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Kinetics and modeling study of magnesium hydride with various additives at constant pressure thermodynamic driving forces

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ABSTRACT

In this research a comparison was made of the reaction kinetics of MgH_2 ball milled with 4 mol% of TiH_2, Nb_2O_5 or Mg_2Ni. This comparison was made using a novel procedure in which the ratio of the equilibrium plateau pressure (P_m) to the opposing pressure (P_{op}) was the same in all cases. TPD analysis showed that the addition of 4 mol% of the various additives to MgH_2 resulted in a reduction of the onset temperature of MgH_2 by as much as 120 °C. Kinetic data showed that the reaction rates with additives are in the order: $TiH_2 < Mg_2Ni < Nb_2O_5$. These data were fitted to models for a moving boundary mechanism, a diffusion-controlled process, and nucleation and growth. It was found that a moving boundary mechanism best fit the data and most likely controlled the reaction rates. Kissinger plots showed that the activation energies for the mixtures were in the order: $TiH_2 > Mg_2Ni > Nb_2O_5$.

1. Introduction

Magnesium hydride is an attractive material for hydrogen storage because it has a high hydrogen-holding capacity of 7.6 wt% and it releases hydrogen reversibly via a simple one-step process. However, a major obstacle to its usefulness for hydrogen storage is the slow reaction rates and the high temperature required for it to release hydrogen. Attempts have been made to improve reaction rates and lower the reaction temperature of MgH_2 by ball milling it with various additives such as metal oxides and transition metals [1–5]. For example, Liang et al. [1] studied the catalytic effect of transition metals (ex. Ti, V, Mn, Fe and Ni) on hydrogen sorption by MgH_2. They found that the five 3d-elements had different catalytic effects on the reaction kinetics of the Mg–H system and that the activation energy for desorption of hydrogen from magnesium hydride was reduced drastically. Huot et al. [2] ball milled a mixture of Mg and Ni under hydrogen atmosphere and analyzed the reaction products by Temperature Programmed Desorption, TPD. They found that the presence of Ni lowered the onset temperature for desorption of hydrogen from MgH_2 from 440.7 to 225.4 °C. However, the presence of Mg_2Ni slowed the decomposition kinetics of MgH_2. Oelerich et al. [3] used a variety of metal oxides (ex. Nb_2O_5, Fe_3O_4, V_2O_5, Mn_2O_3, Cr_2O_3, TiO_2, Sc_2O_3, Al_2O_3, CuO, and SiO_2) to improve reaction rates of MgH_2 and found that as little as 0.2 mol% was sufficient to provide fast sorption kinetics. Barkhordarian et al. [4] investigated the efficiency of Nb_2O_5 as a catalyst for the hydrogen sorption reaction of magnesium and compared it to other metal and oxide catalysts. Their results demonstrated that the catalytic effect of Nb_2O_5 is superior in absorption as well as desorption. In another study [5] they further studied the effect of Nb_2O_5 on the sorption kinetics of MgH_2 and found that at 250 °C, absorption and desorption of 6 wt% hydrogen occurred from a 0.5 mol% Nb_2O_5 in Mg–H mixture in 60 and 500 s, respectively. The activation energies for desorption was calculated and found to vary exponentially with Nb_2O_5 concentration. Their results showed that there is a change in the rate-limiting step with catalyst content. In none of these studies has there been an attempt to compare the intrinsic reaction rates of catalyzed magnesium hydride using constant pressure thermodynamic forces. It is important that this be done because, without constant pressure driving forces, results will vary widely as the conditions change. For example, Barkhordarian et al. [5] reported that desorption into a dynamic vacuum at 300 °C occurs in as little as 60 s. Others have reported much slower kinetics when desorbing against a finite pressure [10]. Goudy and co-workers [6–8] first showed the importance of using constant pressure driving forces when they analyzed the kinetic behavior of a series of $LaNi_5$-based intermetallic hydrides. Since that time they have used this technique to study the kinetics of other materials such as sodium alanate [9].

In this present study, an attempt has been made to compare the intrinsic dehydriding kinetics of MgH_2 ball milled with various catalysts using constant pressure thermodynamic driving forces and to determine the rate-controlling process. The results should lead to a better understanding of the role that catalysts may have on reaction temperatures and rates.

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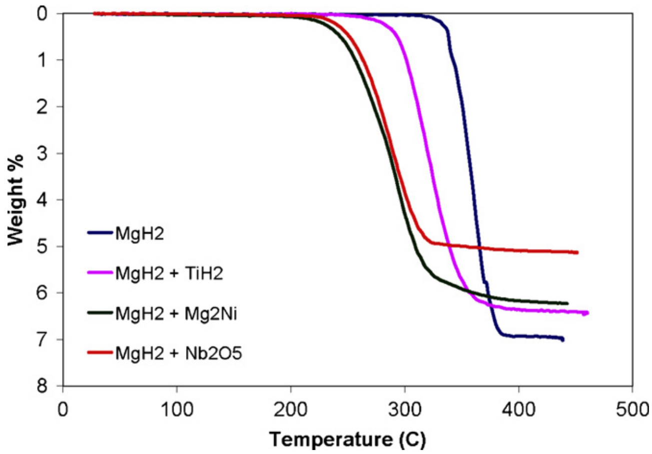

Fig. 1. TPD profiles for catalyzed MgH_2 materials.

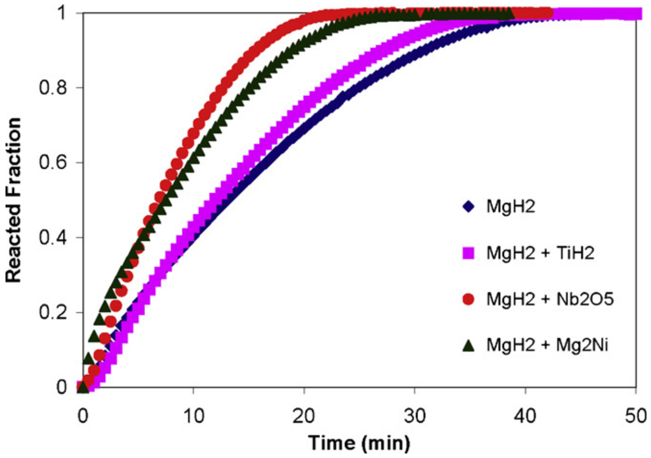

Fig. 2. Desorption kinetics for catalyzed MgH_2 materials at 400 °C and $N = 5$.

2. Experimental details

The starting materials used in this research were obtained from Sigma Aldrich. The MgH_2 powder was hydrogen storage grade and according to the supplier, the total amount of trace metal contaminants in this material was less than 0.1%. All sample handling, weighing and loading were performed in a vacuum atmospheres argon-filled glove box that was capable of achieving less than 1 ppm oxygen and moisture. Prior to analysis, each sample mixture was milled for up to 10 h in a SPEX 8000M Mixer/Mill that contained an argon-filled stainless steel milling pot with four small stainless steel balls. Pressure Composition Isotherm (PCI) analyses and Temperature Programmed Desorption (TPD) were used to evaluate the hydrogen desorption properties of each reaction mixture. These analyses were done in a gas reaction controller unit that was manufactured by the Advanced Materials Corporation in Pittsburgh, PA. The unit was fully automated and was controlled by a Lab View-based software program. PCI analyses were done on freshly ball milled materials and no activation procedure was necessary. The TPD analyses were done in the 30–450 °C range at a temperature ramp of 4°/min. Simultaneous thermal analysis, a combination of Thermal Gravimetric and Differential Thermal Analysis (TG/DTA), was conducted to determine the thermal stability of the mixtures using a Perkin Elmer Diamond TG/DTA. The heating rate was set at 1, 4, 10 and 15°/min when the activation energy of the samples was investigated. The experimental apparatus used to perform kinetics measurements consisted essentially of a stainless steel manifold with ports for adding hydrogen, venting, and evacuating. Pressure regulators were installed to control the hydrogen pressure applied to the sample and to allow hydrogen to flow to or from the sample into a remote reservoir. High purity hydrogen gas of 99.999% purity was used throughout the analyses. Complete details of the experimental procedures used in this research have been published elsewhere [9–11].

3. Results and discussion

Several mixtures were made in which MgH_2 was ball milled with 4 mol% of TiH_2, Nb_2O_5 or Mg_2Ni. After each mixture was ball milled for 10 h, TPD measurements were done in order to determine the effect of each catalyst on the hydrogen desorption properties of MgH_2. The profiles in Fig. 1 show that pure MgH_2 has the highest onset temperature of about 310 °C. The onset temperatures for all the catalyzed mixtures are summarized in Table 1 and are in the order: Pure $MgH_2 > TiH_2 > Nb_2O_5 \geq Mg_2Ni$. The plots also show that all of the mixtures released greater than 6 wt% hydrogen except the Nb_2O_5 catalyzed mixture, which released about 5 wt% hydrogen. This lower weight percentage could possibly result from partial oxidation of the Mg in the alloy caused by the presence of oxide in Nb_2O_5.

Table 1
Kinetics and TPD results for some MgH_2-based systems.

System	Onset temperature (°C)	T_{90} (min)	E_a (kJ/mol)
MgH_2	310	32	174
$MgH_2 + TiH_2$	250	26	131
$MgH_2 + Mg_2Ni$	190	19	98
$MgH_2 + Nb_2O_5$	205	16	95

In addition to lowering reaction temperatures, it is important to have fast reaction rates. Therefore several experiments were done in order to determine the effect of catalyst additives on the hydrogen desorption rates from MgH_2. Fig. 2 contains plots of reacted fraction versus time for the desorption of hydrogen from the MgH_2 mixtures. These desorption measurements were performed using a novel concept of constant pressure thermodynamic driving forces. This was accomplished by first adjusting the hydrogen pressure in the reactor to a value just slightly higher than that of the mid-plateau pressure (P_m), to assure that only the hydrogen rich phase was initially present, and sealing off the reactor. The pressure in the remaining system (P_{op}) was then adjusted to a value such that the ratio of the mid-plateau pressure to the opposing pressure (P_m/P_{op}) was a small whole number. This small whole number in the remainder of the text is defined as the N-value. In these experiments the N-value, and thus the thermodynamic driving force, was the same in all cases. This represents the first time that this technique has been applied to a kinetic study of the MgH_2 system. The plots show that, under the conditions used, the reaction times are in the order: Pure $MgH_2 > TiH_2 > Mg_2Ni > Nb_2O_5$. The times required for 90% of the reaction to be completed are also summarized in Table 1. The rapid kinetics of Nb_2O_5 is in agreement with the results of others [4,5].

The dehydriding reactions can possibly be described by any of several kinetics models. These include: diffusion, moving boundary and nucleation and growth. To determine which, if any, of these kinetics models describe these reactions it was necessary to construct plots corresponding to the theoretical equations. The theoretical equations are summarized below.

$$(1-f)^{1/3} = 1 - \frac{\sqrt{kt}}{R} \tag{1}$$

$$(1-f)^{1/3} = 1 - \left(\frac{k}{R}\right) t \tag{2}$$

$$f = 1 - \exp(-kt^n) \tag{3}$$

In these equations, "f" corresponds to the reacted fraction, "k" is a constant, "t" is the time, "R" is the gas constant and "n" is a constant that depends on the geometry of the system. Eq. (1) corresponds to a diffusion-controlled process; Eq. (2) depicts a process that is limited by reaction at a moving boundary; and Eq. (3) represents a nucleation and growth controlled process. If diffusion were controlling the rates then, according to Eq. (1), a plot of $(1-f)^{1/3}$ versus time$^{1/2}$ should be linear. The nonlinearplot in Fig. 3(c) indicates that

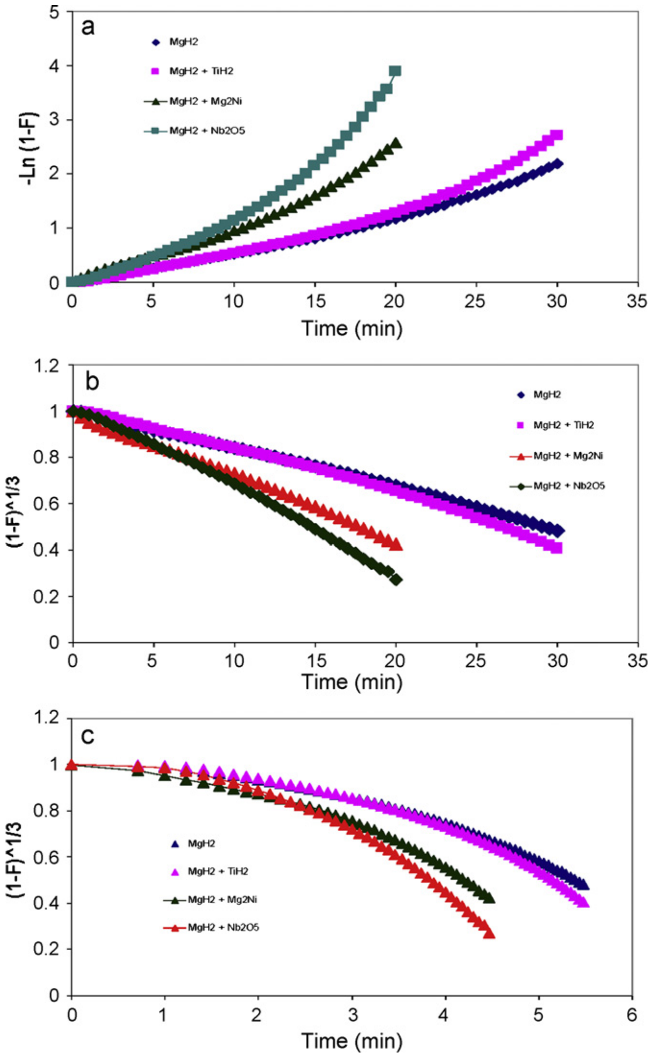

Fig. 3. Modeling for catalyzed MgH_2 materials at 400 °C and $N = 5$ using (a) nucleation and growth, (b) moving boundary and (c) diffusion models.

diffusion does not control the reaction rate. In addition, according to the nucleation and growth model represented by Eq. (3), a plot of $-\ln(1-f)$ versus t should be linear, assuming that $n = 1$. The assumption that $n = 1$ was reached based on a method of comparing the kinetics of solid state reactions that was proposed by Hancock and Sharp [12]. In their method, plots of $-\ln\ln(1-f)$ vs. ln(time) were used to determine values of "n" in Eq. (3). Since values in these experiments ranged from 0.7 to 1.6, it was decided that an average value of 1 would be used for the analyses. The plots based upon a nucleation and growth model shown in Fig. 3(a) have a pronounced curvature, which indicates that the nucleation and growth model is not applicable. That leaves the moving boundary model that is based on equation (2). When a plot of $(1-f)^{1/3}$ versus time was constructed it was found to be more linear than the other plots. Fig. 3(b) contains such plots for each of the four systems studied and they are very nearly linear over five half lives. Therefore the moving boundary model is the most plausible mechanism. It should be noted that since reaction at a moving boundary is a bulk process, this indicates that the additives did not merely coat the surface of the hydride particles upon ball milling but rather they were mechanically alloyed into the MgH_2 phase. If the additives had coated the surface then a surface reaction would have controlled the rate and a plot of reacted fraction vs. time would be linear. We did not observe this.

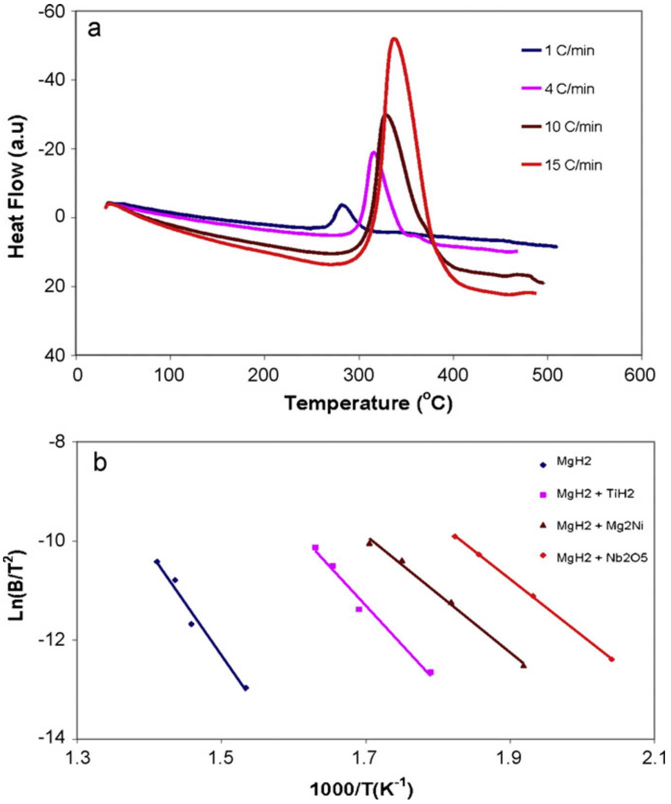

Fig. 4. (a) DTA for MgH_2 catalyzed with TiH_2 done at different scan rates. (b) Kissinger plots for catalyzed MgH_2 materials.

To further understand the effects of catalyst additives on the dehydrogenation of MgH_2, the activation energy of dehydrogenation for the samples with different catalysts were investigated using an isoconversion method based on the Kissinger equation [13]:

$$\ln\left(\frac{\beta}{T_{\max}^2}\right) = -\frac{E_a}{R}\left(\frac{1}{T_{\max}}\right) + F_{KAS}(\alpha) \tag{4}$$

where $T_{\max}$ is the temperature at the maximum reaction rate, β the heating rate, E_a the activation energy, α the fraction of transformation, $F_{KAS}(\alpha)$ a function of the fraction of transformation, and R is the gas constant.

Fig. 4(a) shows the DTA curves for MgH_2–TiH_2 mixtures. As expected the endothermic peak corresponding to the maximum rate of dehydrogenation shifts to higher temperatures as the heating rate is increased. The same trend was also observed for the samples with Mg_2Ni and Nb_2O_5 additives. The plot based on the Kissinger equation is shown in Fig. 4(b). It is seen that good linear relationships between $\ln(\beta/T_{\max}^2)$ and $1/T_{\max}$ are present for all the samples and that the activation energy of dehydrogenation can be calculated from the slope of the straight lines. The calculated activation energies are summarized in Table 1 and are in the order: Pure $MgH_2 > TiH_2 > Mg_2Ni > Nb_2O_5$. It should be noted that the desorption kinetics follows the same trend as the activation energies in so far as mixtures with lower activation energies have faster kinetics. A similar trend can be seen in the desorption temperatures. Mixtures with lower activation energies have lower desorption temperatures. However, there is one exception. The mixture containing Mg_2Ni has a slightly lower desorption temperature than the one containing Nb_2O_5 even though theNb_2O_5-containing mixture has a faster desorption rate and lower activation energy. The reason for this is not clearly understood at this time but it could simply be because their catalytic effects are too close.

4. Conclusions

This study has shown that it's possible to compare the intrinsic dehydriding rates of MgH_2 mixed with various additives. Since constant pressure driving forces were used, it is evident that the desorption rates are in the order $Nb_2O_5 > Mg_2Ni > TiH_2 >$ pure MgH_2. As expected, the mixtures with the fastest reaction times also had the lowest activation energies. In addition, the mixtures with the fastest reaction times generally had the lowest reaction temperatures. The one exception is that Nb_2O_5 had a slightly higher desorption temperature than Mg_2Ni even though it reacted faster than Mg_2Ni. Modeling studies indicate that reaction at a moving boundary is the most probable rate-controlling process for desorption of hydrogen from MgH_2.

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