

Hydrogen Sorption Behavior of the MgH₂-Ni Prepared by Reactive Mechanical Alloying

Mustanir¹ and Zulkarnain Jalil¹

Abstract—Regarding the use of hydrogen in fuel cell for mobile or stationary applications, metal hydrides can offer a high hydrogen volume capacity and a safe alternative compared with liquid storage or with compressed gas. Among the metal hydrides, magnesium is considered as one of potential hydrogen storage materials because of its high capacity (7.6 wt%), lightweight and low cost. However, high work temperature would slow down kinetics reaction and harden activation process limit practical application of Mg-based hydrides as well. Recently, the high energy ball milling was successfully introduced to prepare hydrogen storage materials. In this work, MgH₂ catalyzed with Ni nanoparticles was synthesized by planetary type ball milling under high pressure of hydrogen at 100 bar (10 MPa). As a result, small amount of Ni in nanometer scale acts as a suitable catalyst for kinetics improvement of MgH₂ which could absorb 5.3 wt% of hydrogen within 5 minutes at 300°C. It is obvious that small amount Ni (2 mol%) has much better catalyst than catalyst in nanoparticle size; and at the same time, it is allowed to reduce the milling process for short time (2 hours).

Keywords—Hydrogen storage, magnesium, metal hydrides, ball milling.

I. INTRODUCTION

Among the metal hydrides, magnesium theoretically has the highest capacity for hydrogen storage (7.6 wt.%), lightweight and a reasonably low cost (Zaluska *et al.*, 1999). However, high working temperature, slow reaction kinetics and difficult activation would limit practical application of Mg-based hydrides. Many efforts have been done to improve sorption properties and reaction kinetics such as element substitution (metal or metal oxides) as catalyst in nanometer scale and modification of ball milling technique as well (Oelerich *et al.*, 2001; Liang, 2004; Ichikawa *et al.*, 2005; Varin *et al.*, 2007). Recently, the reactive ball milling under hydrogen atmosphere was successfully introduced to prepare hydrogen storage materials (Gennari *et al.*, 2001; Tessier and Akiba, 1999; Herrich *et al.*, 2004; Gutfleisch *et al.*, 2005). Usually the milling was performed in “mild” condition with relatively low hydrogen pressure. This paper is going to reveal how the sorption behavior of MgH₂ catalyzed with small amount of Ni nanoparticles is prepared by reactive ball milling under 100 bar hydrogen.

II. EXPERIMENTAL

MgH₂ (Goldschmidt, 95+%), Ni (99.9%, Sigma Aldrich, ~90 nm) powders were used. The powders were filled into a hardened steel vial and sealed together with 13 balls (9.5 mm in diameter) and reactively milled in a

planetary mill Fritsch (P6) at a rotational speed of 400 rpm (ball to powder ratio 10:1) for 2 hours under hydrogen atmosphere (0-100 bar). Structural changes during milling were characterised by XRD (Co-K α) and high resolution scanning electron microscopy. Hydrogen sorption properties have been studied by gravimetric analysis (IGA-Hiden at IFW Dresden, Germany) in a wide temperature and pressure range for absorption (1-10 bar, 50-300°C) and desorption (250-350°C, 50 mbar-1 bar). Thermal properties of samples were studied using a differential scanning calorimeter with H₂ (3 bar) flow rate of 10 K/min.

III. RESULT AND DISCUSSION

A. Structural Investigations

1. X-ray diffraction

Fig. 1 shows the evolution of the XRD diffraction pattern for MgH₂-Ni as a function of milling time. The starting mixture shows the presence of microcrystalline magnesium hydride and Ni nanoparticles. It can be seen that during milling MgH₂ and Ni diffraction peaks were broaden; however, there were no changes in the 2 θ position at early stage of milling.

The as-received sample was composed mainly MgH₂ and a small peak of Ni. The same result was also found in the sample of further milling time (1-2 hours). However, for the sample after desorption, the composition has already changed and it was mainly composed by Mg. Therefore, it can be noted down that after desorption, It would completely react to produce only magnesium.

2. Electron microscopy

The SEM micrographs of Fig. 2 shows secondary electron image of powders reactively milled in the planetary mill for 2 hours. The surface of the powder is irregular, as a result of the fracturing during the milling process. This is consistent with the structural analysis of the 2 h milled powder.

Backscattered electron (BSE) image in Fig. 3 shows that the catalyst Ni nanoparticles (white spot) are uniformly distributed on the magnesium surface. This indicates, when small particles of catalyst are uniformly distributed on the metal surface, a small amount of catalysts is sufficient for improving the reaction kinetics.

B. Hydrogen Sorption Behavior

The hydrogen stored and released properties of Ni-catalyzed MgH₂ that were measured by gravimetric method. The intelligent gravimetric analysis (IGA) measurements confirm the catalytic effect of nickel nanoparticle on magnesium hydride hydrogenation and dehydrogenation. Fig. 4 shows the hydrogen absorption curves of MgH₂-2mol% Ni nanoparticles compared to microparticles and pure MgH₂ samples at constant

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temperatures (300°C) and pressures (10 bar) after reactive ball milling under 100 bar H₂ for 2 hours.

The catalytic effect of nickel nanoparticles was magnified especially during absorption: actually, the absorption in the sample catalyzed with Ni nanoparticles took less than 5 minutes for up-taking 5.3 wt% H₂. Compare to the sample catalyzed with Ni microparticles took more than 60 minutes to absorb 5.3 wt% of hydrogen, and the same result for pure MgH₂. As observed above, the Ni catalyst absorb large amount of hydrogen for short time in the form of nanoparticles. And large particle catalyst requires a longer time to finish the absorption. Thus, smaller size catalysts are suitable for short time ball milling. On the contrary larger catalyst requires process time longer than smaller one (Kanoya *et al.*, 2002).

Through the XRD profiles, it is clear that the materials are composed by single phase (MgH₂), because Ni acts as catalyst. Hong *et al.* (2002) showed the appearances of the composition of β-Mg and the Ni-rich eutectic phase. They observed that the excellent hydrogenation properties and reaction kinetics of the Mg-9 mass% Ni alloy depended on nickel composition, and the β-Mg phase acts as a hydrogen storage system and the eutectic structure as the catalytic system.

It is obvious that Ni is better catalyst in nanoparticle size in the absorption and desorption processes. This is also one reason for the great interest in the use of nanoparticle catalyst in order to improve the hydrogen sorption properties of MgH₂. However, the addition of Ni nanoparticles has no effect on the operation temperature in which MgH₂ still need high temperature, higher than 300°C, to complete the absorption. Similar to desorption, 350°C is needed to desorb 5.3 wt% of hydrogen as shown in Fig. 5. Noritake *et al.* (2002) suggested that the weak covalency of Mg-H bond may be advantageous on hydrogenation and dehydrogenation performance as well. They revealed that the bonding nature of MgH₂ is a mixture of covalent and ionic bonds. Thus, the lower ionicity of hydrogen enhances the sorption performances.

It is important to note down that the kinetics of absorption/desorption was relatively fast, as they could work only in 5 minutes. Compare to the microparticle catalyst which has longer time, more than 60 minutes, to absorb and desorb hydrogen. It can be seen clearly, the addition of metal nanoparticles leads to a notable enhancement of both the absorption and desorption kinetics. In this case, it can be concluded that this enhancement in the hydrogen sorption kinetics properties is due to the presence of Ni nanoparticle as a catalyst in MgH₂ and the high pressure of milling as well.

The investigations of ball milling conditions such as milling time and different additives have been performed to study the microstructure evolution and its effect on hydrogenation absorption properties (Yao *et al.*, 2006). Yao observed that with increasing milling time, the

average crystallite size of grains decreases, which significantly enhances both the hydrogen absorption capacity and kinetics. However, the grains produced by the ball milling technique are not uniform. Some large grains exist and cannot be fully hydrided, leading to a gap between the real capacity and the theoretical capacity for hydrogen uptake.

IV. CONCLUSION

MgH₂ catalyzed with small amount of nickel nanoparticles prepared via high pressure reactively milling has been done. This process results in high surface area powders with finely dispersed Ni-particles on the surface of Mg. This material exhibits excellent hydrogen absorption/desorption kinetics properties, absorb/desorb within 5 minutes, which are stable upon cycling and far superior to purify magnesium hydride. The metallic Ni in nanometer scale acts as a catalyst for improving the kinetics of MgH₂ for hydrogen storage material and, at the same time, for reducing the milling process time into 2 hours.

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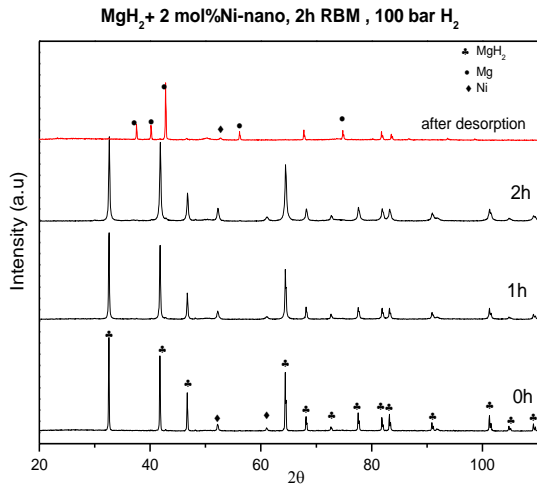


Fig. 1. X-ray diffraction patterns of MgH₂-2mol%Ni nanoparticle produced via reactive ball milling for 2 hours and after H₂ absorption/desorption cycling, ended with desorption at 350 °C, 50 mbar

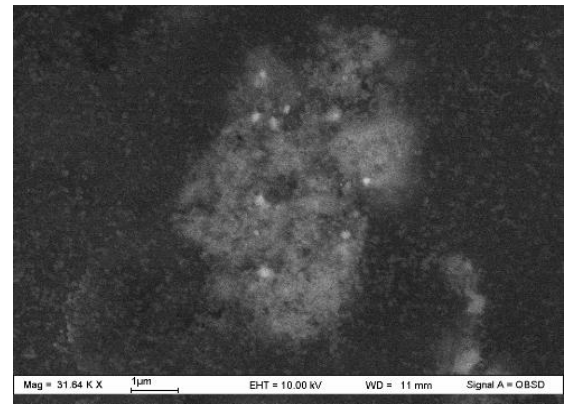


Fig. 3. BSE image of MgH₂-2 mol% Ni nanoparticle after desorption

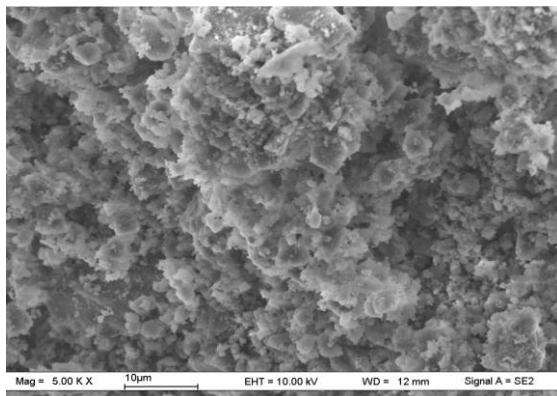


Fig. 2. SEM image of MgH₂-2 mol% Ni nanoparticle after high pressure reactive milling for 2 hours

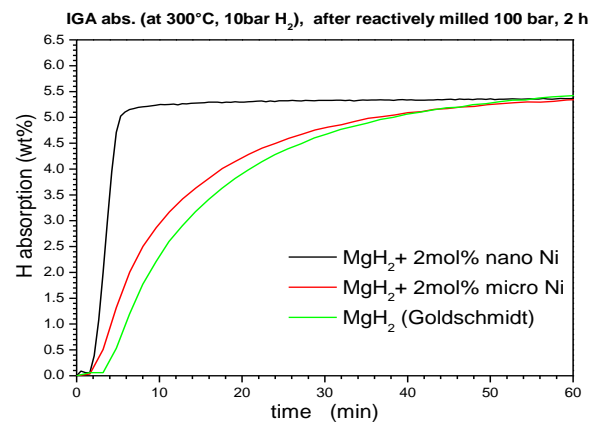


Fig. 4. Hydrogen absorption of MgH₂-2mol% Ni nanoparticles compare to microparticles and pure MgH₂ samples at constant temperatures and pressures after reactive milling under 100 bar H₂ for 2 hours

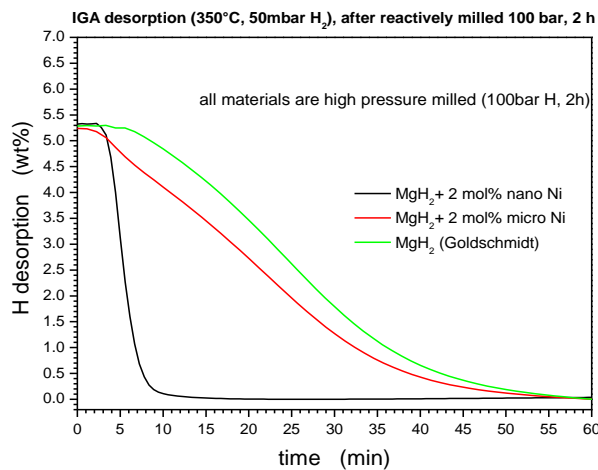


Fig. 5. Hydrogen desorption of MgH₂-2mol% Ni nanoparticles compare to microparticles and pure MgH₂ samples at constant temperatures and pressures after reactive milling under 100 bar H₂ for 2 hours