

Investigations on synthesis and hydrogenation properties of Mg–20 wt% Ni–1 wt% TiO₂ composite prepared by reactive mechanical alloying

Fabing Li^{*}, Lijun Jiang, Jun Du, Shumao Wang,
Xaiopeng Liu, Feng Zhan

*Energy Material and Technology Research Center, General Research Institute for Nonferrous Metal,
Beijing 100088, PR China*

Received 22 September 2006; received in revised form 10 November 2006; accepted 10 November 2006
Available online 12 December 2006

Abstract

Reactive mechanical alloying (RMA) was used to prepare Mg–20 wt% Ni–1.0 wt% TiO₂ composite materials. A nanocrystalline composite of MgH₂ and Mg₂NiH₄ formed after 60 h of ball-milling. An increase of the nanocrystalline size was found after 20 hydriding/dehydriding cycles. It absorbed more than 80% of its full capacity in the temperature range of 363–543 K within less than 1 min and desorbed 3.22 mass% of hydrogen at 578 K under a hydrogen pressure of 0.1 MPa in 1 h. DSC analysis shows that the thermodynamic property of Mg-based hydrogen storage alloys do not be changed by the addition of TiO₂ and ball-milled process.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Reactive mechanical alloying; Hydriding/dehydriding; Magnesium-based hydrogen storage materials

1. Introduction

In recent years much attention has been paid to magnesium-based system for hydrogen storage because of its high volumetric and gravimetric storage capacity. However, the hydriding/dehydriding reaction of magnesium and magnesium-based alloys is too slow and higher temperature than 573 K is needed for practical application. One way to overcome these drawbacks is by reducing the grain size into nanocrystalline dimensions, which significantly improves the diffusion of hydrogen atoms [1,2]. More recently, it has been reported that binding Mg with various additives by reactive mechanical alloying improves hydrogen absorption and desorption kinetics [3–5].

TiO₂ as an important catalyst has been used to improve the hydrogen absorption kinetics of Mg [6–8]. In this work, we investigated the synthesis and hydrogen storage properties of Mg–20 wt% Ni–1 wt% TiO₂ composite prepared by ball milling under a hydrogen atmosphere. This composite showed

very good hydriding/dehydriding kinetics at relatively low temperature.

2. Experimental details

Magnesium and nickel powders (>99 mass% purity, –200 mesh) were provided by manufacturer Beijing Chemical Reagent Company. Mg, Ni and TiO₂ (Anatase, 20 nm, 99%) powders with the mix ratio 79:20:1 (wt%) were placed into a stainless steel jar with 300 ml inner volume and evacuated to 10^{–3} MPa prior to filling with hydrogen gas (3 MPa, 99.9% purity). The jar was refilled every 5 h of milling in order to prevent from any leakage. The mixed powders of 5 g and 25 pieces of Cr steel balls with a diameter of 9 mm were brought into the jar. The ball to powder weight ratio was 10:1. Mechanical milling was carried out in a Spex 8000 ball miller with 1425 rpm and milling time was up to 60 h. After milling, 500 mg samples were removed from the jar and loaded into the double wall reactor. All the handlings were performed in an argon glove box.

The hydrogen storage properties of milled composite were evaluated by using a volumetric method. Absorption rate was calculated by the pressure drop in a constant volume as a function of time. Similarly desorption rate was measured by the pressure increase from the initial pressure set at 0.1 MPa.

X-ray diffraction was performed before and after milling using Cu K α radiation on a MXP21 VAHF diffractometer. The diffraction angle was from 10 to 90° with the scan rates 0.01° per step and 2°/min. The microstructure of the composite was examined by scanning electron microscopy (HITACHI-S4800). The

^{*} Corresponding author. Tel.: +86 10 82241241; fax: +86 10 62001412.
E-mail address: lfbml@yahoo.com.cn (F. Li).

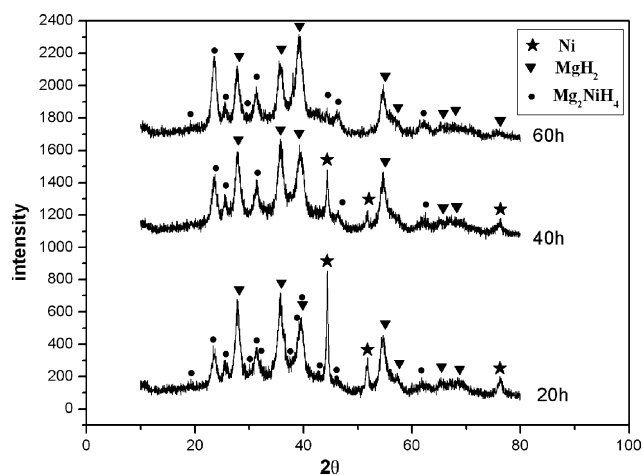


Fig. 1. The X-ray diffraction pattern of Mg–20 wt% Ni–1 wt% TiO₂ composite prepared by RMA.

thermal properties of samples were studied by differential scanning calorimetry (DSC, Netzsch 409) with heating rate of 10 °C min⁻¹ and argon flow rate of 18 ml min⁻¹.

3. Results and discussion

3.1. Phase change and morphological observations

Mechanical milling of Mg–20 wt% Ni–1 wt% TiO₂ under a hydrogen atmosphere directly led to the composite MgH₂ and Mg₂NiH₄ (see Fig. 1). The diffraction peaks of Mg and Ni disappeared completely after 60 h milling. The diffraction peaks of TiO₂ cannot be seen with 1 wt% addition. The broadening of peaks indicated that the crystallite size was reduced to the nanometer range. The crystallite size of MgH₂ and Mg₂NiH₄ after 60 h milling was calculated by Scherrer's equation from XRD data and shown in Table 1.

Fig. 2 shows the X-ray diffraction pattern of this composite after 20 hydriding/dehydriding cycles at 623 K. All Bragg reflections of MgH₂ and Mg₂NiH₄ disappeared after desorption. The final composite consisted of Mg and Mg₂Ni. Table 2 was the crystallite size of Mg and Mg₂Ni after 20 hydriding/dehydriding cycles. It could be seen that the crystallite size increased after hydriding/dehydriding cycles, comparing with milled composite. The reason for the crystallite sizes increase is the

Table 1
Crystallite size of phases after 60 h milling

Phases	Crystallite size (nm)
MgH ₂	24
Mg ₂ NiH ₄	27

Table 2
Crystallite size of phases after 20 hydriding/dehydriding cycles

Phases	Crystallite size (nm)
MgH ₂	63
Mg ₂ NiH ₄	86

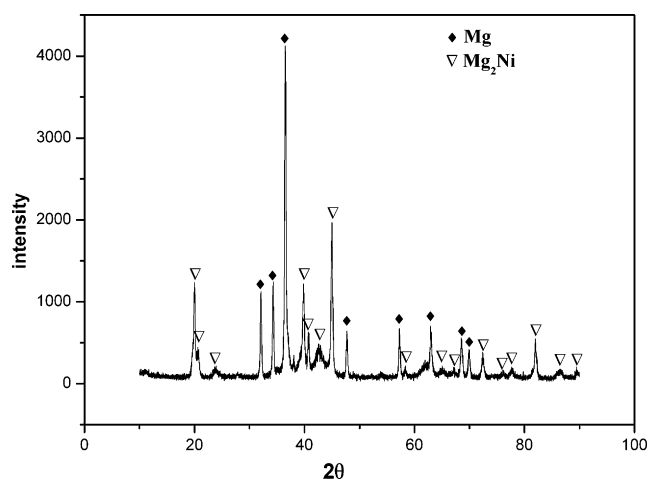


Fig. 2. The X-ray diffraction pattern of Mg–20 wt% Ni–1 wt% TiO₂ composite after 20 hydriding/dehydriding cycles.

elimination of stress and growth of the fine grains during hydriding/dehydriding cycles at a bit high temperature.

Fig. 3 was the scanning electron micrograph of the 60 h ball milled composite. The continuous cold welding and fracturing roughened the surface of the ball-milled powders. With further ball milling, the agglomerates with many finer particles formed as the final ball-milling effects. SEM images showed that the particles are typically around a few micrometers in size.

3.2. Hydrogen storage properties

The composite powders after 60 h of milling were loaded into the reactor, pumped for 10 min, then heated to 623 K for dehydriding. After five absorption–desorption cycles, the hydriding/dehydriding capacity and rate remain almost the same. The kinetic curves at various temperature and pressure were measured.

Fig. 4 shows the absorption kinetic curves for the 60 h ball milled composite at different temperature under 3.0 MPa hydrogen pressure. This composite, showing good hydriding properties, can absorb 2.70 mass% of hydrogen even at

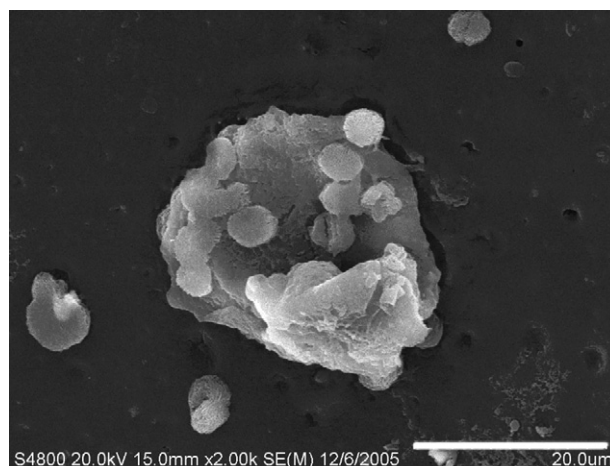


Fig. 3. SEM morphology of the composite milled for 60 h.

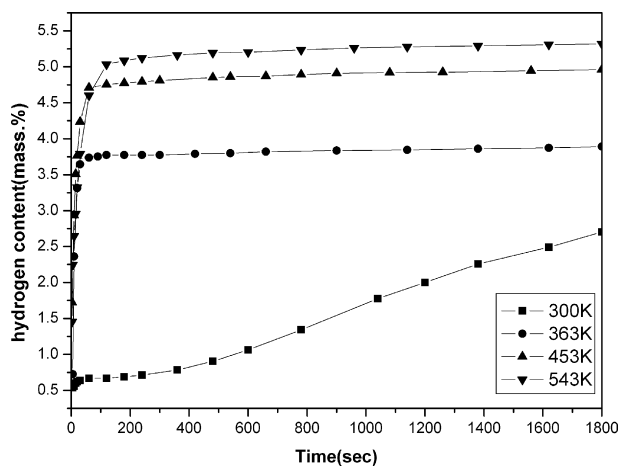


Fig. 4. Hydrogen absorption kinetics curves of Mg–20 wt% Ni–1 wt% TiO₂ composite at different temperatures under a hydrogen pressure of 3.0 MPa.

room temperature within 30 min. It was seen that the composite can absorb more than 80% of the full hydrogen storage capacity in 1 min within the temperature range 363–543 K under 3.0 MPa hydrogen pressure. The maximum hydrogen storage capacity of Mg–20 wt% Ni–1 wt% TiO₂ composite at 543 K was 5.32 mass%. The absorption rate strongly depended on the absorption temperature. The hydriding properties of the composite at 453 K under different hydrogen pressure were also investigated and shown in Fig. 5. The hydrogen absorption rate increased with the increasing hydrogenation pressure.

The desorption curves of the composite materials are given in Fig. 6. This composite desorbed 3.22 mass% of hydrogen at 578 K and 3.76 mass% of hydrogen at 593 K in 1 h under a hydrogen pressure of 0.1 MPa. The dehydriding rate increases with the increase of reaction temperature.

Fig. 7 shows the DSC profile of 60 h milled of Mg–Ni–TiO₂ composite. The curve showed a double endothermic peak, the 525.6 K of endothermic peak attributed to hydrogen desorption from Mg₂NiH₄ and 574.1 K of endothermic peak attributed to

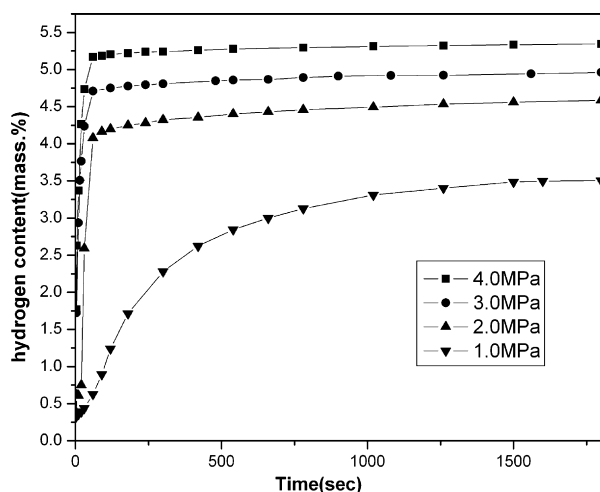


Fig. 5. Hydrogen absorption kinetics curves of Mg–20 wt% Ni–1 wt% TiO₂ composite under different hydrogen pressure at 453 K.

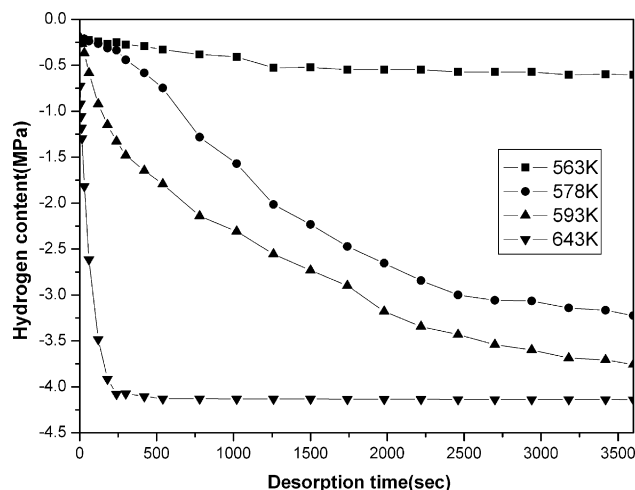


Fig. 6. Hydrogen desorption curves of the composite at different temperature under a hydrogen pressure of 0.1 MPa.

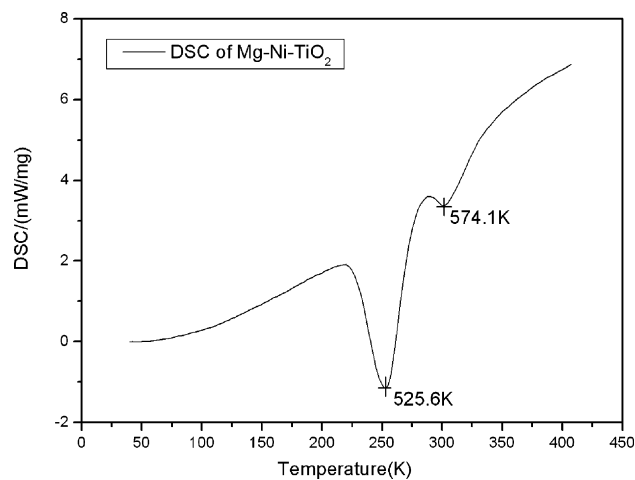


Fig. 7. DSC curve of the Mg–Ni–TiO₂ milled for 60 h.

hydrogen desorption from MgH₂. The thermodynamic properties of the composite did not change.

Henrich et al. has studied the sorption of hydrogen at TiO₂ surfaces and found that perfect TiO₂-single crystal surfaces are inert towards reactions with H₂. However, H₂ can be absorbed by TiO₂ surfaces that contain a higher density of defects in the crystal structure [9–10]. During high energy ball milling, high defect density is introduced at the surface of the metal oxide particles. Ball milling also introduces much grain boundaries and disorder into nanocrystalline composite. Furthermore, Mg₂Ni hydride has well catalytic effects on absorption/desorption of Mg and MgH₂ [11]. The nanocrystalline Mg₂NiH₄ and TiO₂ catalytic phases enable quick and effective absorption/desorption of hydrogen at lower temperature.

4. Conclusions

Reactively mechanical milling has been used to produce MgH₂ + Mg₂NiH₄ + TiO₂ composite material. Under 3.0 MPa hydrogen pressure, it absorbed more than 80% of its full capacity in the range of 363–543 K for less than 1 min. The maximum

capacity at 543 K is 5.32 mass%. The thermodynamic properties of this composite did not change after the addition of TiO₂ by reactive mechanical alloying.

Acknowledgement

The work is supported by the Ministry of Science and Technology, China (Grant No. 2000 026405).

References

- [1] N. Hanada, T. Ichikawa, H. Fujii, *J. Phys. Chem. B* 109 (2005) 7188–7194.
- [2] S. Orimo, H. Fujii, *Appl. Phys. A* 72 (2001) 167–186.
- [3] J.-L. Bobet, B. Chevalier, M.Y. Song, B. Darriet, J. Etourneau, *J. Alloys Compd.* 332 (2002) 292–296.
- [4] G. Liang, J. Huot, S. Boily, A. Van Nestea, R. Schulz, *J. Alloys Compd.* 297 (2000) 261–265.
- [5] M. Au, *Mater. Sci. Eng. B* 117 (2005) 37–44.
- [6] W. Oelerich, T. Klassen, R. Bormann, *J. Alloys Compd.* 315 (2001) 237–242.
- [7] P. Wang, A.M. Wang, H.F. Zhang, B.Z. Ding, Z.Q. Hu, *J. Alloys Compd.* 313 (2001) 218–223.
- [8] T. Schober, *J. Less-Common Met.* 89 (1983) 63.
- [9] V. Henrich, *Prog. Surf. Sci.* 9 (1979) 143.
- [10] V. Henrich, *Rep. Prog. Phys.* 48 (1985) 1481.
- [11] H.H. Uchida, H.-G. Wulz, E. Fromm, *J. Less Common Met.* 172–174 (1991) 1076.