

Hydrogen storage properties of mechanical milled MgH_2 -nano Ni for solid hydrogen storage material

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Abstract. Among the metal hydrides, magnesium has the theoretically highest weight capacity for hydrogen storage (7.6 wt.%), lightweight and a reasonably low cost. However, high working temperature ($>300^\circ\text{C}$), slow reaction kinetics (need more than 1 hour to produce 5 wt% of hydrogen) and difficult activation limit the practical application of Mg-based hydrides. In order to improve their performance, MgH_2 was catalyzed with Ni nanoparticles which reactively milled under hydrogen atmosphere. Phase identification and microstructure were characterised by XRD and scanning electron microscope (SEM). Hydrogen sorption properties was studied by gravimetric analysis method. The results showed that, small amount of Ni in nanometer scale proved to be as a suitable catalyst for improvement the kinetics of MgH_2 and at the same time allowed to reduce the milling time process.

1. Introduction

Mg-based metal hydrides are promising candidates for reversible hydrogen storage because of their high capacity (7.6 wt%), lightweight, and low cost [1]. However, relatively high sorption temperatures ($>300^\circ\text{C}$) and low kinetics are the major difficulties hindering its commercial use. Many efforts have been done to improve the hydriding and dehydriding properties such as element substitution (metal or metal oxides) as catalyst in nanometer scale and modification of ball milling technique have been used to improve sorption and kinetics properties [2-4]. Recently, the reactive ball milling under hydrogen atmosphere was successfully introduced to prepare hydrogen storage materials [5-8]. Aims of this study to observe MgH_2 catalyzed with small amount of Ni in nanoparticles scale and the preparation by reactive ball milling under 10 bar hydrogen.

2. Materials and method

MgH_2 (Goldschmidt, 95+%), Ni (99.9%, Sigma Aldrich, ~ 90 nm) powders were used to prepare the samples. 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 (10 bar). Phase identification and microstructure were characterised by XRD using a Philips 1050 diffractometer (Co- $\text{K}\alpha$ radiation) and scanning electron microscope (FEGSEM LEO 1530). Hydrogen sorption properties were studied by



gravimetric analysis in a wide temperature range for absorption (50-300 °C) and desorption (250-350 °C).

3. Results and discussion

Figure 1 shows the evolution of the XRD diffraction pattern for MgH_2 -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 the MgH_2 and Ni diffraction peaks broaden but no changes in the 2θ position at early stage of milling. The as-received sample composed mainly MgH_2 and a small peak of Ni. The same result found after 1 h milling. Then after 2 hour of milling the peaks are broaden. It can be also note that after desorption hydrogen completely react to produce only magnesium. It can be concluded that MgH_2 completely desorp after only two hours milling.

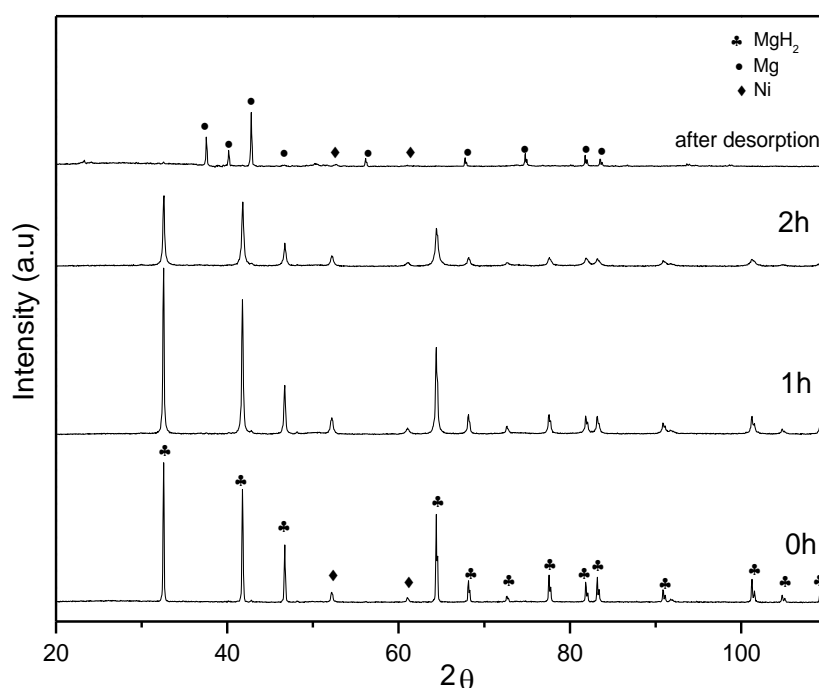


Figure 1. X-ray diffraction patterns of MgH_2 -2 mol% nano-Ni reactively milled for 2 hours in 10 bar H_2 .

It was shown that after H_2 absorption/desorption cycling, ended with desorption at 350 °C, 50 mbar. It was also observed that with increasing milling time the crystallite sizes decrease further to finally stabilize around 10 nm. Thus, the used of hydrogen pressure during milling promotes the formation of larger amounts of MgH_2 [9-11].

The hydrogen storage and release properties of Ni-catalyzed MgH_2 were measured by gravimetric method. The gravimetric analysis measurements confirm the catalytic effect of nickel nanoparticle on magnesium hydride hydrogenation and dehydrogenation. Figure 2 shows the hydrogen absorption curves of MgH_2 -2mol% Ni nanoparticles compare to microparticles and pure MgH_2 samples as well at constant temperatures (300 °C) and pressures (10 bar) after reactive ball milling under 10 bar H_2 for 2 hours.

The catalytic effect of nickel nanoparticles is magnified especially during absorption: actually, the absorption in the sample catalyzed with Ni nanoparticle took less than 5 minutes for up-taking 5.3 wt% H_2 . Compare to the sample catalyzed with Ni microparticles took more than 60 minutes to absorb 5.3 wt% of hydrogen, and similar result for pure MgH_2 as well.

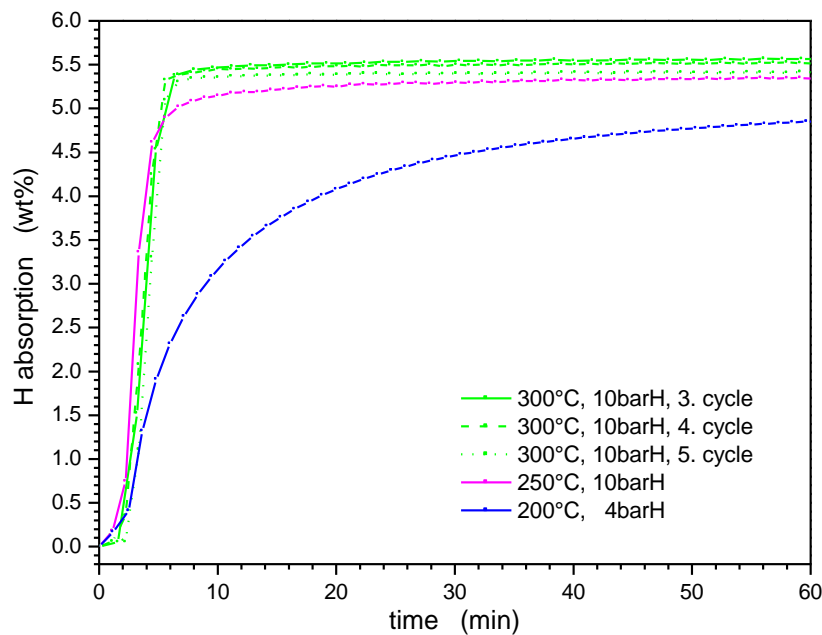


Figure 2. Hydrogen absorption of MgH_2 -2 mol% nano-Ni reactively milled for 2 hours in 10 bar H_2 reactive milling under 10 bar H_2 .

The results show that the Ni catalyst absorb large amount of hydrogen for short time in the form of nanoparticles. And the large particle catalyst requires a longer time to finish the absorption. It is obvious that Ni has much better as catalyst in nanoparticle size in the absorption and desorption processes. This is also one reason for the great interest in the use of nanoparticles catalyst in order to improve the hydrogen sorption properties of MgH_2 . However, Ni nanoparticles has no effect on the operation temperature, which needed high temperature, more than 300 °C, to complete the absorption.

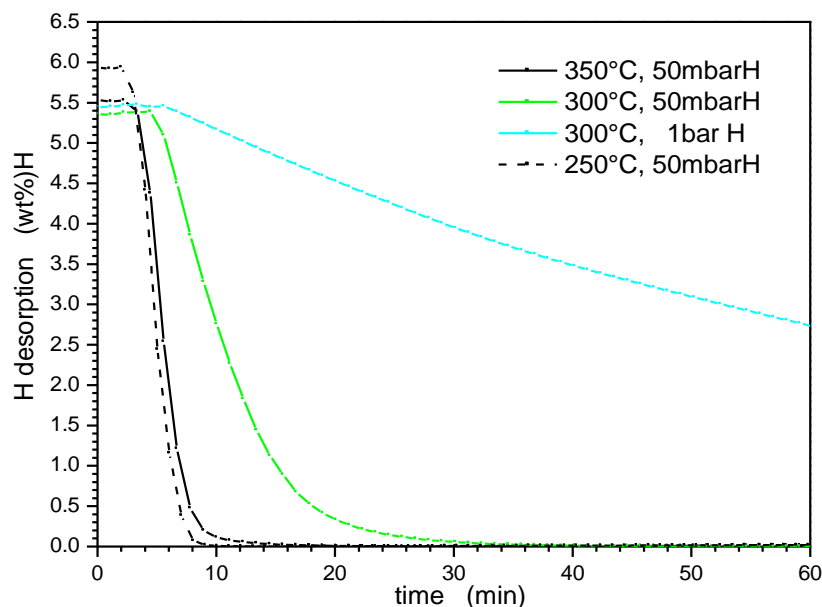


Figure 3. Hydrogen desorption of MgH_2 -2 mol% nano-Ni reactively milled for 2 hours in 10 bar H_2 reactive milling under 10 bar H_2 .

Similar to desorption, its needed 350 °C to desorp 5.3 wt% of hydrogen as shown in Figure 3. But, the kinetics of absorption/desorption was extremely fast, which work only in 5 minutes. As 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 MgH_2 and the high pressure of milling as well.

A fundamental study of the role of catalysts in MgH_2 nanoclusters was provided by carrying out based on density functional theory [12]. Interesting to note that the diffusion mechanism may account for the fact that a small amount of catalysts is sufficient in improving the MgH_2 kinetics, which is essential for the use of this material for hydrogen storage application.

The SEM micrographs of Figure 4 show secondary electron image of powders reactively milled in the planetary mill for 2h (a) and 2h (b). The areas with the white contrast (Mg) disappear with increasing milling time leading to improved homogeneity. The surface of the powder is irregular, as a result of the fracturing during the milling process [13, 14].

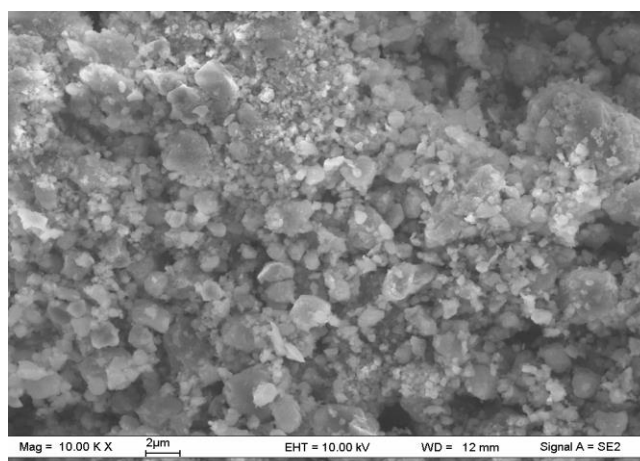


Figure 4. Secondary electron (SE) image of MgH_2 -2 mol% Ni nanopowders reactively milled in the planetary mill for 2h.

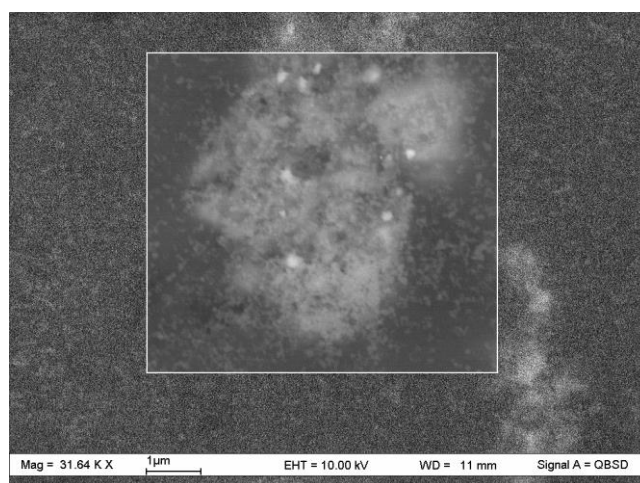


Figure 5. Backscattered electron (BSE) image of MgH_2 -2 mol% Ni nanopowders after gravimetric desorption.

Backscattered electron (BSE) image of MgH_2 -2 mol% Ni nanoparticles after gravimetric analysis desorption (see Figure 5) shows that the catalyst Ni nanoparticles (white spot) were uniformly distributed on the magnesium surface. This indicates that when small particles of catalyst is uniformly distributed on the metal surface, a small amount of catalysts is sufficient for improving the reaction kinetics.

4. Conclusions

MgH_2 catalyzed with small amount of nano-Ni as catalyst has been prepared via reactive milling. This high energy planetary ball mill (HEPBM) produced a high surface area powders and showed the nano-Ni particles dispersed on the surface of Mg uniformly. The MgH_2 -2mol% Ni nanopowders exhibited the sorption kinetics properties, absorp/desorp 5.3 wt% of hydrogen within 5 minutes. It was also clear that, the used of nanopowder Ni and reactive milling method were very effective to reduce the milling process in short time.

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