Magnetic field effects on the hydrogen isotope separation with metal hydrides

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Abstract

Hydrogen isotope separation experiments were conducted under the influence of magnetic field with the ferromagnetic LaCo5 and the paramagnetic LaNi5 compound as working materials. The deuterium concentration in the gas phase after hydrogen-absorbing reactions depended on applied magnetic fields for LaCo5, but not for LaNi5. The isotope separation factor α=(D/H)gas/(D/H)solid increased from 1.54 in zero field to 2.25 at 13 T in the β+γ region for the system LaCo5–(H2+D2). The increase in α is related to the magnetic field effect on the equilibrium pressure in ferromagnetic metal hydrides.

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1. Introduction

Metal hydrides have potential applications to energy technology and materials processes including hydrogen isotope separation of protium H, deuterium D and tritium T [1]. This method is due to the hydrogen isotope effect on the equilibrium pressure between the protide MH, deuteride MD, and tritide MT. In this paper, the terms ‘hydrogen’ and ‘hydride’ represent every element H, D and T and every compound MH, MD, and MT, respectively. If, for instance, the equilibrium pressure of the deuteride $P_D$ is larger than that of the protide $P_H$ in zero field, we can enhance it by applied magnetic fields [2,3].

Some ferromagnetic hydrides exhibit a magnetic field effect where the equilibrium hydrogen pressure is changed with increasing applied magnetic fields B according as

$$P_B = P_0 \exp \left( \frac{2B\Delta M_s}{RT} \right)$$

where $P_B$ is the equilibrium pressure in the magnetic field and $P_0$ is that in zero field. This magnetic field effect originates from the ferromagnetic property of the hydrides which is expressed by the change in the saturation magnetization per mole of desorbed hydrogen, $\Delta M_s$ [4]. For the system LaCo5–H2, as a matter of fact, $P_0=232$ kPa in zero field and $P_B=281$ kPa in 15 T in the β+γ region with $\Delta M_s=15.7 \text{ J T}^{-1} (\text{mol H})^{-1}$ at 303 K [5,6]. The same magnetic effect occurs for the corresponding deuterium system LaCo5–D2 because the magnetic properties of the deuteride LaCo5D are the same as those of the corresponding protide LaCo5H in the magnetic fields below 35 T which are currently available as steady magnetic fields [7]. Consequently, the value of $\Delta M_s$ is common to the protide and the deuteride. Even so, Eq. (1) implies that the pressure difference $P_D^0 - P_D^H$ in zero field is increased with increasing applied magnetic fields.

Assuming that the isotope separation ability is related to the pressure difference $P_D^0 - P_D^H$, we can enhance it by applied magnetic fields. In this work, we investigate the magnetic field effect on the isotope separation ability with the ferromagnetic LaCo5 compound. In addition, we examined the paramagnetic LaNi5 compound for comparison: The system LaNi5–H2 shows the isotope effect on the equilibrium pressure because of non-ferromagnetic property. We presume that the latter system does not show such a magnetic field-induced enhancement of the isotope separation ability.

2. Pressure–composition isotherms

LaCo5 and LaNi5 compounds were prepared by arc melting cobalt and rare earth metals in an argon atmosphere. The purity

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of the raw materials was 99.99% for Co and Ni and 99.9% for La. The ingots were annealed at 1223 K for 48 h for homogenization. The samples were pulverized in an argon atmosphere in sizes under 10 \( \mu \text{m} \). X-ray powder diffraction showed that they were single phase with the CaCu5 structure.

Pressure–composition isotherms (PCTs) were measured by the volumetric method in the pressure ranges of 1–1000 kPa at ordinary temperatures. The purity of the gas was 99.99999% for protium and 99.5D/(D+H)% for deuterium. The experimental error was \( \pm 3\% \) for the hydrogen composition \( x \) in \( \text{MH}_x \).

Fig. 1(a) and (b) show the PCTs for the systems \( \text{LaCo}_5–\text{H}_2(\text{D}_2) \) at 273 K and \( \text{LaNi}_5–\text{H}_2(\text{D}_2) \) at 303 K, respectively. The Co-system has two plateaus of the \( \alpha + \beta \) region \( (0.3 < x < 3.4) \) and the \( \beta + \gamma \) region \( (3.4 < x < 4.3) \). The equilibrium pressure of the deuteride \( P_D \) is higher than that of the protide \( P_H \) in both regions and this isotope effect is more appreciable in the \( \beta + \gamma \) region than the \( \alpha + \beta \) region. On the other hand, the Ni-system has one plateau of the \( \alpha + \beta \) region \( (0.3 < x < 6) \). The deuterium pressure is lower than the protide pressure at this temperature \( (P_D/P_H = 0.915) \). Table 1 lists the observed values of the pressure ratio observed, including the literature data for the Ni-system at 313 K.

3. Isotope separation experiment

The isotope separation experiment was performed under the influence of magnetic fields with the apparatus shown in Fig. 2, by which the deuterium/protium concentration in the gas phase was measured before and after the hydrogen-absorbing reaction of the compounds. First, the 1:1 mixed gas of \( \text{H}_2 \) and \( \text{D}_2 \) was prepared in a tank with the volume of 500 cm\(^3\) at a pressure of 1.2 MPa. This mixed gas was stored for 24 h for homogenization at room temperature. Then, the mixed gas was introduced to a reservoir with the volume of 59.3 cm\(^3\) at an initial pressure \( P_{\text{initial}} \). Next, we introduced this gas into a reactor to react with about 2 g of the \( \text{LaCo}_5 \) or \( \text{LaNi}_5 \) compound. Here, the reactor was situated in the center of a cryo-cooled superconducting magnet with a maximum field of 13 T and an inner bore of 100 mm (JMTD-13T100EF3, Japan Superconducting Technology, Inc.). The temperature of the reactor was controlled at 303.0 \( \pm 0.1 \) or 313.0 \( \pm 0.1 \) K by circulating temperature-controlled water in a water jacket.

### Table 1

Collected data of the hydrogen isotope separation with metal hydrides under the influence of magnetic fields

| System      | Region | Temp. (K) | Pressure ratio\(^a\), \( P_D/P_H \) | Magnetic field (T) | Separation factor, \( \alpha \) | \( \Delta M_s \) (J T\(^{-1}\) (mol H)\(^{-1}\)) | Pressure difference\(^b\), \( P_D - P_H \) (kPa) |
|-------------|--------|-----------|-------------------------------------|--------------------|-------------------------------|---------------------------------|---------------------------------|
| \( \text{LaNi}_5–(\text{H}_2+\text{D}_2) \) | \( \alpha + \beta \) | 303       | 0.915                               | 0                  | 0.954                         | ~0                              | -17.8                           |
|             |        |           |                                     | 13                 | 1.05                          |                                 |                                 |
|             |        |           |                                     | 0                  | 1.90                          |                                 |                                 |
|             |        |           |                                     | 5                  | 1.78                          | ~0                              | 44.6\(^c\)                      |
|             |        |           |                                     | 13                 | 1.70                          |                                 |                                 |
| \( \text{LaCo}_5–(\text{H}_2+\text{D}_2) \) | \( \alpha + \beta \) | 303       | 1.16                                | 0                  | 1.19                          | 8.7                             | 1.114                           |
|             |        |           |                                     | 5                  | 1.19                          | 1.153                           |                                 |
|             |        |           |                                     | 10                 | 1.45                          | 1.394                           |                                 |
|             |        |           |                                     | 13                 | 1.53                          | 1.219                           |                                 |
|             |        |           |                                     | 0                  | 1.54                          | 15.7                            | 288.78                          |
|             |        |           |                                     | 5                  | 1.95                          | 307.36                          |                                 |
|             |        |           |                                     | 10                 | 2.00                          | 327.13                          |                                 |
|             |        |           |                                     | 13                 | 2.25                          | 339.60                          |                                 |
|             | \( \beta + \gamma \) | 303       | 2.18                                | 0                  | 1.54                          | 15.7                            | 288.78                          |

\(^a\) Pressure ratio in zero field.

\(^b\) The values in 0 T are observed and those in 5–13 T are calculated.

\(^c\) After Biris et al. \[3\]..

Fig. 1. Pressure–composition isotherms for the systems (a) \( \text{LaCo}_5–\text{H}_2(\text{D}_2) \) at 273 K and (b) \( \text{LaNi}_5–\text{H}_2(\text{D}_2) \) at 303 K.
The process of hydrogen absorption was monitored by the pressure in the reservoir with a strain-gauge type transducer. After 3–5 min from the start of reaction, the pressure attained a constant value when the hydrogen absorption was completed at the final pressure $P_{\text{final}}$. Eventually, the hydride $\text{LaCo}_5(\text{H,D})_x$ or $\text{LaNi}_5(\text{H,D})_x$ was formed, where $x$ was the final hydrogen composition. The deuterium/protium concentration in the initial or final gas was measured by a mass spectrometer (Quadstar TM 421 QMS200, Balzers Co. Ltd). The experimental error of the composition was less than $1.5\%$. Because the gas included a small amount of HD molecules, we divided them into the H and D concentration equally.

Before the main isotope separation experiment, we operated this experimental apparatus without samples in the reactor. As a result, the deuterium concentration was measured to be 55.0% in the initial gas and 54.6% in the final gas, which agree with each other within the experimental error. This confirmed that the deuterium concentration in the reservoir is not affected by the gas handling itself.

Fig. 3 exemplifies the time-variation of the pressure in the gas phase during the isotope separation experiment where a magnetic field of 13 T at 303 K was applied to the $\beta + \gamma$ region for the system $\text{LaCo}_5(\text{H}_2\text{D}_2)$ was examined at 303 K under the influence of a magnetic field of 13 T. The pressure was $P_{\text{initial}} = 0.564$ kPa and $P_{\text{final}} = 0.137$ kPa and the deuterium concentration was 54.4% in the initial gas and 68.7% in the final gas. The final hydrogen composition in the solid phase was $x = 3.8$ in the $\beta + \gamma$ region. As a consequence, the ratio between hydrogen isotopes was estimated to be $(\text{D/H})_{\text{gas}} = 2.19$ in the gas phase and $(\text{D/H})_{\text{solid}} = 0.975$ in the solid phase after the completion of hydrogen absorption.

Fig. 4 illustrates the magnetic field dependence of deuterium concentration in the gas phase for the isotope separation experiment at 303 K. In both the $\alpha + \beta$ and the $\beta + \gamma$ regions for the Co-system, deuterium is concentrated in the gas phase after the reaction. Moreover, the deuterium concentration increased with increasing magnetic fields and this magnetic field effect is more appreciable in the $\beta + \gamma$ region than the $\alpha + \beta$ region. In contrast to this, the Ni-system shows a little decrease in the deuterium concentration in the final gas in zero field. But the deuterium concentration hardly changed by the applied field of 13 T.

One of measures for the isotope separation ability of metal hydrides is the isotope separation factor defined by

$$\alpha = \frac{(\text{D/H})_{\text{gas}}}{(\text{D/H})_{\text{solid}}}$$

where the isotope separation ability is increased as the $\alpha$ value deviates from unity. For instance, we obtained $\alpha = 2.25$ in the
separation experiment shown in Fig. 3 where \( (D/H)_{\text{gas}} = 2.19 \) and \( (D/H)_{\text{solid}} = 0.975 \). The observed values of the separation factor are summarized in Table 1, which indicates the following features with some explanations.

1. Deuterium is concentrated in the gas phase after the reaction under zero field in the \( \alpha + \beta \) and \( \beta + \gamma \) regions for the Co-system at 303 K and in the \( \alpha + \beta \) region for the Ni-system at 313 K. On the contrary, hydrogen is concentrated in the gas phase in the \( \alpha + \beta \) region for the Ni-system at 303 K. This satisfies the basic principle of the hydrogen isotope separation with metal hydrides, namely the gas with the higher equilibrium pressure is concentrated in the gas phase.

2. In zero field, the separation factor is nearly proportional to the pressure ratio \( P_D/P^H \) both in the La- and Ni-systems. This is simply explained by the thermodynamic model that the separation factor is determined by the pressure ratio, that is, \( \alpha = P_D/P^H \). This model assumes the equilibrium state between \( H_2, D_2, MH \), and \( MD_x \) [1].

3. The magnetic field effect on the isotope separation factor is exhibited for the Co-system, but not for the Ni-system. This is ascribed to the magnetic properties of the hydrides: The former system has a significant magnetic field effect on the equilibrium pressure but the latter system has no effect because the \( \text{LaCo}_5\text{(H,D)}_x \) is ferromagnetic and the \( \text{LaNi}_5\text{(H,D)}_x \) is paramagnetic.

4. For the Co-system, the magnetic field effect on the separation factor in the \( \beta + \gamma \) region is greater than that in the \( \alpha + \beta \) region. This can be connected to the value of \( \Delta M_s \), which is 15.7 and 8.7 J \( T^{-1} \text{mol} \text{H}^{-1} \) for the \( \beta + \gamma \) and the \( \alpha + \beta \) regions, respectively.

We consider the origin of magnetic field effect on the isotope separation factor. The pressure ratio \( P_D/P^H \) remains constant with increasing magnetic fields because Eq. (1) applies to the protide \( \text{LaCo}_5\text{H}_x \) and the deuteride \( \text{LaCo}_5\text{D}_x \) with the same value of \( \Delta M_s \). This means that the separation factor depends not only on the pressure ratio \( P_D/P^H \) but also, to an extent, on some other factor, which is considered to be the pressure difference \( P_D - P^H \). The pressure difference \( P_D - P^H \) is increased, even if the value of \( \Delta M_s \) is the same for the protide and deuteride, according as:

\[
P_D^D - P^H_D = (P_D^0 - P^H_0) \exp \left( \frac{2B\Delta M_s}{RT} \right) \tag{3}
\]

The calculated values of the pressure difference are listed in Table 1. It is observed that the separation factor is increased with increasing magnetic field, associated with the increase in the pressure difference. There is no reasonable explanation of this fact at the moment, but it is speculated that the separation factor is also dominated by the reaction kinetics which is related to the pressure difference \( P_D - P^H \).

In conclusion, the isotope separation ability is enhanced with increasing magnetic fields with the ferromagnetic metal hydride. This enhancement can be explained by the magnetic field effect on the equilibrium hydrogen pressure in ferromagnetic metal hydrides. The isotope separation factor \( \alpha \) increased from 1.54 at zero field to 2.25 at 13 T in the \( \beta + \gamma \) region for the \( \text{LaCo}_5\text{H}_2(\text{D}_2) \) system.

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