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Influences of misch metal on hydrogen storage properties of $FeTi_{1.3}$ alloy①

Ma Jianxin(马建新), Pan Hongge(潘洪革), Chen Yun(陈 昀),
Wang Xinhua(王新华), Chen Changpin(陈长聘)
Department of Materials Science and Engineering,
Zhejiang University, Hangzhou 310027, P.R. China

Abstract: The influences of misch metal (Mm) on the hydrogen storage properties of $FeTi_{1.3}$ alloy have been studied in detail. The results show that the activation behavior of the alloy can be improved dramatically when a small quantity of Mm is added. It suggested that this activation behavior is due to the cracks, which was produced in the FeTi matrix by the expansion of misch metal inclusions coming from preferential hydrogen absorption. As a result, FeTi phase with fresh oxide-free surfaces through which hydrogen can be absorbed easily is provided. In addition, hydrogen storage properties of alloy can be influenced by Mm content. The results show that the overall hydrogen storage properties of $FeTi_{1.3}$ + 6.0% Mm alloy are the best among all alloys studied.

Key words: mischmetals; FeTi alloy; hydrogen storage alloys; activation **Document code**: A

1 INTRODUCTION

It is well known that the FeTi alloy has many favorable characteristics for hydrogen storage application, such as high hydrogen storage capacity, good thermodynamics properties and low material cost. But the activation behavior of FeTi alloy is rather poor. It has to be activated by heating up to 670 K in a hydrogen atmosphere or in vacuum, followed by cooling to room temperature and by applying high-pressure hydrogen[1~3]. Poor activation behavior of FeTi alloy has impeded its applications. How to make the activation behavior of FeTi alloy better becomes an important research subject in the field of metal hydride.

It is generally accepted that one of the major factors affecting the activation behavior of FeTi alloy is a passive oxide layer formed easily on the surface of alloy which makes a baffling between H_2 and the material. Up to now a number of mechanisms of activation of FeTi alloy have been proposed. Schlapbach *et al*[4] proposed the surface segregation theory in which the existence of metallic iron clusters on activated FeTi alloy surface is believed to be the catalytic centers for hydrogen absorption. Schober *et al*[5] considered that some ordered oxides i. e. $FeTiO_x$ and TiO_2 formed on the surface of the activated alloy are the catalytic active centers during hydrogenation reaction. There are some measures which can improve the activation behavior of FeTi alloy, such as alloying with other elements, for example Mn, Cr, Co etc[6~8], surface chemical treatment with acid and alkali[9] and mechanical alloying[10]. Alloying is thought to be the most effective way among them to improve the activation behavior of FeTi alloy.

The activation behavior of FeTi alloy can also be improved by excessive Ti in FeTi alloy[11] or by the addition of a small quantity of Mm[12]. The alloy modified by Ti or Mm can absorb hydrogen at room temperature without any previous activation treatments. But at same time it

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worsens some other hydrogen storage properties such as a decreased hydrogen storage capacity and a sloped plateau.

In this paper, the influences of misch metal (Mm) on the hydrogen storage properties of $FeTi_{1.3}$ alloy are studied.

2 EXPERIMENTAL

The raw materials used are iron (purity 99.5%) and titanium (purity 99.5%). The composition of misch metal (Mm) is listed in Table 1. The specimens were prepared in an induced furnace with copper crucible in an argon atmosphere. The ingots were turned and remelted four times in order to get a good homogenization. No further annealing or homogenization of these alloys was conducted. After being ground into powder in air, the hydrogen storage properties of the specimens were tested immediately. The purity of hydrogen used in the experiment is 99.999%.

Table 1 Composition of misch metal(%)

La	Ce	Pr	Nd	Fe	Ca
24.26	51.75	6.08	18.11	2.26	<0.01

The hydriding rate was measured using a conventional high-pressure volumetric system[13]. For each run, about 10 g of alloy powder were loaded into a reactor, then the reactor was sealed and evacuated to 0.1 Pa. Hydrogen gas at 4.0 MPa was then introduced into the reactor. The pressure change of hydrogen was recorded as a function of time by sensor and X—Y recorder. During dehydrogenation, the reactor was heated by the water bath followed by evacuation.

The microstructures of as-cast ingots were investigated by optical metallography.

3 RESULTS

3.1 Effect of Mm content on hydriding rate of alloys

One of the key parameters characterizing the activation behavior of hydrogen storage materials is the initial hydriding rate of alloy without any previous activation treatment at room temperature. Fig. 1 shows the initial hydriding curves of the $FeTi_{1.3} + x\%Mm(x = 1.5, 3.0, 4.5, 6.0)$ alloys at room temperature under an initial hydrogen pressure of 4.0 MPa. In the graph the hydrogen storage capacity of alloy, which is expressed as the ratio of hydrogen atoms to the total number of metal molecule (H/M), is plotted against the reaction time. It can be seen that, all alloys began to absorb hydrogen at an increasing rate after a short incubation period and the rate slowed down again before approaching the saturated hydrogen content. The incubation time changed as the Mm content increased. For example, the incubation time is 25, 15, 8, 12 min with x being 1.5, 3.0, 4.5, 6.0, respectively. It indicated that when the Mm content is smaller than the critical value 4.5%, the incubation time becomes short with increasing the Mm content, while the Mm content further increases, the incubation time becomes longer instead. The incubation time of the $FeTi_{1.3} + x\%$ Mm alloys is rather short in comparison with that of $FeTi_{1.3}$ alloy. In a word, the activation behavior of alloy is improved dramatically and the incubation period is shortened when a small quantity of Mm is added to $FeTi_{1.3}$ alloy.

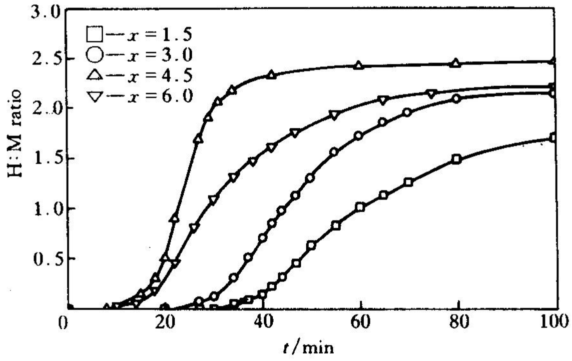

Fig.1 Initial hydriding curves of $FeTi_{1.3} + x\%Mm(x = 1.5, 3.0, 4.5, 6.0)$ alloys at room temperature(298 K)

After the first cycle of hydrogenation and dehydrogenation, the hydrogen absorption rates for these alloys become very rapid. The hydriding rates of $FeTi_{1.3}$ + x% Mm(x = 1.5, 4.5) alloys in different absorption-desorption cycles are shown in Fig.2 and Fig.3. The results show that all the alloys could be fully activated only through two or four cycles at room temperature under the initial hydrogen pressure of 4.0 MPa, while about ten cycles were required for FeTi alloy under the same conditions.

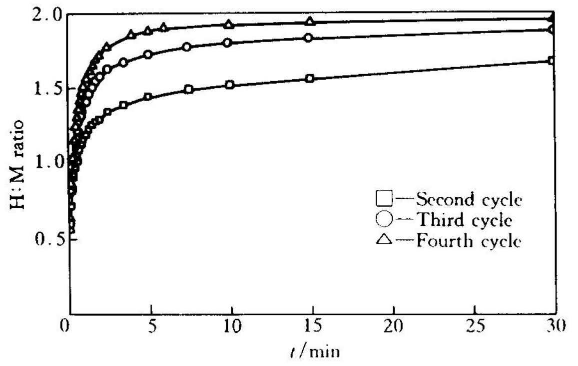

Fig.2 Hydriding curves of $FeTi_{1.3}$ + 1.5% Mm alloy after different cycles at room temperature (298 K)

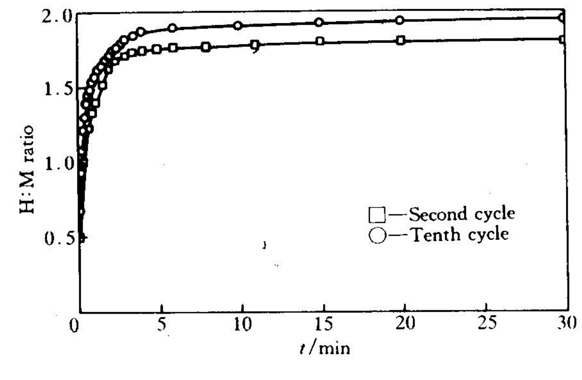

Fig.3 Hydriding curves of $FeTi_{1.3}$ + 4.5% Mm alloy after different cycles at room temperature(298 K)

3.2 Effect of Mm content on hydrogen storage capacities of alloys

Hydrogen storage capacities of $FeTi_{1.3}$ + x% Mm(x = 1.5, 3.0, 4.5, 6.0) alloys after different absorption-desorption cycles are listed in Table 2. The results show that the initial absorption capacities of all alloys are larger than that of the second cycle, which indicate that stable hydrides are formed during the first hydrogenation. It can also be found that the capacities after different cycles are dependent on the Mm content. For example, the capacities in tenth cycle, which can be considered to be the reversible absorption capacity, are 175.1, 173.8, 180.2, 187.2 mL/g with the Mm content x being 1.5, 3.0, 4.5, 6.0, respectively. After all alloys are fully hydrided at room temperature, hydrides decompose at different temperature in atmosphere. The desorption capacities of $FeTi_{1.3}$ + x% Mm(x = 1.5, 3.0, 4.5, 6.0) alloys at different temperatures are listed in Table 3. It can be seen that the higher the reaction temperature, the higher the desorption capacities. Taking the $FeTi_{1.3}$ + 4.5% Mm alloy as an example, the desorption capacities are 99.6, 163.5, 169.5 mL/g with the reaction temperature being 298 K, 318 K, 333 K, respectively. It can also be found that the capacity is influenced slightly by the Mm content. As the Mm content further increases, the desorption capacity at the same temperature increases. For example, when the reaction temperature is 333 K, the capacities of $FeTi_{1.3}$ + x% Mm alloy are 164.4, 165.3, 169.4, 177.8 mL/g with x being 1.5, 3.0, 4.5, 6.0, respectively.

According to the results, it is obvious that, hydrogen storage capacities of the $FeTi_{1.3}$ + x% Mm alloys are comparable with, even higher than that of AB_5 type hydrogen storage alloys,

Table 2 Hydrogen absorption capacities of $FeTi_{1.3}$ + x% Mm(x = 1.5, 3.0, 4.5, 6.0) after different hydrogen absorption-desorption cycles at room temperature(298 K) (mL/g)

Alloy	Capacities after different absorption-desorption cycles		
	1	2	10
$FeTi_{1.3}$ + 1.5% Mm	170.0	156.5	175.1
$FeTi_{1.3}$ + 3.0% Mm	202.3	164.7	173.8
$FeTi_{1.3}$ + 4.5% Mm	223.7	177.5	180.2
$FeTi_{1.3}$ + 6.0% Mm	209.5	181.2	187.2

Table 3 Hydrogen desorption capacities of $FeTi_{1.3}$ + x % Mm(x = 1.5, 3.0, 4.5, 6.0) at different temperatures (mL/g)

Alloy	Capacities at different temperature		
	298 K	318 K	333 K
$FeTi_{1.3}$ + 1.5% Mm	94.9	147.0	164.4
$FeTi_{1.3}$ + 3.0% Mm	112.5	153.5	165.3
$FeTi_{1.3}$ + 4.5% Mm	99.6	163.5	169.4
$FeTi_{1.3}$ + 6.0% Mm	114.1	165.3	177.8

however the cost of the latter is much higher. And the activation behavior of $FeTi_{1.3}$ + x % Mm alloys is also improved dramatically. Among all alloys studied in this work, the overall hydrogen storage properties of $FeTi_{1.3}$ + 6.0% Mm alloy are the best. The alloy is prospective for hydrogen storage applications.

4 DISCUSSION

According to the results mentioned above, there are amounts of hydrogen in the form of stable hydrides retained in alloy after the initial hydriding, which could not decompose during cycling. The formation of stable hydride is related to the existence of a small amount of Mm in alloy. It was reported[12] that La (one major constituent of Mm) can absorb hydrogen very rapidly at room temperature, and at least 13% volume expansion followed. The other major constituent of Mm—Ce can also react with hydrogen readily accompanying 16% volume expansion. The optical micrographs of $FeTi_{1.3}$ + x % Mm(x = 3.0, 6.0) are shown in Fig.4 and Fig.5. It can be seen from the pictures that the misch metal is dispersed in the form of small inclusions throughout the FeTi matrix. It can also be found that the size of these inclusions becomes larger and the number of the inclusions becomes small as the Mm content increases (Fig.4, 5).

The misch metal inclusions dispersed in alloys absorb hydrogen preferentially to form stable hydrides during hydrogenation reaction, in the same time a great deal cracks were produced because of volume expansion. The cracks may expand to FeTi matrix. As a result FeTi phase with fresh oxide-free surfaces through which hydrogen can be absorbed easily is provided. The activation behavior of the alloy is improved because hydrogen can contact with FeTi phase with fresh oxide-free surfaces through cracks and react readily to form $FeTiH_x$ hydrides. Furthermore, Hydrogen storage properties of $FeTi_{1.3}$ + x % Mm alloy is also influenced by the Mm content. When the Mm content was below the critical value, the activation behavior of alloy was further improved with increasing the Mm content because the number of Mm inclusions increased and the interface between the FeTi matrix and the Mm inclusions also increased. When the Mm content is further increased, where the number

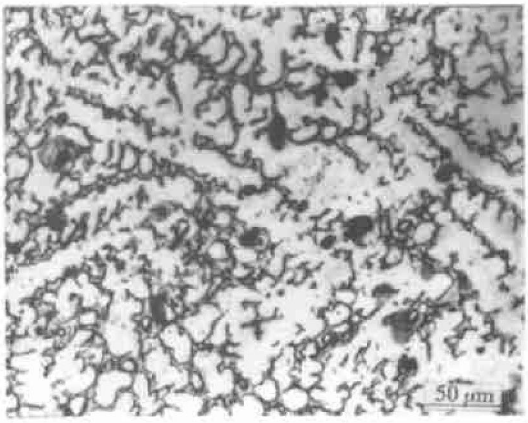

Fig.4 Microstructure of $FeTi_{1.3}$ + 3.0% Mm alloy

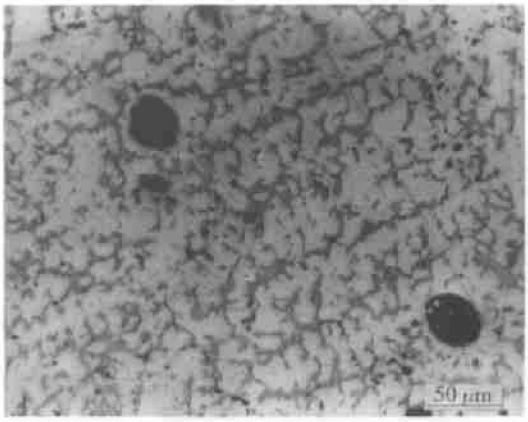

Fig. 5 Microstructure of $FeTi_{1.3}$ + 6.0% Mm alloy

of Mm inclusions become less on the contrary because the Mm inclusions get together, the activation behavior of alloy became worse.

5 CONCLUSIONS

(1) The activation behavior of $FeTi_{1.3}$ + x%Mm alloy is improved when a small quantity of misch metal (Mm) is added.

(2) Hydrogen storage properties of $FeTi_{1.3}$ + x% Mm alloy is influenced by the Mm content. The overall hydrogen storage properties of $FeTi_{1.3}$ + 6.0%Mm are the best among all alloys studied.

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