

## Dehydriding reaction of metal hydrides and alkali borohydrides enhanced by microwave irradiation

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Effects of microwave irradiation on metal hydrides (LiH, NaH, MgH<sub>2</sub>, CaH<sub>2</sub>, and TiH<sub>2</sub>) and alkali borohydrides (LiBH<sub>4</sub>, NaBH<sub>4</sub>, and KBH<sub>4</sub>) were systematically investigated for the first time. TiH<sub>2</sub> was heated to 600 K by microwave irradiation for 3.5 min, at which less than 0.16 mass % of hydrogen was desorbed from surface of the powder. On the other hand, LiBH<sub>4</sub> was heated rapidly above 380 K, at which almost all hydrogen, 13 mass %, was desorbed. The rapid heating of TiH<sub>2</sub> is mainly due to conductive loss, while that of LiBH<sub>4</sub> is related to a structural transition at approximately 380 K. © 2006 American Institute of Physics. [DOI: 10.1063/1.2185079]

Recently, the microwave process has attracted increasing interest as a clean and energy saving process for the preparation of organic and inorganic materials. It has been reported that the reactions in the microwave process proceed rapidly and homogeneously in comparison with those in the external heating process in an electric furnace because microwave energy is absorbed directly by the materials. Thus far, rapid microwave-induced reactions of oxides,<sup>1,2</sup> nitrides,<sup>3</sup> fluorides,<sup>4</sup> chlorides,<sup>4</sup> as well as some metals<sup>5,6</sup> have been investigated. To our knowledge, the microwave heating of hydrides has not yet been systematically investigated, with the exception of hydrogen plasma,<sup>7</sup> reduction reaction,<sup>8</sup> and the dehydriding reaction of carbon-related materials.<sup>9,10</sup>

Some types of hydrides have attracted considerable attention as hydrogen storage materials for developing hydrogen energy systems. The required properties of hydrogen storage materials are low reaction temperatures and fast kinetics.<sup>11</sup> In order to decrease the reaction temperatures, the stabilities of the hydrides were controlled by alloying in the case of metal hydrides<sup>12,13</sup> and by substitution or fabricating appropriate composites in the case of complex hydrides.<sup>14–16</sup> For improving the kinetics of the reactions, transition metals,<sup>12</sup> oxides,<sup>17</sup> and chlorides<sup>14,18</sup> are added as catalysts. To date, the dehydriding and hydriding reactions of hydrogen storage materials are carried out mainly by heating in an electric furnace.

In this letter, we propose the application of the energy saving microwave process to the hydrogen storage system. The effects of microwave irradiation on the dehydriding reactions of metal hydrides (LiH, NaH, MgH<sub>2</sub>, CaH<sub>2</sub>, and TiH<sub>2</sub>) and alkali borohydrides (LiBH<sub>4</sub>, NaBH<sub>4</sub>, and KBH<sub>4</sub>) are investigated for the first time. Furthermore, the dielectric constants  $\epsilon'_r$  and loss values  $\epsilon''_r$  of TiH<sub>2</sub> and LiBH<sub>4</sub>, which undergo rapid dehydriding reactions, are investigated in order to determine the reason for the rapid heating by microwave irradiation.

Microwave irradiation for the hydrides was carried out as follows: approximately 100 mg of hydride was placed in a crucible of Al<sub>2</sub>O<sub>3</sub> (for LiBH<sub>4</sub>) or SiO<sub>2</sub> (for the others). It was placed in an airtight Teflon container inside an argon glove

box. The container, which was equipped with a K-type thermocouple and a pressure gauge, was inserted into a microwave cavity (Mitsubishi Corp. RO-1500, multimode with 500 W, 2.45 GHz) wherein microwave irradiation was carried out for 30–60 min. After irradiation, powder x-ray diffraction measurement (PANalytical X'PERT with Cu K $\alpha$  radiation) was performed. The dielectric constant  $\epsilon'_r$  and loss value  $\epsilon''_r$  were measured by the coaxial line method using a network analyzer (Advantest Network Analyzer, R3765G) in the frequency range of 0.1–3 GHz. The pressed toroidal sample was set in the airtight sample holder inside the argon glove box to measurement of  $\epsilon'_r$  and  $\epsilon''_r$ .

Figure 1 shows the temperature and pressure changes as a function of the microwave irradiation time for LiH, CaH<sub>2</sub>, and TiH<sub>2</sub>. The results of the crucible without any sample are also shown in Fig. 1 for reference. The temperature and pressure changes of LiH were the same as those of the crucible, indicating ineffective heating by microwave irradiation. The same tendency was observed in NaH and MgH<sub>2</sub> (not shown). CaH<sub>2</sub> exhibited a slightly higher temperature than that of the crucible. On the other hand, a rapid increase in the temperature and pressure was observed in TiH<sub>2</sub> by microwave irra-

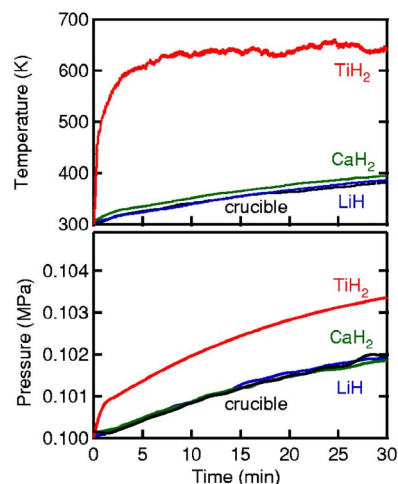


FIG. 1. (Color online) Temperature and pressure changes as a function of microwave irradiation time for LiH, CaH<sub>2</sub>, TiH<sub>2</sub>, and the crucible without any sample.

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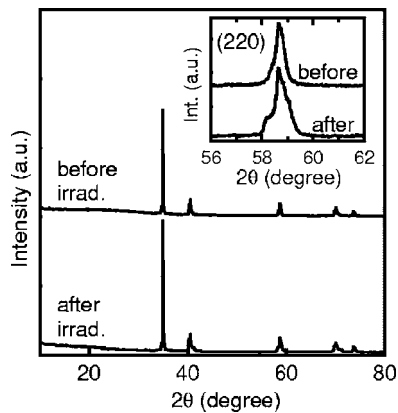


FIG. 2. Powder X-ray diffraction profiles of  $\text{TiH}_2$  before and after microwave irradiation. Inset shows the enlargement of (220) peaks.

radiation. It should be emphasized that  $\text{TiH}_2$  was heated up to 600 K by microwave irradiation for only 3.5 min. The powder x-ray diffraction profiles of  $\text{TiH}_2$  before and after microwave irradiation are shown in Fig. 2. The diffraction peaks observed after irradiation were broader than those observed before irradiation. It has been reported that the lattice of  $\text{TiH}_2$  shrank,<sup>19</sup> and the crystal structure transformed from cubic to tetragonal<sup>20</sup> during the dehydriding reaction. The powder x-ray diffraction profiles indicated that after microwave irradiation, some of the  $\text{TiH}_2$  was transformed into phases of  $\text{TiH}_{1.92-1.971}$ , while the remaining part was unchanged. The origin of the inhomogeneous phases of  $\text{TiH}_2$  and  $\text{TiH}_{1.92-1.971}$  is related to the microwave penetration depth, which will be discussed later. Under the assumption that the entire amount of  $\text{TiH}_2$  is transformed into  $\text{TiH}_{1.92}$ , only a small amount of hydrogen (0.16 mass %) can be desorbed theoretically, which is not sufficient for practical hydrogen storage materials (>6 mass %).<sup>11</sup>

Next, the dehydriding reactions of  $\text{MBH}_4$  ( $M=\text{Li, Na, or K}$ ) during microwave irradiation were investigated, and the results are shown in Fig. 3. The following three tendencies were observed: ineffective heating of  $\text{NaBH}_4$ , slight increase in temperature for  $\text{KBH}_4$  in comparison with the crucible, and rapid heating and increase in the pressure for

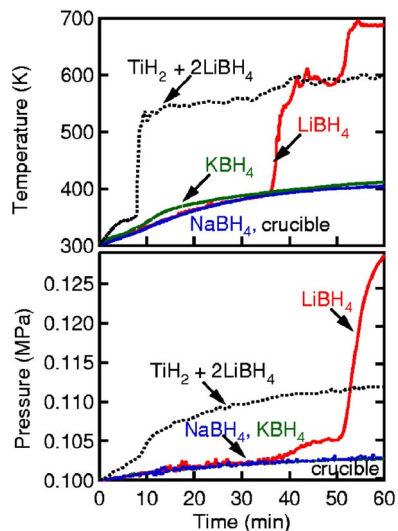


FIG. 3. (Color online) Temperature and pressure changes as a function of microwave irradiation time for  $\text{MBH}_4$  ( $M=\text{Li, Na, or K}$ ) and the crucible. Results of the composite of  $\text{TiH}_2$  and  $\text{LiBH}_4$  are shown by the dotted line.

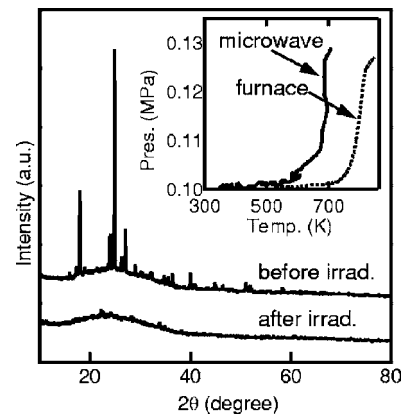


FIG. 4. Powder X-ray diffraction profiles of  $\text{LiBH}_4$  before and after microwave irradiation. Inset shows the thermal desorption profiles of  $\text{LiBH}_4$  upon heating in a microwave cavity and an electric furnace.

$\text{LiBH}_4$  at a temperature above 380 K. It has been reported that the overall dehydriding reaction of  $\text{LiBH}_4$  upon heating in an electric furnace proceeds as follows:<sup>21</sup>



13.8 mass % of hydrogen can be theoretically desorbed in the overall reaction shown in Eq. (1); this value exceeds the required amount as hydrogen storage materials (>6 mass %). The inset of Fig. 4 shows the thermal desorption profiles of  $\text{LiBH}_4$  upon heating in the microwave cavity and in the electric furnace at a heating rate of 5 K/min. The thermal desorption peak of  $\text{LiBH}_4$  in the microwave cavity is similar to that of  $\text{LiBH}_4$  in the electric furnace; however, the former peak is at a lower temperature than the later one. Moreover, the weight loss of  $\text{LiBH}_4$  after microwave irradiation was approximately 13 mass %. Therefore, an increase in the pressure of  $\text{LiBH}_4$  at temperatures higher than 380 K is expected originating from the dehydriding reaction according to Eq. (1). However, there is no powder x-ray diffraction peak in  $\text{LiBH}_4$  after microwave irradiation, as shown in Fig. 4. The absence of the x-ray diffraction peaks and the lower thermal desorption peak of  $\text{LiBH}_4$  under microwave irradiation might be due to the effect of the electromagnetic field and/or the rapid cooling rate (approximately 50 K/min). Recently, a microwave-induced amorphous phase has been reported in  $\text{Al}_2\text{O}_3$ .<sup>22</sup>

The frequency dependence of the dielectric constants  $\epsilon'_r$  and loss values  $\epsilon''_r$  of  $\text{TiH}_2$  and  $\text{LiBH}_4$  are shown in Fig. 5. The  $\epsilon''_r$  value of  $\text{TiH}_2$  is proportional to the inverse of the frequency at room temperature. Based on this result, it can be inferred that the microwave heating of  $\text{TiH}_2$  is due to the conductive loss.<sup>23</sup> In fact, the electrical resistivity of  $\text{TiH}_{1.86}$  is approximately  $120 \mu\Omega \text{ cm}$  at room temperature; in other words,  $\text{TiH}_{1.86}$  is a metallic conductor.<sup>24</sup> We predict that metal hydrides, which exhibit metallic behavior,<sup>12</sup> e.g.,  $\text{RH}_3$  ( $R=\text{rare earth}$ ),  $\text{ZrH}_2$ ,  $\text{HfH}_2$ ,  $\text{VH}_2$ ,  $\text{NbH}_2$ ,  $\text{TaH}_{0.5}$ , and  $\text{PdH}$ , can also be heated rapidly by microwave irradiation.

On the other hand,  $\text{LiBH}_4$  is an insulator; its  $\epsilon'_r$  and  $\epsilon''_r$  values are approximately 5 and 0, respectively, over the entire frequency range at room temperature. However, these values drastically increase at temperatures higher than 380 K, at which rapid increase in temperature and pressure was observed by microwave irradiation. The crystal structure of  $\text{LiBH}_4$  was transformed from orthorhombic to hexagonal at approximately 380 K, at which the  $(\text{BH}_4)^-$  tetrahedron

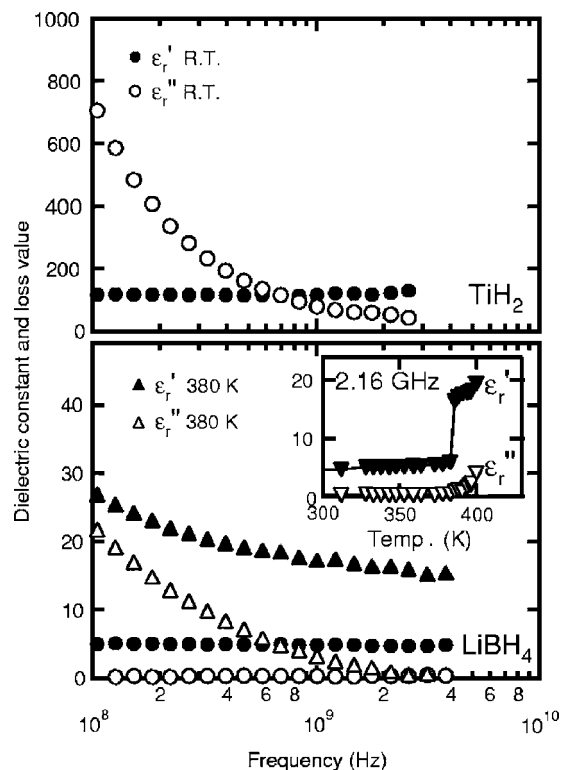


FIG. 5. Dielectric constants  $\epsilon_r'$  (closed symbols) and loss values  $\epsilon_r''$  (opened symbols) as a function of frequency. The measurements were done at room temperature for  $\text{TiH}_2$  and at room temperature (circles) and 380 K (triangles) for  $\text{LiBH}_4$ . Inset shows the temperature dependence of the  $\epsilon_r'$  and  $\epsilon_r''$  values of  $\text{LiBH}_4$  at a frequency of 2.16 GHz. Sample was pressed into toroidal shape with thickness of approximately 1 mm without sintering. Therefore, the results of  $\epsilon_r'$  and  $\epsilon_r''$  values are apparent values composed of the sample and argon gas.

was rearranged along the  $c$  axis.<sup>25</sup> Therefore, the effective heating and dehydrogenating reaction of  $\text{LiBH}_4$  at temperatures above 380 K are related to this structural transition. The dielectric loss value  $\epsilon_r''$  of  $\text{LiBH}_4$  is proportional to the inverse of the frequency at temperatures above 380 K. The Li ion of  $\text{LiBH}_4$  might become conductive at 380 K. The conductive property of  $\text{LiBH}_4$  is presently being investigated in detail.

It should be noted that less than 0.16 mass % of hydrogen (corresponding to 4% of the desorbed hydrogen from  $\text{TiH}_2$  into Ti) is desorbed from  $\text{TiH}_2$ , whereas more than 13 mass % of hydrogen (corresponding to 94% of desorbed hydrogen of Eq. (1)) is desorbed from  $\text{LiBH}_4$  by microwave irradiation. The amount of desorbed hydrogen is related to the electromagnetic penetration depth. In a metallic conductor, the microwave penetration depth is less than a few  $\mu\text{m}$ , while that in an insulator is considerably larger.<sup>24</sup> The particle sizes of  $\text{TiH}_2$  and  $\text{LiBH}_4$  are approximately 45  $\mu\text{m}$  and 50–200  $\mu\text{m}$ , respectively. Therefore, only a small amount of hydrogen near the surface area is desorbed from  $\text{TiH}_2$ . On the other hand, almost all the hydrogen can be desorbed from  $\text{LiBH}_4$ .

Because  $\text{TiH}_2$  and  $\text{LiBH}_4$  were heated rapidly and entirely, respectively, their composite prepared by mechanical milling under an argon atmosphere was investigated. The results are shown by the dotted line in Fig. 3. The temperature and pressure of the composite gradually increase until 9 min and then rapidly increase. This behavior is similar to a superimposition of the individual behaviors of  $\text{TiH}_2$  and  $\text{LiBH}_4$ . Fabricating suitable composite is useful for control-

ling rapid heating and for maintaining the amount of desorbed hydrogen.

In summary, the effects of microwave irradiation on metal hydrides ( $\text{LiH}$ ,  $\text{NaH}$ ,  $\text{MgH}_2$ ,  $\text{CaH}_2$ , and  $\text{TiH}_2$ ) and alkali borohydrides ( $\text{LiBH}_4$ ,  $\text{NaBH}_4$ , and  $\text{KBH}_4$ ) were systematically investigated for the first time. Among the metal hydrides,  $\text{TiH}_2$  exhibits rapid heating under microwave irradiation due to the conductive loss. However, because the particle size is larger than the microwave penetration depth, a small amount of hydrogen is desorbed from the surface area. On the other hand,  $\text{LiBH}_4$  is heated by microwave irradiation at a temperature above 380 K, at which more than 13 mass % of hydrogen is desorbed. This is due to a change in the conductivity accompanied by a structural transition. The composite of  $\text{TiH}_2$  and  $\text{LiBH}_4$  exhibits the behaviors of both materials. Therefore, the energy saving microwave process can be applied to the hydrogen storage system. Microwave-induced rehydrogenating reactions are currently being investigated.

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