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Hydrogen absorption kinetics of the catalyzed MgH_2 by niobium oxide

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Abstract

The hydrogen absorption kinetics of magnesium hydride (MgH_2) composite doped with 1 mol% Nb_2O_5 prepared by ball milling was examined under various temperatures and pressures. The composite after dehydrogenation at 200 °C absorbs gaseous hydrogen of ∼4.5 mass% within 15 s even at room temperature under 1.0 MPa hydrogen pressure or at 0 °C under 3.0 MPa, and finally their capacities reach up to 5 mass%. At 150 and 250 °C, a large amount of hydrogen gas of more than 5.0 mass% is absorbed within 30 s and their capacity reach up to 5.7 mass% under 1.0 MPa. Interestingly, the absorption kinetics of the catalyzed Mg shows two unusual behaviors in the initial reaction stage of the time scale within 30 s. One is that the kinetics decreases with increase in the temperature from 150 to 250 °C under any pressures (0.2, 1.0 and 3.0 MPa). The other is that the amount of hydrogen absorption drastically increases with increase in the initial pressure from 1.0 to 3.0 MPa at 0 °C or from 0.2 to 1.0 MPa at room temperature (∼20 °C). These behaviors may be explained by taking into account heat generation of Mg due to fast hydrogen uptake in such a short time.
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Keywords: Hydrogen absorbing materials; Ball milling; Kinetics; Catalysis

1. Introduction

Magnesium hydride (MgH_2) has been considered as one of the attractive hydrogen storage materials because it possesses high hydrogen capacity of 7.6 mass% and abundant resources. However, the reaction speed of hydrogen absorption and desorption is too low, and it needs a higher temperature than 300 °C for hydrogen desorption under a 0.1 MPa hydrogen atmosphere. Some Mg or MgH_2 composites with a small amount of transition metals prepared by ball milling have been studied to improve the kinetics of hydrogen absorption/desorption reactions without reducing the high hydrogen capacity [1–3]. Further, the hydrogen storage properties of MgH_2 with a small amount of transition metal oxides as a catalyst have been also examined [4–12]. Especially, Barkhordarian et al. have claimed that Nb_2O_5 revealed the best catalytic effect on the hydrogen storage properties among the oxide catalysts in their trials [9–11]. According to their reports, MgH_2 catalyzed with 0.5 mol% Nb_2O_5, which was prepared by ball milling for 100 h, desorbs almost all the hydrogen within 90 s under a vacuum condition at 300 °C, and after that, the dehydrogenated product absorbs up to ∼7 mass% hydrogen within 60 s under a 0.84 MPa hydrogen pressure.

Motivated by their reports, we have prepared the MgH_2 composites with a small amount of some transition metals and metal oxides by the ball milling method and studied the hydrogen storage properties till now [13–16]. Among all the additives we doped, we clarified that the 1 mol% Nb_2O_5-catalyzed MgH_2 exhibited the most superior hydrogen desorption properties. The product just after milling desorbed ∼6 mass% hydrogen in temperature range from 200 to 250 °C at a heating rate of 5 °C/min under a purified helium flow, while the product after rehydrogenation at 200 °C desorbed ∼6 mass% hydrogen in lower temperature range from 150 to 200 °C [14].

Furthermore, the kinetics of hydrogen absorption and desorption reactions was examined on the Nb_2O_5-catalyzed MgH_2 [15]. Interestingly, the composite after dehydrogenation at 200 °C absorbed gaseous hydrogen of ∼4.5 mass% even at room temperature (RT) under 1 MPa hydrogen gas pressure within 15 s and finally its capacity reached up to 5 mass%. In addition, the catalyzed MgH_2 after rehydrogenation desorbed ∼6 mass% hydrogen at 160 °C under a purified He flow, where the desorption kinetics followed a first order reaction. From the Kissinger

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plot, the activation energy for hydrogen desorption was estimated to be ~71 kJ/mol H_2. This indicates that the surface of the product MgH_2 was almost completely activated due to the catalytic effect of Nb_2O_5.

In this paper, especially the hydrogen absorption kinetics of MgH_2 catalyzed with Nb_2O_5 is examined under various temperatures and pressure conditions. The absorption kinetics shows specific temperature and pressure dependence and the origin of these properties are discussed in this paper.

2. Experimental procedures

Magnesium hydride powder (the purity is 90 mass%, 9 mass% is unreacted Mg and the rest of 1 mass% are impurities; the size of several tens of micrometers) and niobium oxide Nb_2O_5 with mesoporous of 3.2 nm pore size (99.5% purity) were purchased from Sigma–Aldrich. First of all, the mixture of 300 mg MgH_2 and 1 mol% Nb_2O_5 were put into a Cr steel vessel (30 cm^3 inner volume) together with 20 steel balls (7 mm in diameter). After the vessel was evacuated below 1×10^{-4} Pa for 12 h, highly pure hydrogen gas (7 N) of 1.0 MPa was introduced into it. Then, the mixture was mechanically milled for 20 h at 400 rpm using a planetary ball milling apparatus (Fritsch P7). The samples before and after ball milling were always handled in a glovebox filled with a purified Ar gas so as to minimize the oxidation on the samples. To examine the hydrogen desorption properties for the ball milled product, thermal desorption mass spectroscopy (TDMS) and thermogravimetry (TG) measurements [13] were performed.

To produce the dehydrogenated states of the catalyzed MgH_2, the ball milled product was dehydrogenated under high vacuum condition for 8 h at 200 °C (catalyzed Mg). For examining the hydrogen absorption properties, about 100 mg of the product was loaded into a sample cell and was kept at each different programmed temperature under high vacuum. After reaching the programmed temperatures, the valve, which combines a hydrogen reservoir tank with the sample cell, is quickly opened and the corresponding variations of pressure and temperature were monitored.

3. Results

Fig. 1 shows the hydrogen absorption curves for Mg catalyzed by 1 mol% Nb_2O_5 at 0, RT (~20 °C), 150 and 250 °C under three different hydrogen pressures of 0.2, 1.0 and 3.0 MPa, where the temperatures and pressures are the initial ones of the examinations. For the curves under 0.2 MPa hydrogen pressure at 0 °C and RT, the amounts of absorbed hydrogen are only 0.1 and 0.6 mass% within ~30 s, respectively (Fig. 1(a)). Similarly, the curve under 1.0 MPa at 0 °C indicates hydrogen absorption of only 0.2 mass% within ~30 s. On the contrary, very fast absorption kinetics is shown at RT under 1.0 MPa within the same time scale. Actually, the amount of hydrogen absorption reaches more than 4.3 mass% within 15 s. Under 3.0 MPa, both of the reaction kinetics at 0 °C and RT are very fast as well, where the amount of hydrogen absorption reaches more than 4.5 mass% within 15 s. Therefore, the above results indicate that the catalyzed Mg quickly absorbs large amount of hydrogen even at 0 °C under 3.0 MPa or RT under 1.0 MPa. However, as is evident from Fig. 1(a), the increase of the reaction speed with increasing hydrogen pressure at 0 °C and RT is quite drastic. On the other hand, for the curves at 150 and 250 °C, the absorption reactions proceed at a relatively rapid rate even under 0.2 MPa comparing with the reactions at 0 °C and RT in the short time scale as shown in Fig. 1(a). Moreover, the reaction speed at 250 °C is lower than at 150 °C under 0.2 MPa. The 4.0 and 2.4 mass% of hydrogen are absorbed within 15 s at 150 and 250 °C, respectively. The phenomenon, in which the reaction speed decreases with increasing temperature in a short time scale, is also observed under 1.0 and 3.0 MPa. Under 1.0 MPa, we notice that the reaction speed decreases with increasing temperature from RT to 250 °C. Under 3.0 MPa, the reaction speed also decreases with increasing temperature from 150 to 250 °C.

In Fig. 1(b), the hydrogen absorption curves of the catalyzed Mg by 1 mol% Nb_2O_5 at 0, RT (~20 °C), 150 and 250 °C under three different hydrogen pressures of 0.2, 1.0 and 3.0 MPa in a time scale of ~5 h. In such a long time scale, we notice that the absorption rate and amount of hydrogen absorption increase

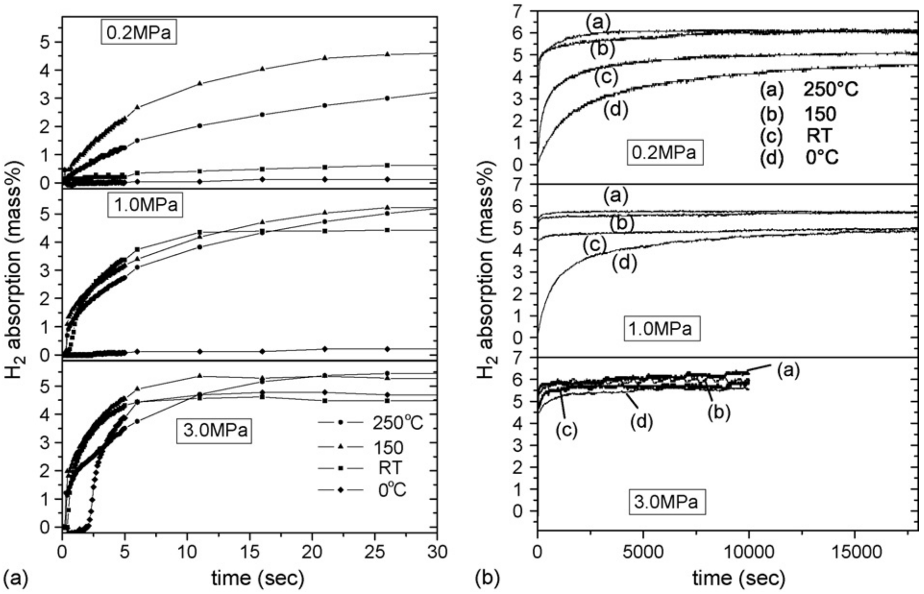

Fig. 1. The hydrogen absorption curves of the catalyzed Mg at 0 °C, room temperature (RT, ~20 °C), 150 and 250 °C under 0.2, 1.0 and 3.0 MPa hydrogen pressure as a function of reaction time up to (a) 30 s and (b) 18,000 s under 0.2 and 1.0 MPa and 10,000 s under 3.0 MPa.

with the increasing temperature under all the pressure conditions we applied.

Generally, the kinetics of hydrogen absorption has been considered to be controlled by a thermally activated process like the Arrenius-type one. Therefore, the hydrogen absorption kinetics in the long time scale could be understood to be originated in the diffusion process of hydrogen atom in the inner part of Mg metal itself. However, the hydrogen absorption process in the initial short time region shows opposite behavior to thermally activated process. Similar results have been also reported by Barkhordarian et al. at high temperatures of 250 and 300 °C [9,10]. It seems likely that these behaviors are characteristic in the Mg system catalyzed well.

4. Discussion

In Fig. 2, the amounts of hydrogen absorption at 6 s passed from the starting time are plotted as a function of reaction temperature under three different pressures of 0.2, 1.0 and 3.0 MPa for the Nb_2O_5-catalyzed Mg system. We notice that the absorption kinetics shows two unusual characteristics in such a short time scale. One is that the absorption reaction speed decreases with increasing temperature above 150 °C under any pressures in this work. The other is that the amount of hydrogen absorption drastically increases with increasing pressure at the lower temperatures (0 °C and RT). With respect to the decrease in reaction speed with the increasing temperature, there are two possibilities to be considerable as the reason of this phenomenon. One is due to the appearance of the reverse reaction. The other is due to the variation of surface coverage of hydrogen atoms on the Mg surface with temperature.

Firstly, we argue about the appearance of the reverse reaction. The hydrogen absorption reaction can be simply expressed by the following differential equation if we assume that the reaction in the catalyzed Mg follows a first order reaction,

$$\frac{dy}{dt} = k_a(1-y)P - k_d y, \tag{1}$$

where y indicates a normalized hydrogen concentration in the hydrogenated state and P is the hydrogen partial pressure. The reaction velocity constants for absorption and desorption are given by k_a and k_d, respectively,

$$k_a = k_{0a} \exp\left(\frac{-E_a}{RT}\right) \tag{2}$$

and

$$k_d = k_{0d} \exp\left(\frac{-E_d}{RT}\right). \tag{3}$$

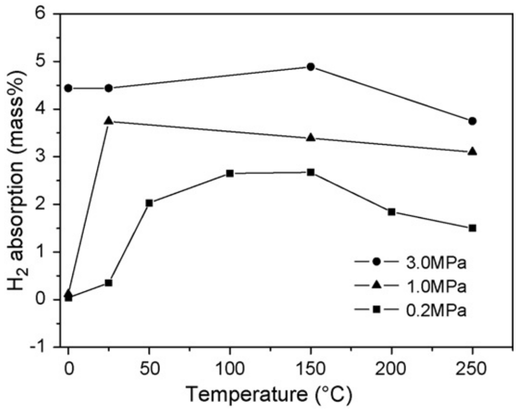

Fig. 2. The amounts of hydrogen absorption in the reaction time 6 s corresponding to absorption curves of Fig. 1. The data at 50, 75 and 100 °C under 0.2 MPa are also obtained by the same procedure as the others. (These absorption curves are not shown in Fig. 1.)

If both the activation energies of absorption and desorption are sufficiently decreased by the catalytic effect of Nb_2O_5, E_a and E_d should be, respectively, ~0 kJ/mol and the same as the reaction enthalpy change of ΔH (~74 kJ/mol H_2). Actually, the activation energy E_d for hydrogen desorption was estimated to be ~71 kJ/mol H_2 in our previous paper [15]. Therefore, at lower temperature (0 °C or ~RT), the absorption velocity constant k_a remains a finite value, while the desorption velocity constant k_d is quite small. As a result, at lower temperature (0 °C or RT), the reaction velocity in the absorption process is not suppressed by the reverse reaction of hydrogen desorption. On the other hand, at higher temperature than 250 °C, since the desorption velocity constants k_d possess a finite value but not small, the reaction velocity of the hydrogen absorption is suppressed by developing the reverse desorption reaction. In addition, if there is no effect of reverse reaction, the reaction velocity should be proportional to hydrogen pressure in low temperature from the reaction equation (see Eq. (1)). However, the experimental results in this work do not coincide with the above simple consideration. Therefore, the first assumption cannot explain both unusual characteristics of the absorption kinetics.

Secondly, we argue about the variation of surface coverage of hydrogen atoms on the Mg surface with reaction temperature. The elementary steps of hydrogen absorption are described as follows,

$$H_2 \leftrightarrow 2H \tag{4}$$

and

$$Mg + 2H \leftrightarrow MgH_2. \tag{5}$$

Here, if it is considered that the surface is completely activated by catalyst Nb_2O_5, the reaction of Eq. (4) should be in an equilibrium state and Eq. (5) should be a rate determining step for whole reaction. With respect to Eq. (4), the equilibrium constant is expressed as follows,

$$K = \frac{k_a}{k_d} = \frac{\theta^2}{P(1-\theta)^2}, \tag{6}$$

θ is the surface coverage of hydrogen atoms on the Mg surface, P the hydrogen partial pressure and k_a and k_d are the reaction velocity constants of adsorption and desorption, respectively. Therefore, the surface coverage θ is given by the following formula:

$$\theta = \frac{(KP)^{1/2}}{1+(KP)^{1/2}}. \tag{7}$$

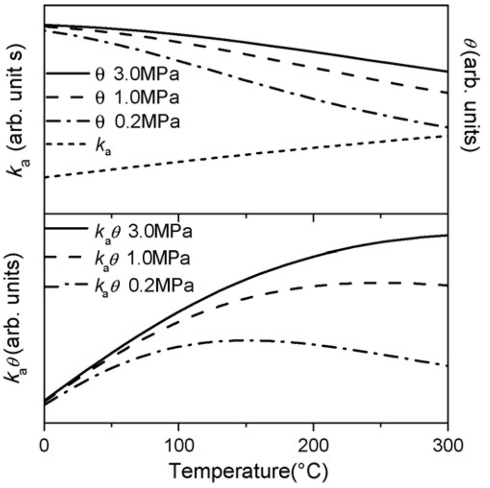

Fig. 3. Temperature dependence of the reaction velocity constants (k_a), the surface coverage of hydrogen atoms (θ) and the reaction velocity ($k_a\theta$) correspond to the case of the hydrogen pressure 0.2, 1.0 and 3.0 MPa.

Because the absorption rate should be proportional to surface coverage, the hydrogen absorption reaction can be simply expressed by the following differential equation,

$$\frac{dy}{dt} = k_a(1 - y)\theta - k_d y. \quad (8)$$

When it is an initial stage of the reaction ($t \sim 0$), dy/dt is rewritten to be $k_a\theta$. The temperature dependence of k_a, θ and $k_a\theta$ under various hydrogen pressures of 0.2, 1.0 and 3.0 MPa is drawn in Fig. 3, where the parameters used are $\Delta H^0 = 30$ kJ/mol, $\Delta S^0 = 65$ J/mol ($K = \exp(-(\Delta H^0 - T\Delta S^0)/RT)$) and $E_a = 5$ kJ/mol. In lower temperature region (0–50 °C), the value of θ is large and the pressure dependence is very small. In high temperature region (above 150 °C), θ largely decreases with increasing temperature and the decrease rate of θ with increase in the temperature is larger under lower pressures. Therefore, the temperature dependence of reaction velocity $k_a\theta$ under a 0.2 MPa is consistent with the experimental results, where the reaction velocity increases with increasing temperature from 0 to 150 °C but decreases with the increasing temperature from 150 to 250 °C. However, the temperature dependence under high pressure (1.0 and 3.0 MPa) does not coincide with the experimental results, in which the reaction velocity at 3 MPa is almost constant with increase in the temperature from 0 to 150 °C as shown in Fig. 2. Furthermore, its pressure dependence in low temperature is too small comparing with the experimental results. Therefore, the second assumption cannot explain the behavior at high pressure in the experimental results.

In order to explain both the temperature and pressure dependence of the reaction velocity in details, it is necessary to take account of heat generation effect of Mg caused during the absorption reaction. When 100 mg of Mg, which is a standard sample amount used for our absorption measurement, absorbs 4 mass% hydrogen, the reaction heat of ∼150 J is generated, but the heat capacity corresponding to 100 mg of Mg is only ∼0.1 J. Therefore, if Mg receives the whole reaction heat in the short time adiabatically, the absorption reaction stops after reaching equilibrium temperature, indicating that 4 mass% hydrogen cannot be absorbed in Mg. However, if Mg radiates the heat to outside of the system after reaching equilibrium temperature, the sample can continue to absorb hydrogen in the short time. Therefore, it seems likely that the high reaction speed at a relatively low temperature under a relatively high pressure in the short time range is mainly originated in the temperature increase by heat generation of Mg due to the hydrogenation. Although, the reaction kinetics in the low temperature should be slow according to thermally activated process of Arrenius-type, the high pressure leads to high reaction speed due to the increasing temperature from the low temperature to the equilibrium temperature by yielding large heat generation of Mg. Actually, in the fast kinetics under high pressure (1.0 and 3.0 MPa at RT or 3.0 MPa at 0 °C), the temperatures of the sample increased by at least 20 °C in the short time range (∼30 s) from the starting temperature, while, in the slow kinetics under low pressure (0.2 MPa at RT or 0.2 and 1.0 MPa at 0 °C), the temperatures of the sample did not increase from the starting temperature. From these phenomena, a threshold temperature seems to exist under each condition of the initial pressure. Therefore, the drastic changes in the short time absorption kinetics were found at 0.2 MPa between RT and 50 °C and at 1.0 MPa between 0 °C and RT.

On the other hand, with respect to the decrease in the reaction speed with increasing temperature around 150–250 °C, the behavior may be explained as follows. The absorption speed under 1.0 MPa is suppressed when local Mg temperature increases up to 400 °C by heat generation due to hydrogen uptake because the equilibrium temperature of this reaction is as low as 400 °C under a 1.0 MPa hydrogen pressure. Therefore, the sample in lower starting temperature about 150 °C can absorb hydrogen more than that in higher starting temperature about 250 °C, leading to the decrease in reaction speed with increasing temperature from 150 to 250 °C. In other words, the larger the difference between the equilibrium temperature and starting one is, the faster the absorption reaction becomes in the short time.

5. Conclusion

The hydrogen absorption kinetics of MgH_2 composite doped with 1 mol% Nb_2O_5 prepared by ball milling was investigated under various temperatures and pressures. The composite after dehydrogenation at 200 °C absorbs gaseous hydrogen up to ∼4.5 mass% even at room temperature under 1.0 MPa hydrogen pressure or 0 °C under 3.0 MPa within 15 s and finally its capacity reaches up to 5 mass%. At 150 and 250 °C, a large amount of hydrogen gas more than 5.0 mass% is absorbed within 30 s and its capacity reached up to 5.7 mass% under 1.0 MPa. The interesting points are the kinetics decreases with increase in the temperature from 150 to 250 °C under any pressures (0.2, 1.0 and 3.0 MPa), and the amount of hydrogen absorption drastically increases with increase in pressure from 1.0 to 3.0 MPa at 0 °C or from 0.2 to 1.0 MPa at RT. The decrease in reaction speed with increasing temperature from 150 to 250 °C is considered from the appearance of the reverse reaction or from the decrease in surface coverage of hydrogen atoms on the Mg surface with temperature. However, both assumptions do not explain the phenomena. As the next consideration, the temperature increase by heat generation of Mg during fast hydrogen uptake in the short time was taken into account to understand the overall experimental results, leading to an acceptable explanation.

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