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Phase diagram of Hf–H alloy

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The equilibrium phase diagram was investigated for hafnium–hydrogen binary system. Using a modified Sieverts' apparatus, pressure–composition–temperature (*P–C–T*) relationships were measured for the hafnium–hydrogen systems at low temperature. Because the allotropic transformation temperature of pure hafnium is about 2000 K, the hafnium–hydrogen phase diagram could not be obtained directly at high temperature. Therefore, based on the Duhem–Margules equation, the partial molar free energy of hydrogen can be estimated at high temperature.

1. Introduction

Metal hydrides are exceptional materials which may be used as a clean fuel in the future and also as an energy storage medium. It is important, therefore, that the equilibrium phase diagram is studied. Using a modified Sieverts' apparatus, *P–C–T* relationships have been investigated for metal–hydrogen systems [1–5]. The Group IVa metals (titanium, zirconium, hafnium) absorb large quantities of hydrogen and form pseudo-hydrides (MH_2) [4, 5]. The partial phase diagrams of titanium–hydrogen [3] and zirconium–hydrogen [5] binary systems were calculated using thermodynamic functions. The hafnium–hydrogen system can be measured at low temperatures, below 1000 K; however, because the allotropic transformation is too high (2000 K), the diagram at high temperature has not yet been clarified.

Therefore, the purpose of the present work was to obtain the partial phase diagram of the Hf–H binary system by using the Duhem–Margures equation.

2. Experimental procedure

Using a Sieverts' apparatus shown schematically in Fig. 1, the *P–C–T* relationships for the hafnium–hydrogen system were measured [5, 6]. The apparatus consists of four parts: the evacuation apparatus, the hydrogen gas supply, the equilibrium pressure measuring system and the reaction tube. The apparatus was evacuated to 1×10^{-4} Pa for 1 week before measurements. A leak rate of less than 8×10^{-7} Pa l sec^{-1} was obtained.

The purity of the specimen was at least 98%, the main impurity being zirconium. Rectangular specimens weighing about 400 to 500 mg were polished in mineral oil and washed with pure acetone just before mounting in the reaction tube. The specimen was degassed in the reaction tube at about 1100 K, until a leak rate of less than 8×10^{-7} Pa l sec^{-1} was obtained.

Hydrogen gas was obtained from the thermal decomposition of titanium hydride and was purified by passage through the heated palladium–alloy tube. The amount of hydrogen gas absorbed by the solidus specimen was measuring using the gas burette and the mercury manometer, M_1, and was calculated from the ideal gas law. The equilibrium pressure was measured by the McLeod gauges (Mc_1, 10^{-4} to 10^0 Pa; Mc_2, 10^0 to 10^2 Pa) and the mercury manometer (M_2, 10^2 to 10^4 Pa).

Because of the large temperature difference between the reaction tube and the measuring apparatus with the liquid nitrogen trap, the following correction was used in the determination of the hydrogen. The apparatus was set up without a specimen in the reaction tube and a normal measurement was performed. The hydrogen pressure registered on the gauge corresponded to the residual gas equilibrium pressure, when a specimen attained equilibrium with hydrogen. The actual measurements were subtracted from the total amount of hydrogen gas supplied. Figure 2 shows the correction line for the apparatus.

3. Results and discussion

Figure 3 shows the *P–C–T* relationships for the hafnium–hydrogen system. The equilibrium pressure, P_{H_2}, increases with the amount of hydrogen dissolved in the hafnium. The line conforms to Sieverts' law of the solid solution [4–6]. When the hydridephase begins to precipitate, the isotherm does not change further with changing hydrogen increment, in accordance with the requirements of the phase rule; it depends only on the temperature.

The isotherm shows a plateau at lower temperature which tends to increase in length and miscibility gaps at higher concentrations. The hydrogen–metal ratio approaches 2.0 (66 at %) with decreasing temperature. This shows that the dihydride of hafnium is formed at lower temperatures. The isotherms do not describe the plateau in the high-temperature range. Their gradients change with increasing hydrogen concentration, a phenomenon which is caused by the hydrogen absorbed by another phase.

Figure 4 shows the change in the equilibrium hydrogen pressure with reciprocal temperature.

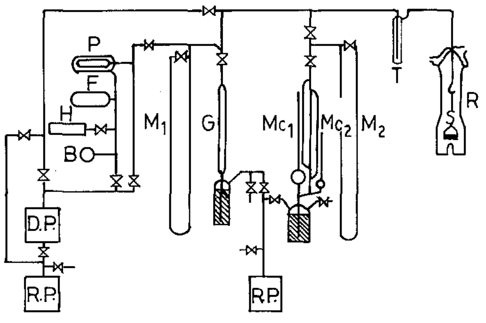

Figure 1 Schematic diagram of the Sieverts' apparatus. P, Permeable palladium tube; F, TiH_2 tank, H, hydrogen gas supply; R, reaction tube; S, sample; M_1, M_2, mercury manometers; T, nitrogen cold trap; Mc_1, Mc_2, McLeod gauge; G, gas burette; R.P., rotary pump; D.P., oil diffusion pump.

The dissolution of hydrogen in the α- and β-hafnium phase is given by the equations

$$1/2H_2(\text{gas}) \rightleftharpoons \text{H (dissolved in } \alpha\text{-hafnium)} \quad (1)$$

$$1/2H_2(\text{gas}) \rightleftharpoons \text{H (dissolved in } \beta\text{-hafnium)} \quad (2)$$

The free energy of the equilibrium conditions were given by

$$1/2F_{H_2}(\text{gas}) = F_H(\alpha) \quad (3)$$

$$1/2F_{H_2}(\text{gas}) = F_H(\beta) \quad (4)$$

Here, F_{H_2}(gas) is the free energy of hydrogen in the gas phase, $\bar{F}_H(\alpha)$ and $\bar{F}_H(\beta)$ are the partial molar free energy in the α- and β-phases. Although the hydrogen atoms could be dissociated in the metal into the form of ions, it was assumed that hydrogen existed as atoms in the lattices.

Because the gas phase is assumed to be ideal for these conditions, the following equation was proposed

$$1/2F_{H_2}(\text{gas}) = 1/2F^0_{H_2}(\text{gas}) + 1/2RT \ln P_{H_2} \quad (5)$$

Hence,

$$\Delta F_{H_2} = 1/2RT \ln P_{H_2} \quad (\text{in } \alpha \text{ and } \beta \text{ phase}) \quad (6)$$

The free energy of solution is expressed as

$$\Delta F(\alpha_{\text{Hf-H}}) = N_H\bar{F} + N_{\text{Hf}}\bar{F}_{\alpha\text{Hf}} \quad (7)$$

$$\Delta F(\beta_{\text{Hf-H}}) = N_H\bar{F} + N_{\text{Hf}}\bar{F}_{\beta\text{Hf}} \quad (8)$$

where N_{Hf}, N_H are atomic fractions and $\bar{F}_{\text{Hf}}$, $\bar{F}_H$ are partial molar free energy.

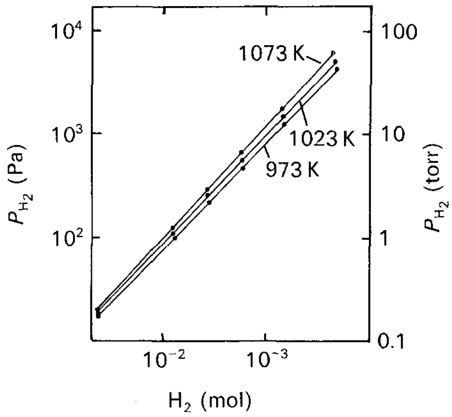

Figure 2 Calibration curves for dead space. H_2 is the amount of residual gas; P_{H_2} is the equilibrium pressure.

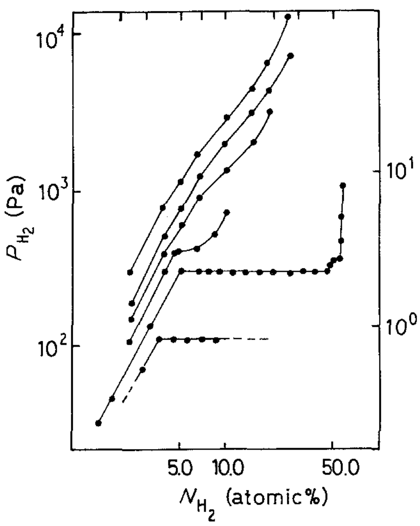

Figure 3 Isothermal pressure-concentration curves for the Hf-H system.

The Duhem-Margules equation is

$$N_{\text{Hf}}\mathrm{d}\bar{F}_{\text{Hf}} + N_H\mathrm{d}\bar{F}_H = 0 \quad (9)$$

$$N_{\text{Hf}}\mathrm{d} \ln N_{\text{Hf}} + N_H \,\mathrm{d} \ln N_H = 0 \quad (10)$$

and from Equation 6

$$\mathrm{d}\bar{F}_H = RT \,\mathrm{d} \ln nP^{1/2}_{H_2} \quad (11)$$

Equation 9 divided by N_{Hf} gives

$$\mathrm{d}\bar{F}_{\text{Hf}} = -N_H/N_{\text{Hf}}\mathrm{d}\bar{F}_H = -RTN_H/N_{\text{Hf}}\mathrm{d} \ln P^{1/2}_{H_2} \quad (12)$$

Equation 10 multiplied by RT and divided by N_{Hf} gives

$$RT \,\mathrm{d} \ln N_{\text{Hf}} + RTN_H/N_{\text{Hf}} \,\mathrm{d} \ln N_H = 0 \quad (13)$$

Rearranging and collecting Equations 12 and 13 produces

$$\mathrm{d}\bar{F}_{\text{Hf}} = RT \,\mathrm{d} \ln N_{\text{Hf}} - RTN_H/N_{\text{Hf}} \,\mathrm{d} \ln P^{1/2}_{H_2}/N_H \quad (14)$$

$$\bar{F}_{\text{Hf}} - F_{\text{Hf}} = RT\left[\ln N_{\text{Hf}} - \int_0^{N_H} N_H/N_{\text{Hf}} \,\mathrm{d} \ln P^{1/2}_{H_2}/N_H\right] \quad (15)$$

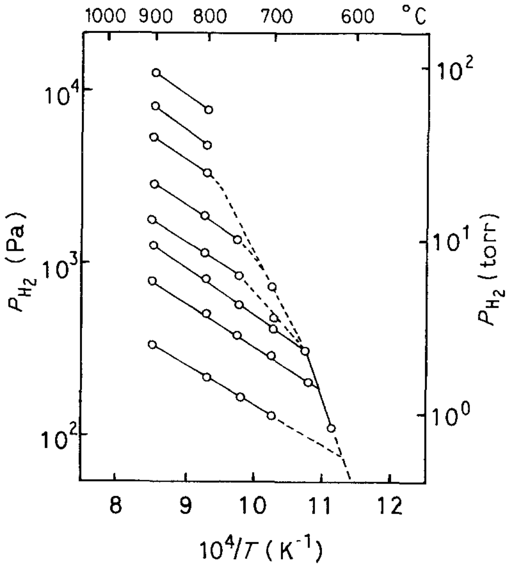

Figure 4 Pressure-temperature curves of isocomposition for the Hf-H system.

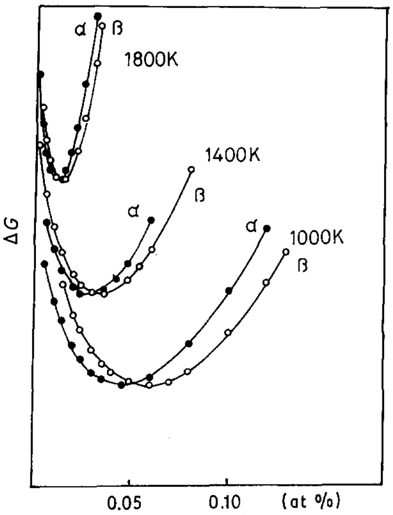

Figure 5 The free energy of the Hf–H system as a function of concentration at a number of temperatures.

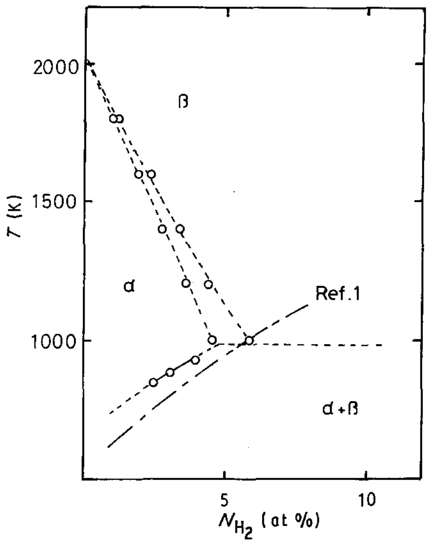

Figure 6 Partial phase diagram of the Hf–H system.

If the change in the activity coefficient of hafnium is negligibly small, equation 15 can be rewritten as

$$\int_0^{N_H} N_H/N_{Hf}\, d \ln P_{H_2}^{1/2}/N_H \qquad (16)$$

and differentiating both sides by N_H by assuming ln $P_{H_2}^{1/2}/N_H = X$ gives

$$dX/dN_H = -1/N_H \qquad (17)$$

$$\therefore dX = -1/N_H \, d\, N_H \qquad (18)$$

Therefore

$$\begin{aligned} \int_0^{N_H} N_H/N_{Hf}(-1/N_H)\, d\, N_H &= -1/N_{Hf} \int_0^{N_H} d\, N_H \\ &= -1/N_{Hf}[N_H]_0^{N_H} \\ &= N_H/N_{Hf} \qquad (19) \end{aligned}$$

If the activity of hafnium equals 1, Equation 15 may be rearranged as follows

$$\begin{aligned} \bar{F}_{Hf} - F_{Hf}^0 &= \Delta F(1 - N_H) \\ &= RT\{[\ln(1 - N_H)] + N_H/(1 - N_H)\} \qquad (20) \end{aligned}$$

The free energy of the hafnium–hydrogen solution is expressed as

$$\begin{aligned} \Delta F(\alpha, \beta_{Hf\text{-}H}) = {} & 1/2 N_H RT(\ln k + Q/RT + 2 \ln N_H) \\ & + RT(1 - N_H)\{[\ln(1 - N_H)] \\ & + N_H/(1 - N_H)\} \qquad (21) \end{aligned}$$

Equations 6 and 20 are used to calculate the partial molar free energy of hydrogen in α and β solutions. The partial molar free energy of hafnium in each solution as a function of hydrogen concentration is deduced from the Duhem–Margules equation. The total free energy of both the α and β solutions at any temperature can be given in terms of the free energies of pure α and β hafnium at that temperature

Figure 5 shows the free energy–concentration curves for α and β solutions of hydrogen in hafnium constructed at different temperatures. The tangents are drawn to the point of the α and β curves. They correspond to the values of hydrogen concentration at which the α and β solutions co-exist.

Because of the agreement between *P–C–T* measurements and calculation of Zr–H system has been investigated [5], the partial phase diagram at high temperatures of the hafnium–hydrogen system can be drawn as shown in Fig. 6. This is constructed from Figs 3 and 5. The allotropic transformation point of pure hafnium coincides with the value of extrapolation from the points of α/(α + β) and β/(α + β) and the existence of the eutectoid point can be estimated.

4. Conclusion

Using a modified Sieverts' apparatus, *P–C–T* relationships of hafnium–hydrogen system were measured at low temperature. Based on the Duhem–Margules equation, the *P–C–T* at high temperature could be calculated.

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