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# Hydrogen absorption and desorption characteristics of mechanically milled Mg–35wt.%$FeTi_{1.2}$ powders

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## Abstract

Mg–35wt.%$FeTi_{1.2}$ hydrogen storage materials were made by mechanical milling of mixed elemental magnesium and $FeTi_{1.2}$ alloy powders. The hydrogen absorption and desorption characteristics of powders milled for various times were evaluated. The results show that the *P–C–T* characteristics, hysteresis, plateau pressure, storage capacity, and hydriding and dehydriding rates change substantially with increasing milling time. Mechanical milling produces fine powder with nanometer-sized grains and large microstrain, which results in an increase in the hydriding and dehydriding rates.

*Keywords:* Hydrogen absorption; Hydrogen desorption; Mechanical milling

## 1. Introduction

In recent years, many attempts have been made to use mixtures of metals and alloys as hydrogen storage materials, in order to improve the kinetic properties of hydriding and dehydriding of Mg or initial activation of FeTi compounds by catalysts such as metals or $LaNi_5$ [1–3].

Mechanical alloying is a very simple method of producing composite powders and has been used to synthesize hydrogen storage materials [4–6]. In those works, it was shown that mechanical alloying has considerable advantages over conventional procedures. It produces hydrogen storage materials by ball milling mixed powders in a short time, the powders have high purity surface and homogeneous composition, and the powders are hydrided at an appreciable rate even in initial hydriding [7].

Magnesium hydride is the most promising hydrogen storage material because of its high absorption capacity, but its hydriding and dehydriding kinetics are very slow. Some work has been done to improve the reaction kinetics of Mg by mechanical milling of Mg with transition metals [4]. Here, we report the effects of ball milling on the structure and hydrogen absorption and desorption behavior of Mg–35wt.%$FeTi_{1.2}$ composite powders.

## 2. Experimental procedure

$FeTi_{1.2}$ compound was prepared by arc melting and crushed into powder with less than 80 mesh. The $FeTi_{1.2}$ and Mg powders (98.5% pure, −200 mesh) were mixed in the composition Mg–35wt.%$FeTi_{1.2}$. Mechanical milling was carried out in an attritor ball mill under the protection of high purity argon gas. Chromium steel balls 6 mm in diameter and a stainless steel vial were used for milling. The ball to powder weight ratio was 20:1 and the rotational velocity was kept at 300 rev $min^{-1}$.

After the selected duration of milling, a small amount of sample was removed from the vial for X-ray diffraction (XRD) analysis using a Rigaku/max-rB X-ray diffractometer with Cu K$\alpha$ radiation. The hydrogen absorption and desorption measurements were taken using the volumetric method.

## 3. Results

### 3.1. Mechanical milling

XRD patterns of Mg–35wt.%$FeTi_{1.2}$ mechanically milled for various times are shown in Fig. 1. We observe that an increasing milling time produces broadening of the Mg and FeTi peaks and a decrease in peak

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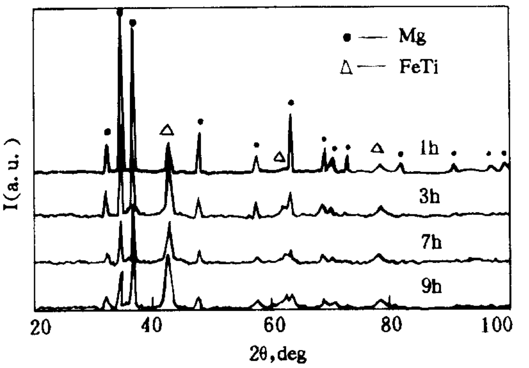

Fig. 1. XRD patterns of Mg-35wt.%FeTi$_{1.2}$ powders milled for various times.

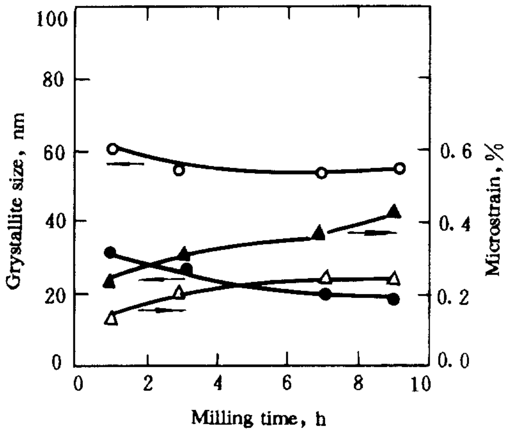

Fig. 2. Crystallite size and microstrain of milled powders (● ▲) and powders after eight hydriding and dehydriding cycles (○ △).

height, indicating a continuous decrease in crystal size of the powders due to plastic deformation. Indeed, measurements of the width at half-maximum of the peaks confirmed that the crystallite size of Mg decreased to nanometer size after 9 h milling as shown in Fig. 2. Mechanical milling also results in a high microstrain in the crystal lattice. No new phase was found in milled powders in addition to the Mg and FeTi phases.

### 3.2. Hydriding and dehydriding rates

Samples milled for various times were selected for the hydrogen absorption test. All the samples were exposed to 3.0 MPa hydrogen gas at room temperature, but a very small absorption of hydrogen was observed (1 h milled, 0.596 wt.%; 3 h milled, 0.48 wt.%; 7 h milled, 0.34 wt.%; 9 h milled, 0.21 wt.%). The capacity of hydrogen absorption at room temperature decreased with increasing milling time.

When the sample was heated to 673 K at a pressure of 3 MPa with a heating rate of 25 K min$^{-1}$, the hydrogen absorption rate became very fast. After several hydriding and dehydriding cycles, the hydrogen absorption and desorption capacities reached saturation values as shown in Fig. 3. The saturation storage capacity increased at the starting milling stage, to a maximum value of 2.7 wt.% for 7 h milled powders, and then decreased to 2.3 wt.% after 9 h milling. The absorption and desorption capacities of hydrogen are shown in Fig. 4.

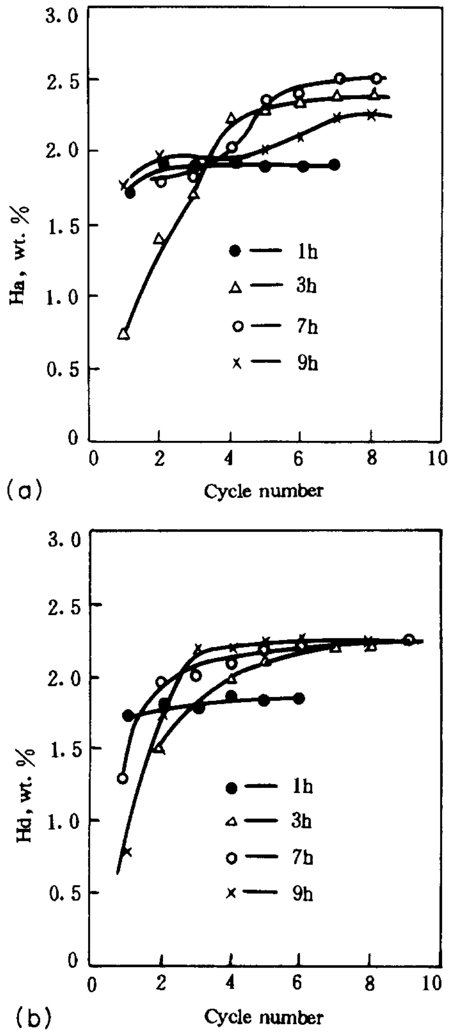

Fig. 3. Hydrogen absorption capacity (a) at 3 MPa, 673 K and desorption capacity (b) at 0.1 MPa, 673 K for powders milled for different times.

Fig. 5 shows the hydriding and dehydriding rates of powders mechanically milled for various times. We observe that the kinetic characteristics of hydriding and dehydriding improved with ball milling, but increasing the milling time did not accelerate the hydriding and dehydriding rates further after 7 h milling, and the hydrogen storage capacity decreases.

### 3.3. P–C–T curves

Fig. 6 shows the P–C–T curves of powders mechanically milled for various times. We observe that powders milled for 1 h and 3 h have a low plateau pressure, high slope and serious hysteresis, while powders milled for 7 h and 9 h have a high plateau pressure, low slope and small hysteresis.

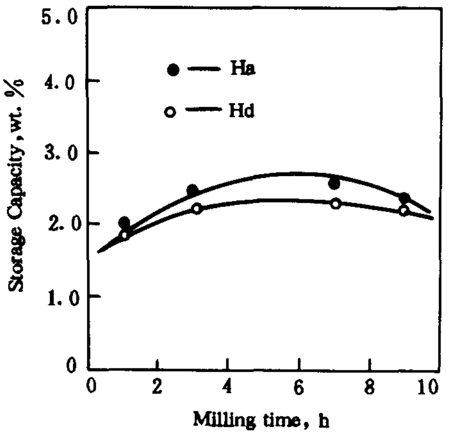

Fig. 4. Hydrogen absorption and desorption capacities as a function of milling time.

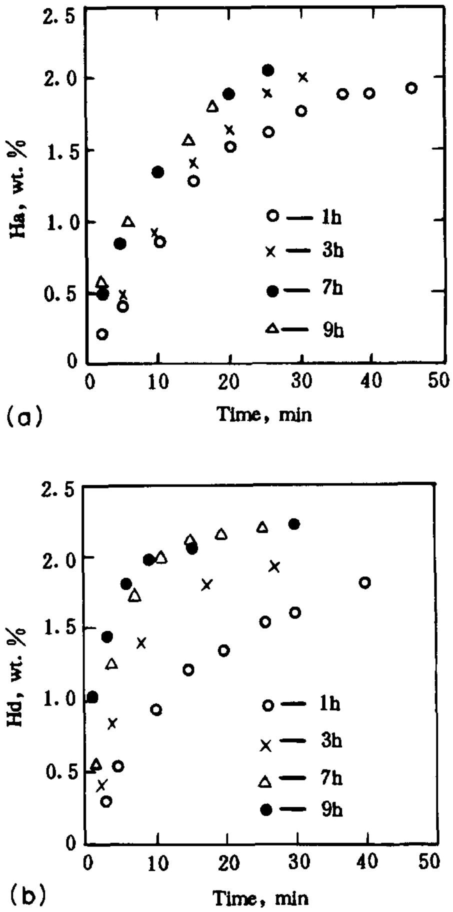

Fig. 5. Hydriding rate (a) at 3.0 MPa, 673 K and dehydriding rate (b) at 0.1 MPa, 673 K for powders milled for different times.

Fig. 7 shows the *P–C–T* curves of 9 h milled powders at various temperatures. The hydrogen storage capacity decreased at low temperature. Based on the relationship of the logarithm of the equilibrium pressure with reciprocal temperature, the following equation was obtained:

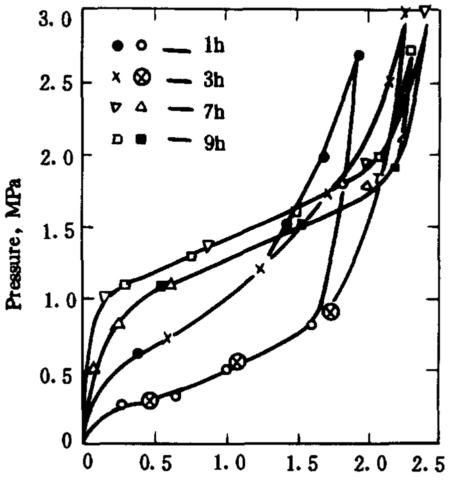

Fig. 6. *P–C–T* curves at 673 K for powders milled for various times.

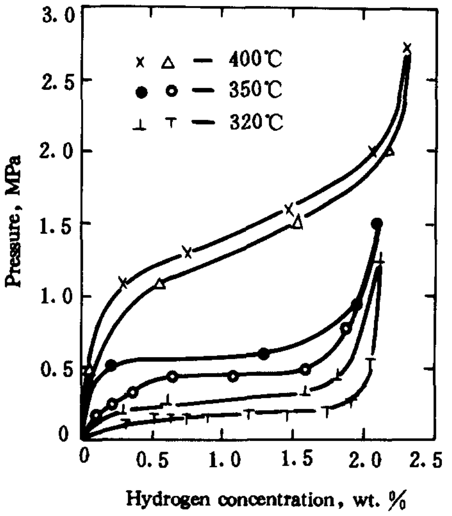

Fig. 7. *P–C–T* curves at various temperatures for powders milled for 9 h.

$$\ln p = -\frac{16670}{T} + 53$$

Furthermore, the thermodynamic data calculated according to the Van't Hoff equation are $\Delta H = -68.3$ kJ mol$^{-1}$, $\Delta S = -220$ J mol$^{-1}$ K$^{-1}$. Judging from these values, we see that the formation enthalpy is equal to the formation enthalpy of $MgH_2$, indicating that the hydrogen absorption phase in 9 h milled powders is magnesium.

## 4. Discussion

Mechanical milling produces composite powders of Mg–35wt.%$FeTi_{1.2}$. The main effects of mechanical milling on the materials are an increase in the surface area and the creation of many defects on the surface and in the interior. However, annealing during hydriding and dehydriding cycling at 673 K may decrease the surface area by sintering (after several cycles, the powders sintered to porous bulk with relatively high strength) and diminution of the number of defects. As shown in Fig. 2, we observed an increase in crystallite size and reduction of microstrain of Mg after eight hydriding and dehydriding cycles. However, the crystallite size of Mg is still less than 100 nm, and the microstrain is still about 0.2%, suggesting that there remain a number of grain boundaries and defects on the surface and in the interior of the material as nucleation sites for magnesium hydride [8]. The lattice defects may aid the diffusion of hydrogen in materials by providing many sites with low activation energy of diffusion [4], and the increasing microstrain may reduce the hysteresis of hydrogen absorption and desorption [9]. It may also accelerate the hydriding and dehydriding rates. When the milling time exceeds 7 h, there are no obvious changes in the grain size and microstrain of Mg crystals with increasing milling time (see Fig. 2). So the hydrogen absorption and desorption properties do not change at the final milling stage.

In addition, the observed optimum storage capacity of about 2.7 wt.% at 673 K for Mg-35wt.%$FeTi_{1.2}$ indicates that a large proportion of Mg participates in hydrogen absorption and desorption. Fig. 8 shows XRD patterns of powders after eight hydriding and dehydriding cycles at 673 K; only $MgH_2$, Mg and FeTi were found, and no new phases formed. This also indicates that the main hydrogen absorption phase is Mg with nanometer-size grains. The observed optimum storage capacity is much smaller than the theoretical value of 5.2 wt.% for the composite powders, owing to the existence of a large amount of non-dehydriding Mg.

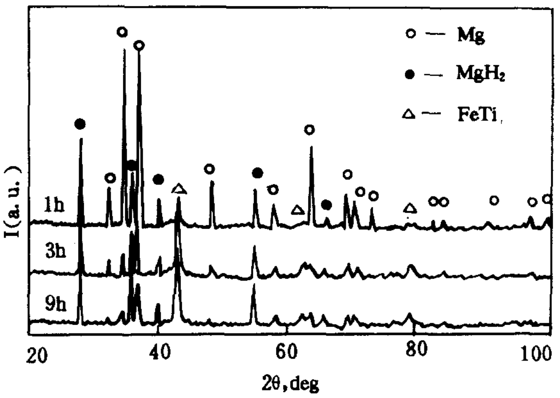

Fig. 8. XRD patterns of powders milled for various times after eight cycles of hydriding and dehydriding.

## 5. Conclusions

The hydrogenation behavior of the new composite material Mg-35wt.%$FeTi_{1.2}$ synthesized by mechanical milling was studied; the following conclusions can be drawn.

(1) The Mg-35wt.%$FeTi_{1.2}$ powder composed of Mg and FeTi only; the storage capacity is due mainly to the absorption of hydrogen by Mg.

(2) The hydriding and dehydriding rates increased obviously with increasing milling time at the starting milling stage, and there was no further improvement in kinetic characteristics at the final milling stage when the milling causes no structural change of the powder.

(3) The hydrogen storage capacity has a maximum value of 2.7 wt.% for powder subjected to 7 h milling, and a further increase in milling time causes a reduction in storage capacity.

(4) Powder milled for long times (7 h and 9 h) have a higher plateau pressure, lower slope and smaller hysteresis than powder milled for short times.

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