TiCr_2$-H.
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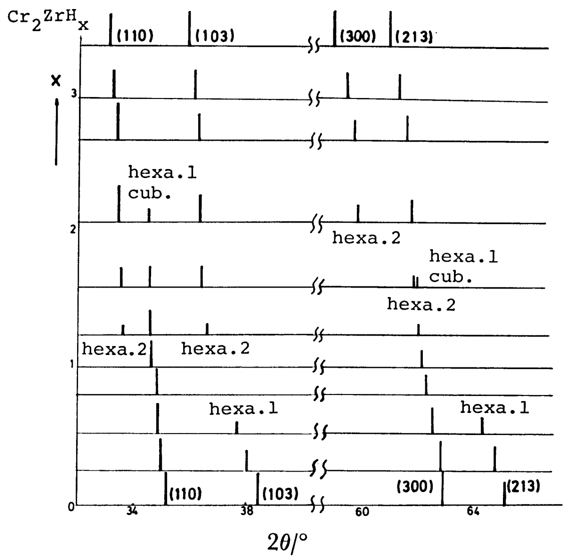

Fig. 3. Observed reflection-angles and -intensities of the powder X-ray diffration of $ZrCr_2H_x$.

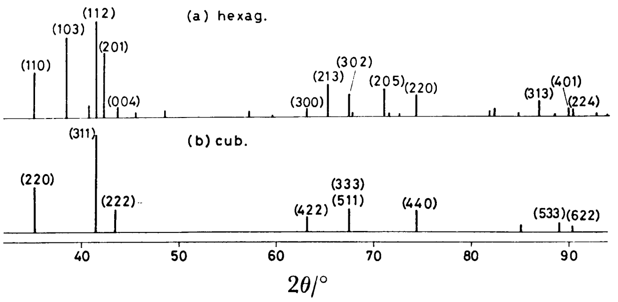

Fig. 4. Calculated reflection-angles and -intensities of the powder X-ray diffraction of $ZrCr_2$.
(a) The structure is assumed to be hexagonal Laves phase; (b) The structure is assumed to be cubic Laves phase.

dependence of the plateau pressure. The isotherms for the $ZrCr_2$-H system with plateaus showed that two phases coexist in the samples in the $1<x<2.5$ region, and the X-ray data confirmed it. A hydrogen-rich phase (α' phase) with a hexagonal $MgZn_2$-type structure (C14) and a hydrogen-poor phase with a cubic $MgCu_2$-type structure were observed with the X-ray techniques in the samples in the two-phase region. While the powder pattern of the hydrogen-rich phase did not change with the x value except for the lattice expansion, a gradual variation in the powder pattern was observed in the samples with low hydrogen concentrations, as is shown in Fig. 3. The powder pattern of the sample with $x=1.0$ is identical with the calculated pattern of the cubic structure (C15), while the pattern of the sample with a very low hydrogen concentration is similar to the hexagonal structure (C14) (Fig. 4). The sample with x value between these two extremes have powder patterns generated by the superposition of these two patterns. Though the calculated patterns of the hexagonal and cubic structures are very similar, some reflections, such as (103) and (213), of the hexagonal structure do not correspond to any reflection of the cubic phase. From the measurements of the intensities of these reflections, the following was concluded: the starting material, $ZrCr_2$, which has been prepared by the dehydrogenation of $ZrCr_2H_x$, as has been described in the Experimental section, consists *ca.* 40% of the cubic (α_c) and *ca.* 60% of the hexagonal (α_h) phase. The samples with $x<0.8$ also consist of cubic (α_c) and hexagonal (α_h) phases, but the percentage of the cubic phase increase with the x value until it reaches 100% at $x=0.8$.

Table 1. Lattice constants of $ZrCr_2H_x$ and $TiCr_2H_x$
Standard deviations in parentheses.

	a/Å	c/Å
$ZrCr_2$ (α_h)	5.107(3)	8.290(8)
$ZrCr_2H_{0.250}$ (α_h)	5.119(2)	8.356(6)
$ZrCr_2H_{0.516}$ (α_h)	5.141(3)	8.383(8)
$ZrCr_2H_{1.582}$ (α')	5.342(2)	8.747(6)
$ZrCr_2H_{2.047}$ (α')	5.354(1)	8.746(10)
$ZrCr_2H_{2.824}$ (α')	5.376(1)	8.774(3)
$ZrCr_2H_{2.953}$ (α')	5.386(1)	8.801(3)
$ZrCr_2H_{3.340}$ (α')	5.420(1)	8.856(6)
$TiCr_2$	4.923(2)	7.990(4)
$TiCr_2H_{0.171}$	4.938(3)	8.026(10)
$TiCr_2H_{0.318}$	4.946(3)	8.074(12)
$TiCr_2H_{0.526}$	4.967(5)	8.131(14)
$ZrCr_2$ (α_c)	7.211(3)	
$ZrCr_2H_{0.250}$ (α_c)	7.237(2)	
$ZrCr_2H_{0.516}$ (α_c)	7.264(1)	
$ZrCr_2H_{0.795}$ (α_c)	7.298(4)	
$ZrCr_2H_{1.012}$ (α_c)	7.306(2)	
$ZrCr_2H_{1.232}$ (α_c)	7.322(3)	
$ZrCr_2H_{1.582}$ (α_c)	7.328(3)	

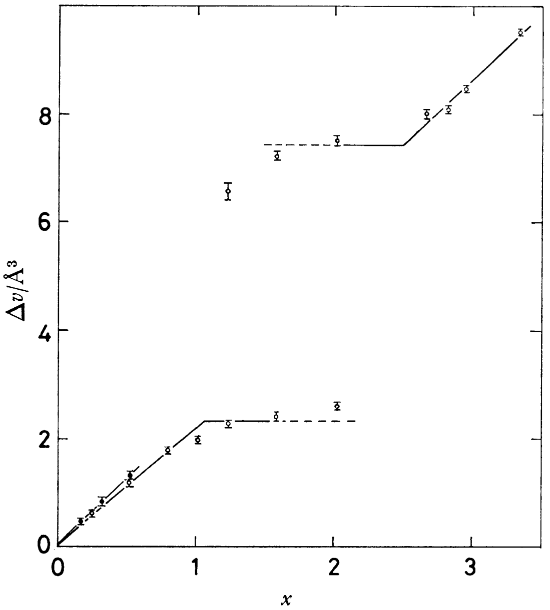

Fig. 5. Hydrogen-concentration dependence of the volume of MCr_2H_x with standard derviations.
M is Ti (filled circles) or Zr (unfilled circles). Δv means $\Delta V/Z$, where ΔV is the increase of the unit-cell volume of MCr_2H_x and Z is the number of MCr_2H_x units in a unit cell. $ZrCr_2H_x$) $0<x<1$) has two stuructures, but their Δv's are practically equal.

In contrast with $ZrCr_2H_x$, $TiCr_2H_x$ ($x<0.6$) had only a hexagonal $MgZn_2$-type structure (C14). The lattice constants of $ZrCr_2H_x$ and $TiCr_2H_x$ are shown in Table 1, while the increase of the volumes with the x value is shown in Fig. 5. The volume increase per hydrogen atom was 2.5 Å^3 for $TiCr_2H_x$ and 2.2 Å^3 for $ZrCr_2H_x$. These values are a little smaller than the values for palladium alloy–hydrogen systems reported by Baranowski *et al.* (11.5/4 Å^3=2.9 Å^3).[6)]

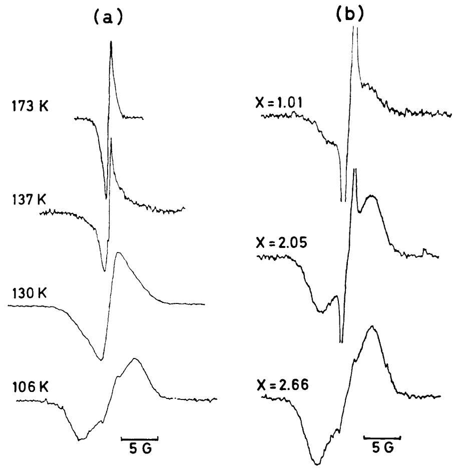

Fig. 6. ^{1}H-NMR spectrum of $ZrCr_2H_x$ at 3700 G.
(a) Temperature-dependence of the ^{1}H-NMR spectrum of $ZrCr_2H_{2.66}$; (b) Hydrogen-concentration dependence of the ^{1}H-NMR spectrum of $ZrCr_2H_x$ at 106 K.

The temperature dependence of the ^{1}H-NMR spectrum of $ZrCr_2H_x$ is shown in Fig. 6. A widening of the signal of hydrogen in the α' phase was observed at 173—106 K, but the signal of hydrogen in the α_c and α_h phases showed motional-narrowing even at 106 K. The second moment of the $ZrCr_2H_{2.66}$ sample at 106 K was 7.2 G^2 (1 G=10^{-4} T).

Discussion

The dissociation pressures of the $ZrCr_2$–H system obtained by the present authors are higher than those reported by Pebler and Gulbransen, as is shown in Fig. 1. To explain this discrepancy, the present authors assume some width of the nonstoichiometry of the $ZrCr_2$ phase, as in the case of $TiCr_2$, though it has not yet been reported how wide the phase is. Therefore, the difference in the dissociation pressure of $ZrCr_2H_x$ probably depends on the composition of the $ZrCr_2$ phase. A very small difference may be enough to explain the discrepancy in these two sets of data. The small variation in the dissociation pressure in the two-phase region ($1.0<x<2.5$) may also be caused by the nonstoichiometry of $ZrCr_2$, since a small inhomogeneity may inevitably be brought about in the sample prepared by arc-melting, which causes a fluctuation in the dissociation pressure of the sample.

In a Laves-phase compound, AB_2, if it has the ideal structure of the Laves phase, there are 24 tetrahedral holes around one larger atom, A, whether its structure is the $MgZn_2$ type or the $MgCu_2$ type. All these holes have the same size, and hydrogen atoms are assumed to enter into these holes, because they are the largest ones. If all these holes were filled with hydrogen atoms, the composition of the compound would be AB_2H_{12}. Because the c/a ratios of the lattice constants of hexagonal $ZrCr_2$ and $TiCr_2$ are very close to the value of the ideal structure, $2\sqrt{6}/3$, and since they change very slightly with the x value, we can assume in the following discussions that they have the ideal structure of the Laves phase.

The tetrahedral holes in $ZrCr_2$ and $TiCr_2$ are all of almost the same size. Strictly speaking, the radii of the largest spheres that these holes can hold are calculated to be 0.349 Å for $ZrCr_2$ and 0.360 Å for $TiCr_2$ if we assume the atomic radii to be 1.2866 Å for chromium, 1.4615 Å for titanium, and 1.6027 Å for zirconium,$^{7)}$ and if we assume the unit-cell volumes to be equal to the observed values of $ZrCr_2$ and $TiCr_2$. Therefore, the difference in the hydrogen-absorption ability between $ZrCr_2$ and $TiCr_2$ can not be attributable to the difference in the size of the holes of each intermetallic compound.

Since, around 106 K, the ^{1}H-NMR spectrum of $ZrCr_2H_{2.66}$ did not broaden as the temperature decreased, the hydrogen atoms are thought to form a rigid lattice. Therefore, the second moment of the spectrum can be compared with the theoretical value calculated using the following equation:$^{8)}$

$$M = \frac{9}{10}\gamma^2 N^{-1} \sum_{j \neq k} r_{jk}^{-6}$$

where M, γ, N, and r_{jk} are the second moment, the magnetic moment of a proton, the number of protons, and the distance between the protons j and k respectively. If we assume a random distribution of hydrogen atoms in all of the tetrahedral holes mentioned above, we get 77.9 G^2 as M, which is much larger than the observed value (7.2 G). This discrepancy suggests that a hydrogen atom occupying a hole prevents other hydrogen atoms from entering the neighboring holes. This seems probable, because the distance between the nearest holes are only about 1.2 Å. For the purpose of getting an approximate value of the second moment for the restricted random distribution in which a hydrogen atom has no neighbor within 1.5 Å, the above equation, excluding the terms in which r_{jk} is less than 1.5 Å has been calculated. The result of this calculation was 14.2 G^2; this value agrees better with the observation.

The transformation from the hexagonal α_h phase to the cubic α_c phase shown by the intensity variation in the X-ray diffraction in $ZrCr_2H_x$ is not analogous to any other found in metal–hydrogen systems, but the facts described below may support the occurrence of this transformation. The only difference between the two structures is their stacking order, the cubic phase having the ABCABC....order and the hexagonal phase having the ABAB....order.$^{9)}$ Therefore, the transformation between the two structures may take place easily by means of a shear mechanism; indeed, in the $TiFe_2$ system a martensitic transformation between these structures has been proposed on the basis of the temperature dependence of the electric conductivity at low temperatures.$^{10)}$ The reason why the coexistence of these two phases has not been shown by the isotherms may be that the plateau pressure is lower than the measured pressure range.

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