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Hydrogen absorption of TiFe alloy synthesized by ball milling and post-annealing

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Abstract

The correlation of the hydrogen absorption properties to the phase structure of the TiFe alloys prepared by mechanical allying was investigated. In the mechanical alloying process, the crystalline or amorphous phases of TiFe alloy were formed. It found that TiFe amorphous phase recrystallized around 750 K. From the above results, the mixture of Ti and Fe prepared by short period ball milling was post annealed over 773 K. As the results, TiFe alloy was successfully synthesized. These TiFe alloys are able to absorb the hydrogen without activated treatment and it was found that the plateau pressure was controlled by post-annealing temperature.

Keywords: Mechanical alloying; Intermetallics; Thermal analysis; Hydrogen storage materials

1. Introduction

Mechanical alloying (MA) is able to synthesize various non-equilibrium alloys so that it has been widely applied to modify properties of a hydrogen storage alloy. In particular, there have been many reports about improving the hydrogen sorption properties by surface modification with catalysis [1–4]. It is well known that the TiFe alloy also is very difficult to be activated to hydrogen under normal conditions. High temperature and high pressure (∼773 K, 6.5 MPa) are necessary in order to start hydrogenation [5]. Improving this characteristic, the nano-crystalline and amorphous TiFe alloys synthesized by MA has been extensively studied [6,7] and recently these alloys were also applied for the Ni-MH batteries [8].

MA is an attractive method for developing of novel materials in shown above but there are actually problems. Because the alloying process generally needs long duration and high excess energy, i.e., mechanical energy and/or super cooling, to synthesize alloys. Contamination from ball or vessel, increase in temperature and sticking of powders to vessel or balls during mechanical alloying should have a great influence on the structures of the synthesized alloy [9,10]. It is, therefore, difficult to control the microstructure and hydrogen properties (pressure–composition curve) of alloys prepared by MA. This is very important issue practically.

In this study, TiFe alloy was synthesized by short period of ball milling and post-annealing at relatively low temperatures in order to solve these problems. This alloying process is discussed from the thermodynamic point of view and the relations between annealing temperature and hydrogen absorption properties of synthesized TiFe alloys was investigated.

2. Experimental

Fe and Ti powers, 99.5% of purity, smaller than 150 μm were mixed in an atomic ratio TiFe = 1:1. A mixture of the powders and stainless steel balls together were sealed in a stainless steel pot under the evacuated atmosphere (<10 Pa). The ball-to-sample ratio in weight was 40:1. The diameter of each ball was 12.1 mm. MA was carried out for maximum 40 h at a speed of 710 rpm and the MA system was water-cooled by high-power ball-milling apparatus (NEV-MA8, Nissin-Giken, Japan).

The samples prepared by ball-milling were removed from the pot in a glove box under argon. The samples were put into the stainless steel reactor and annealed for 3 h at 573 ∼ 873 K in the atmosphere of <10 Pa. Subsequently, the reactor was cooled gradually to room temperature. These samples continued to be subjected to the examination of hydrogen absorption properties in the same reactor for a Sieverts' type apparatus. The pressure–composition (P–C) isotherms were measured using a hydrogen gas with a purity of 99.99999%.

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The phases of the prepared samples were determined by X-ray diffraction (XRD) analysis. The microstructure and alloy composition were observed using scanning electron microscope equipped with an energy dispersive X-ray (SEM-EDX) analysis. The thermal stability of the phase was determined differential scanning calorimeter (DSC).

3. Results and discussion

3.1. TiFe alloy on MA process

Fig. 1 shows the XRD patterns of the TiFe mixtures mechanically alloyed with different milling times. After a milling time of 5 h, Fe and Ti peaks still are present, in particularly a strong Fe peak at $2\theta = 44^\circ$. After 10 h milling, the XRD pattern was dominated by peaks from TiFe phase. In fact, the height of the Fe and Ti peaks became the background level. Moreover, when MA proceeded longer, the sample milled for 20 h seemed to become amorphous and milling for 40 h yielded crystallization of TiFe. However, the peaks form TiFe phase for MA 40 h is slightly broadened compared with those for MA 10 h. The lattice parameter of the TiFe for MA 10 h and 40 h estimated to be 2.982 Å, 2.987 Å, respectively.

Fig. 2 shows the collecting efficiency of samples after ball-milling for various times. This result is well consistent to the result of XRD analysis. When the XRD peaks of TiFe phase appeared clearly, the collection efficiency always is very low because the powders stuck on the inside surface of the vessel and ball surface. On the other hand, when XRD patterns show broad peaks implying the existence of the amorphous phase, the efficiency is good every time. The SEM images of prepared powders are shown in Fig. 3. The surface morphology of crystalline TiFe alloy synthesized by MA 10 h is equivalent to that of mixture for MA 5 h. The particle size of these samples is less than 100 μm. The particle of the amorphous TiFe alloy by MA 20 h is the agglomerate less than 10 μm consisted of the minimum 2–3 μm powders. In addition, the chemical composition of the samples milled with differential time was determined and shown in Table 1. The contents of Cr, respectively were 0.4, 1.6, 4.7 at.% for MA 5 h, 10 h, 20 h. The contamination of Cr to the

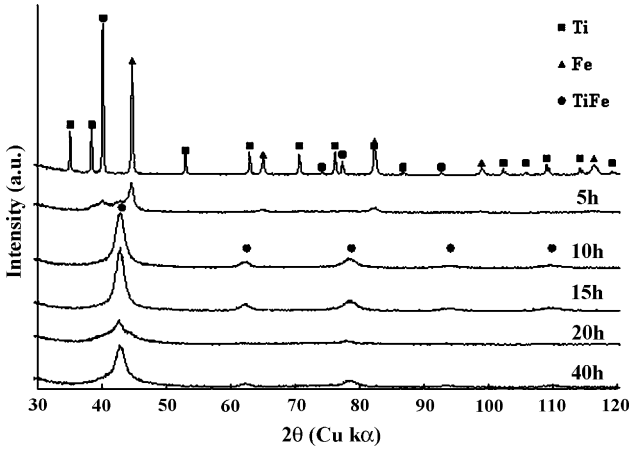

Fig. 1. XRD patterns of the TiFe mixtures mechanically alloyed with different milling times.

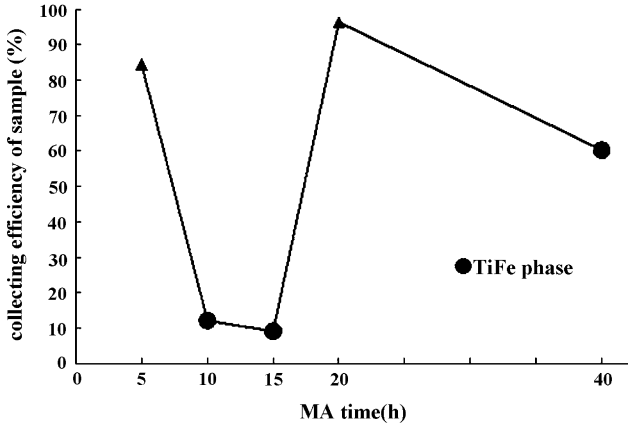

Fig. 2. The collecting efficiency of samples after ball-milling for various times.

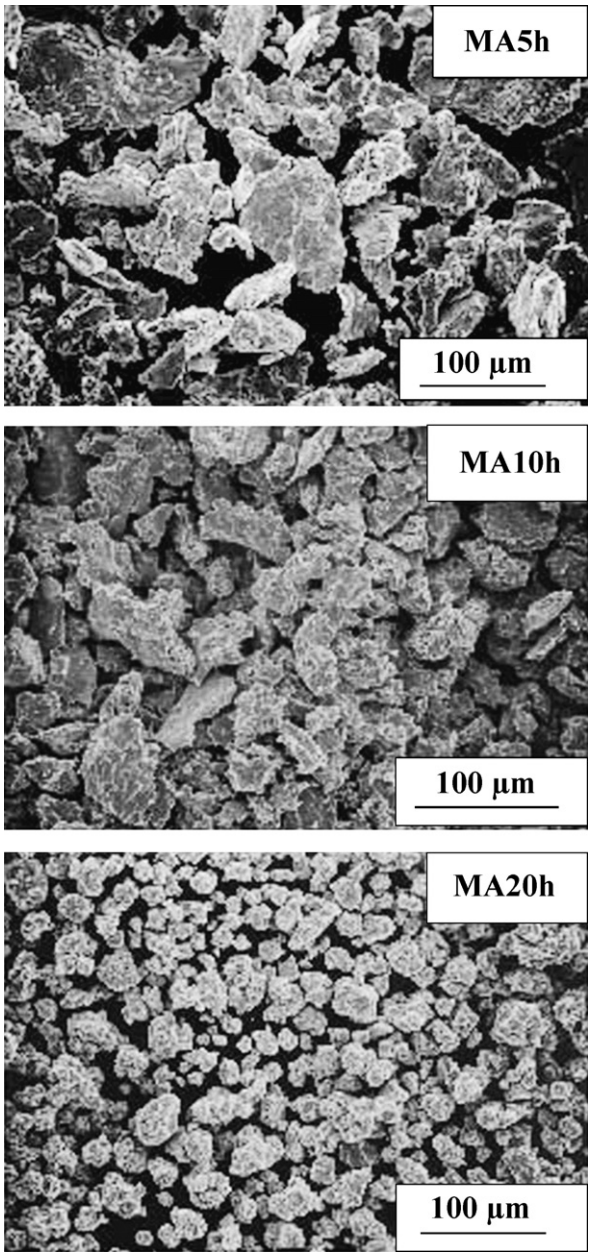

Fig. 3. SEM observations of TiFe alloy powders milled for various times.

Table 1
Chemical composition of the sample milled for various times (at.%)

Milling time (h)	Ti	Fe	Cr
5	51.4	48.2	0.4
10	53.0	45.4	1.6
20	55.7	39.6	4.7

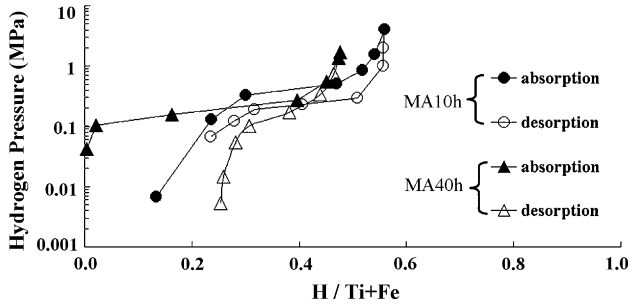

Fig. 4. Pressure–composition isotherms at 295 K of TiFe alloy synthesized by MA for 10 h, 40 h.

sample powders from stainless steel vial and balls increased with milling time. From these results, the contents of contamination and the particle size seem to be related to the milling time so that longer MA should not be favorable.

Fig. 4 shows P–C curves on two samples prepared for MA for 10 and 40 h. Both samples are able to absorb hydrogen readily after heat treatment at 573 K for 3 h. However, the TiFe prepared by MA 40 h could not desorb hydrogen completely. This indicated that the hydride of TiFe synthesized for longer milling time is stable, corresponding to lower plateau pressure. Furthermore, the structural difference of TiFe alloys prepared by MA was studied by DSC, as shown in Fig. 5. The DSC curves of all sample show an exothermic peak around 750 K. These DSC peaks from an amorphous phase prepared by MA 20 h are sharp but the peak sharpness from mixture for MA 5 h is equivalent to that from TiFe alloys synthesized by MA 10 h and 40 h. From

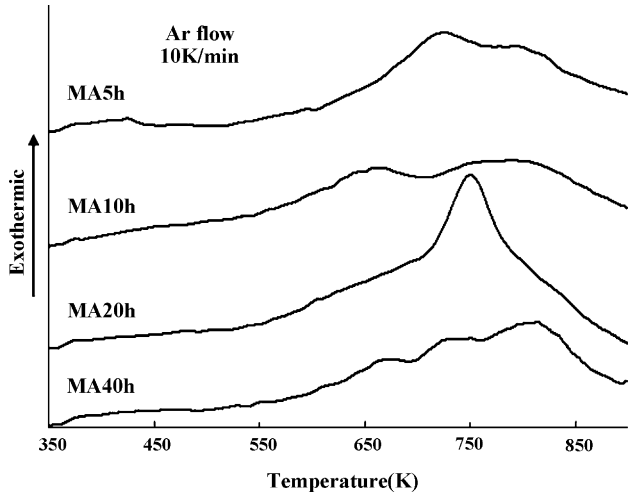

Fig. 5. DSC curves of TiFe alloyed mechanically for various times.

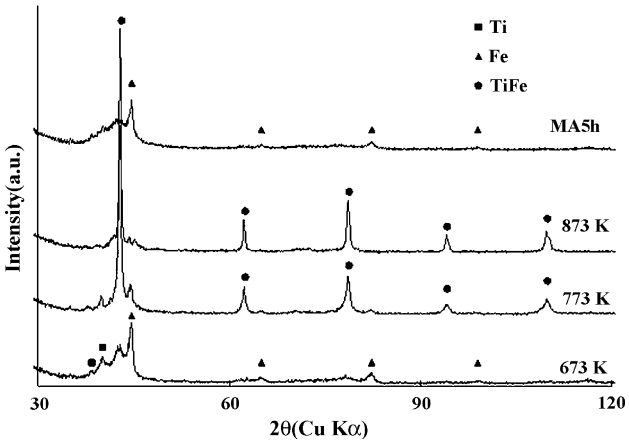

Fig. 6. XRD patterns of the samples annealed for 3 h at various temperatures after MA 5 h.

these results, the sample mechanically alloyed recrystallized at about 750 K.

3.2. TiFe alloy on short ball-milling and annealing

Based on the result of DSC, we tried to synthesize TiFe alloy by post-annealing after short period of ball milling, i.e., MA 5 h. The XRD patterns of TiFe alloys after annealing at different temperatures for MA 5 h are shown in Fig. 6. These results imply to synthesize TiFe alloy even from the mixture of Ti and Fe after annealing over 773 K. This condition of MA 5 h is utilized well because the collection efficiency of samples powder is relatively good (over 85%) as shown in Fig. 2 and the influence of contamination is relatively low as shown in Table 1.

Fig. 7 shows hydrogen absorption properties of TiFe alloy synthesized after annealing at various temperatures. These samples synthesized after annealing was continuously examined the hydrogen properties in same reactor as mentioned previously. These samples are able to absorb hydrogen ready without initial activation treatment at room temperature. The initial hydrogenation behavior of TiFe alloy was found to be markedly improved compared with a conventional TiFe alloys produced by induction melting.

The sample annealed at 673 K does not exhibit plateau clearly. However, when the annealing temperature is raised, the sample

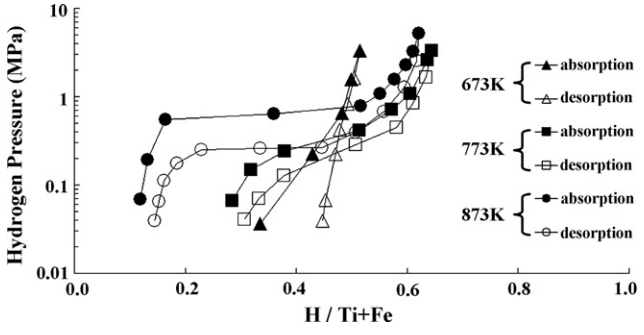

Fig. 7. Pressure–composition isotherms at 295 K of TiFe alloy synthesized by annealing for various temperatures after MA 5 h.

begins to appear plateau gradually. This is well consistent to the XRD results that crystalline TiFe is gradually generated. Finally, the maximum hydrogen storage capacity of TiFe alloy synthesized was about H/Ti + Fe = 0.64 (1.25 wt.%) at 5 MPa H_2. This is approximately the same as maximum value (H/Ti + Fe = 0.56, 1.09 wt.%) of the samples synthesized by MA 10 h in Fig. 4.

In these results, the TiFe alloy synthesized by milling for a longer time seems to have lower plateau pressure. However, the amount of utilized hydrogen reversibly is also low. Solving this problem, post-annealing at lower than 873 K could be effective so that wide plateau area without declining the hydrogen capacity should be obtained. The maximum plateau pressure is about 1.0 MPa for TiFe prepared by the combination of ball milling and post-annealing.

4. Conclusions

The hydrogenation properties (P–C curve) of TiFe alloys prepared by MA is not easily controlled because the phase transformation of crystallization and amorphous repeated on MA process. In this study, we have successfully synthesized TiFe alloys from the mixture of Ti and Fe by short ball milling and post-annealing at higher than 773 K. Using this method, the produced alloys are able to absorb hydrogen without initial activation and be controlled plateau pressure by annealing temperature.

Acknowledgements

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