



Hydrogen desorption properties of MgH_2 -5 at% Ni_3FeMn composite via combined vacuum arc remelting and mechanical alloying

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ABSTRACT

In this study, the composite material with composition of MgH_2 -5 at% Ni_3FeMn has been prepared by co-milling of MgH_2 powder with Ni_3FeMn alloy. The effect of milling time and additive on the hydrogen desorption properties of obtained composite was evaluated by thermal analyzer method and compared with pure un-milled MgH_2 . It has been shown that addition of 5 at% Ni_3FeMn to MgH_2 and mechanical alloying (MA) up to 30h formed a nanocrystalline composite with the average crystallite size of MgH_2 of 17nm and average particle size of 1.4 μm . As a consequence, the desorption temperature of composite material milled for 30 h has decreased from 421°C to 307°C. Furthermore, the dehydrogenation has started at ~ 140°C after 30h MA, revealing catalytic effect of Ni_3FeMn alloy.

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1. Introduction

Hydrogen is an ideal energy carrier and renewable fuel which is considered for future transport, such as automotive applications [1]. Magnesium hydride is one of attractive hydrogen storage materials because of its hydrogen storage capacity (7.6 wt %), low cost, and light weight [2,3]. 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 [4,5]. 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 [1]. Many researchers have investigated mechanical milling of MgH_2 with transition metals [6-8], metal oxides [9-11], none-oxide ceramics [12] and intermetallic compounds [13-15]. Liang et al. [7] found that milled MgH_2 /TM (Ni, Co, Ti, Fe) exhibits higher absorption/desorption kinetics than that of milled MgH_2 . Hanada et al. [16] found that a large amount of hydrogen (6.5 wt%) could be released in the temperature range from 150°C to 250°C from a 2mol% nano-Ni doped MgH_2 composite prepared

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by mechanical alloying.

Some experimental findings have shown that the hydrogen desorption properties of MgH_2 vary with multi-component additions, for example in Mg-Al-Y, Mg-Fe-Ti (Mn) and Mg-Li-Ni-Zn systems [17]. Recently, Dehouche et al. [18] reported the hydrogenation properties of MgH_2 nanocomposites with different families of alloys. Mahmoudi et al. [15] prepared an MgH_2 - $\text{TiCr}_{12}\text{Fe}_{0.6}$ nanocomposite by mechanical alloying and reported that the addition of prealloyed powder decreases the desorption temperature of mechanically activated MgH_2 from 327°C to 241°C. Agarwal et al. [13] investigated the catalytic effect of ZrCrNi alloy on hydriding properties of MgH_2 and showed that the superior hydrogenation performance can be attributed to the combined effects of the catalytic function of ZrCrNi alloy and the nanostructure of MgH_2 . The substantially lowered temperature of hydride decomposition for $\text{Mg}_{87}\text{Ni}_3\text{Al}_3\text{M}_7$ (M=Ti, Mn, Ce, La) alloys obtained by the reactive mechanical alloying (RMA) method was reported Spassove, et al. [19].

The aim of this work has been to study the effect of Ni-Fe-Mn addition on the desorption properties of MgH_2 -based composite obtained by mechanical alloying, as well as investigating the simultaneous effects of these elements on desorption properties of MgH_2 . In this work, the alloy was added to magnesium hydride in the form of as-cast powder and the mixture was mechanically milled over various times. The effect of the Ni_3FeMn addition and mechanical alloying on the dehydrogenation was investigated and compared with pure magnesium hydride. The results improve the current understanding on the effect of the alloying method on the dehydrogenation properties of magnesium hydride

2. Experimental Procedure

The starting materials MgH_2 (98%, <105 μm), Ni (98%, <100 μm), Fe (98%, <150 μm), and Mn (97%, <100 μm) powders were supplied from Merck Germany. To prepare the alloy with nominal composition of Ni_3FeMn (at.%), the elemental powders were mixed in a Tumbling mixer/miller for 30 min and compacted into an ingot of 10 mm diameter. Then, the powder compact was solution-treated and homogenized by being melted in a vacuum arc remelting furnace for three times.

The alloy was mechanically broken into small pieces and then ball milled for 30 min to obtain

small particles (< 106 μm). MgH_2 powder was blended with 5 at.% Ni_3FeMn powder and 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-K α radiation. The crystallite size and lattice strain of β - MgH_2 phase were estimated by broadening XRD peaks using Williamson–Hall method [20]. The size and morphological changes of powder particles upon mechanical alloying were studied by scanning electron microscopy (SEM, KYKY-EM3200). 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, the BET method 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 450°C.

3. Results and Discussion

Fig. 1 shows the XRD patterns of MgH_2 -5 at% Ni_3FeMn composite at the selected milling times.

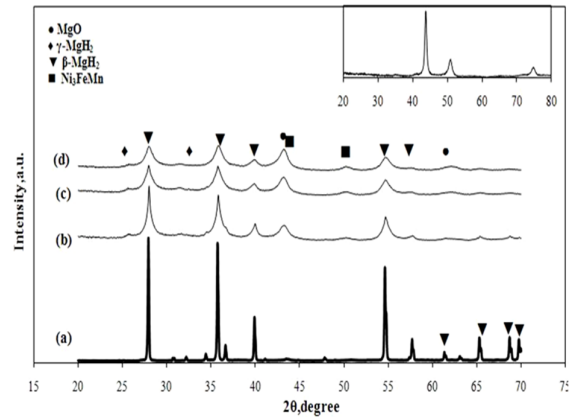


Fig.1. XRD patterns of un-milled MgH_2 (a) and MgH_2 -5wt% Ni_3FeMn composite after mechanical alloying for 5h (b), 15h (c) and 30h (d). The insert figure exhibit the main peaks of the produced Ni_3FeMn alloy.

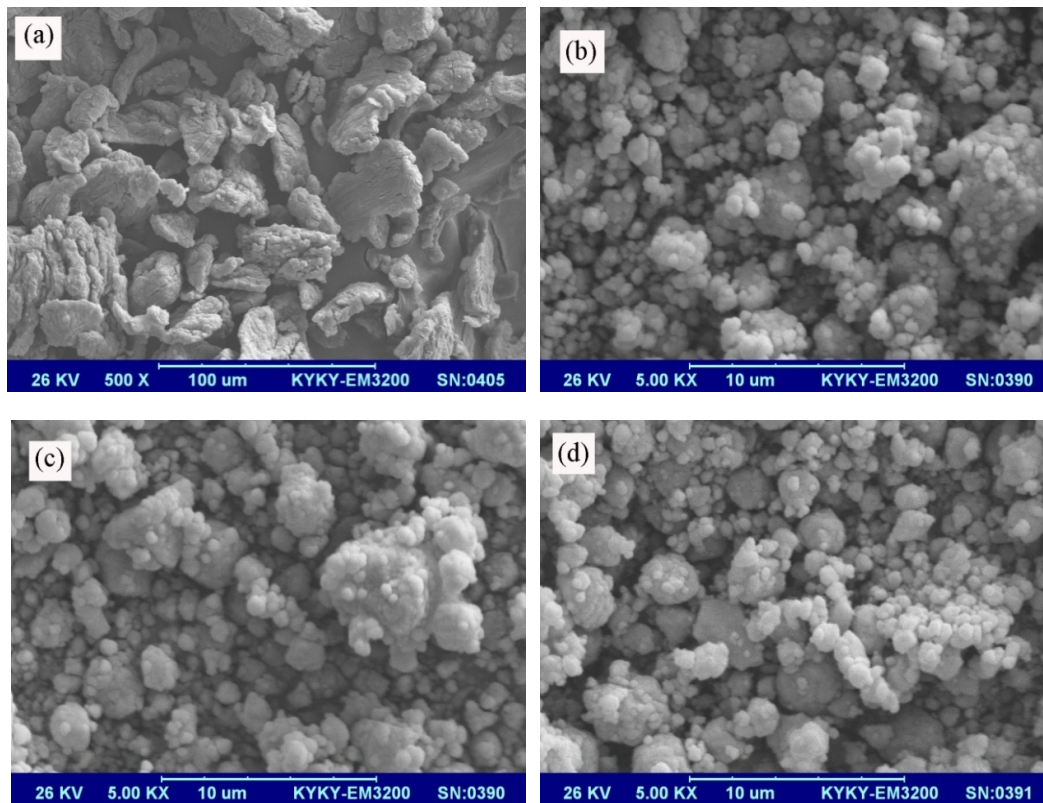


Fig.2. SEM micrographs showing the morphology of pure un-milled MgH_2 (a) and MgH_2 -5 wt% Ni_3FeMn composite after mechanical alloying for 5 h (b), 15 h (c) and 30 h (d).

The XRD peak of pure un-milled MgH_2 powder has diffraction peaks of β - MgH_2 are broadened and decreased evidently due to the high-energy impact of the milling balls. After 5h milling, the diffraction peaks corresponding to γ - MgH_2 were detected. The formation of a small amount of MgO phase was also observed. By the milling time extended up to 15 h and 30h, the diffraction peaks corresponding to β - MgH_2 became broader and less intense, while those corresponding to MgO intensified, showing the presence of higher amounts of this phase by increasing milling time. No new phase formation was noticed at these milling times.

The morphological changes produced by mechanical milling at different times can be observed in Fig.2. A significant particle size refinement is observed after milling up to 30h, the particle size reduced to about 1.4 μm .

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_2 exhibited a single endothermic peak

at 421°C corresponding to the decomposition of hydride (see Fig.3). This value is similar to the values reported in previous studies [21]. A reduction in the dehydrogenation temperature from 421°C to 307°C was achieved via co-milling of MgH_2 with the Ni_3FeMn alloy. Fig.4 shows the thermogravimetry (TG) profiles of the materials as a function of temperature milled for 5h and 30h. As observable, 5h milling of MgH_2 with Ni_3FeNi alloy powder is not sufficient to show the catalytic effect of additive. On the other hand, adding catalyst to MgH_2 via 30h milling could improve the dehydrogenation rate, i.e. the onset temperature of dehydrogenation decreased about 110°C compared with the sample milled for 5h. In order to find the origin of differences, the characteristics of the synthesized composite powders at different milling times were determined. The results are summarized in Table 1. The results show that mechanical milling and Ni_3FeMn addition are favourable with respect to the improvement of the

Table 1. Average particle size (D), specific surface area (S), crystallite size (d), lattice strain (ϵ) and dehydrogenation temperature (T) for MgH_2 -5at% Ni_3FeMn composite

System	Time, h	Phase	D, μm	S, (m^2/g)	d, nm	ϵ , %	T, ($^\circ\text{C}$)
Un-milled MgH_2	0	β	30	2.1	60	0	421
Composite	5	$\beta, \gamma, \text{MgO}$	2	9	24	0.3	332
Composite	15	$\beta, \gamma, \text{MgO}$	1.9	9.3	23	0.6	327
Composite	30	$\beta, \gamma, \text{MgO}$	1.4	10.5	17	0.7	307

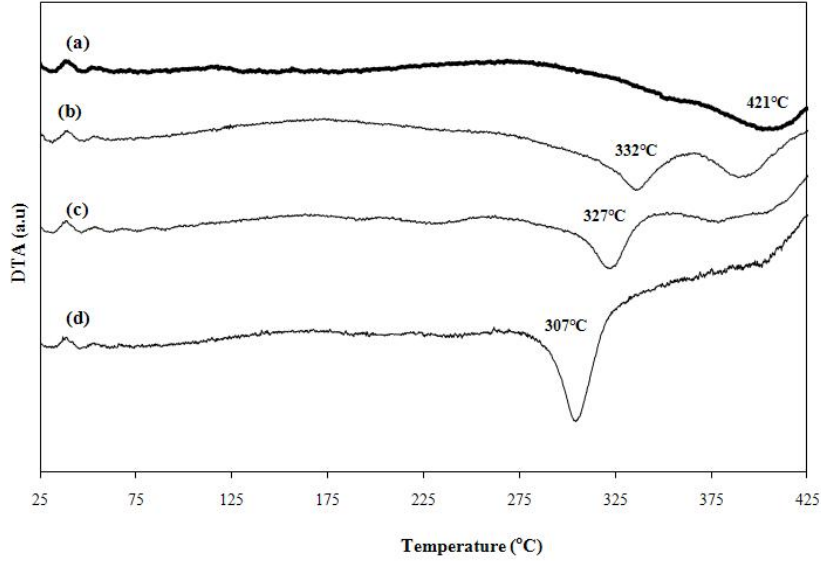


Figure 3. DTA curves of pure un-milled MgH_2 (a) and the composite material after mechanical alloying for 5h (b), 15h (c) and 30h (d).

hydrogendesorption temperature of MgH_2 . Different reasons are identified to explain this behavior. As can be seen in Table 1, the crystallite size gradually decreases from 60nm to 17nm by increasing milling time. Since the diffusion of atoms in grain boundaries is much faster than that of entire lattice [22]

it is acceptable that finer grain structure can promote the dehydrogenation properties. Additionally, a significant particle size refinement is observed, i.e. from $30\mu\text{m}$ to $1.4\mu\text{m}$ after 30h MA. The decrease in particle size should correspond to an increase in the specific surface area. Varin and Czujku [23] reported a profound effect of particle size on the decomposition temperature of 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 MgH_2 is accompanied by fracturing as well as clustering and cold welding into large particles. Here, it seems that the addition of Ni_3FeMn 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 lattice strain also significantly affects the H-kinetics [15]. Based on the XRD results, ternary hydrides are not formed in Mg-Mn-H, Mg-Ni-H and Mg-Fe-H systems during milling MgH_2 with Ni_3FeMn alloy powder. On the other hand, it seems that iron, nickel and manganese play the role of active sites on the surface of the magnesium particles, which is in agreement with previous reports [7,15].

Therefore, a change in the rate limiting step from nucleation and growth to phase boundary migration is expected to occur in the presence of

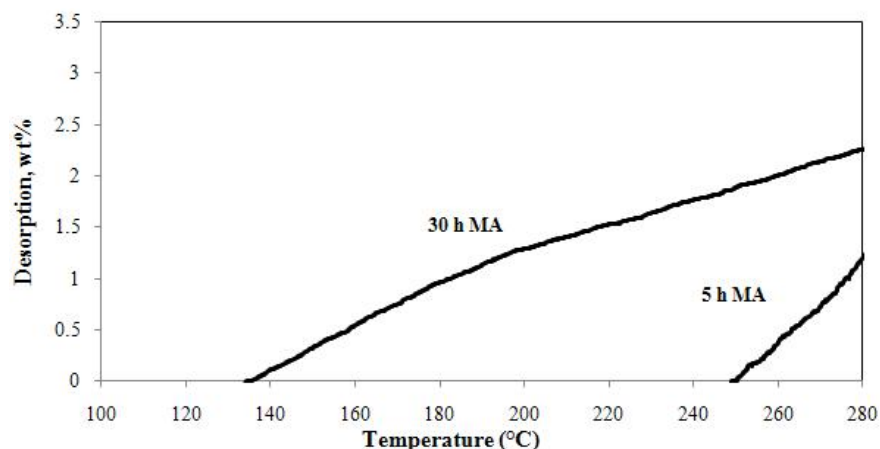


Figure 4. Thermogravimetric (TG) profiles of composite material at some selected milling times.

these elements, which can improve dehydrogenation temperature.

It has also been reported that the addition of a transition metal to MgH_2 generally reduces the stability of MgH_2 , which can lead to the improvement of dehydrogenation properties [24]. On the other hand, the 3d-metal additives could drastically reduce the activation energy of hydrogen desorption, whereas the thermodynamic properties of MgH_2 have not changed. In fact, dissolution of the alloying elements in magnesium hydride reduces the unit cell volume of the matrix, which increases the plateau pressure of hydride [17,24].

According to Van't Hoff equation, an increase in the plateau pressure corresponds to a reduction in the hydrogen desorption temperature. Song et al. [17] showed that the alloying elements of Fe and Ni weaken the bonds between both themselves and the H atoms, and between Mg atoms and H atoms, thereby improving the dehydrogenation properties of MgH_2 .

Liang et al. [7] reported values of 88.1 and 67.6 kJ mol^{-1} for the activation energies in $\text{MgH}_2\text{-Ni}$ and $\text{MgH}_2\text{-Fe}$ systems, respectively, which are much smaller than that of the ball milled pure MgH_2 (120 kJ mol^{-1}). This effect also improves the dehydrogenation of magnesium hydride as explained above. It is worth mentioning here that the formation of $\gamma\text{-MgH}_2$ and MgO may affect the dehydrogenation process. The metastable high-pressure orthorhombic $\gamma\text{-MgH}_2$ phase, which has a lower desorption enthalpy and temperature [25], would affect the thermodynamics and kinetics of dehydrogenation process, so its formation decreases the hydrogen desorption temperature of MgH_2 .

Nevertheless, MgO acts as a barrier between the solid and gas phases by limiting the diffusion of hydrogen atoms through its dense structure. Therefore, MgO can block catalytic active centers and can prevent the dissociation of molecular hydrogen [26].

4. Conclusion

Nanocrystalline $\text{MgH}_2\text{-5at\%Ni}_3\text{FeMn}$ composite powder was synthesized by vacuum arc remelting of the Ni_3FeMn alloy followed by co-milling with MgH_2 . The findings can be summarized as follow:

Addition of 5at% Ni_3FeMn to MgH_2 and mechanical alloying up to 30h formed a nanocrystalline composite containing $\beta\text{-MgH}_2$ and low amounts of $\gamma\text{-MgH}_2$ and MgO with the average crystallite size of MgH_2 of 17nm, specific surface area of $10.5\text{m}^2/\text{g}$ and average particle size of $1.4\mu\text{m}$.

The addition of Ni_3FeMn alloy to magnesium hydride and mechanical alloying for 30h reduced the dehydrogenation temperature of magnesium hydride from 421°C to 307°C , mainly due to reducing the crystallite size and average particle size (increasing the surface area).

The onset temperature of dehydrogenation of milled composite for 30h decreased about 110°C compared to the sample milled for 5h.

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