

# EFFECT OF SiC ADDITION ON HYDROGEN DESORPTION PROPERTIES OF NANOCRYSTALLINE $MgH_2$ SYNTHESIZED BY MECHANICAL ALLOYING

M. Maddah, M. Rajabi\* and S. M. Rabiee

\* m.rajabi@nit.ac.ir

Received: May 2015

Accepted: September 2015

Department of Material Science and Engineering, Faculty of Mechanical Engineering, Babol Noshirvani University of Technology, Babol, Iran.

**Abstract:** In this study, the composite material with composition of  $MgH_2$ -5 wt% SiC has been prepared by co-milling of  $MgH_2$  with SiC powder. The effect of milling time and additive on  $MgH_2$  structure, i.e. crystallite size, lattice strain, particle size and specific surface area, and also hydrogen desorption properties of obtained composite was evaluated by thermal analyzer method and compared with pure un-milled  $MgH_2$ . The phase constituents and grain size of powder were characterized by X-ray diffractometry method. It has been shown that addition of 5 wt% SiC to  $MgH_2$  and mechanical alloying up to 30 h formed a nanocrystalline composite with the average crystallite size of 12 nm, average particle size of 0.5  $\mu m$  and specific surface area of 10  $m^2/g$ . On the other hand, SiC can help to break up particles and reduce the particle size. As a consequence, the desorption temperature of composite material milled for 30 h has decreased from 435 °C to 361 °C.

**Keywords:** Magnesium hydride, Mechanical alloying, Hydrogen desorption temperature, SiC addition.

## 1. INTRODUCTION

Developing highly efficient and safer means for hydrogen storage is one of key technologies to realize future hydrogen energy systems. Magnesium hydride is one of attractive hydrogen storage materials because of its hydrogen storage capacity (7.6 wt %), low cost, and light weight [1, 2]. However, high hydrogen desorption temperature, relatively poor hydrogen absorption-desorption kinetics, and a high reactivity toward air and oxygen can restrict the use of  $MgH_2$  in practical applications [3, 4].

Many efforts have been focused on Mg-based hydrides in recent years to reduce the desorption temperature and to fasten the re/dehydrogenation reactions which could be accomplished, to some extent, by changing the microstructure of the hydride by mechanical alloying which reduces the stability of the hydrides and also by using proper catalysts to improve the absorption/desorption kinetics [5]. Mechanical milling simultaneously produces mechanical deformation, defect formation and surface modification. These structural modifications can lead to the formation of metastable phases, refinement of the microstructure into the

nanometer range, extension of solubility limits, development of amorphous phases, etc. [6]. It has been reported that nanocrystalline magnesium hydride exhibits fast absorption and desorption kinetics at 300 °C when compared with its non-milled counterpart. This behaviour can be attributed to the faster diffusion of hydrogen along grain boundaries and the high number of heterogeneous nucleation sites of the hydrogen on absorption or the pure magnesium phase on desorption [7].

Many researchers have investigated mechanical milling of  $MgH_2$  with transition metals [8, 9], metal oxides [10, 11], none-oxide ceramics [12] and intermetallic compounds [13, 14]. It has been recently found for SiC/ $MgH_2$  nanocomposites prepared by mechanical milling of  $MgH_2$  and SiC that SiC significantly improves the performance of  $MgH_2$  for hydrogen storage [15]. Ranjbar et al. [16] reported the effects of the addition of SiC on the hydrogen storage properties of  $MgH_2$  synthesized by ball milling. In this paper, destabilization of magnesium hydride was observed upon ball milling with SiC. They found that hardness of the SiC facilitates the grain size reduction and expand the surface area of  $MgH_2$  which has positive influence on

hydrogen sorption properties.

The aim of this work has been to study the effect of SiC addition on the desorption properties of MgH<sub>2</sub>-based composite obtained by mechanical alloying. The effect of SiC addition and mechanical alloying on the dehydrogenation was investigated and compared with pure magnesium hydride. Also, the catalytic effect of SiC addition on hydrogen desorption properties was evaluated.

## 2. MATERIAL AND METHODS

The starting materials MgH<sub>2</sub> (98%, <105 μm) and SiC (99%, <100 μm) powders were supplied from Merck Germany. Mechanical alloying was performed in a Retsch PM100 planetary ball mill at room temperature under a high purity argon atmosphere over various times. Ball to powder weight ratio of 20:1 was selected and rotation speed was adjusted to 400 rpm. Weighing, filling and handling of the powders were performed in a glove box under argon atmosphere.

The phase formation and variation of grain structure were investigated by X-ray diffraction method (X'Pert Pro MPD, PANalytical) with Cu-Kα radiation. The crystallite size and lattice strain of β-MgH<sub>2</sub> phase were estimated by broadening XRD peaks using Williamson–Hall method. The

size and morphological changes of powder particles upon mechanical alloying were studied by scanning electron microscopy (SEM, VEGA/TESCAN). The mean particle size of powders was measured using Clemex Vision image analyzer on SEM images. In order to characterize specific surface area of milled powders, a Brunauer-Emmett-Teller analyser (BET, Belsorp-Mini II, Japan) was employed. The dehydrogenation properties were investigated with a simultaneous thermal analyzer (NETSCH STA 409) under argon atmosphere at a heating rate of 5 °C/min up to 500 °C. The catalytic effect of SiC addition on hydrogen desorption properties was evaluated using a volumetric Sievert apparatus and characterized at 350 °C under 0.5 bar of hydrogen pressure.

## 3. RESULTS AND DISCUSSION

Fig. 1 shows the XRD patterns of MgH<sub>2</sub>-5 wt% SiC composite at the selected milling times. The XRD peak of pure un-milled MgH<sub>2</sub> powder has been included in the graph for comparison. As can be seen, with the increase in milling time, all diffraction peaks of β-MgH<sub>2</sub> are broadened and decreased evidently due to the high-energy

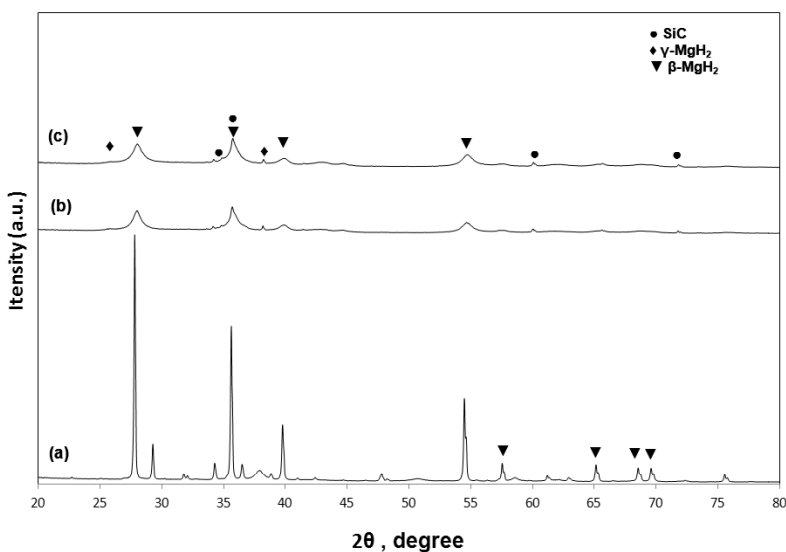


Fig. 1. XRD patterns of un-milled MgH<sub>2</sub> (a) and MgH<sub>2</sub>-5 wt% SiC composite after mechanical alloying for 5 h (b) and 30 h (c).

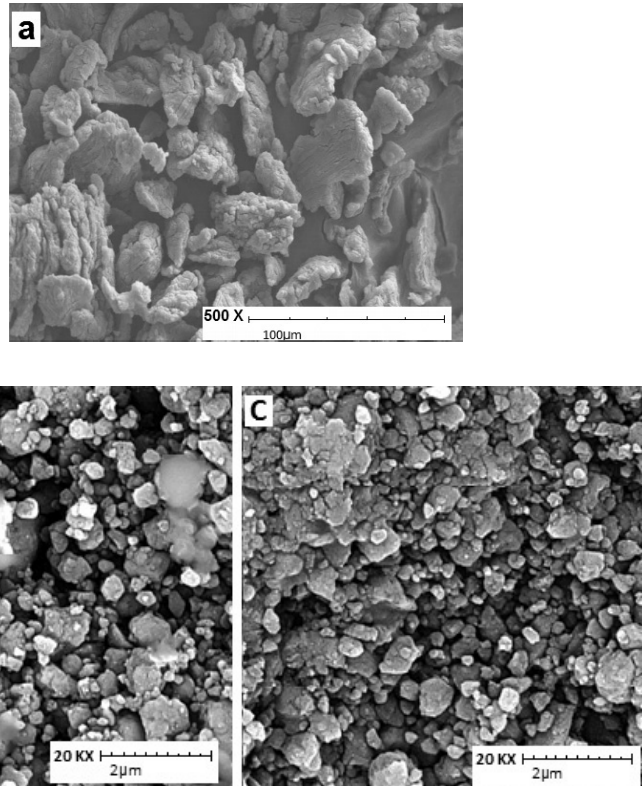


Fig. 2. SEM micrographs showing the morphology of pure un-milled MgH<sub>2</sub> (a) and MgH<sub>2</sub>-5 wt% SiC composite after mechanical alloying for 5 h (b) and 30 h (c).

impact of the milling balls. After 5 h milling, the diffraction peaks corresponding to  $\gamma$ -MgH<sub>2</sub> were detected. By the milling time extended up to 30 h, the diffraction peaks corresponding to  $\beta$ -MgH<sub>2</sub> became broader and less intense, while no new phase formation was noticed at this milling time. The morphological changes produced by mechanical milling at different times can be observed in Fig. 2. A significant particle size refinement is observed and after milling up to 30 h, the particle size reduced to about 0.5  $\mu$ m. Fig. 3 shows the dehydrogenation of the composite material as a function of temperature for the milled material over different times. The as-received MgH<sub>2</sub> exhibited a single endothermic peak at 435 °C corresponding to the decomposition of hydride (see Fig. 3). This value is similar to the values reported in previous studies [17]. A reduction in the dehydrogenation temperature from 435 °C to 361 °C was achieved via co-milling of MgH<sub>2</sub> with the SiC powder. It should be mentioned that the DSC curves for the

milled samples show two endothermic peaks. The reason for the appearance of two peaks in DSC curves may be explained by Varin et al. [18] and Gennari et al. [6]. According to Varin et al. a two-step hydrogen desorption may occur due to the existence of two fractions of powder particles: small and large, which could desorb at lower and higher range of temperatures, respectively. However, Gennari et al. reported that the low-temperature endothermic peak corresponds to the complete dehydrating of  $\gamma$ -MgH<sub>2</sub> and the partial dehydrating of  $\beta$ -MgH<sub>2</sub>, whereas the high-temperature peak corresponds to hydrogen desorption from  $\beta$ -MgH<sub>2</sub>. Fig. 4 shows the desorption kinetics of nanocrystalline MgH<sub>2</sub> with 5 wt% of SiC powder in comparison to the mechanically activated MgH<sub>2</sub>. No significant effect of the SiC addition on the desorption kinetics of magnesium hydride was noticed, thereby, the catalytic effect of SiC addition on H-kinetics was marginal.

In order to find the origin of differences, the

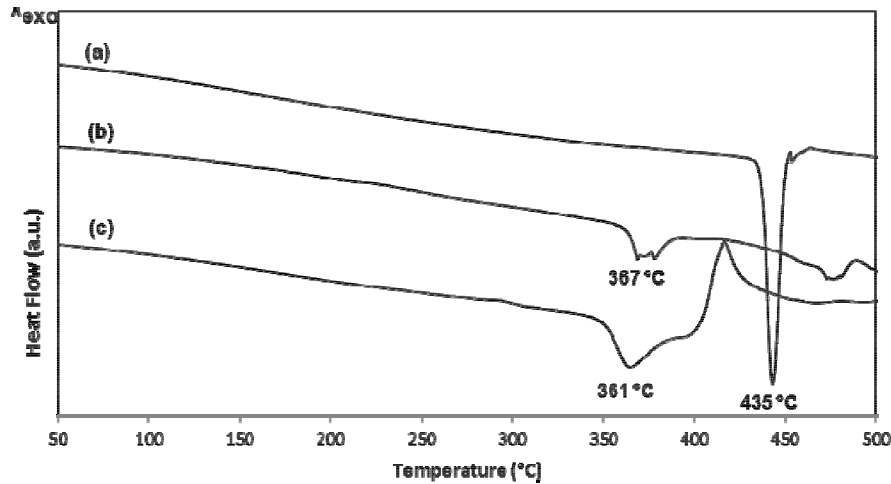


Fig. 3. DSC curves of pure un-milled MgH<sub>2</sub> (a) and the composite material after mechanical alloying for 5 h (b) and 30 h (c).

characteristics of the synthesized composite powders at different milling times were determined. The results are summarized in table 1. The characteristics of the pure mechanically activated MgH<sub>2</sub> powder are included in Table 1 for comparison. The results show that mechanical milling and SiC addition are favourable with respect to the improvement of the hydrogen desorption temperature of MgH<sub>2</sub>. Compared to the mechanically activated MgH<sub>2</sub>, a reduction in the dehydrogenation temperature from 384°C to 367°C (milled for 5 h) and from 375°C to 361°C

(milled for 30 h) has been achieved via co-milling with SiC powder. However, there was no significant difference on the hydrogen desorption temperature of composite material with increasing the milling time from 5 h to 30 h. Different reasons are identified to explain this behavior. As can be seen in Table 1, the crystallite size gradually decreases from 99 nm to 12 nm by increasing milling time. Since the diffusion of atoms in grain boundaries is much faster than that of entire lattice [19], it is acceptable that finer grain structure can promote the dehydrogenation

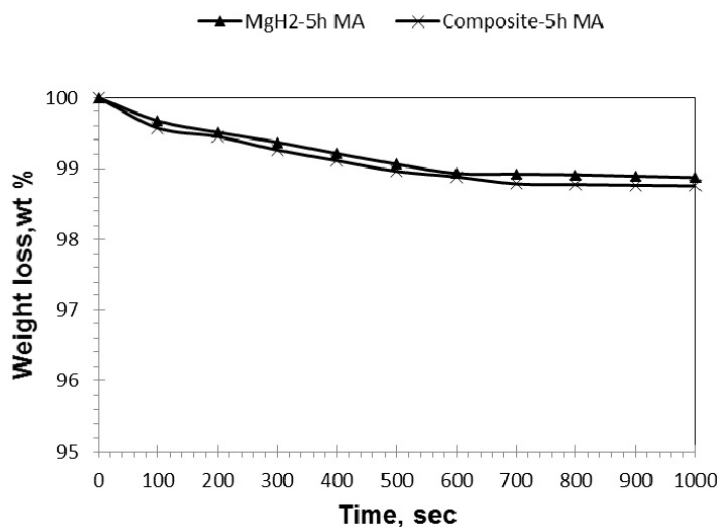


Fig. 4. Hydrogen desorption curves of the mechanically activated MgH<sub>2</sub> prepared without and with SiC powders under a hydrogen pressure of 0.5 bar at 350 °C.

**Table 1.** Average particle size (D), specific surface area (S), crystallite size (d), lattice strain ( $\epsilon$ ) and dehydrogenation temperature (T) for different compositions.

System	Time, h	Phase	D, $\mu\text{m}$	S, ( $\text{m}^2/\text{g}$ )	d, nm	$\epsilon$ , %	T, ( $^{\circ}\text{C}$ )
Un-milled $\text{MgH}_2$	0	$\beta$	30	2.1	99	0	435
Milled $\text{MgH}_2$	5	$\beta, \gamma$	0.95	8.1	21	0.25	384
Milled $\text{MgH}_2$	30	$\beta, \gamma$	0.8	9.2	17	0.3	375
Composite	5	$\beta, \gamma, \text{SiC}$	0.6	9.3	15	0.28	367
Composite	30	$\beta, \gamma, \text{SiC}$	0.5	10	12	0.3	361

properties. Additionally, a significant particle size refinement is observed, i.e. from 30  $\mu\text{m}$  to 0.5  $\mu\text{m}$  after 30 h MA. The decrease in particle size should correspond to an increase in the specific surface area. Varin and Czujku [20] reported a profound effect of particle size on the decomposition temperature of  $\text{MgH}_2$  after a certain critical threshold value ( $\sim 2 \mu\text{m}$ ). The present study has shown that the size of particles is approximately close to this value, so the effect of particle size on the decomposition temperature should be considered. It is reported that mechanical alloying of  $\text{MgH}_2$  is accompanied by fracturing as well as clustering and cold welding into large particles. Here, it seems that the addition of SiC powders can act as a process control agent; inhibiting the micro-welding of the magnesium hydride particles and leading to reduction in the particle size. The decrease in particle size should correspond to an increase in the specific surface area. Based on the XRD results, ternary hydrides are not formed in system during milling  $\text{MgH}_2$  with SiC powder. It is worth mentioning here that the formation of  $\gamma\text{-MgH}_2$  may affect the dehydrogenation process. The metastable high-pressure orthorhombic  $\gamma\text{-MgH}_2$  phase, which has a lower desorption enthalpy and temperature [18], would affect the thermodynamics and kinetics of dehydrogenation

process, so its formation decreases the hydrogen desorption temperature of  $\text{MgH}_2$ .

#### 4. CONCLUSIONS

Nanocrystalline  $\text{MgH}_2$ -5 wt% SiC composite powder was synthesized by mechanical alloying. The findings can be summarized as follow:

1. Addition of 5 wt% SiC to  $\text{MgH}_2$  and mechanical alloying up to 30 h formed a nanocrystalline composite containing  $\beta\text{-MgH}_2$  and low amounts of  $\gamma\text{-MgH}_2$  with the average crystallite size of  $\text{MgH}_2$  of 12 nm, average particle size of 0.5  $\mu\text{m}$  and specific surface area of 10  $\text{m}^2/\text{g}$ .
2. The addition of SiC powder to magnesium hydride and mechanical alloying for 30 h reduced the dehydrogenation temperature of magnesium hydride from 435  $^{\circ}\text{C}$  to 361  $^{\circ}\text{C}$ , mainly due to reducing the crystallite size and average particle size.
3. The hardness of the SiC helps to reduce the particle size and increase the surface area of the  $\text{MgH}_2$ , which is beneficial to the dehydrogenation properties of  $\text{MgH}_2$ .
4. No significant effect of the SiC addition on the desorption kinetics of magnesium hydride was noticed, thereby, the catalytic effect of SiC addition on H-kinetics was marginal.

## REFERENCES

- Bowman, R. C. and Fultz, B., "Metallic hydrides I: hydrogen storage and other gas-phase applications". *MRS Bull.*, 2002, 27, 688-693.
- Maddalena, A., Petris, M., Palade, P., Sartori, S., Principi, G., Settimo, E., Molinas, B. and Lo Russo, S., "Study of Mg-based materials to be used in a functional solid state hydrogen reservoir for vehicular applications". *Int. J. Hydrogen Energy*, 2006, 31, 2097-2103.
- Barkhordarian, G., Klassen, T. and Bormann, R., "Effect of Nb<sub>2</sub>O<sub>5</sub> content on hydrogen reaction kinetics of Mg". *J. Alloys Compds.*, 2004, 36-41, 242-246.
- Varin, R. A., Li, S., Chiu, C., Guo, L., Morozova, O., Khomenko, T. and Wronski, Z., "Nanocrystalline and non-crystalline hydrides synthesized by controlled reactive mechanical alloying/milling of Mg and Mg-X (X = Fe, Co, Mn, B) systems". *J. Alloys Compds.*, 2005, 404-406, 494-498.
- Sakintuna, B., Darkrim, F. L. and Hirscher, M., "Metal hydride materials for solid hydrogen storage: review". *Int. J. Hydrogen Energy*, 2007, 32, 1121-1140.
- Gennari, F. C., Castro, F. J. and Urretavizcaya, G., "Hydrogen desorption behavior from magnesium hydrides synthesized by reactive mechanical alloying". *J. Alloys Compds.*, 2001, 321, 46-53.
- Polanski, M., Bystrzycki, J. and Plocinski, T., "The effect of milling conditions on microstructure and hydrogen absorption /desorption properties of magnesium hydride (MgH<sub>2</sub>) without and with Cr<sub>2</sub>O<sub>3</sub> nanoparticles". *Int. J. Hydrogen Energy*, 2008, 33, 1859-1867.
- Liang, G., Huot, J., Boily, S., Van Neste, A. and Schulz, R., "Catalytic effect of transition metals on hydrogen sorption in nanocrystalline ball milled MgH<sub>2</sub>-Tm (Tm=Ti, V, Mn, Fe and Ni) systems". *J. Alloys Compd.*, 1999, 292, 247-252.
- Mao, J., Guo, Z., Yu, X., Liu, H., Wu, Z. and Ni, J., "Enhanced hydrogen sorption properties of Ni and Co-catalyzed MgH<sub>2</sub>". *Int. J. hydrogen energy*, 2010, 35, 4569-4575.
- Simchi, H., Kafrou, A. and Simchi, A., "Synergetic effect of Ni and Nb<sub>2</sub>O<sub>5</sub> on dehydrogenation properties of nanostructured MgH<sub>2</sub> synthesized by high-energy mechanical alloying". *Int. J. hydrogen energy*, 2009, 34, 7724-7730.
- Aguey-Zinsou, K. F., Ares Fernandez, J. R., Klassen, T. and Bormann, R., "Effect of Nb<sub>2</sub>O<sub>5</sub> on MgH<sub>2</sub> properties during mechanical milling". *Int. J. hydrogen energy*, 2007, 32, 2400-2407.
- Milanovic, I., Milosevic, S., Raskovic-Lovre, Z., Novakovic, N., Vujasin, R., Matovic, L., Fernandez, J. F., Sanchez, C. and Novakovic, J. G., "Microstructure and hydrogen storage properties of MgH<sub>2</sub>-TiB<sub>2</sub>-SiC composites. *Ceram. Int.*, 2013, 39, 4399-4405.
- Agarwal, S., Aurora, A., Jain, A., Jain, I. P. and Montone, A., "Catalytic effect of ZrCrNi alloy on hydriding properties of MgH<sub>2</sub>". *Int. J. hydrogen energy*, 2009, 34, 9157-9162.
- ChitsazKhoyi, L., Raygan, S. and Pourabdoli, M., "Mechanical milling of Mg, Ni and Y powder mixture and investigating the effects of produced nanostructured MgNi<sub>4</sub>Y on hydrogen desorption properties of MgH<sub>2</sub>". *Int. J. hydrogen energy*, 2013, 38, 6687-6693.
- Imamura, H., Nakatomi, S., Hashimoto, Y., Kitazawa, I., Sakata, Y., Maeb, H. and Fujimoto, M., "Synthesis and hydrogen storage properties of mechanically ball-milled SiC/MgH<sub>2</sub> nanocomposites". *J. Alloys Compd.*, 2009, 488, 265-269.
- Ranjbar, A., Guo, Z. P., Yu, X. B., Wexler, D., Calka, A., Kim, C. J. and Liu, H. K., "Hydrogen storage properties of MgH<sub>2</sub>-SiC composites". *Mater. Chem. Phys.*, 2009, 114, 168-172.
- Mahmoudi, N., Kafrou, A. and Simchi, A., "Synthesis of a nanostructured MgH<sub>2</sub>-Ti alloy composite for hydrogen storage via combined vacuum arc remelting and mechanical alloying". *Mater. Lett.*, 2011, 65, 1120-1122.
- Varin, R. A., Czujko, T. and Wronski, Z., "Particle size, grain size and  $\gamma$ -MgH<sub>2</sub> effects on the desorption properties of nanocrystalline commercial magnesium hydride processed by controlled mechanical milling". *Nanotechnology*, 2006, 17, 3856-3865.
- Huot, J., Liang, G., Bobet, S., Van Neste, A. and Schulz, R., "Structural study and hydrogen sorption kinetics of ball-milled magnesium hydride". *J. Alloys Compd.*, 1999, 295, 495-500.
- Varin, R. A. and Czujko, T., "The effect of atomic volume on the hydrogen storage capacity of hexagonal metals/intermetallics". *Scripta Mater.*, 2002, 46, 531-535.