

Dependence of hydrogen storage characteristics of Mg–TiFe_{0.92}Mn_{0.08} composite on amount of TiFe_{0.92}Mn_{0.08}

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Received 1 June 2004; received in revised form 4 October 2004; accepted 12 October 2004
Available online 14 July 2005

Abstract

We investigated the hydrogen storage characteristics of Mg–*x* wt.% TiFe_{0.92}Mn_{0.08} (*x* = 20, 35, and 50) composites prepared by wet mechanical milling. TiFe_{0.92–*x*}Mn_{0.08} and α-Fe phases were formed in these composites by the decomposition of TiFe_{0.92}Mn_{0.08} after activation. The kinetics of the hydrogen absorption at low temperature was improved by increasing the amount of TiFe_{0.92}Mn_{0.08}. These improvements appear to be attributable to the TiFe_{0.92–*x*}Mn_{0.08} phase, which plays an important role as a pathway for the diffusion of hydrogen into the Mg matrix. In contrast, the hydrogen desorption temperature decreased as the amount of α-Fe originating from TiFe_{0.92}Mn_{0.08} increased. The Mg–50 wt.% TiFe_{0.92}Mn_{0.08} composite started to desorb hydrogen at the same temperature as Mg–50 wt.% Fe composite prepared under the same milling conditions although the former had much better hydrogen absorption characteristics than the latter at low temperature. We consider that the presence of α-Fe probably contributes to the improvement in the hydrogen desorption characteristics.

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Keywords: Hydrogen storage materials; High-energy ball milling; Scanning electron microscopy; Thermal analysis

1. Introduction

Mg is an attractive hydrogen absorbing material because of its high capacity (7.6 wt.%) and low cost. However, it requires high temperature to display practical hydrogen absorption–desorption characteristics [1]. There have been many studies designed to produce a composite material to solve this important problem. A significant improvement in hydrogen absorption–desorption kinetics has been achieved by using Mg-based nanostructured composites prepared by the mechanical milling of Mg or MgH₂ and secondary substances, such as catalytic 3d-transition metals, metal oxides, and intermetallic compounds with good hydrogen absorption–desorption characteristics at room temperature [2–6]. We have also demonstrated that Mg–50 wt.% TiFe_{0.92}Mn_{0.08}

composite prepared by wet mechanical milling shows good hydrogen absorption–desorption characteristics. We believe the main factor in the noticeable improvement in the characteristics is the formation of TiFe_{0.92–*x*}Mn_{0.08} and α-Fe due to the decomposition of the TiFe_{0.92}Mn_{0.08} after activation [7]. However, the roles of TiFe_{0.92–*x*}Mn_{0.08} and α-Fe have yet to be understood in detail.

In this study, we investigated the dependence of the hydrogen storage characteristics of Mg–TiFe_{0.92}Mn_{0.08} composite prepared by wet mechanical milling on the amount of TiFe_{0.92}Mn_{0.08} in order to reveal the roles played by TiFe_{0.92–*x*}Mn_{0.08} and α-Fe in hydrogen absorption–desorption.

2. Experimental

Mg powder (Furuuchi Chemical, –100 mesh, 99.9%) and TiFe_{0.92}Mn_{0.08} alloy powder (Japan Metals and Chemicals, –100 mesh, 99.9%) were mixed with a composition of Mg–*x* wt.% TiFe_{0.92}Mn_{0.08} (*x* = 20, 35, and 50). The mixture (1.025 g) was mechanically milled in absolute *n*-hexane

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(4 ml) under an argon atmosphere at a rotation speed of 600 rpm for 80 h. The milling was carried out according to our previous report [7].

The structures of the composites were characterized by X-ray diffraction (XRD, Rigaku, MultiFlex) with Cu K α radiation, and scanning electron microscopy (SEM, Jeol, JXA-8621). The internal structure of a composite particle was observed by using SEM with sliced samples, and the elemental distribution was confirmed by electron probe X-ray micro-analysis (EPMA, Jeol, JXA-8621). The hydrogen storage characteristics of the composites were determined by using an automatic Sievert apparatus (Lesca) and differential scanning calorimetry (DSC, TA Instruments, DSC2910), as described in our previous report [7].

3. Results and discussion

3.1. Microstructure of composites

Fig. 1 shows backscattering electron images of cross-sections of the prepared composite particles. The large dark part and the fine bright particles in the figure were confirmed by EPMA to correspond to Mg and TiFe_{0.92}Mn_{0.08}, respectively. The morphology of the composite was independent of the amount of TiFe_{0.92}Mn_{0.08}. The TiFe_{0.92}Mn_{0.08} particles were uniformly distributed in the Mg matrix and their sizes were similar among the composites.

Fig. 2 shows the XRD patterns of the Mg–TiFe_{0.92}Mn_{0.08} composites with different compositions after activation. All the patterns contained peaks attributable to α -Fe that became clear as we increased the amount of TiFe_{0.92}Mn_{0.08} dispersed in the Mg matrix. This clearly indicates that TiFe_{0.92-x}Mn_{0.08} and α -Fe are formed by the decomposition of TiFe_{0.92}Mn_{0.08} [7].

3.2. Hydrogen absorption characteristics

The hydrogen absorption kinetics and capacities of the composites were examined under a hydrogen pressure of 1.55 MPa after activation. Fig. 3 shows the hydrogen absorption curves of the composites at various temperatures. In order to normalize the hydrogen absorption kinetics, we used a transformed fraction, which we defined as the ratio of the absorbed hydrogen to the hydrogen absorption capac-

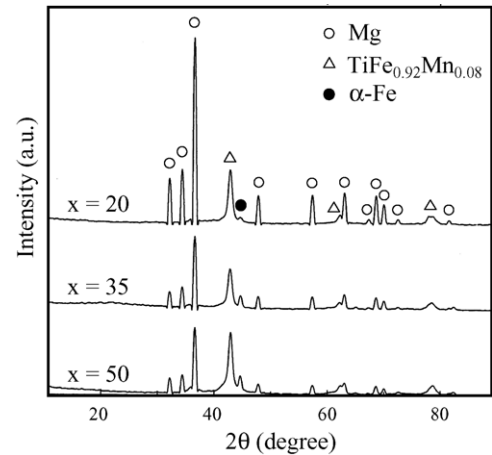


Fig. 2. XRD patterns of Mg– x wt.%TiFe_{0.92}Mn_{0.08} ($x = 20, 35,$ and 50) composites after activation.

ity at 350 °C. All the Mg–TiFe_{0.92}Mn_{0.08} composites showed almost the same hydrogen absorption kinetics at 350 °C because the diffusion of hydrogen into the Mg matrix is very fast and does not appear to affect the hydrogen absorption kinetics. However, when the temperature decreased, the hydrogen absorption kinetics became poor in all the composites and significant differences in the kinetics were observed among the composites. At 100 and 25 °C, the kinetics was improved by increasing the amount of TiFe_{0.92}Mn_{0.08} dispersed in the Mg matrix. This is because the TiFe_{0.92-x}Mn_{0.08} and/or α -Fe phases in the activated composite act as a pathway for the diffusion of hydrogen into the Mg matrix.

Table 1 shows the dependence of the hydrogen absorption capacity on temperature. The capacities in all the composites at 350 °C were similar to their theoretical hydrogen absorption capacities estimated from the Mg content. The reduction in capacity caused by the decrease in temperature became very noticeable as we decreased the amount of TiFe_{0.92}Mn_{0.08} dispersed in the Mg matrix. Mg–50 wt.%TiFe_{0.92}Mn_{0.08} composite can absorb almost all the hydrogen even at 25 °C because the successive diffusion of the hydrogen into the Mg matrix is retained by large amounts of TiFe_{0.92-x}Mn_{0.08} and/or α -Fe.

On the other hand, the kinetics of the Mg–50 wt.% TiFe_{0.92}Mn_{0.08} composite was much better than that of the Mg–50 wt.%Fe composite prepared under the same milling conditions and it retained its hydrogen absorption capac-

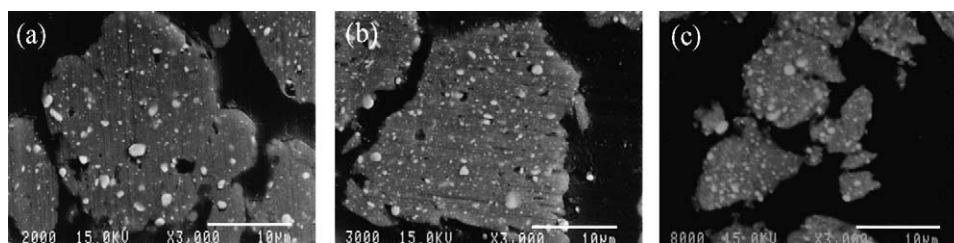


Fig. 1. Backscattering electron images of cross-sections of the composite particles: (a) Mg–20 wt.%TiFe_{0.92}Mn_{0.08}; (b) Mg–35 wt.%TiFe_{0.92}Mn_{0.08}; (c) Mg–50 wt.%TiFe_{0.92}Mn_{0.08}.

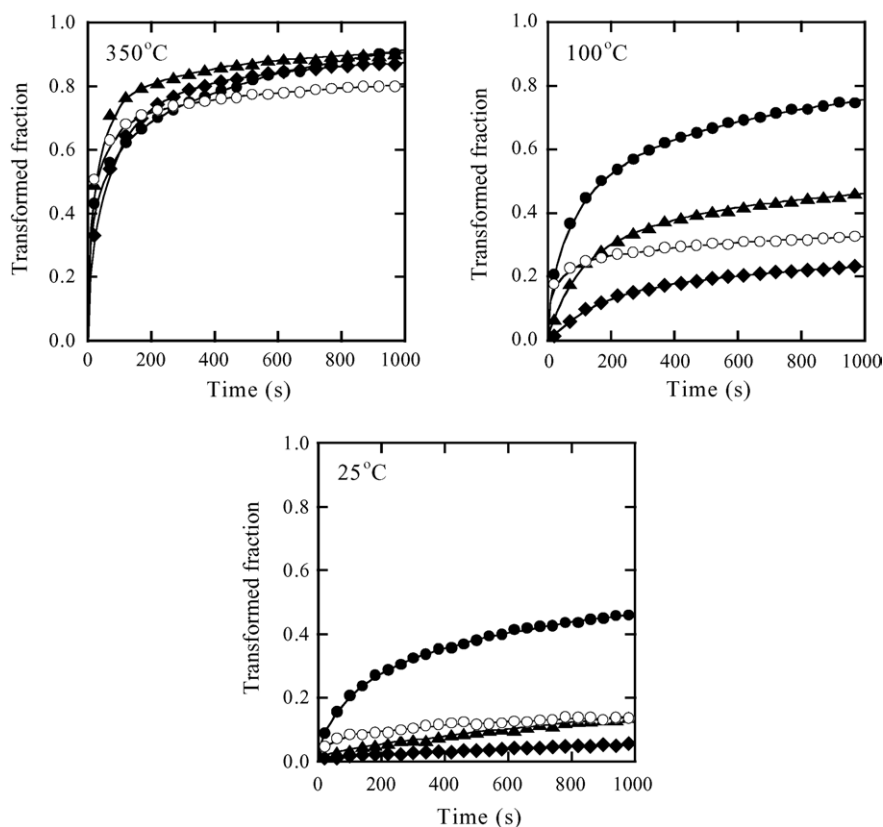


Fig. 3. Hydrogen absorption curves of composites under a hydrogen pressure of 1.55 MPa at 350, 100, and 25 °C: (◆) Mg–20 wt.%TiFe_{0.92}Mn_{0.08}; (▲) Mg–35 wt.%TiFe_{0.92}Mn_{0.08}; (●) Mg–50 wt.%TiFe_{0.92}Mn_{0.08}; (○) Mg–50 wt.%Fe.

ity even at low temperatures below 100 °C. This was despite the fact that the α -Fe particles were dispersed more finely and uniformly in the Mg matrix than the TiFe_{0.92}Mn_{0.08} particles, as shown in Fig. 4. This clearly indicates that TiFe_{0.92-x}Mn_{0.08} is more effective than α -Fe for the diffusion of hydrogen at low temperature.

On the basis of the above results, we consider that the improvement in the hydrogen absorption characteristics at low temperature can be mainly attributed to the TiFe_{0.92-x}Mn_{0.08} phase, which plays an important role as a pathway for the diffusion of hydrogen into the Mg matrix. TiFe_{0.92-x}Mn_{0.08} phase probably provides the interface and the short diffusion paths in the Mg matrix [7]. However, the reason why TiFe_{0.92-x}Mn_{0.08} phase promotes the diffusion more effectively than α -Fe phase is not clear. Further investigation is necessary on this point.

Table 1
Dependence of hydrogen absorption capacity on temperature

Sample	Hydrogen absorption capacity (wt.%)		
	350 °C	100 °C	25 °C
Mg–20 wt.%TiFe _{0.92} Mn _{0.08}	5.6	3.0	1.8
Mg–35 wt.%TiFe _{0.92} Mn _{0.08}	4.7	4.3	2.9
Mg–50 wt.%TiFe _{0.92} Mn _{0.08}	3.6	3.6	3.5
Mg–50 wt.%Fe	3.6	2.4	1.4

3.3. Hydrogen desorption characteristics

The hydrogen desorption characteristics were evaluated using DSC because no hydrogen desorption was detected by the volumetric method at low temperature. Fig. 5 shows DSC profiles of the hydrogenated composites under a hydrogen pressure of 0.1 MPa. The endothermic peak attributed to hydrogen desorption from MgH₂ shifted to a low temperature with increasing amounts of TiFe_{0.92}Mn_{0.08} dispersed in the Mg matrix, that is, the amount of TiFe_{0.92-x}Mn_{0.08}

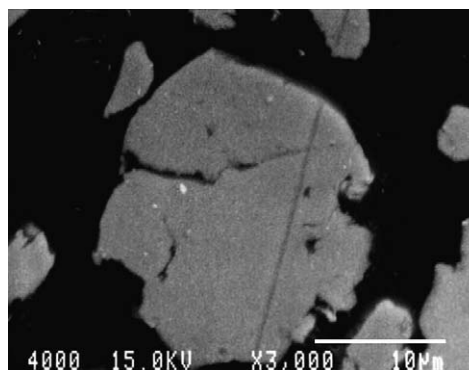


Fig. 4. Backscattering electron image of cross-section of Mg–50 wt.%Fe composite particle.

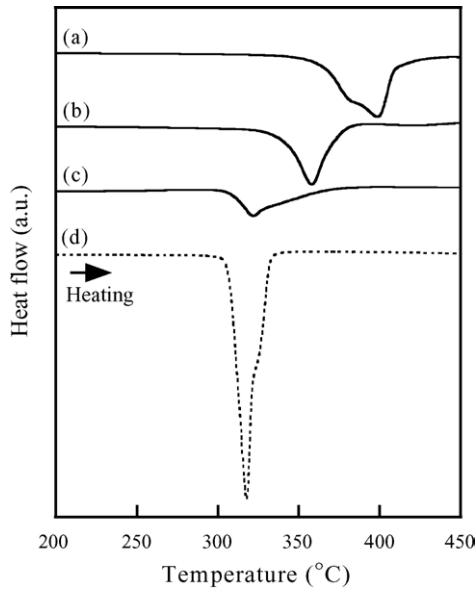


Fig. 5. DSC profiles of hydrogenated composites under a hydrogen pressure of 0.1 MPa: (a) Mg–20 wt.% TiFe_{0.92}Mn_{0.08}; (b) Mg–35 wt.% TiFe_{0.92}Mn_{0.08}; (c) Mg–50 wt.% TiFe_{0.92}Mn_{0.08}; (d) Mg–50 wt.% Fe.

and α -Fe in the activated composite. Furthermore, the Mg–50 wt.% TiFe_{0.92}Mn_{0.08} started to desorb hydrogen at the same temperature as the Mg–50 wt.% Fe composite. These facts suggest that the reduction in the hydrogen desorption temperature is probably due to the catalytic effect of α -Fe in the activated composites. In fact, Fe nano-particles dispersed in the Mg matrix act as a catalyst, resulting in the noticeable improvement in the hydrogen desorption characteristics of Mg [2].

4. Conclusions

We investigated the microstructure and hydrogen storage characteristics of Mg– x wt.% TiFe_{0.92}Mn_{0.08} ($x = 20, 35$, and 50) composites prepared by wet mechanical milling. For all the composites, the TiFe_{0.92}Mn_{0.08} particles were uniformly distributed in the Mg matrix and their sizes were similar. After activation, α -Fe was formed by the decomposition of the TiFe_{0.92}Mn_{0.08} phase and it increased with the amount of TiFe_{0.92}Mn_{0.08} in as-milled composite. The improvement in the hydrogen absorption characteristics at low temperature appears to be attributable to the TiFe_{0.92– x} Mn_{0.08} phase, which promotes the diffusion of hydrogen into the Mg matrix. In contrast, the improvement in the hydrogen desorption characteristics is probably due to the catalytic effect of α -Fe.

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