

# Effect of nanostructure Ni on the sorption properties of mechanical milled MgH<sub>2</sub> for solid hydrogen storage materials

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**Abstract.** Among the metal hydrides, magnesium has the theoretically highest weight capacity for hydrogen storage (7.6wt.%), lightweight and a reasonably low cost. However, high working temperature (>300°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<sub>2</sub> 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 show that, small amount of Ni in nanometer scale proved to be as a suitable catalyst for improvement the kinetics of MgH<sub>2</sub> and at the same time allowed to reduce the milling time process.

## 1 Introduction

Among the metal hydrides, magnesium has the theoretically highest weight capacity for hydrogen storage (7.6wt.%), lightweight and a reasonably low cost [1]. However, high working temperature (>300°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. 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]. Here, we report on MgH<sub>2</sub> catalyzed with small amount of Ni in nanoparticles scale and the preparation was done by reactive ball milling under 10 bar hydrogen.

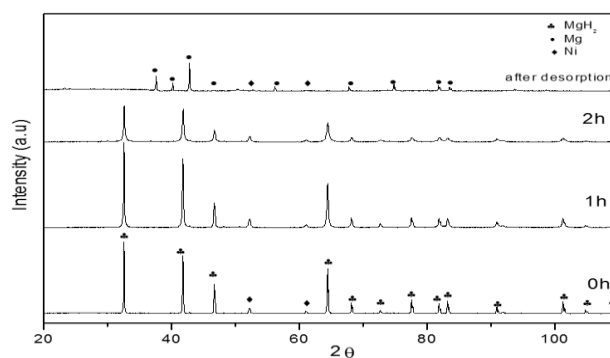
## 2 Materials and Method

MgH<sub>2</sub> (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-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 as a function of milling time. The starting mixture of MgH<sub>2</sub>-2 mol% nano-Ni shows the presence of microcrystalline magnesium hydride and Ni nanoparticles. It can be seen that during milling the MgH<sub>2</sub> and Ni diffraction peaks broaden but no changes in the 2 $\theta$  position at early stage of milling. The as-received sample composed mainly MgH<sub>2</sub> and a small peak of Ni. The same result found after 1 h milling. Then after 2 hour of milling the peaks are broader. It can be also note that after desorption hydrogen completely react to produce only magnesium. We can conclude that MgH<sub>2</sub> completely desorp after milling only two hours.

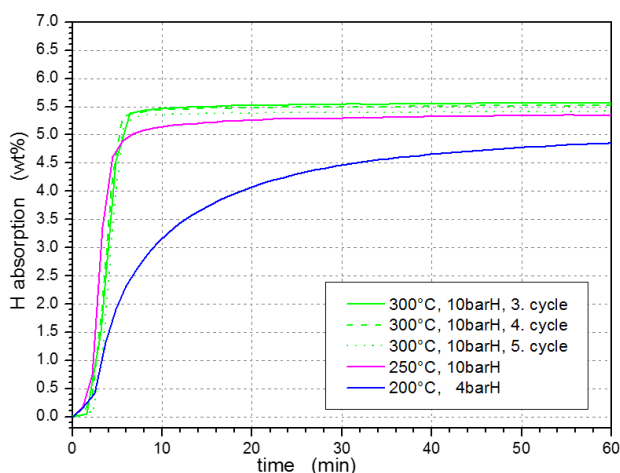


**Fig. 1.** XRD patterns of MgH<sub>2</sub>-2 mol% nano-Ni reactively milled for 2 hours.

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It was also observed that with increasing milling time the crystallite sizes decrease further to finally stabilize around tens nanometer. Thus, making use 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 ( $300^{\circ}C$ ) and pressures (10 bar) after reactive ball milling under 10 bar  $H_2$  for 2 hours.

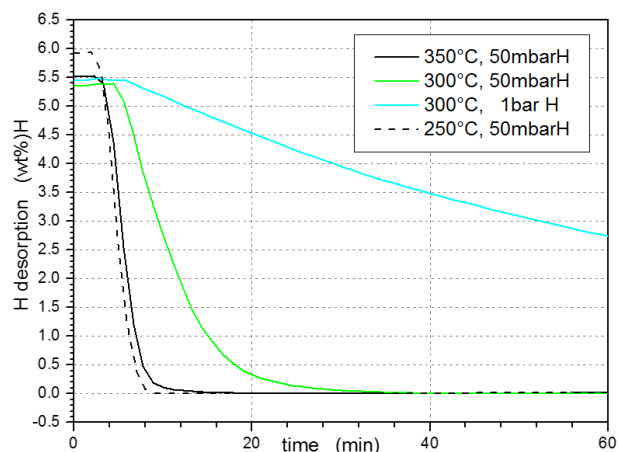


**Fig. 2.** Hydrogen absorption of of  $MgH_2$ -2 mol% nano-Ni reactively milled for 2 hours in 10 bar  $H_2$  reactive milling under 10 bar  $H_2$ .

The 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 the same result for pure  $MgH_2$  as well.

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, the effect of Ni nanoparticles has no effect on the operation temperature

which needed high temperature, more than  $300^{\circ}C$ , to complete the absorption.

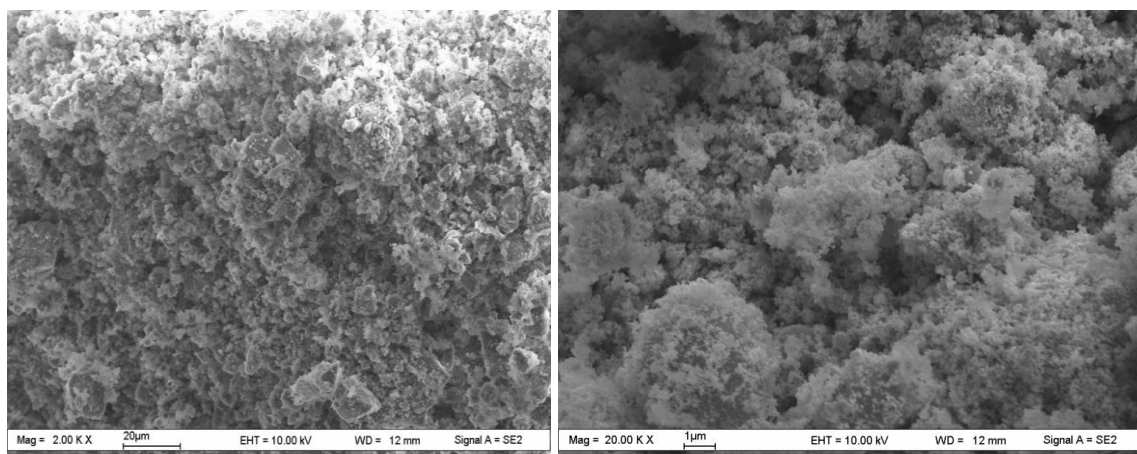


**Fig. 3.** Hydrogen desorption of of  $MgH_2$ -2 mol% nano-Ni reactively milled for 2 hours in 10 bar  $H_2$  reactive milling under 10 bar  $H_2$ .

Similar to desorption, its need  $350^{\circ}C$  to desorp 5.3 wt% of hydrogen as shown in Fig.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 Fig. 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]. From the SEM data inform that at the early milling time, the sampel has particle size about  $20 \mu m$ . Then, after milling the sample has been reduced until  $1 \mu m$ .



**Fig. 4.** SEM image of MgH<sub>2</sub>-2 mol% Ni reactively milled for 2h.

## 4 Conclusions

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

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