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Hydriding kinetics of nano-phase composite hydrogen storage alloys prepared by mechanical alloying of Mg and $MmNi_{5-x}(CoAlMn)_x$

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Abstract

Nano-phase composite hydrogen storage alloys were prepared by mechanical alloying of Mg and $MmNi_{5-x}(CoAlMn)_x$. The hydrogen absorption kinetics of the nano-phase composite and melted $MmNi_{5-x}(CoAlMn)_x$ alloys were measured under isobaric conditions at different temperatures. The obtained hydrogen absorption kinetic curves were fitted using various rate equations to reveal the mechanism of the hydriding reaction process. The results showed that the hydriding reaction kinetics of the nano-phase composite and melted $MmNi_{5-x}(CoAlMn)_x$ were different. For the nano-phase composite, the hydriding reaction was in agreement with an auto-catalysis process. For the melted $MmNi_{5-x}(CoAlMn)_x$, the hydride reaction was in agreement with a nucleation and growth process. The difference in hydriding kinetics of the two alloys is discussed based on the fitting results and the microstructural characteristics of the alloys.

Keywords: Hydrogen storage alloys; Mechanical alloying; Nanocrystalline alloys; Hydrogen absorption kinetics

1. Introduction

Magnesium-based hydrogen storage alloys have a high hydrogen storage capacity and are inexpensive. It would be of great benefit to use them in a Ni–MH battery because the theoretical capacity of electrodes made of these materials is very high [1]. However, the hydriding/dehydriding kinetic properties of Mg-based hydrogen storage alloys are poor. Much research has been carried out to improve the kinetic properties of Mg-based alloys. The main approaches include: (1) adding alloying elements, such as Zr, Al, Co, Mn, Cu, Si, Ca, Ag, etc. [2]; (2) modifying the surface of the alloys by coating with metals such as Ni and Cu [3], or fluoride treatment [4]; (3) using novel methods, such as mechanical alloying (MA) [5], to prepare alloys with nanocrystalline and/or amorphous microstructure [6]; (4) forming composites with other hydrogen storage alloys, such as $LaNi_5$ [7] and La_2Mg_{17} [8], with good kinetic properties.

With respect to composite hydrogen storage alloys [8], it has been found that there is an interaction between the different components of the composite. The component with good kinetic properties can catalyze the hydriding process of the component with poor kinetic properties. The interphase boundary plays a key role in the interaction between the different components. Therefore, it would be very beneficial to increase the density of the interphase boundary. Consequently, nano-phase composite hydrogen storage alloys have been prepared in recent years, especially using MA [9]. It has been well established that the hydriding kinetics of Mg-based alloys are greatly improved due to the formation of a nano-phase composite microstructure by MA [10,11].

Improvement of the hydrogen absorption kinetics of nano-phase composite hydrogen storage alloys would be related to their hydriding mechanism. Generally, the hydriding mechanism can be determined from the rate equation of different hydriding reaction processes [12]. The purpose of the present research was to investigate in detail the hydriding kinetics of nano-phase composite alloys prepared by MA of Mg and $MmNi_{5-x}(CoAlMn)_x$ (denoted below as MmM_5) in previous work [13].

2. Experimental

A powdered mixture of Mg of purity 99.8% and size 200 mesh and MmM_5 pulverized from an ingot was sealed in a stainless steel vial together with hardened steel balls in

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the ratio 1:10 under pure argon. Ball milling was then performed in a Fritsch P5 mill at a rotation speed of 150 rpm for 20 h. Hydrogen absorption kinetics were measured using an apparatus with a pressure transducer and a mass flow meter with a measuring range of 5 to 10^4 standard ml/min and an accuracy of 2%. Hydrogen gas at a constant pressure of 0.6 MPa was introduced into the sample chamber through a pressure regulator. The sample container was a copper cylinder 10 mm in diameter and 30 mm in height. Five grams of the sample was placed in the sample holder and the holder was immersed in a water bath maintained at constant temperature to an accuracy of ±1 K during the measurement. Three hydriding/dehydriding cycles were performed before measuring the hydriding kinetic curves. A CM-200 TEM was used to characterize the microstructure. The specimen was prepared by mixing milled powder with resin and then thinning by ion milling.

3. Results

As reported in previous work [10], the composite alloy obtained by MA of MmM_5 and Mg consists of nanometer-sized MmM_5, Mg and $MmMg_{17}$ phases. Fig. 1 shows the pressure–composition isothermal (PCI) curves for melted MmM_5 alloy and nano-phase composite of composition MmM_5–30% Mg obtained at 303 K. The figure exhibits two plateaus in the PCI of the composite alloy and the amount of hydrogen absorption is larger than that of the melted MmM_5 alloy. This indicates that Mg participates in the hydrogen absorption. However, it is still not clear which phase, Mg or Mm_2Mg_{17}, takes part in the hydrogen absorption. Fig. 2 shows kinetic curves for melted MmM_5 alloy and nano-phase composite of composition MmM_5–10% Mg and MmM_5–30% Mg measured under isobaric conditions at 333 K. This figure clearly shows that the hydrogen absorption rate for the nano-phase composite is higher than that for the melted MmM_5 alloy. However, it can be seen that the ultimate hydrogen absorption content for the nano-phase composite shown in Figs. 1 and 2 is different. This is probably due to the different measuring procedures used for Figs. 1 and 2. In the former case, the hydrogen pressure was increased slowly step by step, while in the latter case a constant pressure of 0.6 MPa was introduced. It is likely that, in the latter case, a dense layer of hydride was formed on the surface of the composite particles due to the initial high H_2 pressure, which acted as an obstacle to further hydriding. Thus, the ultimate hydrogen absorption content was low in the latter case.

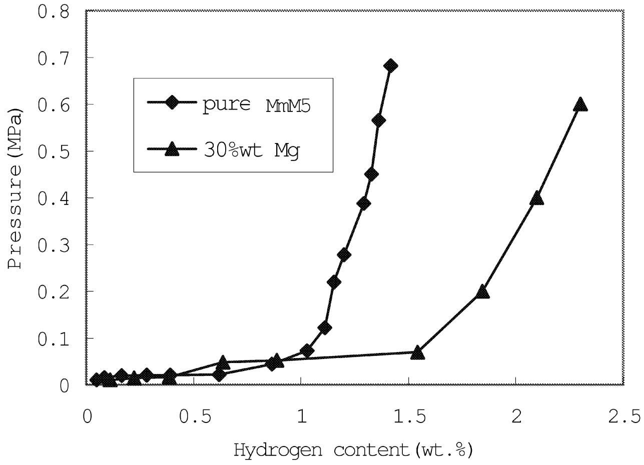

Fig. 1. Pressure–composition isothermal curves for melted MmM_5 alloy and nano-phase composite of composition MmM_5–30% Mg measured at 303 K.

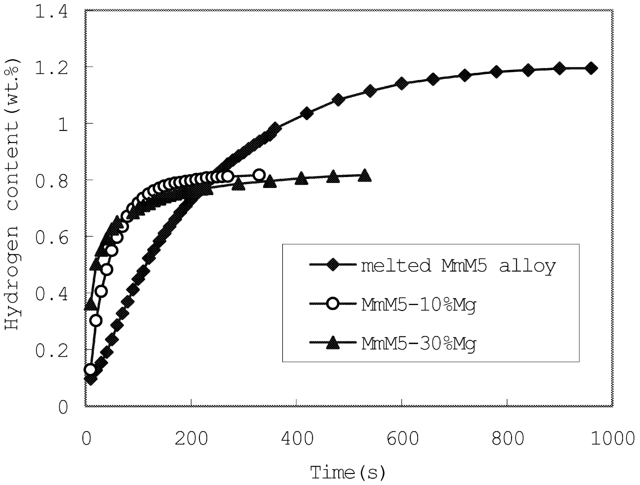

Fig. 2. Kinetic curves for melted MmM_5 alloy and nano-phase composite of compositions MmM_5–10% Mg and MmM_5–30% Mg measured under isobaric conditions at 333 K.

Usually, the reaction mechanism can be analyzed by comparing the observed hydriding rate curve with the rate equation derived from different reaction processes, such as (1) nucleation and growth processes, (2) auto-catalytic reactions, (3) phase-boundary-controlled reactions, and (4) diffusion-controlled reactions [12]. It was found that the experimental data for melted MmM_5 alloy and the MA MmM_5–Mg composite can be best fitted to Eq. (1) (Avrami–Erofeev equation) and Eq. (2) (auto-catalytic reaction), respectively, which was deduced from the nucleation and growth process and the auto-catalytic reaction process, respectively:

$$\alpha = 1 - \exp(-Bt^m) \tag{1}$$

$$\ln[\alpha/(1-\alpha)] = k(t - t_c) \tag{2}$$

where α is the ratio of reacted material to total material, and m, B, k and t_c are constants (see Ref. [12] for details). Fig. 3a–c shows the experimental data for the kinetic measurements and fitting results for melted MmM_5 alloy, and nano-phase composites of compositions MmM_5–10% Mg and MmM_5–30% Mg measured at 353 K. The values of B, m, k and t_c obtained by fitting are listed in Table 1.

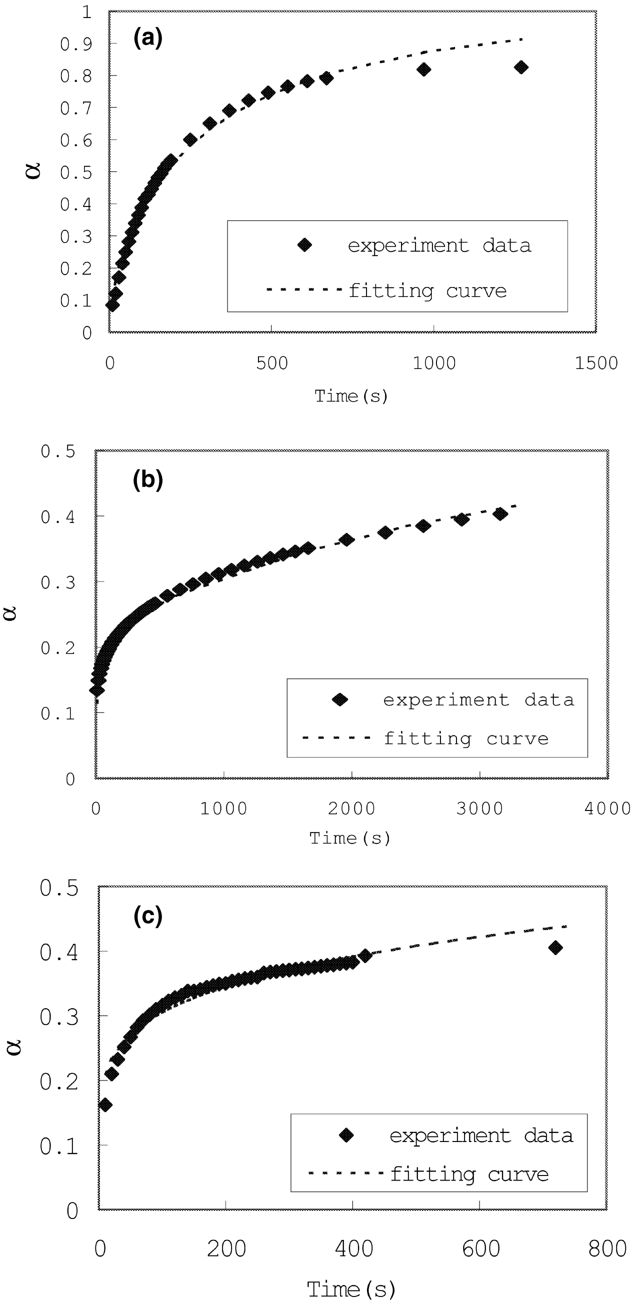

Fig. 3. Hydrogen absorption kinetics measured under 0.6 MPa at 353 K and their fitting curves for different alloys. (a) Melted MmM_5 alloy, (b) nano-phase composite of composition MmM_5–10% Mg and (c) nano-phase composite of composition MmM_5–30% Mg.

The error was estimated by factor *S*, the standard error, and *r*, the correlation coefficient, which are also given in Table 1. It can be seen from the values of *S* and *r* that the fitting is in good agreement with the experiment data.

Although Eq. (1) describes the nucleation and growth process of the hydriding reaction, the rate-controlling steps of the reaction are different with different values of *m*. For instance, the one-dimensional diffusion process and the three-dimensional interface reaction process correspond to an *m* value of 0.62 and 1.07, respectively [12]. From Fig. 3a we obtained that the kinetic curve can be well fitted using Eq. (1) and the value of *m* is about 0.63 (see Table 1), which is very close to 0.62. This result suggests that the hydriding of melted MmM_5 alloy at 353 K is likely to be a one-dimensional diffusion-controlled nucleation and growth process. With respect to MmM_5–10% Mg and MmM_5–30% Mg nano-phase composite alloys, the kinetic curve fits Eq. (2). This suggests that the hydriding of the nano-phase composite is likely to be an auto-catalytic process controlled reaction.

Kinetics measurements showed that temperature has an influence on the kinetics of the hydriding process. Fig. 4a and b show, respectively, the kinetic curves and their fitting curves for melted MmM_5 alloy and nano-phase composite of composition MmM_5–30% Mg measured at different temperatures. It can be seen from Fig. 4a that the hydriding rate increases with increasing reaction temperature. The fitting result shows that all three curves are in accordance with the rate equation of the nucleation and growth process (Avrami–Erofeev equation). However, the values of *m* for each curve are slightly different. As shown in Table 1 the value of *m* increases with decreasing reaction temperature. It is likely that there is a change in the rate-controlling step of the reaction as the reaction temperature varies. For the nano-phase composite alloys the effect of temperature is also clear. As can be seen from the data in Table 1, constants t_c and *k* decrease and increase, respectively, as the reaction temperature increases. This indicates that the auto-catalytic process is enhanced with increasing reaction temperature.

4. Discussion

The results of the hydriding reaction kinetics measurements and fitting described above indicate that the rate-controlling step of the hydriding process of melted MmM_5 alloys is different from that of the Mg-MmM_5 nano-phase composite prepared by MA. This is probably due to their different microstructural characteristics. For the melted MmM_5 alloy, the microstructure is a coarse grain single phase. In this case, the hydriding reaction is likely a process of hydride nucleation at the surface and growth into the interior of the alloy. To maintain hydride growth, a supplement of H atoms to the reaction front through the hydride phase is required. Since the grain is coarse, there are few easy paths, such as grain boundaries and interphase boundaries, for H atoms to diffuse to the reaction front. Thus, as suggested before, the diffusion of H is a limiting process.

For the nano-phase composite, the density of the inter-grain and interphase boundary is very high. As shown in Fig. 5, the microstructure of the composite obtained by milling MmM_5–30% Mg for 20 h is randomly distributed nanometer-sized MmM_5, Mm_2Mg_{17} and Mg phases. In

Table 1
Fitting results for hydriding kinetic curves of melted MmM_5 alloy and nano-phase composites of composition MmM_5–10% Mg and MmM_5–30% Mg

Material	Fitting equation	Parameters obtained by fitting						
		Reaction temp.	B	m	k	t_c	S	r
Melted MmM_5	(1)	290	0.006	0.82			0.016	0.997
		333	0.010	0.80			0.0245	0.994
		353	0.026	0.63			0.0259	0.993
MA MmM_5– 10% Mg	(2)	303			0.106	170.7	0.0296	0.874
		333			0.128	25.0	0.0378	0.923
		353			0.193	15.6	0.0518	0.996
MA MmM_5– 30% Mg	(2)	303			0.097	26.9	0.0329	0.844
		333			0.121	21.7	0.0158	0.94
		353			0.135	19.9	0.0124	0.97

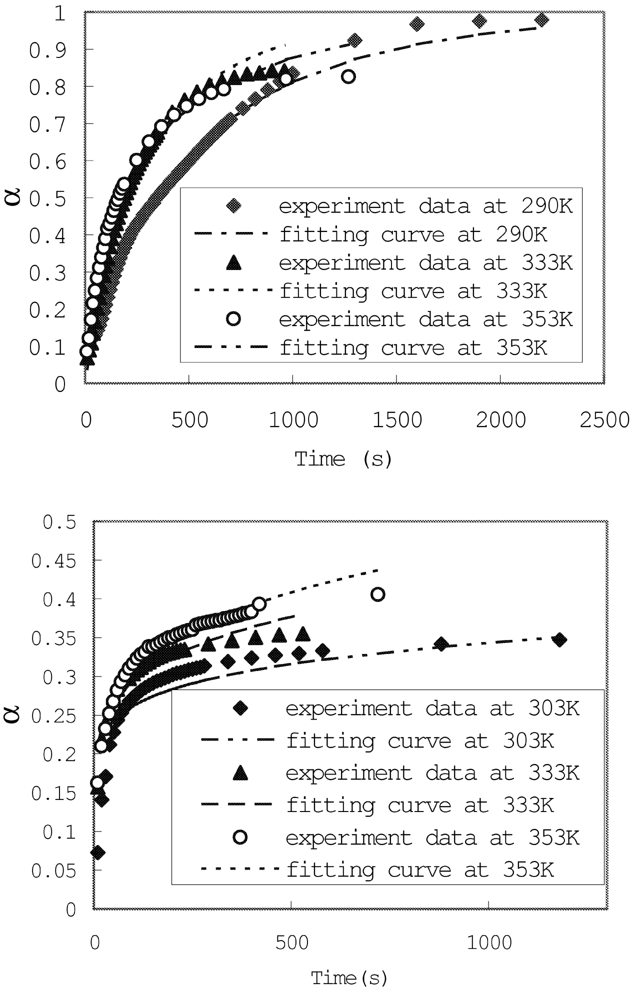

Fig. 4. Hydrogen absorption kinetic curves and their fitting curves measured at different temperatures. (a) Melted MmM_5 alloy and (b) nano-phase composite of composition MmM_5–30% Mg.

this case, H atoms can easily diffuse into the interior of the composite. Therefore, diffusion of H in the nano-phase composite is very fast and should not be a limiting process for the hydriding reaction. On the other hand, however, hydriding of the MmM_5 phase is much easier than that of the Mg or $MmMg_{17}$ phase. It is likely that the hydriding of the MmM_5 phase can catalyze the hydriding of the Mg and/or Mm_2Mg_{17} phase. This is due to the fact that a high density interphase boundary exists in the nano-phase composite, which is beneficial to the interaction between the different phases. The fitting of the kinetic curve agrees with the rate equation of the auto-catalysis process, implying that the limiting process of the hydriding of the nano-phase composite is a catalytic process. This phenomenon was also demonstrated for the Mg/La_2Mg_{17} composite [8]. In this sense, it is suggested that the improvement of the hydriding kinetic properties of Mg-based alloys by forming a nano-phase composite with alloys with good hydriding kinetics is due to the catalysis effect of the phase with good hydriding kinetics on the phases with poor kinetic properties.

5. Conclusions

The hydriding kinetics of melted MmM_5 alloy and nano-phase composite prepared by MA of MmM_5 and Mg were measured under isobaric conditions. The obtained kinetic curves were fitted using various rate equations derived from different hydriding reaction processes. It was found that the hydriding kinetics of the nano-phase composite is in agreement with the rate equation $\ln[\alpha/(1-\alpha)] = k(t-t_c)$ of the auto-catalysis reaction, while that of melted MmM_5 alloy is in agreement with the Avrimi–Erofeev rate equation, $\alpha = 1 - \exp(-Bt^m)$, of the nucleation and growth process. With increasing reaction temperature, the hydriding kinetics also varies. For the nano-phase composite, the constants t_c and k in the rate equation decrease and

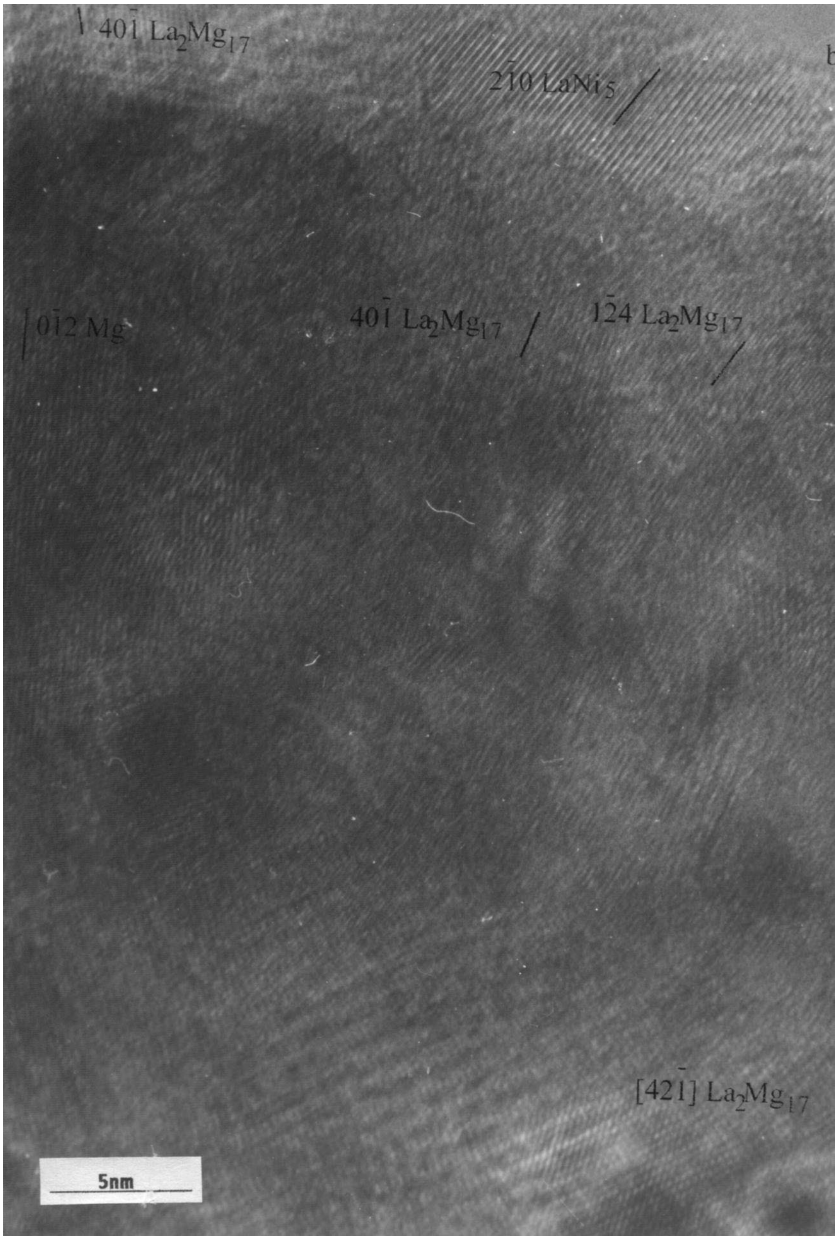

Fig. 5. HREM image of nano-phase composite alloys obtained by milling MmM_5–30% Mg for 20 h.

increase, respectively, with increasing reaction temperature. For the melted MmM_5 alloys, *m* decreases with increasing temperature.

Acknowledgements

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