Journal of Alloys and Compounds 446–447 (2007) 698–702

Journal of ALLOYS AND COMPOUNDS

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Effects of microwave irradiation on metal hydrides and complex hydrides

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Received 31 October 2006; received in revised form 6 March 2007; accepted 12 March 2007
Available online 25 March 2007

Abstract

Effects of single-mode microwave irradiation on metal hydrides, MH_n (LiH, MgH_2, CaH_2, TiH_2, $VH_{0.81}$, ZrH_2, and $LaH_{2.48}$) and complex hydrides MBH_4 ($LiBH_4$, $NaBH_4$, and KBH_4) were systematically investigated. Among the metal hydrides, TiH_2, $VH_{0.81}$, ZrH_2, and $LaH_{2.48}$ exhibit a rapid heating by microwave irradiation, where small amount of hydrogen (less than 0.5 mass%) are desorbed. On the other hand, $LiBH_4$ is heated above 380 K by microwave irradiation, where 13.7 mass% of hydrogen is desorbed. The rapid heating of metal hydrides such as TiH_2, $VH_{0.81}$, ZrH_2, and $LaH_{2.48}$ are mainly due to the conductive loss. Meanwhile the microwave heating in $LiBH_4$ is attributed to the conductive loss which is caused by a structural transition. The difference in the amount of desorbed hydrogen between metal hydrides and complex hydrides might be caused by the different microwave penetration depth and/or the temperature saturation in the microwave irradiation process. Microwave heating might be applied to hydrogen storage system, though further development of hydrides themselves and engineering techniques are required.

Keywords: Hydrogen absorbing materials; Gas–solid reaction; Dielectric response; X-ray diffraction

1. Introduction

The required properties on hydrogen storage materials are low reaction temperature and fast kinetics, and so on. For decreasing the reaction temperature, the stability of hydrides was controlled by alloying [1,2], fabricating appropriate composites [3–5] and considering the electronegativity of cation [6] in metal hydrides and complex hydrides. However, the reaction kinetics generally becomes slower at lower reaction temperatures. In particular, in the complex hydrides, the fast diffusion of not only the hydrogen but also the other elements is required, which is very difficult to be achieved at ambient temperature.

On the other hand, it is well known that microwave heating, that is, heating by microwave irradiation, increased temperature rapidly and reaction proceeds fast in comparison with external heating. For example, domestic microwave ovens with frequency of 2.45 GHz are wildly used for saving time of cooking. The basic mechanism of microwave heating lies in the ability of polarization of the material and the inability of this polarization to follow reversals of the electromagnetic field [7]. This ability and inability are measured by the dielectric constant ε_r' and loss value ε_r''. The larger dielectric loss value makes microwave heating faster (see in Section 3.3). Because complex hydrides have the ability of polarization and poor thermal conductivity due to insulator, microwave heating might be suitable for complex hydrides to realize fast kinetics comparing to external heating.

Recently, we have reported that TiH_2 and $LiBH_4$ can be heated up rapidly and proceeded dehydriding reaction by multi-mode microwave irradiation [8]. Furthermore, it has been predicted that RH_{3-x} (R = rare earth), ZrH_2 and VH_2, can be heated up rapidly by microwave irradiation.

In this study, to prove this prediction, the effects of microwave irradiation on metal hydrides, MH_n (LiH, MgH_2, CaH_2, TiH_2, $VH_{0.81}$, ZrH_2, and $LaH_{2.48}$) were systematically investigated. Additionally, the single-mode microwaves were irradiated to metal hydrides, MH_n and complex hydrides MBH_4 in order to extract the effects of electric field of the irradiated microwaves.

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doi:10.1016/j.jallcom.2007.03.096

To clarify the origin of rapid heating by microwave irradiation, the measurements of the effective dielectric constant ε_r' and loss value ε_r'' were carried out for TiH_2 and $LiBH_4$ which show the rapid dehydriding reactions.

2. Experimental

Metal hydrides MH_n (LiH, MgH_2, CaH_2, TiH_2, $VH_{0.81}$, ZrH_2, and $LaH_{2.48}$) and complex hydrides MBH_4 ($LiBH_4$, $NaBH_4$, and KBH_4) were purchased from Aldrich Co., LTD. Microwave irradiation for the hydrides was carried out as follows: approximately 0.3–0.4 cm^3 of hydride was placed in a crucible of BN which was placed in an airtight Teflon container inside an argon glove box. The container, which was equipped with a K-type thermocouple, was inserted into a microwave cavity (IDX Corp. MS1109A-001, single-mode with 400 W, 2.45 GHz) at the point of maximum of electric field, wherein microwave irradiation was carried out for 10–70 min. In order to investigate the dehydriding reaction during the microwave irradiation, the powder X-ray diffraction measurements (PANalytical X'PERT with Cu Kα radiation) and the hydrogen analysis (Horiba, EMGA-621W) were performed for the samples before and after microwave irradiation. The effective dielectric constant ε_r' and loss value ε_r'' were measured by the coaxial line method using a network analyzer (Advantest R3765G) in the frequency range of 0.1–3 GHz. During these experiments, the samples were handled in a glove box filled with purified argon (dew point below 183 K) by using special airtight container.

3. Results and discussion

3.1. Microwave irradiation on metal hydrides MH_n

Fig. 1 shows the temperature changes as a function of the microwave irradiation time for LiH, MgH_2, CaH_2, TiH_2, $VH_{0.81}$, ZrH_2, and $LaH_{2.48}$. The temperatures change of LiH and MgH_2 were the same as that without sample (not shown) indicating the ineffective heating by microwave irradiation. CaH_2 exhibited a slightly higher temperature than that without sample. On the other hand, a rapid temperature increase was observed in TiH_2, $VH_{0.81}$, ZrH_2, and $LaH_{2.48}$ by microwave irradiation. A considerable change in the temperature increasing rate was observed at 1, 5, and 2 min for TiH_2, ZrH_2, and $LaH_{2.48}$, respectively. This change may be caused by the change of the dielectric loss values by partial dehydriding reaction. In order to investigate the dehydriding reaction during microwave irradiation, powder X-ray diffraction measurements are performed for TiH_2, $VH_{0.81}$, ZrH_2, and $LaH_{2.48}$, which are heated up rapidly. As shown in Fig. 2, the powder X-ray diffraction peaks observed after microwave irradiation became broader and smaller than those observed before irradiation. These changes are probably due to the effect of the electromagnetic field and/or the rapid cooling rate. The diffraction peaks of TiH_2 and $VH_{0.81}$ shift to higher angles after microwave irradiation, while those of ZrH_2 and $LaH_{2.48}$ do not change by microwave irradiation. These results indicate that the progression of the partial dehydriding reactions proceed in TiH_2 and $VH_{0.81}$ [9]; the crystal structure of TiH_2 also transforms from cubic to tetragonal by microwave irradiation [10]. The amount of desorbed hydrogen during microwave irradiation is deduced by subtraction of the amount of hydrogen after irradiation from that before irradiation. The small amount of hydrogen, 0.3 and 0.5 mass%, were desorbed from TiH_2 and $VH_{0.81}$, while no hydrogen desorption was confirmed from ZrH_2 and $LaH_{2.48}$. The possible reason for the small amount of desorbed hydrogen during microwave irradiation will be discussed in Section 3.3.

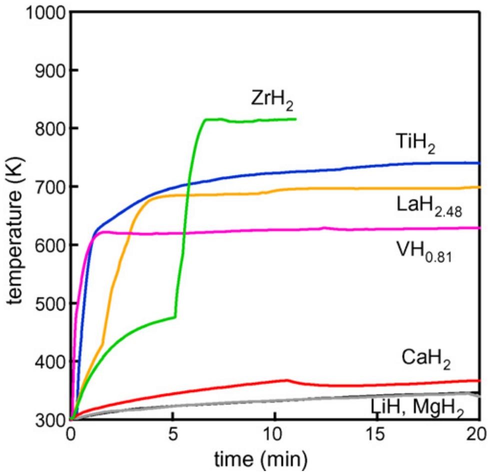

Fig. 1. Temperature changes as a function of single-mode microwave irradiation time for LiH, MgH_2, CaH_2, TiH_2, $VH_{0.81}$, ZrH_2, and $LaH_{2.48}$.

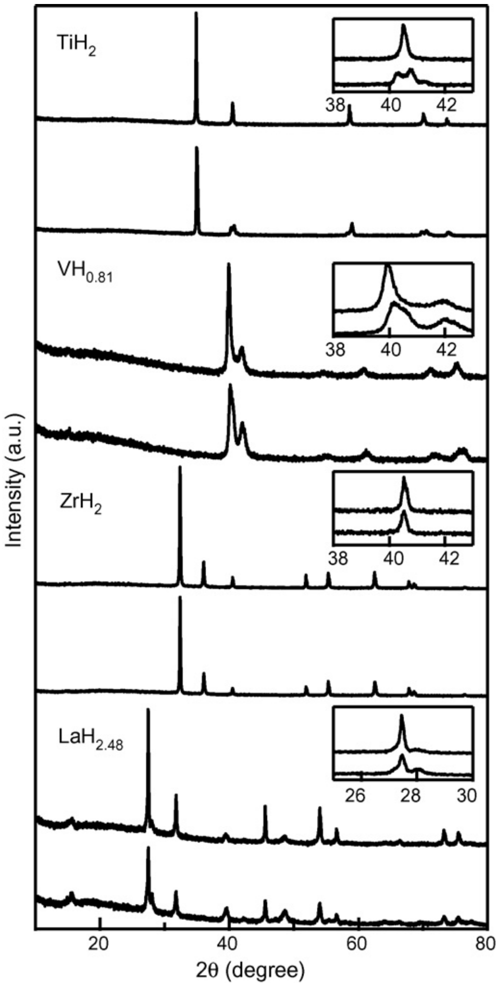

Fig. 2. Powder X-ray diffraction profiles of TiH_2, $VH_{0.81}$, ZrH_2, and $LaH_{2.48}$ before and after microwave irradiation. The diffraction profiles at top and bottom in each panel show before and after microwave irradiation, respectively. Insets show the enlargements of (2 0 0), (1 0 1), (0 0 2) and (1 1 1) peaks for TiH_2, $VH_{0.81}$, ZrH_2, and $LaH_{2.48}$, respectively.

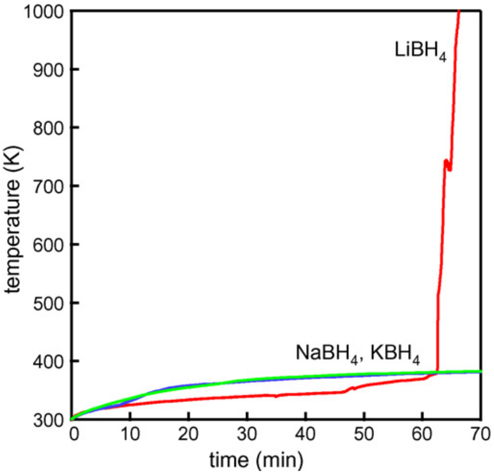

Fig. 3. Temperature changes as a function of single-mode microwave irradiation time for $LiBH_4$, $NaBH_4$, and KBH_4.

3.2. Microwave irradiation on complex hydrides MBH_4

The temperature changes of MBH_4 ($LiBH_4$, $NaBH_4$, and KBH_4) during microwave irradiation are shown in Fig. 3. The following two tendencies were observed: ineffective heating for $NaBH_4$ and KBH_4, and a rapid heating above 380 K for $LiBH_4$. In the powder X-ray diffraction profile, small peaks of LiH were confirmed after microwave irradiation for $LiBH_4$, as shown in Fig. 4. Thus, the dehydriding reaction in $LiBH_4$ is expressed as follow [11]:

$$LiBH_4 \rightarrow LiH + B + \tfrac{3}{2}H_2 \qquad (1)$$

This is the same overall dehydriding reaction as that by heating in an electric furnace, where 13.8 mass% of hydrogen desorbed theoretically. The hydrogen analyses before and after irradiation indicated that 13.7 mass% of hydrogen was desorbed during microwave irradiation, which is in a good agreement with the amount of desorbed hydrogen of Eq. (1). However, no diffraction peak of boron was observed after microwave irradiation. Thus the precipitated boron is considered to be in an amorphous phase [12].

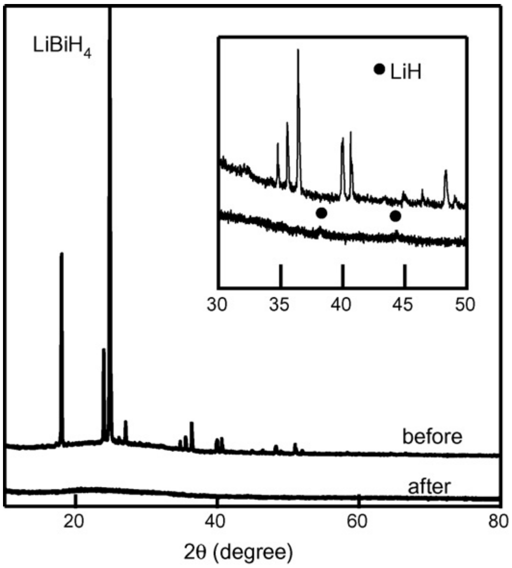

Fig. 4. Powder X-ray diffraction profiles of $LiBH_4$ before and after microwave irradiation. Insets show the enlarged X-ray pattern in the 2θ range from 30 to 50°.

3.3. Mechanism of rapid heating of TiH_2 and $LiBH_4$

Metal hydrides, TiH_2, $VH_{0.81}$, ZrH_2, and $LaH_{2.48}$, were heated up rapidly by microwave irradiation, whereas small amounts of hydrogen (less than 0.5 mass%) were desorbed by microwave irradiation. On the contrary, complex hydride, $LiBH_4$, desorbed all amount of hydrogen at a temperature above 380 K by microwave irradiation. The possible reasons of the different behavior by microwave irradiation are briefly discussed on the basis of dielectric properties of the materials.

Generally, the generation power P by microwave irradiation is expressed as follows [7]:

$$P = 2\pi f E^2 \varepsilon''. \qquad (2)$$

Here, f, E, and ε'' are frequency, electric field and dielectric loss value, respectively. In the conductor, the dielectric loss ε'' can be expressed as follows:

$$\varepsilon'' = \frac{\sigma}{2\pi f} + \varepsilon''_{\text{dipole}} \qquad (3)$$

where σ is conductivity of the material, namely $\sigma/2\pi f$ is the contribution from the conductivity loss, and $\varepsilon''_{\text{dipole}}$ is that from the dipole loss. In this study, f and E are invariable. Therefore, dielectric loss value ε'' of the material is an important factor for heating by microwave irradiation. The effective dielectric constant ε'_r and loss value ε''_r were measured for TiH_2 and $LiBH_4$, and the results are shown in Fig. 5 [8]. The ε''_r value of TiH_2 is inversely proportional to the frequency at room temperature. So, it was inferred that the microwave heating of TiH_2 is caused by the conductive loss. In fact, the electrical resistivity of $TiH_{1.86}$ is approximately 120 $\mu\Omega$ cm at room temperature; in other words, $TiH_{1.86}$ is a metallic conductor [13]. $VH_{0.81}$, ZrH_2, and $LaH_{2.48}$ also show metallic conduction [13]. Therefore, these metal hydrides are heated up rapidly mainly due to the conductive loss. The rest of hydrides, MH_n, LiH, MgH_2, and CaH_2, which indicate ineffective heating by microwave irradiation, have ionic bond and are insulators. These results indicate that the hydrides having a relatively high electrical conductivity can be heated up rapidly by microwave irradiation.

On the other hand, $LiBH_4$ is an insulator; its ε'_r and ε''_r values are approximately 5 and 0, respectively, over the entire frequency range at room temperature. This is a typical frequency dependence of insulator without dielectric dipole loss. However, ε'_r and ε''_r drastically increase at temperatures higher than 380 K, at which rapid increase in temperature was observed by microwave irradiation. The crystal structure of $LiBH_4$ is transformed from orthorhombic to hexagonal at approximately 380 K, at which the $[BH_4]^-$ tetrahedron was rearranged along the c-axis [14]. Therefore, the effective heating at temperatures above 380 K is related to the change in the electrical property by this structural transition. Since the dielectric loss ε''_r of $LiBH_4$ is inversely

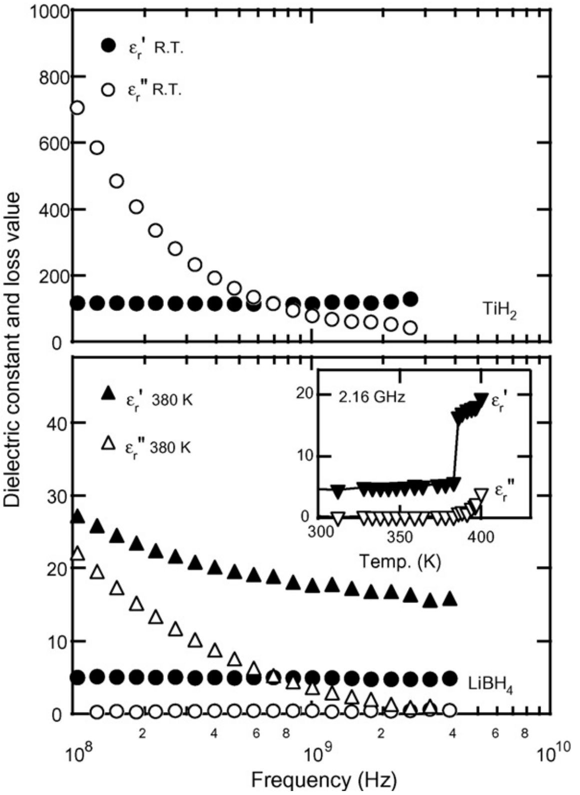

Fig. 5. The relative dielectric constant ε_r' (closed symbols) and loss value ε_r'' (opened symbols) as a function of frequency. The measurements were carried out at room temperature for TiH_2 and at room temperature (circles) and 380 K (triangles) for $LiBH_4$. Inset shows the temperature dependence of the ε_r' and ε_r'' values of $LiBH_4$ 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 ε_r' and ε_r'' values are apparent values composed of the sample and argon gas [8].

proportional to the frequency at the temperatures above 380 K, high electrical conductivity due to Li ion or hydrogen diffusion, might be achieved at temperatures above 380 K. More detailed investigations for the conductive and dielectric losses of $LiBH_4$ are now in progress.

3.4. Difference of the amounts of desorbed hydrogen between TiH_2 and $LiBH_4$

One of the reasons for the difference of the amount of desorbed hydrogen can be related to the skin effect [7]. From the Maxwell equation, the penetration depth of the electromagnetic wave δ is expressed as follow:

$$\delta = \left[\frac{\omega^2\varepsilon\mu}{2}\left(\sqrt{1+\frac{1}{\omega^2\varepsilon^2\rho^2}}-1\right)\right]^{-1/2}, \tag{4}$$

where ω is angular frequency (i.e., $2\pi f$) and μ is magnetic permeability. In the case of the metallic conductor, ρ is so small that the term $\omega^2\varepsilon^2\rho^2$ becomes small enough to unity. Hence, Eq. (4) is rewritten as follow:

$$\delta = \sqrt{\frac{2\rho}{\omega\mu}} \tag{5}$$

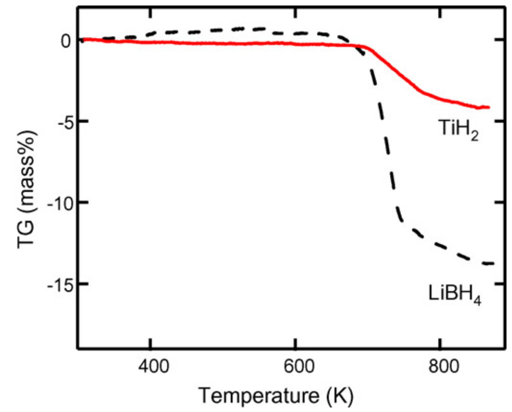

Fig. 6. Thermogravimetry of TiH_2 and $LiBH_4$ upon heating in an electric furnace (the He gas flow rate is 100 ml/min and the heating rate is 5 K/min).

The penetration depth δ of TiH_2 is deduced to be 11 μm, using $\rho = 120\,\mu\Omega\,\mathrm{cm}$, $\mu_r = 1$ ($\mu_r = \mu/\mu_0$; μ_0 is the magnetic permeability of vacuum) and $f = 2.45$ GHz. On the other hand, the penetration depth of the insulator is considerably large. The particle size of TiH_2 and $LiBH_4$ is approximately 45 and 50–200 μm, respectively. Therefore, only a small amount of hydrogen near the surface area can be desorbed from TiH_2, whereas almost all the hydrogen can be desorbed from $LiBH_4$.

Another possibility is the saturation temperature by microwave irradiation. The saturation temperature of TiH_2 is 740 K by microwave irradiation (Fig. 1), while the dehydriding reaction finishes at approximately 850 K by using an electric furnace as shown in Fig. 6. $LiBH_4$ was heated up to above 1000 K by microwave irradiation (Fig. 3), at which the dehydriding reaction has proceeded completely as shown in Fig. 6.

We are now continuing to investigate the effects of microwave heating on composites of TiH_2 and $LiBH_4$ in order to simultaneously achieve both rapid heating and large amount of hydrogen desorption [15]. The possibility of hydrogen absorption reactions by microwave irradiation is also being investigated.

4. Summary

The effects of the single-mode microwave irradiation on metal hydrides, MH_n (LiH, MgH_2, CaH_2, TiH_2, $VH_{0.81}$, ZrH_2, and $LaH_{2.48}$) and complex hydrides, MBH_4 ($LiBH_4$, $NaBH_4$, and KBH_4) have been systematically investigated. Metal hydrides TiH_2, $VH_{0.81}$, ZrH_2, and $LaH_{2.48}$ exhibited a rapid heating by microwave irradiation; a small amount of hydrogen (less than 0.5 mass%) was desorbed. On the other hand, a rapid heating was observed in the complex hydrides $LiBH_4$ at a high temperature above 380 K accompanied by the 13.7 mass% of hydrogen desorption. The rapid heating of TiH_2, $VH_{0.81}$, ZrH_2, and $LaH_{2.48}$ are mainly due to the conductive loss, while the microwave heating in $LiBH_4$ is attributed to the conductive loss which is caused by a structural transition. The difference of the amount of desorbed hydrogen might be caused by the difference of the microwave penetration depth or the temperature saturation. Microwave heating might be applied to hydrogen storage system, though further development of hydrides themselves and engineering techniques are required.

Acknowledgements

This work is the Collaborative Research in Center for Interdisciplinary Research, the Inter-University Cooperative Research Program of the Institute for Materials Research, Tohoku University. This study was partially supported by the Ministry of Education, Science, Sports and Culture, Grant-in-Aid "#18070001", "Scientific Research (A), #18206073" and by Japan Science and Technology Agency, promotion of seed program.

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