



## Hydrogen storage properties of ball-milled Mg-based composite with PdCl<sub>2</sub> additive\*

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**Abstract:** Mg-25 wt% Mg<sub>2</sub>Ni composite was prepared by sintered method, hydrided at 613 K and then ball-milled with 1.5 wt% PdCl<sub>2</sub> additive for 51 h. The effects of PdCl<sub>2</sub> on the hydriding and dehydriding behavior of Mg-25 wt% Mg<sub>2</sub>Ni composite were investigated. The absorption and desorption rate of the composite with PdCl<sub>2</sub> is fast and the hydrogen storage capacity is more than that of the composite without PdCl<sub>2</sub>. The maximum hydrogen storage capacity reached 3.48 wt% at 373 K, and 5.05 wt% H at 453 K, respectively. The improvement of sorption and desorption kinetics is attributed to the catalytic effect of PdCl<sub>2</sub>, and the grain refining and lattice strain introduced by ball milling.

**Key words:** Hydrogen storage, Mg-based composite, PdCl<sub>2</sub> additive, Ball milling

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### INTRODUCTION

Much effort has been concentrated on studies of metal hydrides for hydrogen storage, magnesium metal or magnesium-containing systems are considered as promising candidate materials because of their high hydrogen storage capacity and low cost (Schulz *et al.*, 1999; Stander, 1977; Imamura *et al.*, 1983; Wang *et al.*, 2000). However, due to the hydride stability and slow sorption kinetics, the actual applications are limited. The sorption kinetics of Mg-based alloys can be improved by addition of catalysts such as transition metals (Bobet *et al.*, 2001), metal oxides (Oelerich *et al.*, 2001) and metal chloride (Yu *et al.*, 2002), thus forming a composite with low temperature hydride (Sun *et al.*, 1999; Wang *et al.*, 2005; Zhu *et al.*, 1999), or by using multiphase systems, or by surface modification (Bouaricha *et al.*, 2000; Cui *et al.*, 1999). The oxides are brittle, and thus may be pulverized

during ball milling. The added oxides and/or their pulverization during ball milling may help the Mg particles to become finer. According to Yu *et al.* (2002)'s result, the addition of CrCl<sub>3</sub> in Mg composite may be attributed to two aspects: (1) The CrCl<sub>3</sub> can promote breaking of MgO membrane covering the surface of Mg grains; (2) The Cr<sup>3+</sup> of Cr<sub>2</sub>O<sub>3</sub> plays a key role in catalytic process as Cr<sup>3+</sup> of Cr<sub>2</sub>O<sub>3</sub> in hydriding/dehydriding process.

Composite formation with other hydrogen storage material is a main approach to improve the hydrogenation properties of Mg-based alloy. Mg<sub>2</sub>Ni hydride has lower stability than MgH<sub>2</sub>, therefore Mg<sub>2</sub>Ni in the composite can be hydrided with low activation energy. The exothermic reaction provides energy for the hydrogen absorption by Mg to some extent. It is known that ball milling may change the properties of materials, as a result of the formation of special microstructures, metastable phase and modified surfaces. Hydrogen properties are very sensitive to these modifications. The brittle Mg-based hydrides can accelerate the ball milling process compared with the ductile Mg-based alloy (Huot *et al.*,

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1999). In this work, the hydriding/dehydriding properties of Mg-25 wt% Mg<sub>2</sub>Ni composite with 1.5 wt% PdCl<sub>2</sub> addition was investigated, and the effect of PdCl<sub>2</sub> on the sorption and desorption kinetics of the composite was also discussed.

## EXPERIMENTAL DETAILS

Magnesium and nickel powders (99.9% purity, 200 mesh), corresponding to a weight proportion of Mg-25 wt% Mg<sub>2</sub>Ni were mechanically mixed under argon in a planetary ball mill machine for 1 h. After the milling, the mixture was cold pressed into a pellet under a pressure of 800 MPa and sintered at 823 K for 3 h in argon atmosphere. The sintered alloy pellet was pulverized to powder smaller than 100 mesh. Then the Mg-25 wt% Mg<sub>2</sub>Ni powders with or without 1.5 wt% PdCl<sub>2</sub> particles were ball-milled for 1 h, and activated at 613 K at 4.0 MPa H<sub>2</sub> for 8 h. Thereafter, the multi-phase hydrides were ball-milled for 51 h under argon with a ball-to-powder weight ratio of 20:1. The phase structures of the hydride powders before and after ball-milling were examined by X-ray diffraction (XRD, Philips PW1050 diffractometer, CuK $\alpha$  radiation).

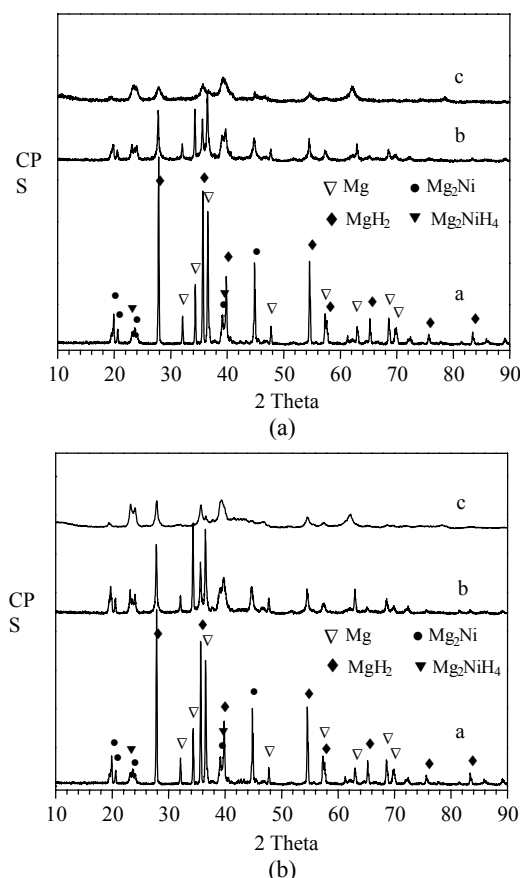
The apparatus for hydriding/dehydriding measurements is similar to the equipment described in (Wang *et al.*, 2005). The vessel filled with a 3.0 g powder sample was evacuated to 10<sup>-2</sup> Pa by a rotary vacuum pump and heated to 573 K for 1 h. Then the temperature was set equal to the determined absorption temperature, and hydrogen was introduced at initial pressure of 4 MPa. After measuring the hydrogen absorbing behavior, the vessel was evacuated to 0.1 MPa and heated to 543 K to desorb the hydrogen.

## RESULTS AND DISCUSSION

### Mechanical milling process

The evolution of the X-ray diffraction spectra as a function of milling time for two composites, Mg-25 wt% Mg<sub>2</sub>Ni and Mg-25 wt% Mg<sub>2</sub>Ni-1.5 wt% PdCl<sub>2</sub>, is shown in Figs. 1a and 1b, respectively. From these figures, it can be clearly seen that the intensities of the

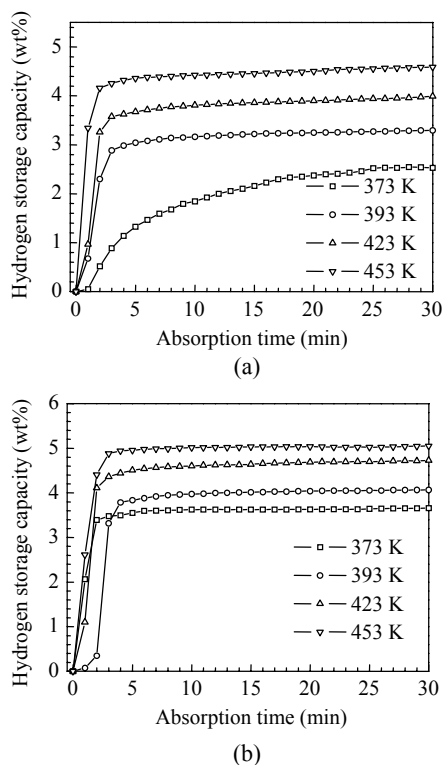
diffraction peaks reduce and the widths of the peaks increase with the increase of milling time. It indicates the grain refining and the introduction of plastic deformation and lattice strain into the powders during ball milling. From the patterns a in Figs. 1a and 1b, there exist four phases of Mg, MgH<sub>2</sub>, Mg<sub>2</sub>Ni and Mg<sub>2</sub>NiH<sub>4</sub>, suggesting that Mg and Mg<sub>2</sub>Ni partly react with hydrogen during the initial hydriding process at 613 K. In this work, the purpose of initial hydriding treatment at 613 K is to accelerate the subsequent ball milling process. The XRD diffraction peaks of ball-milled composite in Figs. 1a and 1b indicate that partly hydriding here is enough to promote the ball milling process. Besides, since the proportion of PdCl<sub>2</sub> is only 1.5 wt%, the diffraction peaks of the two composites do not change significantly, while the peaks of PdCl<sub>2</sub> do not appear in the XRD pattern at all.



**Fig.1** XRD patterns of Mg-25 wt% (a) Mg<sub>2</sub>Ni composite and (b) Mg<sub>2</sub>Ni-1.5 wt% PdCl<sub>2</sub> composite. Curves a, b and c represent the patterns after being partly hydrided, ball milling for 23 h, ball milling for 51 h, respectively

### Hydrogen storage properties

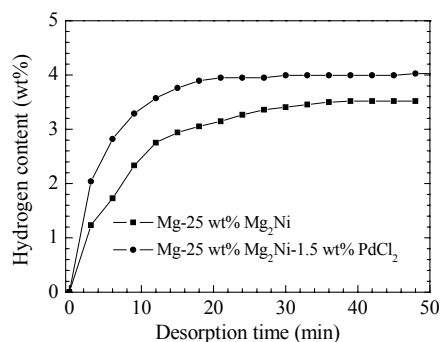
After being dehydrided at 573 K, the as-milled composites need no activation for rapid hydrogen absorption. Figs.2a and 2b present the hydriding kinetics curves of Mg-25 wt% Mg<sub>2</sub>Ni and Mg-25 wt% Mg<sub>2</sub>Ni-1.5 wt% PdCl<sub>2</sub> composites at different temperatures under initial 4.0 MPa H<sub>2</sub>, respectively. The absorption rate of the composite with PdCl<sub>2</sub> additive is fast and the hydrogen storage capacity is more than that of the sample without PdCl<sub>2</sub>, especially at the lower temperature. Mg-25 wt% Mg<sub>2</sub>Ni composite with PdCl<sub>2</sub> reacts rapidly with hydrogen at 373 K. The hydriding process is finished within 5 min with the maximum hydrogen storage capacity reaching 3.48 wt%. However, the composite without PdCl<sub>2</sub> reacts slowly with hydrogen at 373 K and the hydrogen storage capacity is 2.52 wt% in 30 min. With increasing hydriding temperature, the hydrogen storage capacities of both the composites increase. In the case of Mg-25 wt% Mg<sub>2</sub>Ni-1.5 wt% PdCl<sub>2</sub> composite, the hydrogen absorption capacity is 4.06 wt%, 4.72 wt% and 5.05 wt% H at 393 K, 423 K and 453 K, respectively; while the maximum hydrogen storage capacity



**Fig.2** Hydrogen absorption kinetics curves of Mg-25 wt% (a) Mg<sub>2</sub>Ni and (b) Mg<sub>2</sub>Ni-1.5 wt% PdCl<sub>2</sub> at different temperatures under initial 4.0 MPa H<sub>2</sub>

of Mg-25 wt% Mg<sub>2</sub>Ni is 3.30 wt%, 3.98 wt% and 4.58 wt% at 393 K, 423 K and 453 K, respectively. Theoretically, the maximum hydrogen storage capacity of Mg-25 wt% Mg<sub>2</sub>Ni composite is 6.3 wt%.

On the desorption side, the composite with PdCl<sub>2</sub> additive also exhibited rather high rates. Fig.3 presents the hydrogen desorption kinetics curves of Mg-25 wt% Mg<sub>2</sub>Ni and Mg-25 wt% Mg<sub>2</sub>Ni-1.5 wt% PdCl<sub>2</sub> at 543 K under 0.1 MPa H<sub>2</sub>. As shown in Fig.3, the addition of PdCl<sub>2</sub> particles also accelerates the hydrogen desorption rate. The Mg-25 wt% Mg<sub>2</sub>Ni composite with PdCl<sub>2</sub> releases 4.0 wt% H in 30 min while the composite without PdCl<sub>2</sub> can only desorb 3.5 wt% H<sub>2</sub> in 40 min under the same desorption conditions. From the above results, it can be concluded that the addition of PdCl<sub>2</sub> particles could improve the hydriding/dehydriding kinetics to some extent.



**Fig.3** Hydrogen desorption kinetics curves of Mg-25 wt% Mg<sub>2</sub>Ni and Mg-25 wt% Mg<sub>2</sub>Ni-1.5 wt% PdCl<sub>2</sub> at 543 K under 0.1 MPa H<sub>2</sub>

The improvement of the absorption/desorption kinetics of the composite was attributed to the catalytic effect of PdCl<sub>2</sub>. Yu *et al.*(2002) reported that CrCl<sub>3</sub> had catalytic effect on the hydrogen absorption and desorption process of Mg-Ni system materials, and that CrCl<sub>3</sub> was very helpful in peeling off the membrane MgO from the Mg grain surface. In this work, it is believed that PdCl<sub>2</sub> dispersed on the surface of Mg-based alloy by ball milling shows important catalytic effect on the hydriding/dehydriding process. In addition, the grain refining and lattice strain introduced by ball milling affect the absorption/desorption kinetics. The interface between the Mg and Mg-Ni can act as an active nucleation sites for Mg-based hydrides. In general, the key step in the absorption/desorption process is the diffusion of hydrogen in

the hydrides. Mechanical milling can facilitate nucleation by creating many defects on the surface and/or in the interior of Mg-based alloy, or by an additive acting as active sites for the nucleation, and shorten the diffusion distance by reducing the effective particle sizes of Mg-based hydrogen storage material.

## CONCLUSION

Mg-25 wt% Mg<sub>2</sub>Ni composite was prepared by sintering method, hydrided at 613 K and then ball-milled with 1.5 wt% PdCl<sub>2</sub> particles for 51 h. After being dehydrided at 573 K, the as-milled composites need no activation for rapid H-absorption. The absorption rate of the composite with PdCl<sub>2</sub> was fast and the hydrogen storage capacity was more than that of the composite without PdCl<sub>2</sub>, especially at lower temperatures. Mg-25 wt% Mg<sub>2</sub>Ni-1.5 wt% PdCl<sub>2</sub> reacted rapidly with hydrogen at 373 K, the hydriding process was finished within 5 min and the maximum hydrogen storage capacity reached 3.48 wt%. The improvement of the absorption/desorption kinetics was attributed to the catalytic effect of PdCl<sub>2</sub>, and the grain refining and lattice strain introduced by ball milling.

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