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Dehydrogenation characteristics of Ti- and Ni/Ti-catalyzed Mg hydrides

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ABSTRACT

The desorption capacity, thermodynamics, and kinetics of Ti- and Ni/Ti-catalyzed Mg hydrides were investigated using Sievert-type apparatus and differential scanning calorimetry. Based on analysis of the van't Hoff equation and the Kissinger equation, the addition of Ti and Ni as catalysts has been found to play a key role in improving the thermodynamic and kinetic properties of MgH_2 by decreasing the desorption temperature and the activation energy. A combination of Ti and Ni is a more effective catalyst than either Ti or Ni alone, suggesting the existence of a synergetic effect.

1. Introduction

The increasing demand for "clean" energy sources has drawn attention to the prospects for a "Hydrogen Economy", in which hydrogen is used as the main energy carrier to provide a long-term solution to a sustainable future as well as energy security [1]. Being a gas, however, hydrogen faces great challenges in terms of practical storage, especially in on-board storage systems for hydrogen-powered vehicles. A suitable material for hydrogen storage is one of the key requirements for any future hydrogen economy. The MgH_2 system is one of the most promising metal hydrides because it can store hydrogen reversibly up to 7.6 wt.% and has a high volumetric hydrogen density of 106 kg H_2/m^3. Furthermore, magnesium is abundant and inexpensive.

However, the use of magnesium as a practical storage material is hindered by its slow sorption kinetics. It has been previously demonstrated that additives can significantly improve the reaction kinetics, which enables hydrogen to be desorbed at temperatures far below 300 °C [2–5]. Among the additives used in different studies, the catalytic effect of Ti and Ni alone [3] and the transition-metal compounds show high potential [6,7]. However, in the ball-milled Ti-catalyzed MgH_2 system, the addition of Ti does not change the thermodynamic properties of MgH_2, despite a significant reduction in the activation energy of hydrogen desorption [3]. Catalysts consisting of mixed transition metals were found to have synergetic catalytic effects which significantly improved the hydrogen dissociation and diffusion characteristics in nanostructured magnesium [8,9]. Moreover, Ni element is effective in promoting the hydrogenation kinetics of Mg-based alloys [3] and often plays a vital catalytic role in Ti-based alloy electrodes during electrochemical reactions [10]. The Mg–Ni–Ti ternary alloys have also been studied as hydrogen storage electrodes using electrochemical method [11]. However, only few studies have been carried out about synergetic catalytic effects of Ni and Ti elements on Mg hydride, especially using van't Hoff equation and the Kissinger equation. Furthermore, the storage capacity, kinetics, and desorption temperature are the most important parameters for the application of hydrides as hydrogen storage materials [12]. The desorption behavior is more important than the absorption behavior because a material can only be regarded as a suitable hydrogen storage material if it has favorable hydrogen desorption characteristics [12].

In this work, the storage capacity, thermodynamics, and kinetics of the hydrogen desorption performance of nanocrystalline Mg hydrides catalyzed by Ti element alone and the combination of Ni and Ti elements have been studied using Sievert-type apparatus and differential scanning calorimetry (DSC).

2. Experimental

The elemental powders with high purity (>99 wt.%) from Sigma–Aldrich were used for the experiments. The following ratios were used for the catalyzed Mg hydrides: MgH_2–x at.% Ti (x = 1 and 5) and MgH_2–Ni/Ti (Ni:Ti = 1:1 in molar ratio, with 16.7 at.% Ni, and Ni:Ti = 4:1, with 26.7 at.% Ni). The samples were prepared by ball milling under hydrogen atmosphere at an initial pressure of about 7 atm for 35 h. The ball-milling equipment was a magnetically controlled Uni-Ball-Mill with a rotational speed of 60 rpm. All powders were handled in a glove box with an

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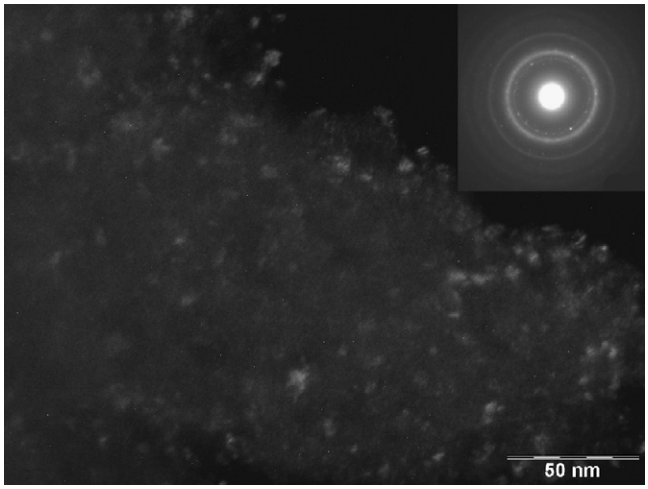

Fig. 1. TEM dark-field image of the MgH_2–Ni/Ti (Ni:Ti = 4:1) sample after ball milling. Inset shows a selected area electron diffraction (SAED) pattern.

argon atmosphere to prevent the oxidation of the samples. Transmission electron microscopy (TEM) was performed using a JEOL 2011 analytical instrument to investigate the morphology and crystallography of the products with dark-field imaging and selected area electron diffraction (SAED). TEM samples were prepared by dispersing powders on lacy carbon support films. The dehydrogenation behavior was studied using a Sievert-type apparatus from the Advanced Materials Corporation (USA). The as-milled samples were activated at 380 °C under a hydrogen pressure of 30 atm and evacuated at the end of 1 h. The activation energy for the hydrogen desorption kinetics was obtained using DSC techniques (TA Instruments Q100) with different linear heating rates under an argon flow rate of 50 mL min^{-1}. The argon pressure inside the DSC cell was 1.0 atm.

3. Results and discussion

The grain size after ball milling is important for an understanding of hydrogen sorption behavior. As shown previously [2,13], the catalyst in the nanoscale is very essential for improving the kinetics of hydrogen sorption. The nanostructured alloys reveal improved hydrogen storage properties, mainly due to the large volume fraction of the grain-boundary regions. The mean grain size of the as-received magnesium particles was found to be about 10 μm, and it was reduced to 15 nm after the ball-milling process as determined by TEM (Fig. 1).

Fig. 2 shows the hydrogen desorption capacity by ramping up the temperature to 400 °C under 0.1 atm hydrogen pressure. The measured hydrogen desorption capacities, by taking the total mass of the sample into account, were 4.9 wt.%, 4.5 wt.%, and 2.9 wt.% for the 1 at.% Ti, the 5 at.% Ti, and the Ni–Ti samples. Moreover, the addition of Ti significantly decreases the desorption temperatures. In contrast, the Ni/Ti-doped MgH_2 composites have the lowest desorption temperature (about ~200 °C). This means that the addition of elemental Ti and Ni/Ti can significantly improve the dehydriding property of MgH_2 compared with the non-catalyzed MgH_2.

The pressure–composition isotherm (PCI) desorption curves for the MgH_2–Ni/Ti (4:1) sample at temperatures of 340 °C, 360 °C, 400 °C and 420 °C have been shown in Fig. 3. Only one plateau pressure was observed in the PCI desorption curves, and this indicated that there was only one phase transformation during the hydrogen desorption process [9], which was associated with MgH_2 in our case. The thermodynamic properties, such as the dissociation enthalpy (ΔH) and the entropy (ΔS), were derived from the van't Hoff equation:

$$\ln\left(\frac{P_{eq}}{P_0}\right) = \frac{\Delta H}{RT} - \frac{\Delta S}{R} \quad (1)$$

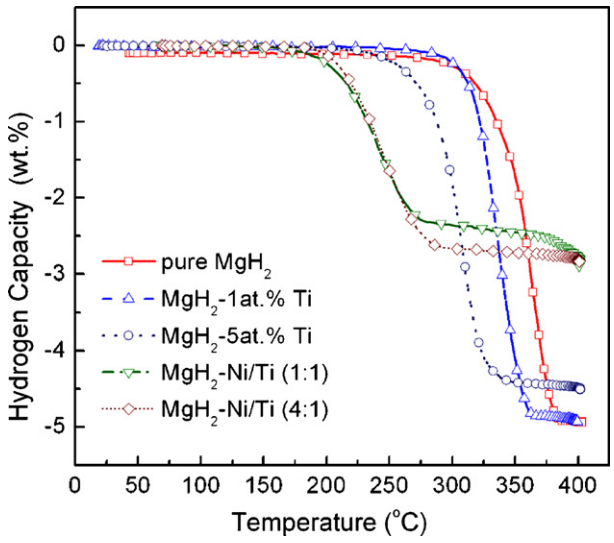

Fig. 2. Hydrogen desorption capacity measured using the volumetric method by ramping the sample temperature from room temperature to 400 °C at 0.1 atm hydrogen pressure. The heating rate was 23 °C/min.

where P_{eq} is the equilibrium pressure, P_0 is the reference pressure (taken to be 1.0 atm herein), T is the isothermal temperature, and R is the gas constant. The corresponding van't Hoff plot for this MgH_2–Ni/Ti (4:1) sample, based on the plateau pressures and isothermal temperatures, is also presented (Fig. 3 inset). The thermodynamic values of ΔH and ΔS for this sample are -67.8 ± 0.1 kJ mol^{-1} and 128.3 ± 0.2 J mol^{-1} K^{-1}, respectively, which are lower than those of pure MgH_2 (-76.7 kJ mol^{-1} and 139.2 J mol^{-1} K^{-1}), as shown in Table 1. The calculated desorption temperature, T_{des}, of the MgH_2–Ni/Ti (4:1) sample at 1.0 atm of hydrogen pressure, based on its experimental values for ΔH and ΔS is 256 ± 1 °C, which is 22 °C lower than that of our pure MgH_2. The values of ΔH, ΔS, and T_{des} for the other Ti-and Ni/Ti-catalyzed MgH_2 samples are also listed in Table 1. It can be seen from Table 1 that the samples doped with Ti and Ni/Ti have the lower values of ΔH, ΔS and T_{des} compared with those of pure MgH_2. As Zaluski et al. pointed out [14], transition metals are known to enhance the rate of hydrogen desorption, and the "spill-over" process seems to

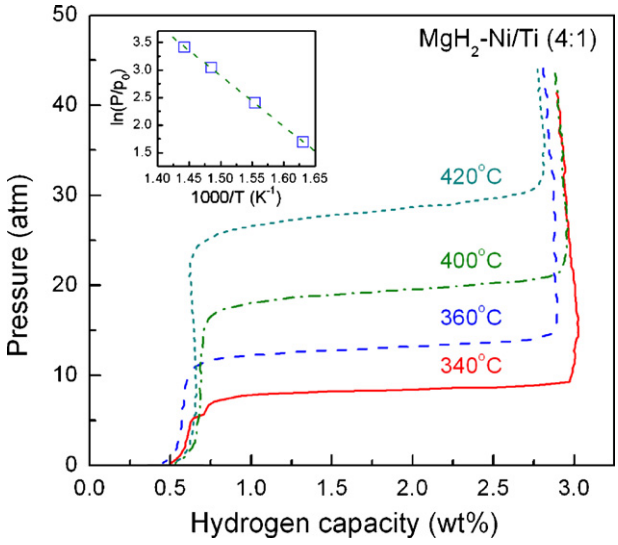

Fig. 3. The pressure–composition isotherms (PCI) desorption curves of the MgH_2–Ni/Ti (4:1) sample at different temperatures. The inset shows the van't Hoff plot derived from the PCI curves.