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# Microstructure and hydrogen absorption properties of nano-phase composite prepared by mechanical alloying of $\text{MmNi}_{5-x}(\text{CoAlMn})_x$ and Mg

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## Abstract

In this work high energy ball milling was used to prepare composite hydrogen storage alloy in the  $\text{MmNi}_{5-x}\text{M}_x\text{-Mg}$  system. X-ray diffraction and TEM analysis were used to characterise the microstructure of the composite alloy obtained by ball milling. It has been shown that the grain size of  $\text{MmNi}_{5-x}\text{M}_x$  and Mg components were reduced to nanometre range after about 20 h of milling. Besides, a  $\text{Mm}_2\text{Mg}_{17}$  phase of nanometre size was also formed in the milling process. Thus, a composite alloy, referred to as nano-phase composite here, composed of  $\text{MmNi}_{5-x}\text{M}_x$ , Mg and  $\text{Mm}_2\text{Mg}_{17}$  phase of nanometre size was obtained. Hydrogen storage behaviour of the nano-phase composite was compared with that of conventional  $\text{MmNi}_{5-x}\text{M}_x$  alloy by measuring PCT and kinetics. It showed that the hydrogen absorption properties were improved. © 1999 Elsevier Science S.A. All rights reserved.

**Keywords:** Hydrogen storage alloys;  $\text{MmNi}_5\text{-Mg}$  composite; Mechanical alloying; Nanocrystalline alloys

## 1. Introduction

Since the development of hydrogen storage alloys, such as  $\text{LaNi}_5$ ,  $\text{ZrV}_2$ ,  $\text{FeTi}$  and Mg systems, a lot of effort has been devoted to improve the properties of these alloys by various methods, such as alloy addition [1], surface treatment [2], rapid solidification [3] and mechanical alloying (MA) [4]. Particularly, the synthesis of nanocrystalline hydrogen storage alloys, such as  $\text{TiFe}$  [5],  $\text{LaNi}_5$  [6] and  $\text{Mg}_2\text{Ni}$  [7], by MA has been of great interest in recent years. This is due to the fact that MA is a convenient way of manufacturing nanocrystalline materials in large quantity, and to the consideration that nanocrystalline structure induced by MA may improve the properties of hydrogen storage alloys because nanocrystalline materials have a very high volume ratio of boundary region. Indeed, activation was much easier or even unnecessary for hydrogen storage alloys prepared by MA. To a certain extent, however, most of the hydrogen storage alloys could not satisfy the multiple requirements of practical applications. For instance, hydrogen absorption capacity of Mg is the largest among the hydrogen storage alloys developed so far, but it absorbs/desorbs hydrogen at high temperature

and its kinetics is poor, which limits its application. On the other hand,  $\text{MmNi}_5$  alloys exhibit good hydrogen absorption/desorption kinetics, but its hydrogen storage capacity is not high with relatively higher specific weight. There were many attempts to synthesise composite hydrogen storage alloys in trying to obtain alloys with better comprehensive properties [8,9]. It was speculated that the advantages of hydrogen storage properties of constituent phases could be combined well in nano-phase composite for there is very high volume ratio of boundary region in nanocrystalline materials. In this work nano-phase composite hydrogen storage alloy was prepared by mechanical alloying of Mg and  $\text{MmNi}_{5-x}(\text{CoAlMn})_x$  (denoted as  $\text{MmNi}_{5-x}\text{M}_x$  here). The microstructure and hydrogen storage properties were investigated.

## 2. Experimental procedures

$\text{MmNi}_{5-x}\text{M}_x$  alloy was prepared by induction melting under protection of pure argon. The ingot was crushed to powder with dimensions of about 1–2 mm. The Mg used was commercial powder with purity of 99.9% and size of 100 mesh. Powder mixtures with composition of  $\text{MmNi}_{5-x}\text{M}_x-x$  wt.% Mg ( $x=5, 10, 30, 50$ ) were prepared for composite alloy by high energy ball milling. The

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milling process was performed by sealing the powder mixture in a stainless steel vial together with hardened steel balls in a glove box filled with argon. The weight ratio of ball to powder was 10:1. Ball milling was carried out using a Fritsch P-5 planetary ball mill with rotational speed of 150 rev./min. X-ray diffraction and TEM analysis were used to characterise the microstructure of the milled sample. The X-ray diffractometer and TEM used were a Rigaku D/MAX-RC with Cu  $K_{\alpha}$  radiation and a JEM-100cx TEM, respectively. The preparation of thin foil for TEM observation is similar to that described before [10]. Hydrogen absorption properties of samples were evaluated by measuring pressure–composition–temperature relation (PCT) and hydrogen absorption kinetics using a gas flow counter together with pressure gauge at different temperatures.

### 3. Results and discussions

#### 3.1. Microstructure of nano-phase composite obtained by MA

X-ray diffractograms a, b and c placed in Fig. 1 were obtained from  $MmNi_{5-x}M_x-10\%Mg$ ,  $MmNi_{5-x}M_x-30\%Mg$  and  $MmNi_{5-x}M_x-50\%Mg$  powder mixtures milled for 20 h. The X-ray diffractogram d of  $M_x-30\%Mg$  milled for 0.5 h, which was used as reference state, was also placed in Fig. 1 for comparison. It can be seen that diffraction patterns broadened apparently after milling,

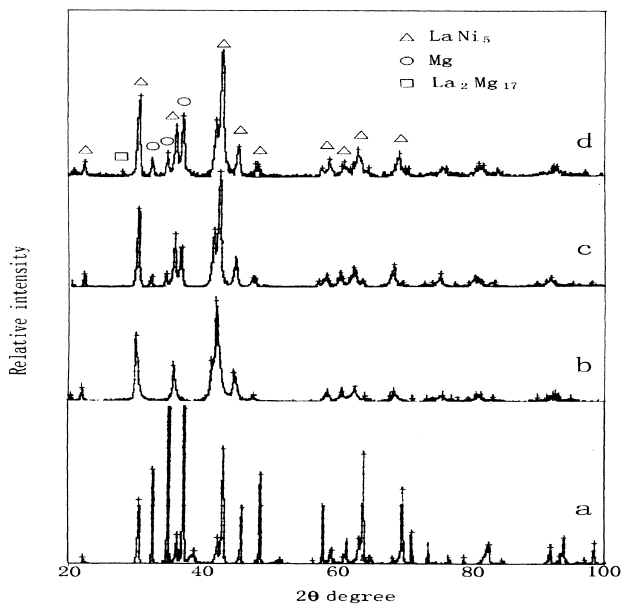


Fig. 1. X-ray diffractograms of  $MmNi_{5-x}M_x-30\%Mg$  powder mixture milled for 0.5 h (a),  $MmNi_{5-x}M_x-10\%Mg$  powder mixture milled for 20 h (b),  $MmNi_{5-x}M_x-30\%Mg$  powder mixture milled for 20 h (c) and  $MmNi_{5-x}M_x-50\%Mg$  mixture milled for 20 h (d).

which indicates the apparent reduction of grain size and increment of internal strain of components phases. The grain size of  $MmNi_{5-x}M_x$  and Mg components of  $MmNi_{5-x}M_x-30\%Mg$  milled for 20 h, for instance, reached 23 and 16 nm, respectively, as estimated from broadening of full width at half maximum of diffraction peaks [11]. In other words, nanocrystalline composite of  $MmNi_{4.5}M_{0.5}$  and Mg was obtained by high energy ball milling. It should be pointed out, however, that the Mg content has a strong influence on the grain size of  $MmNi_{4.5}M_{0.5}$  phase. The grain size of  $MmNi_{4.5}M_{0.5}$  phase increased as the Mg content increased. This is owing to the fact that Mg is softer than  $MmNi_{4.5}M_{0.5}$  phase. It is likely that Mg acted as a buffer to the impact to  $MmNi_{5-x}M_x$  phase in the milling process.

Analysing Fig. 1 in more detail, it can be noted that the relative intensity of the diffraction peaks of Mg reduced in comparison with that of  $MmNi_{5-x}M_x$  as milling proceeded. Meanwhile, the diffraction pattern of  $La_2Mg_{17}$  phase appeared (since  $MmNi_{5-x}M_x$  was used, the phase formed in the milling process was actually  $Mm_2Mg_{17}$  phase). The formation of  $Mm_2Mg_{17}$  phase was further proved by TEM observation. The morphology and corresponding electron diffraction pattern obtained from  $MmNi_{5-x}M_x-10\%Mg$  milled for 20 h is given in Fig. 2. Fig. 2a is a bright field image. Fig. 2b is the diffraction pattern corresponding to Fig. 2a and the indexing of it. The indexing of the electron diffraction pattern clearly verified the presence of  $MmNi_{5-x}M_x$ , Mg and  $Mm_2Mg_{17}$  phases. The dark field images formed by taking a set of diffraction halo of  $Mm_2Mg_{17}$  and  $LaNi_5$ , respectively, are given in Fig. 2c and d. It can be seen that the grain size is about the same order as that obtained from X-ray diffraction analysis. Thus, we obtained a composite alloy composed of nanometre-sized  $MmNi_{5-x}M_x$ , Mg and  $Mm_2Mg_{17}$  phases, which we refer to as nano-phase composite.

The formation of  $Mm_2Mg_{17}$  phase meant that solid state reaction between  $MmNi_{4.5}M_{0.5}$  and Mg took place in the milling process. The mechanism of the reaction is likely similar to that previously reported in many systems [12,13]. It was probably that part of the Mm atom in  $MmNi_{4.5}M_{0.5}$  was caught by Mg to form  $Mm_2Mg_{17}$ . This consideration was further supported by measurement of the lattice constant. The lattice constant of  $LaNi_5$  phases in  $MmNi_{5-x}M_x-30\%Mg$  powder mixture milled for different times was measured by using pure silicon powder as inner indexing standard and the result is shown in Fig. 3. It can be seen that the lattice constant  $a$  and  $c$  decreases as the milling time increases. According to Ref. [14], the atomic radius of La and Ni are 0.187 and 0.125 nm, respectively. Therefore, the lattice constant should decrease if the atom ratio of the bigger atom, Mm is less than the stoichiometric ratio of  $LaNi_5$  phase. In other words, the reduction of lattice constant of  $MmNi_{5-x}M_x$  phase with the proceeding of milling meant that part of the Mm atom was caught by the Mg atom and formed  $Mm_2Mg_{17}$  phase. The  $Mm_2Mg_{17}$

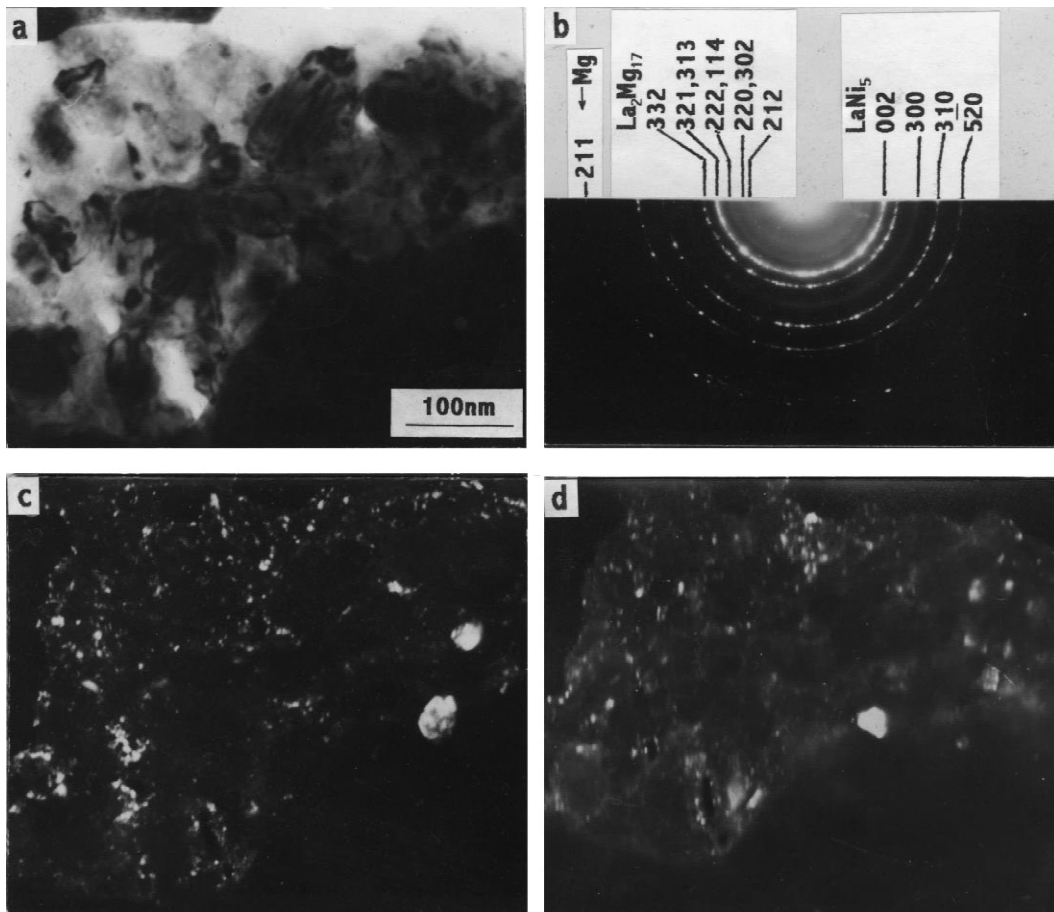


Fig. 2. Morphology and electron diffraction pattern of  $\text{MmNi}_{5-x}\text{M}_x-10\%\text{Mg}$  powder mixture milled for 20 h, (a) bright field image, (b) electron diffraction pattern, (c) dark field image formed by a set of 222 reflection halo of  $\text{La}_2\text{Mg}_{17}$ , (d) dark field image formed by a set of 300 reflection halo of  $\text{MmNi}_{4.5}\text{M}_{0.5}$ .

phase may also be formed by another mechanism. For instance, if the reaction  $\text{MmNi}_5 + \text{Mg} \rightarrow \text{Mm}_2\text{Mg}_{17} + \text{Mg}_2\text{Ni}$  took place in the milling process,  $\text{Mm}_2\text{Mg}_{17}$  phase should be formed also. Further investigation has been undertaken

to clarify the mechanism for the formation of  $\text{Mm}_2\text{Mg}_{17}$  phase.

### 3.2. Hydrogen absorption behaviour of the nano-phase composite

The nano-phase composite obtained by mechanical alloying of  $\text{MmNi}_{5-x}\text{M}_x$  and Mg exhibited different hydrogen storage behaviour in comparison with the conventional  $\text{MmNi}_{5-x}\text{M}_x$  sample. First of all, the activity of the nano-phase composite obtained by ball milling was much better than that of conventional  $\text{MmNi}_{5-x}\text{M}_x$  sample. For the former one, it absorbed hydrogen almost immediately when exposed to hydrogen at room temperature and activation treatment was not necessary. For the latter one, several activation cycles were required before it started to absorb hydrogen. Besides, the hydrogen absorption kinetics of the nano-phase composite prepared by ball milling was also much better than that of conventional  $\text{MmNi}_{5-x}\text{M}_x$  sample. Fig. 4 shows the hydrogen absorption kinetic curves, which were obtained by keeping a constant hydrogen pressure of 0.55 MPa in the sample

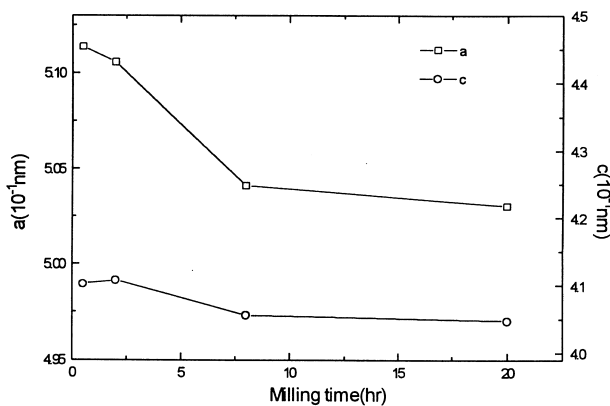


Fig. 3. Dependence of lattice constant of  $\text{MmNi}_{4.5}\text{M}_{0.5}$  phase on time of milling obtained in  $\text{MmNi}_{5-x}\text{M}_x-30\%\text{Mg}$  powder mixture.

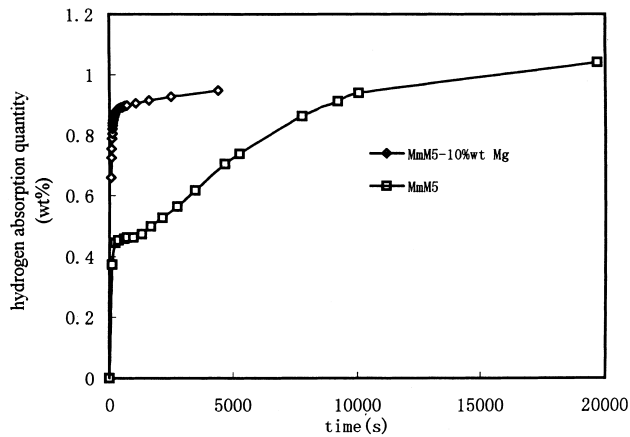


Fig. 4. Hydrogen absorption kinetic curve of as-melted  $\text{MmNi}_{5-x}\text{M}_x$  alloy and  $\text{MmNi}_{5-x}\text{M}_x-10\%\text{Mg}$  milled for 20 h.

chamber at  $30^\circ\text{C}$ , of  $\text{MmNi}_{5-x}\text{M}_x-10\%\text{Mg}$  powder mixture milled for 20 h and conventional  $\text{MmNi}_{5-x}\text{M}_x$  sample. It can be seen that absorption speed of the former is about 10 times faster than that of the latter. The great improvement of activity and kinetics of the ball milled sample is probably due to the fact that nanostructure was induced into the sample. The high ratio of interface and grain boundary of nano-phase composite resulted in high chemical activity and high density and easy diffusion path for the hydrogen atom.

Fig. 5 shows the PCT curves, which were measured at the temperature indicated inside the figure, of the nano-phase composite of different Mg content prepared by 20 h of milling. The PCT curve of the conventional  $\text{MmNi}_{5-x}\text{M}_x$  alloy was also placed in this figure for comparison. It is evident that the PCT curve of nano-phase composite prepared by ball milling differs from that of conventional  $\text{MmNi}_{5-x}\text{M}_x$  alloy in the following two aspects. The first difference is that the hydrogen absorption capacity of the nano-phase composite is larger than the

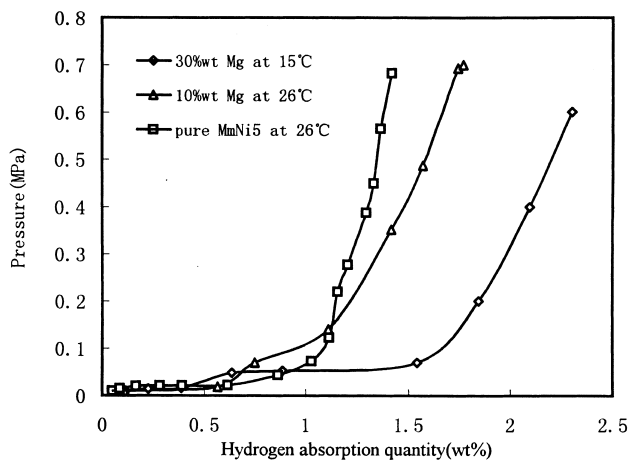


Fig. 5. PCI curves of hydrogen absorption of as-melted  $\text{MmNi}_{5-x}\text{M}_x$  (a),  $\text{MmNi}_{5-x}\text{M}_x-10\%\text{Mg}$  milled for 20 h (b),  $\text{MmNi}_{5-x}\text{M}_x-30\%\text{Mg}$  milled for 20 h (c).

conventional  $\text{MmNi}_{5-x}\text{M}_x$  alloy. Taking the hydrogen absorption capacity at 0.6 MPa, it is 1.25%, 1.7% and 2.3% (wt.%) for the conventional  $\text{MmNi}_{5-x}\text{M}_x$  alloy, nano-phase composites obtained by milling mixture of  $\text{MmNi}_{5-x}\text{M}_x-10\%\text{Mg}$  and  $\text{MmNi}_{5-x}\text{M}_x-30\%\text{Mg}$  for 20 h, respectively. This result means that Mg mechanically alloyed with  $\text{MmNi}_{5-x}\text{M}_x$  has substantial contribution to the hydrogen absorption. As described before, however, the Mg was in the form of  $\text{Mm}_2\text{Mg}_{17}$  and Mg phase. The exact role they played is not clear at the moment, and how the  $\text{MmNi}_{5-x}\text{M}_x$ ,  $\text{Mm}_2\text{Mg}_{17}$  and Mg phases interacted with each other in the course of hydrogen absorption. Anyway, it is likely that mechanical alloying of  $\text{MmNi}_{5-x}\text{M}_x$  with Mg makes Mg, maybe not in the form of pure Mg but other Mg-containing phases, that participate in hydrogen absorption at room temperature. This is really a very interesting result considering that Mg normally absorbs hydrogen at about  $300^\circ\text{C}$ . The second difference is that there are two plateaus in the PCT curve of the nano-phase composite prepared by ball milling. This was also evidence that the hydrogen was absorbed by two different phases. The lower pressure plateau in the PCT curve of the nano-phase composite prepared by milling is close to the pressure plateau of the as-melted  $\text{MmNi}_{5-x}\text{M}_x$ , which indicates that the lower pressure plateau in the PCT curve of nano-phase composite corresponds to hydrogen absorption by  $\text{MmNi}_{5-x}\text{M}_x$ . With respect to the higher pressure plateau, it is not clear yet whether Mg or  $\text{Mm}_2\text{Mg}_{17}$  phase is responsible for it. Further investigation is required to fully understand the situation.

The PCT curves of the nano-phase composite at different temperatures were also measured. Fig. 6 is the result obtained in  $\text{MmNi}_{5-x}\text{M}_x-30\%\text{Mg}$  mixture milled for 20 h. The enthalpy of reaction corresponding to the lower and higher pressure plateau was calculated according to the Van't Hoff equation. The enthalpy corresponding to lower and higher pressure plateau is 19.5 and 22.1 kJ/mol,

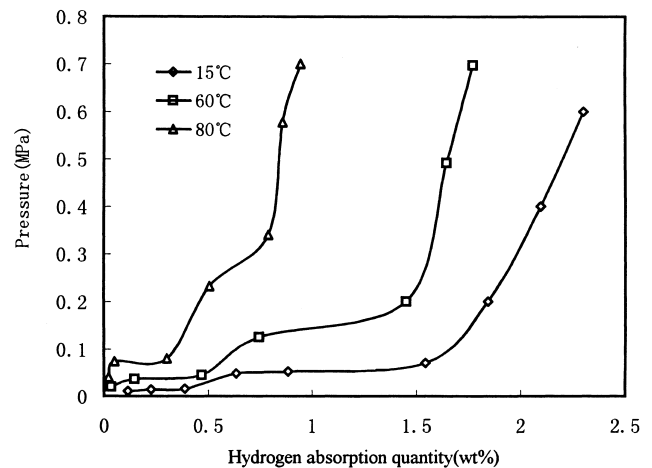


Fig. 6. PCI curves of hydrogen absorption of  $\text{MmNi}_{5-x}\text{M}_x-30\%\text{Mg}$  milled for 20 h measured at different temperatures: (a)  $15^\circ\text{C}$ , (b)  $60^\circ\text{C}$  and (c)  $80^\circ\text{C}$ .

respectively. The reaction enthalpy of the as-melted  $\text{MmNi}_{5-x}\text{M}_x$  is 18.5 kJ/mol. It can be seen that the reaction enthalpy corresponding to the lower pressure plateau in the PCI curve of nano-phase composite is close to that of as-melted  $\text{MmNi}_{5-x}\text{M}_x$ . This gave further support to the statement that the lower pressure plateau in the PCI curve of nano-phase composite was related to the hydrogen absorption by  $\text{MmNi}_{5-x}\text{M}_x$  phase.

#### 4. Conclusions

In this work, high energy ball milling was used to prepare a nano-phase composite in  $\text{MmNi}_{5-x}\text{M}_x$ -Mg system. Based on the experimental results obtained from X-ray diffraction analysis, TEM observation and hydrogen storage properties evaluation, the following conclusions can be made.

1.  $\text{Mm}_2\text{Mg}_{17}$  phase has been formed by solid state reaction between  $\text{MmNi}_{5-x}\text{M}_x$  and Mg in the ball milling process.
2. Nano-phase composite consisting of  $\text{MmNi}_{5-x}\text{M}_x$ , Mg and  $\text{Mm}_2\text{Mg}_{17}$  phases has been obtained by ball milling. The grain size of the phases is about 20 nm.
3. Hydrogen absorption kinetics of nano-phase composite is much better than that of conventional  $\text{MmNi}_{5-x}\text{M}_x$  alloy.
4. There are two pressure plateaus in the PCI curve of the nano-phase composite and the hydrogen absorption capacity of the nano-phase composite is much bigger than that of as-melted single phase  $\text{MmNi}_{5-x}\text{M}_x$ .

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