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Hydrogen-desorbing behavior of the hydrides in 15 rare earth elements measured by temperature swing column chromatography

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Abstract

Hydrogen-desorbing behavior of the hydrides in 15 rare earth elements (Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu) was examined by temperature swing column chromatography from room temperature to 1273 K. As a result, it was found that hydrogen-desorbing profiles of the rare earth hydrides except Eu had two peaks. The first peaks were located on low-temperature zone of about 600–700 K, the second peaks were located on high-temperature zone of about 700–900 K, and the peaks were separated. The cause of separation was the bonding type between hydrogen and metals, not from hetero-reaction of dehydrogenation. The bonding between hydrogen and metals seemed to be two types.

In addition, the first peaks had two types, sharp one and broad one. The first peaks of Y and heavy rare earth Tb–Lu showed sharp one and those of light rare earth La, Ce, Pr, Nd showed broad one. Sm, Eu and Gd showed complex hydrogen-desorbing behavior. Molar ratio of the first bonding hydrogen atom dissociated at low-temperature zone to the second bonding hydrogen atom dissociated at high-temperature zone was approximately 1–2.

Keywords: Hydrogen storage materials; Metals; Gas–solid reaction; Thermal analysis

1. Introduction

In research of a switchable mirror [1–5], in order to change the transmissivity of light by making hydrogen desorbs from the hydride, it is very important what quantity of hydrogen is desorbed at a certain pressure and a certain temperature. Moreover, in research of a HDDR process [6–11], after carrying out hydrogenation processing, it is necessary to extract hydrogen completely. Therefore, the hydrogen-desorbing behavior from a hydride is very important. As basic research of a hydrogen storage alloy, the research that clarifies the bonding state of rare earth metal and hydrogen is important. Measurement of the hydrogen-desorbing characteristic gives the important key that knows a bonding state. For this reason, fundamental research of the hydrogen-desorbing behavior from rare earth hydrides is especially important. However, there is no research, which measured the hydrogen-desorbing behavior from the hydrides of all rare earth elements with the equipment of the column chromatography method to the high temperature to 1273 K under Ar flow atmosphere. In this research, the hydrogen-desorbing behavior from the hydrides of all rare earth elements was measured with the equipment of the column chromatography method to the high temperature to 1273 K under Ar flow atmosphere. State of hydrogen bonding were also considered in regard to the hydrogen desorption behavior of 15 types of hydrogenated rare earth elements (Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu).

2. Experimental procedure

The 15 rare earth elements used in this study had purities of 99.9% in rare earth metal base, and composition of impurities

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was a maximum of 200 ppm of carbon, a maximum of 0.8% of oxygen and a maximum of 200 ppm of hydrogen (Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu). These materials were activated in a vacuum (treatment temperature 573 K) and then hydrogenated using ultra-high purity hydrogen gas (2 MPa, 303 K hydrogen desorption was measured in real time with up to a temperature of 1273 K using hydrogen analysis equipment (EMGA651, Horiba Seisakusho) by temperature swing column chromatography. The hydride sample was heated in graphite crucible furnace and the resulting mixed gas was fed along with carrier gas (Ar) into various chromatographic columns where desorption and elimination of gases other than the hydrogen occurred. The amount of hydrogen present was then quantified using a thermal conductivity measurement device. After sealing a defined quantity of the sample in a pre-weighed Sn capsule in the Ar gas glove box, approximately 2 g of Sn flux was added, and the hydrogen desorption per unit time was measured while increasing the temperature from room temperature to 1273 K at $dT/dt = 1\ K\ s^{-1}$.

3. Result and discussion

Fig. 1 presents the reproducibility of the hydrogen desorption profile of the Lu hydride as an example of the analysis results. The reproducibility is good, as seen in the results over three measurement runs. The curve plotted in Fig. 1(a) shows the hydrogen desorption intensity, and the curve plotted in Fig. 1(b) shows the hydrogen desorption (H/M) integrated over temperature. H/M represents the number of desorbed hydrogen atoms per single atom of rare earth metal. The first desorption peak for Lu hydride occurs at a temperature of approximately 650 K. Desorption is then suspended at 700 K, but is followed by a second desorption peak at 750K. The hydrogen desorption H/M during this time is approximately 2.8. Eu hydride adsorbs hydrogen at an H/M ratio of approximately 2, and the other fourteen hydrides absorb hydrogen at H/M ratios of approximately 3. In all rare earth hydrides, the measured values for hydrogen absorption and desorption are consistent. Measurements were carried out three times for all of the rare earth elements, and reproducibility was good with the exception of Eu hydride. The hydrogen desorption profiles for the 15 rare earth elements are presented in Fig. 2. Desorption of hydrogen is seen in two stages for all of the hydride samples. A trend is observed in which desorption temporarily stops after desorption of hydrogen at a lower temperature of about 600–700 K (the first desorption peak),

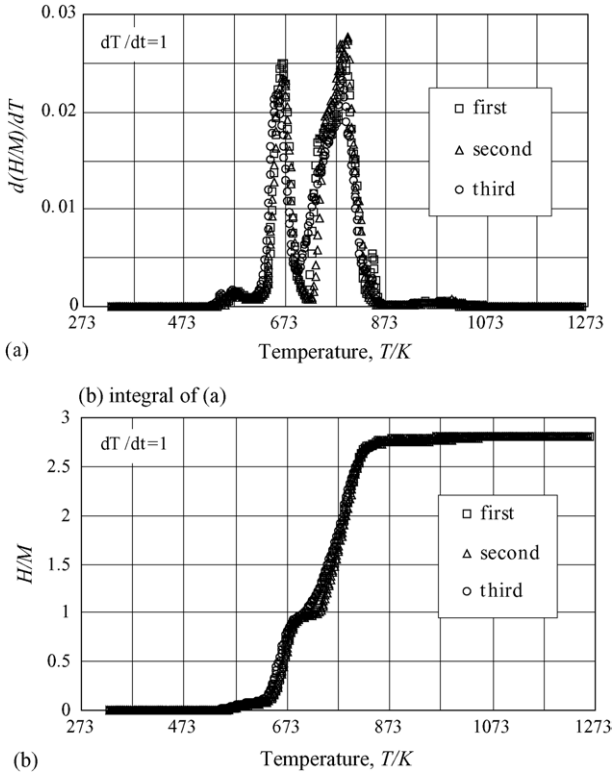

Fig. 1. (a and b) The reproducibility of the hydrogen desorption profile of the Lu hydride, increasing temperature at 1273 K at $dT/dt = 1\ K\ s^{-1}$.

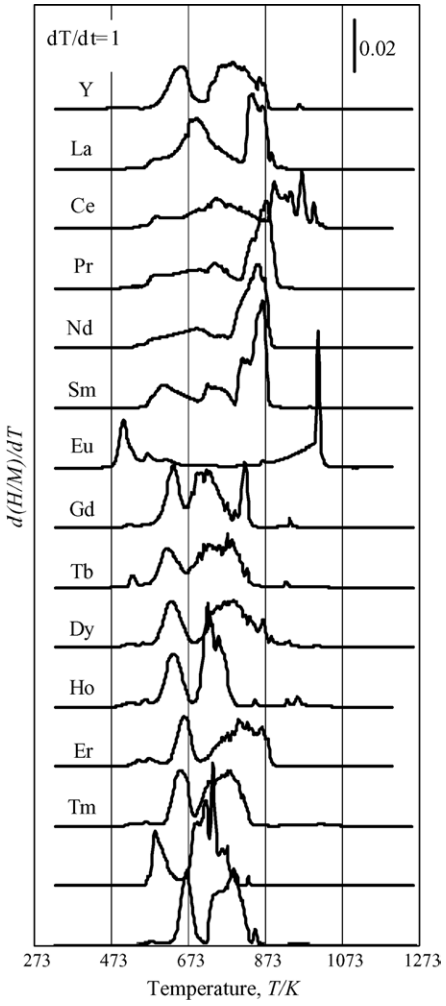

Fig. 2. The hydrogen desorption profiles for the 15 rare earth elements, increasing temperature to 1273 K at $dT/dt = 1\ K\ s^{-1}$.

above which hydrogen desorption occurs again at 750–850 K (the second desorption peak). Both sharp and broad peaks are produced for the first desorption peak. The elements exhibiting a sharp first desorption peak are Y, with the lowest atomic number of the examined elements, and Tb and elements with higher atomic numbers. The hydrides exhibiting broad desorption peak are La, Ce, Pr and Nd, which have low atomic numbers. Sm, Eu and Gd exhibit complex desorption peak profiles. The ratio of the first desorption peak and the second one is about 1:2.

The hydrogen atoms in hydrogenated rare earth elements are thought to be present as either bonded hydrogen atoms that desorb at a lower temperature, or bonded hydrogen atoms that desorb at higher temperature. However, the effects of the capsule and the Sn flux used in these experiments should be considered. Consequently, it is conceivable that the two desorption peaks are present as an artifact of the non-uniform reaction between the hydride and the Sn. In order to confirm this possibility, similar experiment were carried out using Ni capsules. The difference between the hydrogen desorption profile obtained either Sn or Ni capsules is shown in Fig. 3. With Y, La and Ce hydride samples desorption at the two peaks is favorable when a Ni capsule is used. With Y, the temperature differential between the first and second desorption peaks is about 100 K when a Sn capsule is used, but about 400 K with a Ni capsule. With La and Ce, the first desorption peak is extremely broad, and the ratio between the two is approximately 1:2. In order to confirm that peak separation does not occur due to non-uniform reactions, Fig. 4 shows the hydrogen desorption profile for La hydride when the material was held for a period of 600 s at the first desorption peak temperature (690 K). The results indicate that the amount of the hydrogen desorption at the first desorption peak does not increase even when the material is retained at that

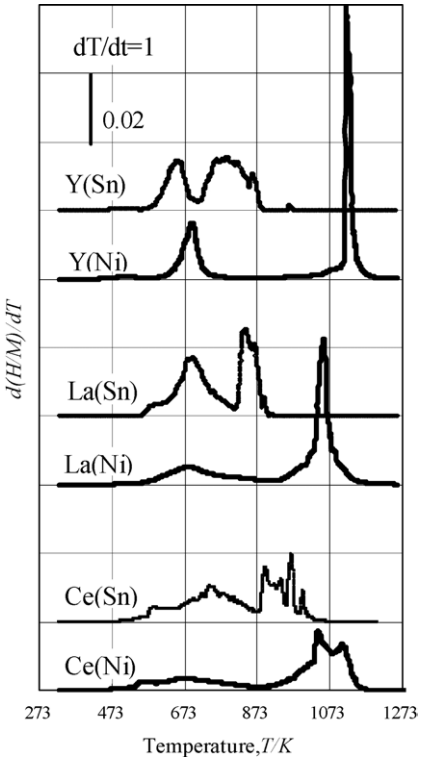

Fig. 3. The difference between the hydrogen desorption profile obtained either Sn or Ni capsules.

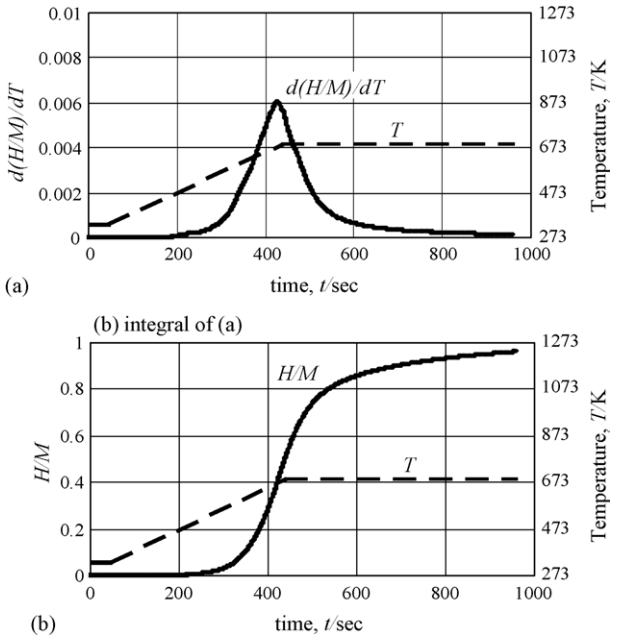

Fig. 4. (a and b) The hydrogen desorption profile for La hydride when the material was held for a period of 600 s at the first desorption peak temperature (690 K).

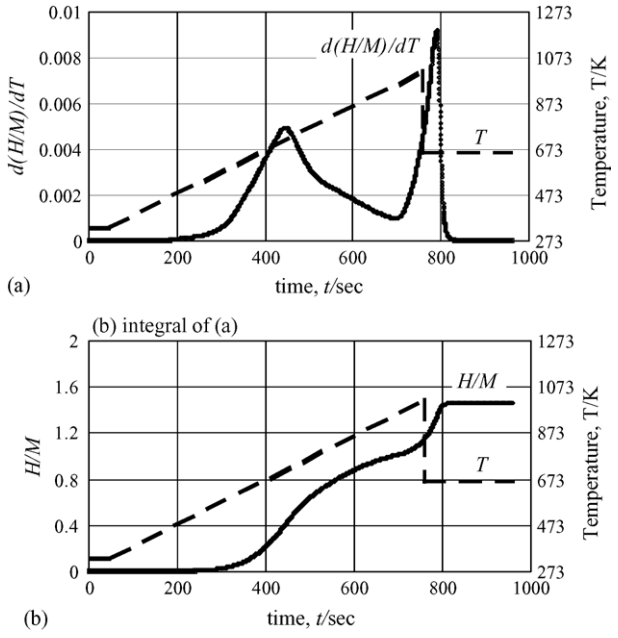

Fig. 5. (a and b) The hydrogen desorption profile for the material upon increasing the temperature to the second desorption peak (1030 K) and then reducing the temperature back to the first desorption peak temperature and maintaining that temperature.

temperature. Fig. 5 shows the hydrogen desorption profile for the material upon increasing the temperature to the second desorption peak (1030 K) and then reducing the temperature back to the first desorption peak temperature and maintaining that temperature. The results indicate no increase in hydrogen desorption. From these results, the two desorption peaks seen for rare earth hydrides do not appear to be separated as an artifact of non-uniform reactions, indicating that the two peaks are caused by the desorption of the two types of hydrogen bonds. The hydrogen desorbed at the respective desorption peak temperature is taken as generally specified values under these experimental conditions.

4. Conclusion

This investigation of the hydrogen desorption behavior of 15 rare earth elements (Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu) by swing column chromatography revealed the following:

1. The hydride of these 15 rare earth elements exhibit two separated hydrogen desorption peaks.
2. Hydrogen in these hydrides appears to be bonded by two types of bond: one that allows for desorption at lower temperature, and one that allows for desorption at higher temperature.
3. These hydrides exhibit both sharp and broad first desorption peaks at low temperature. The elements exhibiting sharp desorption peaks are Y, with the lowest atomic number, and elements with atomic numbers corresponding to Tb or higher. The elements exhibiting desorption broad peak are La, Ce, Pr and Nd, with low atomic numbers. Sm, Eu and Gd exhibit complex desorption peak profiles that have a combination of the broad and sharp features.

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