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Magnetic field effect on the equilibrium hydrogen pressure for the $PrCo_5$–H system

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Abstract

The equilibrium hydrogen pressures in the $\beta_I+\gamma$ region of the ferromagnetic hydride $PrCo_5H_x$ have been investigated as a function of the hydrogen composition x under the influence of magnetic fields up to 5 T at 273.2 K. The logarithmic pressure change is increased linearly with increasing magnetic fields and depends on the hydrogen composition. The value ΔM_S (the change in saturation magnetization per desorbed molH) is calculated from the relationship between the pressure change and the magnetic field. The results show a peculiar dependence of the ΔM_S on the hydrogen composition. The maximum value of ΔM_S of 25 J T^{-1} $molH^{-1}$ at $x=4.3$ is much larger than that observed in other metal–hydrogen systems.

Keywords: Metal–hydrogen systems; Hydrogen pressure; Magnetic field effects

1. Introduction

In previous papers increases of equilibrium hydrogen pressure were reported for the $LaCo_5$–H [1,2] and $SmCo_5$–H [3,4] systems under the influence of magnetic fields. In both the systems, the logarithmic pressure change, ln (P^*/P_0) was proportional to the magnetic fields according to the thermodynamic equation based on the magnetostatic energy — $B\Delta M_S$ [5]

$$\ln\left(\frac{P^*}{P_0}\right)=\frac{2B\Delta M_S}{RT} \qquad (1)$$

where, P^* and P_0 are the equilibrium hydrogen pressures under a magnetic field and zero field, respectively, B is the magnetic field, R is the gas constant, and T is the absolute temperature. The parameter ΔM_S is the change in the saturation magnetization per desorbed 1 mol hydrogen atom. Its value is 16.4 J T^{-1} $(molH)^{-1}$ for the $\alpha+\beta$ region of $LaCo_5$–H system at 293.2 K [5]. Although such a large magnetic field effect has been observed for the $LaCo_5$–H system, a much larger effect is expected for the $PrCo_5$–H system because the saturation magnetization showed a strong dependence on the hydrogen composition [6].

The $PrCo_5$–H system exhibits three hydride phases, namely β_{II}, β_I and γ phases on increasing the hydrogen composition. The pressure–composition isotherm (PCT) curve shows that the $\beta_{II}+\beta_I$ plateau pressure vanishes above room temperature [6].

In the present paper the hydrogen composition dependence of the magnetic field-induced change in pressure has been investigated for the $\beta_I+\gamma$ region of $PrCo_5H_x$ with $3.9<x<4.7$ in magnetic fields up to 5 T at 273.2 K. The results are discussed in comparison with the $LaCo_5$–H system.

2. Experiment

The $PrCo_5$ alloy was prepared in an argon atmosphere by arc-melting Pr and Co metals (99.9% purity), followed by annealing at 1223 K for 24 h for homogenization. The reactor including the $PrCo_5$ of 17.85 g was connected to the gas reservoir with a volume of 22.54 cm^3 and was placed at the center of a superconducting magnet (Sumitomo Heavy Industries Co. Ltd., type HF5-56VT-1). Activation cycles were repeated five times: the alloy was hydrogenated with high purity-hydrogen gas (7N) of 5 MPa at room temperature, and then it was degassed in vacuum at 573 K.

A hydrogen composition of $PrCo_5H_{4.69}$ was prepared in the $\beta_I+\gamma$ region via a desorption process by using Sieverts method. The hydrogen pressure was measured under the influence of magnetic fields. The reactor was soaked into a bath with ice and water, thus the temperature of the sample maintained at 273.2 K. The hydrogen pressure was mea-

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sured by using a pressure transducer (Minebea Co. Ltd., type DHF-50) in a magnetic flux-free position. A computer logged the hydrogen pressure, sample temperature, room temperature and magnetic field at intervals of 10 s. The equilibrium pressure was measured when the pressure was no longer changed. Similarly, the measurements were performed for the $\beta_I + \gamma$ region of the hydride $PrCo_5H_x$ with $x = 4.55$, 4.42, 4.31, 4.16, 4.00 and 3.93.

3. Results and discussion

Fig. 1 shows an example of the time variations in the magnetic field, sample and room temperatures, and hydrogen pressure for $PrCo_5H_{4.42}$ under the influence of the magnetic fields up to 5 T. The hydrogen pressure started increasing as soon as the field was applied. However, it took a few minutes to attain the equilibrium. Although the response to the field was quick, the process itself was a slow endothermic reaction. In spite of the equal 0.5 T increase in the field at each step, the periods necessary to attain equilibrium were gradually prolonged with increasing magnetic fields and hydrogen pressures. The change in pressure from the initial to the final states for each step was enhanced exponentially with increasing the initial pressure P_0 according to Eq. (1). The equilibrium hydrogen pressure of $PrCo_5H_{4.42}$ increased by 116 kPa from 2.375 MPa at zero fields to 2.491 MPa at 5 T. The increase in the hydrogen pressure was inevitably accompanied with the decrease in the hydrogen composition of the solid hydride because the volume of the gaseous phase was constant. But the change in the composition was negligibly small ($\Delta x < 0.02$) in the present experimental arrangement. While the magnetic field was removed, the hydrogen pressure was observed to decrease toward the initial pressure. However, the final pressure in zero fields was higher than the initial one because of the hysteresis in the pressure.

The equilibrium hydrogen pressures were measured for the hydrides with various hydrogen compositions in different fields. Then, the data are represented by the logarithmic pressure changes LPC according to Eq. (1) as shown in Fig. 2. For example, the value of LPC was calculated to be 0.0474 for the $PrCo_5H_{4.42}$ at 5 T. All of the hydrides show the increase in the pressure under the influence of the magnetic fields up to 5 T. However, the LPC at 5 T are not constant, depending on the hydrogen composition.

Fig. 3 illustrates the gradient dLPC/dB between 3 T and 4 T and the ΔM_S value calculated from the gradient dLPC/dB according to Eq. (1). They vary strikingly with the hydrogen composition, showing a maximum in the middle of the plateau region: the largest gradient was observed at $x = 4.31$ near the center of the $\beta_I + \gamma$ region. In accordance with this, the maximum value of the ΔM_S is equal to 24.6 J T^{-1} $molH^{-1}$ for $PrCo_5H_{4.31}$.

Up to date, the magnetic field effects have been investigated for some ferromagnetic hydride–hydrogen systems, especially in detail for the $LaCo_5$–H system. We have already reported that the values of ΔM_S are independent of the hydrogen composition for the $\beta + \gamma$ plateau region of

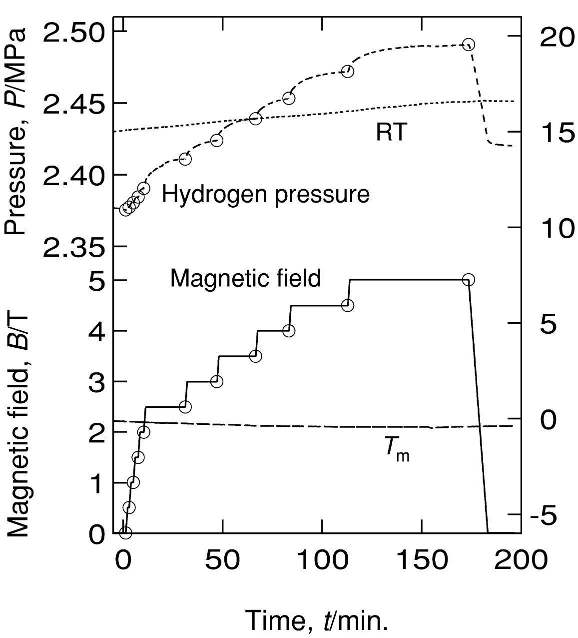

Fig. 1. Time variations in magnetic field (solid curve, left-lower axis), hydrogen pressure (broken curve, left-upper axis), room temperature (dotted curve, right axis) and sample temperature (chained curve, right axis) in the case of $PrCo_5H_{4.42}$. The stepwise field was applied up to 5 T and then the field was removed. The circles on the curves indicate the equilibria.

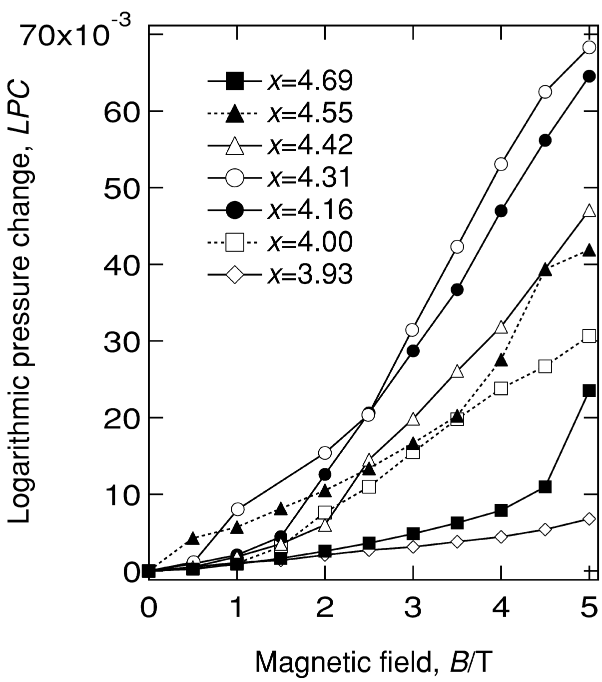

Fig. 2. Magnetic field dependence of the logarithmic pressure change LPC for $PrCo_5H_x$ at 273.2 K.

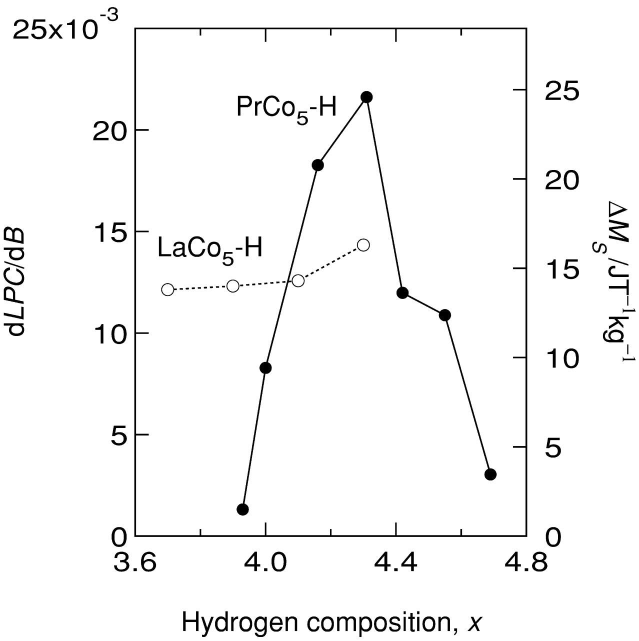

Fig. 3. Hydrogen composition dependence of the gradient of the logarithmic pressure change against the field (left-hand axis), and ΔM_S (right-hand axis) for $PrCo_5H_x$ at 273.2 K. Open marks indicate the ΔM_S for $LaCo_5H_x$ at 293.2 K.

the $LaCo_5$–H system and for the $\alpha+\beta$ region of the $SmCo_5$–H system [4]. The ΔM_S for $LaCo_5H_{4.2}$ maintains a constant value of 16.4 J T^{-1} $molH^{-1}$ at 293.2 K still in strong magnetic fields up to 26 T [1].

The ΔM_S of $PrCo_5H_{4.31}$ observed in the present study is 1.5 times as large as that of the $LaCo_5$–H system. The dependence of the hydrogen composition of ΔM_S are different from each other as shown in Fig. 3. The reason why the $PrCo_5$–H system shows this peculiar behavior is not understood at the present time.

If the ΔM_S is not changed even in high magnetic fields, the equilibrium hydrogen pressure of $PrCo_5H_x$ at $x=4.3$ becomes higher than that at $x=4.7$. But such a PCT cannot occur taking account of thermodynamics. It is considered that the increase in the pressure of the $PrCo_5H_{4.3}$ reaches saturation in higher magnetic fields accompanying the reduction in ΔM_S. Thus, it is desired to investigate the LPC for the hydrides under the influence of magnetic fields greater than 5 T.

4. Conclusion

The hydrogen pressure in the $\beta_I+\gamma$ region of the $PrCo_5$–H system has been investigated with various hydrogen compositions under the influence of magnetic fields up to 5 T. The change in the equilibrium pressure due to the magnetic field of 5 T varies with hydrogen composition. The equilibrium hydrogen pressure of $PrCo_5H_{4.3}$ was increased largely by the magnetic fields compared with the higher and lower composition hydrides. The hydrogen composition dependency of saturation magnetization, ΔM_S is observed to be 24.6 J T^{-1} $molH^{-1}$ for $PrCo_5H_{4.3}$. To our knowledge, this is the largest parameter as the magnetic field effects on the equilibrium pressure change based on the magnetostatic energy — $B\Delta M_S$.

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