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Hydrogen storage properties of V+ $TiFe_{0.85}Mn_{0.15}$ multi-phase alloys made by mechanical alloying①

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[Abstract] The mechanical alloying technique was used to make multi-phase alloys V+ $TiFe_{0.85}Mn_{0.15}$. Their hydrogen storage properties were characterized and compared with that of the polycrystalline alloys made by casting. It was found that the ball milled alloys can absorb hydrogen at room temperature in the first cycle without prior activation. The 40% V + 60% $TiFe_{0.85}Mn_{0.15}$ alloy made by mechanical alloying shows the best hydrogen storage property with the valid hydrogen capacity up to 220 mL/g at 293 K and 4.0 MPa, and the P-C-T behavior is also improved. The XRD and EDX analyses also show that the phase of these alloys contains V, TiFe, γ-TiMnx, $TiFe_2$ and α-FeV. The composition of these phases affects significantly the hydrogen storage properties of alloys.

[Key words] V-based alloys; TiFeMn; hydrogen storage property; mechanical alloying (MA)
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1 INTRODUCTION

Recently, hydrogen storage alloys are enthusiastically studied for future application on fuel cell. Vanadium or V-based alloys are known to have a relatively high hydrogen capacity (up to 3.8%). Activated vanadium can react with hydrogen readily, and form two types of hydride, VH and VH_2. The hydrogen diffusivity in vanadium or V-based alloys with BCC crystal structure is rather high[1]. Besides, the equilibrium pressure of hydrogenation between VH and VH_2 is appropriate for utilization[2].

However, despite these interesting characteristics, the activation of pure vanadium is quite difficult. Heat treatment with high temperature (up to 573 K~ 773 K) and dozens of absorption-desorption cycles are needed for complete activation of pure vanadium[3], and only half of the hydrogen absorbed by the activated vanadium could be released. Thus, the emphasis of the research work on V-based alloys is to improve the activation characteristic of pure vanadium, as well as to enhance the hydrogen capacities of V-based alloys. Up to now, much effort has been exerted, such as heat treatment, film plating with Pd, Pt on the surface of vanadium[4] and partial substitution of V by transition elements Ti, Fe, Cr, Co, Ni, etc[5,6]. Apart from these, V-based alloys modified by ball milling with additives, such as MgNi and $LaNi_5$, have also been reported[7,8]. However, the reversible hydrogen capacities of these resulted ternary/quaternary V-based alloys are always lowered, and the slopes of the plateaus increase, too.

TiFe-based alloys have been studied for applications on Ni/MH batteries and Proton Exchange Membrane Fuel Cell (PEMFC)[9~11] etc. $TiFe_{0.85}Mn_{0.15}$ compound has relatively high hydrogen capacity (1.6~ 2.0H/M), and with the adding of Mn, its activation characteristic has become better. In this paper, pure vanadium is mixed with $TiFe_{0.85}Mn_{0.15}$ alloy, comprising new V-based multi-phase alloys by mechanical alloying. The hydrogen storage properties of this new type V-based alloy, including activation characteristics, hydrogen capacity, property of P-C-T (pressure-composition-temperaure) curves and the phase structure transformation, will be studied.

2 EXPERIMENTAL

All the as-cast (100- x)% V + x% $TiFe_{0.85}Mn_{0.15}$ (x= 50, 60, 70) alloy used in this study were prepared by arc-melting in an atmosphere of high purity argon from the component metals, with a purity above 99.9%. The ingots were turned and remelted several times for homogenization. No further annealing or homogenization of these alloys was conducted.

The ball-milled alloys were prepared through directly milling the mixtures of pure vanadium powder, which has a purity above 99.9%, and the $TiFe_{0.85}Mn_{0.15}$ powder that was made by arc-melting and has a rather high purity. The initial particle size of these two component powder was smaller than 74 μm. Each mixture was milled in a 100 mL vial with mass ratio of 30∶1 ball-to-powder. The vial was evacuated and filled with high purity argon up to 0.5 MPa first.

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The rotating speed was fixed at 225 r/min.

The activation characteristics of experimental alloys were measured using a Sievert's type apparatus at a temperature of 298 K. The powder samples of about 5 g were loaded into a reactor, which was evacuated to 0.1 Pa and then filled with hydrogen up to 6.0 MPa. The pressure change, which was continuously monitored by a sensitive pressure transducer, was used to determine the rate of hydrogen absorption during the hydriding process. After the hydrogen pressure has maintained constant for a period, the hydrogen was released and the reactor was evacuated to 0.1 Pa again. Then, the next hydrogenation cycle began. After the specimens were fully activated, pressure-composition isotherms at different temperatures were plotted. The phase composition of specimens was determined by X-ray diffraction (XRD) using a Philips X'Pert-MPD type X-ray diffractometer with CuKα radiation.

3 RESULTS AND DISCUSSION

3.1 Activation characteristics of experimental alloys

Figs. 1~3 show the hydrogen absorption rates of unactivated ball-milled $(100-x)\%\,V+x\%\,TiFe_{0.85}Mn_{0.15}$ (x = 50, 60, 70) alloys at 298 K under an initial hydrogen pressure of 10.0 MPa. It can be seen that all of these quaternary alloys can react with hydrogen without any heat treatment only after a short period of incubation, which decreases as the content of $TiFe_{0.85}Mn_{0.15}$ increases. For the alloys with x = 50 and 60, the incubation periods are 2 min and 3 min respectively, with hydrided fractions up to 80% and 75% respectively. When the value of x increases to 70, the incubation period is shorten to 1 min, while the first hydrided fraction drops to 30% at the same time.

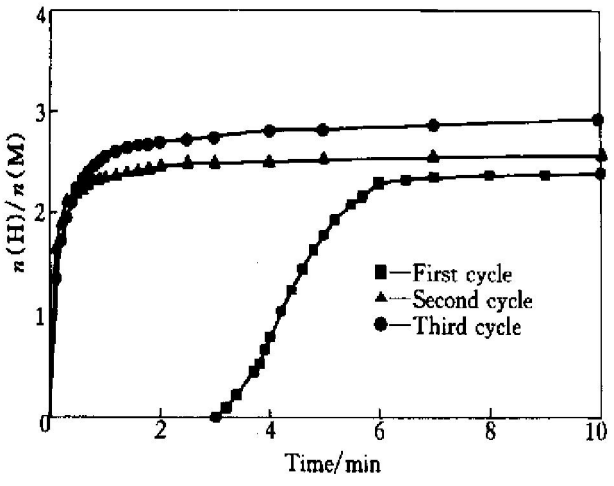

Fig. 1 Initial hydrogen absorption rates of unactivated 50% V+ 50% $TiFe_{0.85}Mn_{0.15}$ alloy made by MA at 298 K and 6.0 MPa

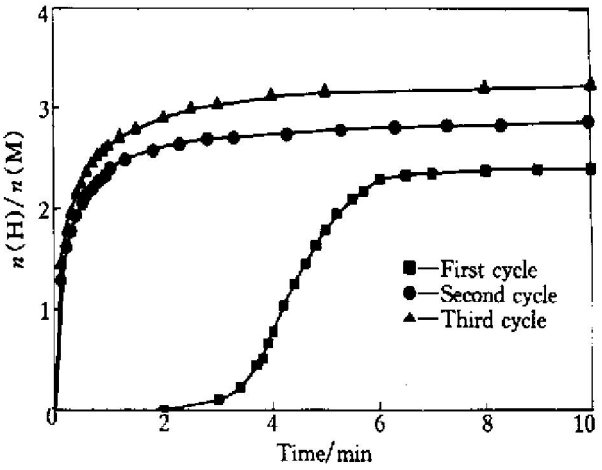

Fig. 2 Initial hydrogen absorption rates of unactivated 40% V+ 60% $TiFe_{0.85}Mn_{0.15}$ alloy made by MA at 298 K and 6.0 MPa

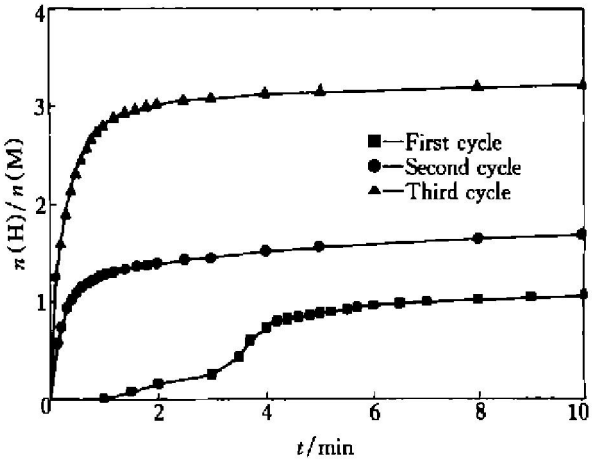

Fig. 3 Initial hydrogen absorption rates of unactivated 30% V+ 70% $TiFe_{0.85}Mn_{0.15}$ alloy made by MA at 298 K and 6.0 MPa

The hydrided fractions of these three experimental alloys increase with increasing the absorption-desorption cycles. After three absorption-desorption cycles, all of these three alloys are fully activated. It is believed that the excellent activation characteristic of these ball-milled V-based alloys is mainly due to the removal of oxidized film on the surface of vanadium during milling process.

3.2 Properties of P-C-T curves and thermodynamics for experimental alloys

The hydriding curves at different temperatures of the $(100-x)\%\,V+x\%\,TiFe_{0.85}Mn_{0.15}$ alloys made by mechanical alloying are illustrated in Figs. 4~6. Unlike TiFe-based or V-based alloys, all these three experimental alloys exhibit two plateau regions in the P-C-T curves, the low one corresponding to V-H system and the high one corresponding to TiFe-H system. When the value of x increases, it can be seen from the P-C-T curves that the low plateau narrows while the high plateau broadens, and the equilibrium

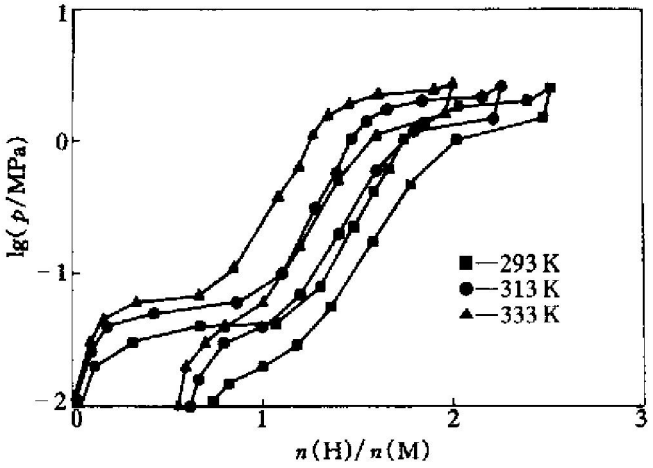

Fig. 4 Pressure-composition isotherms of 50% V + 50% $TiFe_{0.85}Mn_{0.15}$ alloy made by MA

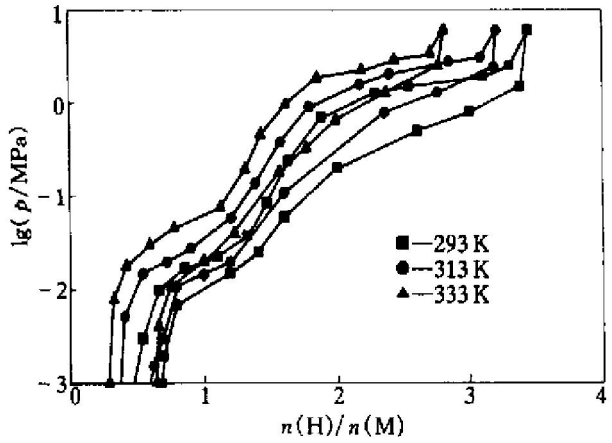

Fig. 5 Pressure-composition isotherms of 40% V + 60% $TiFe_{0.85}Mn_{0.15}$ alloy made by MA

pressure also decreases. For the alloys with x = 50 and 60 at 293 K, the equilibrium pressures at low plateau are 0.04 MPa and 0.02 MPa respectively, while the equilibrium pressures at high plateau are 2.0 MPa and 1.5 MPa respectively. When x increases to 70, the equilibrium pressure at low plateau drops too low and the hydride formed is too stable.

Comparing the P-C-T curves of these three alloys

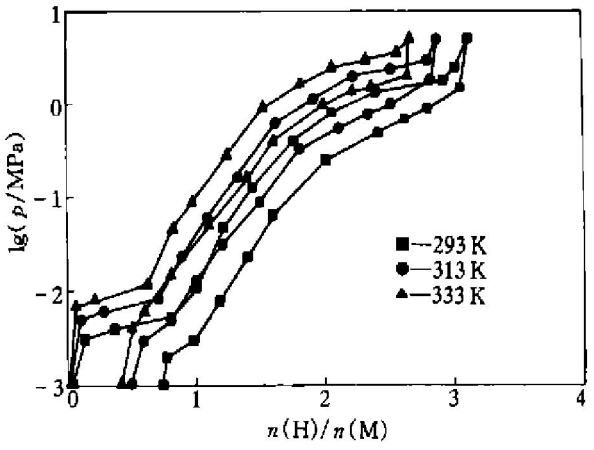

Fig. 6 Pressure-composition isotherms of 30% V + 70% $TiFe_{0.85}Mn_{0.15}$ alloy made by MA

at different temperatures, it can be found that the alloy with x = 60 has the largest reversible hydrogen capacity among all these three alloys.

The thermodynamics parameters of the hydrides calculated through Van' t Hoff equation, as well as hysteresis coefficient (H_f) and slope of plateau (S_f) derived from the P-C-T curves, are all listed in Table 1. Those of as-cast alloys are also listed for comparison. It can be found that the values of H_f and S_f of experimental alloys decrease with increasing the $TiFe_{0.85}Mn_{0.15}$ amount, and are all smaller than those of corresponding as-cast alloys. In the contrast, the values of ΔH° for experimental alloys increase as the amount of $TiFe_{0.85}Mn_{0.15}$ additive increases. When the amount of $TiFe_{0.85}Mn_{0.15}$ is up to 60%, the experimental alloy has almost the same ΔH° as the pure vanadium. At the same time, all the experimental alloys have bigger ΔH° than Ti-$Fe_{0.85}Mn_{0.15}$, which indicates that the hydrides formed from experimental alloys are more stable than that of $TiFe_{0.85}Mn_{0.15}$ and have almost the same stabilities as pure vanadium. It is also inferred from Table 1 that, the hydrogen capacity of the ball-milled alloys is higher than that of as-cast alloys, and the plateau pressure is more suitable. Besides, the values

Table 1 Properties of P-C-T curves and thermodynamics for experimental alloys

Synthesis method	Experimental alloy	Chemical formula of corresponding hydride	$-\Delta H^\ominus(H_2)$ / (kJ·mol^{-1})	$\Delta S^\ominus(H_2)$ / (J·K^{-1}·mol^{-1})	H_f	S_f
Mechanical alloying	50% V + 50% $TiFe_{0.85}Mn_{0.15}$	$V_{2.03}TiFe_{0.85}Mn_{0.15}H_{2.5}$	36.4	140.9	0.79	2.05
	40% V + 60% $TiFe_{0.85}Mn_{0.15}$	$V_{1.36}TiFe_{0.85}Mn_{0.15}H_{3.4}$	40.3	141.8	0.41	1.86
	30% V + 70% $TiFe_{0.85}Mn_{0.15}$	$V_{0.87}TiFe_{0.85}Mn_{0.15}H_{3.1}$	42.7	150.2	0.53	1.77
As-cast	50% V + 50% $TiFe_{0.85}Mn_{0.15}$	$V_{2.03}TiFe_{0.85}Mn_{0.15}H_{2.3}$	34.8	138.5	0.92	2.30
	40% V + 60% $TiFe_{0.85}Mn_{0.15}$	$V_{1.36}TiFe_{0.85}Mn_{0.15}H_{3.2}$	37.1	140.3	0.87	2.15
	30% V + 70% $TiFe_{0.85}Mn_{0.15}$	$V_{0.87}TiFe_{0.85}Mn_{0.15}H_{2.8}$	40.2	143.2	0.75	1.98
	Pure vanadium	VH_2	40	142	1.6	0.2
	$TiFe_{0.85}Mn_{0.15}$	$TiFe_{0.85}Mn_{0.15}H_{1.9}$	29.5	107.0	0.62	0.95

of ΔH° for ball-milled alloys are all lower than those of corresponding as-cast alloys, which indicates that hydrides formed from ball-milled alloys have much stability.

3.3 Phase structure of experimental alloys

Fig. 7 shows XRD patterns of ball-milled $(100-x)\%$ V + $x\%$ $TiFe_{0.85}Mn_{0.15}$ alloys. The XRD pattern of as-cast 40% V + 60% $TiFe_{0.85}Mn_{0.15}$ is also put together for comparison. All samples show multi-phase structure. V and TiFe are the major phase with $TiFe_2$ phase and γ-$TiMn_x$ phase as the minor one. For the alloys with x = 60 and 70, a small amount of σ-FeV phase appears. It can also be found that, with x = 70, the intensity of V peak is weakened and that of $TiFe_2$ and σ-FeV strengthened, while with x = 50, the intensity of TiFe peak is weakened and that of V strengthened. This definitely infers that either excess or deficiency for the amount of $TiFe_{0.85}Mn_{0.15}$ would equally cause reduction of hydriding phase (V or TiFe) and augment of unhydriding phase ($TiFe_2$ or σ-FeV). Compared with Fig. 7(d), it can be apparently seen that, after mechanical milling, the Bragg peaks of all phase elements are broadened and shifted to the left, which indicates reduction of the grain size of elemental particle. This may be one of the main cause for the improvement of activation characteristics.

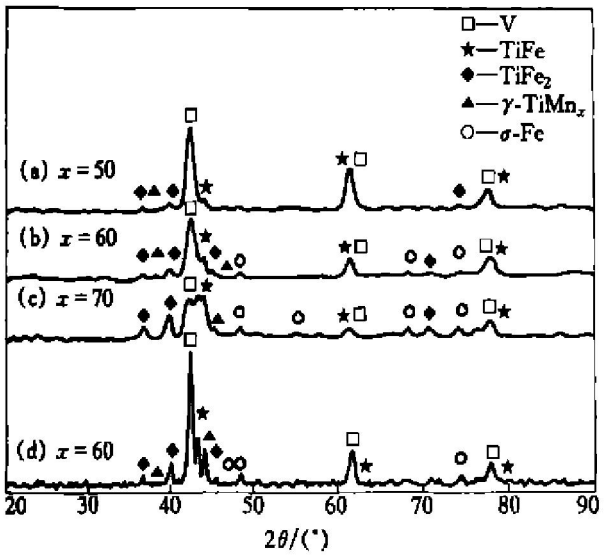

Fig. 7 XRD patterns of $(100-x)\%$ V + $x\%$ $TiFe_{0.85}Mn_{0.15}$
(a), (b), (c) —Ball-milled; (d) —As-cast

Fig. 8 shows the SEM image of the ball-milled alloy with x = 60. The SEM-EDX analysis gives the composition at different regions denoted with A, B, C, D and E in Fig. 8. The composition at regions denoted with A, B, D and E are V base phase, TiFe phase, γ-$TiMn_x$ phase and σ-FeV phase respectively. In the region denoted with C, $TiFe_2$ phase is the major composition while V base phase also

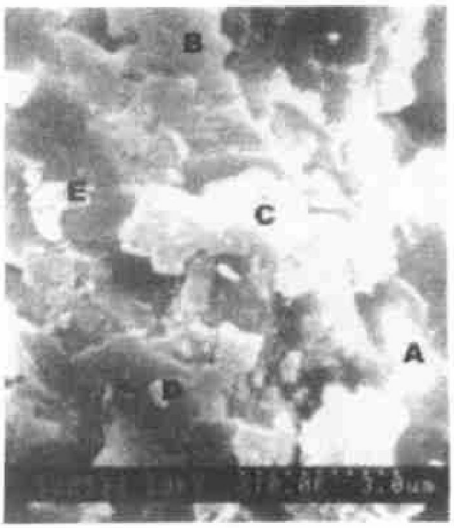

Fig. 8 SEM image of 40% V + 60% $TiFe_{0.85}Mn_{0.15}$

detected.

Among these five phases, $TiFe_2$ is believed to be the major unhydriding phase, whose content affects the hydrogen capacity markedly. Besides, for the alloy with x = 60, the lattice parameter of $TiFe_2$ phase for the ball-milled alloy (a = 4.912 Å, b = 7.831 Å, c = 1.644 Å) is apparently larger than that of C14 Laves $TiFe_2$ phase for the as-cast alloy. This is definitely due to the substitution of little iron atom by large V atom in $TiFe_2$ phase. The SEM-EDX analysis of composition at region denoted with C in Fig. 8 also confirms the exist of V in $TiFe_2$ phase. The work of Miyamura has already reveals that the C14 Laves phase formed by partial substitution of $TiFe_2$ phase by V can absorb hydrogen readily[12]. Thus, to improve the hydrogen capacity of V-based multi-phase alloy, modification of the unhydriding phase is also effective, apart from merely reducing its amount.

4 CONCLUSIONS

1) Ball milling V with $TiFe_{0.85}Mn_{0.15}$ alloy can effectively improve the activation characteristics of vanadium. Ball-milled $(100-x)\%$ V + $x\%$ $TiFe_{0.85}Mn_{0.15}$ alloys can react with hydrogen at room temperature without any heat treatment. Removal of the oxidized film on the surface of vanadium during milling process and prior hydrogenation of the readily-hydrided phase among multi-phase structure are believed to synthetically contribute to the improvement of activation characteristics of vanadium.

2) When the amount of $TiFe_{0.85}Mn_{0.15}$ additive is up to 60%, the alloy exhibits the best hydrogen storage properties with the broadest plateau and largest reversible hydrogen capacity. Excess $TiFe_{0.85}Mn_{0.15}$ additive causes too low plateau and less reversible hydrogen capacity.

3) Both as-cast and ball-milled alloys comprise

with hydriding phase of V, TiFe, γ-TiMnx and unhydriding phase of $TiFe_2$ and σ-FeV. Appropriate fraction of V to $TiFe_{0.85}Mn_{0.15}$ and suitable synthesis method through mechanical alloying both contribute to the augment of hydriding phase and reduction (or transformation) of unhydriding phase.

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