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Hydrogen absorption and modulated structure in Ti–V–Mn alloys

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Abstract

In order to apply hydrogen-absorbing alloys to new energy carrier uses, such as hydrogen storage tanks or Ni–MH batteries, a drastic increase in the hydrogen capacity of these alloys is required. For years, intermetallic compounds or single-phase alloys have been studied as hydrogen-absorbing materials. New approaches to alloy design, relating to multiphase alloys, are proposed and verified. These approaches help to identify a new structure on a multiphase alloy. As a result, a new hydrogen-absorbing alloy, consisting of a nano-structure having a large hydrogen capacity and good desorbing properties, was found.

Keywords: Hydrogen-absorbing alloy; Alloy design; Microstructure control; Spinodal decomposition; Nano structure; Environmental issue

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1. Introduction

Refractive energy sources, such as solar, nuclear, hydroelectric, wind, geothermal and waste heat recovery, which do not produce carbon dioxide, have been proposed as replacements for fossil-fuel derived energy [1] for environmental reasons. A system that utilizes electrolyzed hydrogen produced form solar energy or hydro-electric power is the ultimately clean system, as the hydrogen is formed from water, and water is reproduced following combustion of the hydrogen. However, the storage and transport of hydrogen is the one of the most important issues to be resolved in the realization of the hydrogen energy network because conventional gas cylinders for storage and transportation have low hydrogen densities and are difficult to handle.

As a method for the storage and transport of hydrogen, a hydrogen-absorbing alloy can have a hydrogen capacity which is more than 1000 times the alloy's volume. This volume density of hydrogen is as high, or even higher than that of liquid or solid hydrogen. Table 1 classifies typical hydrogen-absorbing alloys based on their structure, capacity and the difficulty in controlling their hydriding properties [2–4]. The AB_5 alloy, originated from $LaNi_5$, whose properties can be easily controlled, is currently commercialized for Ni–MH battery electrode use. The AB_2 (Laves phase) alloy [5] is considered to be a next generation material for the Ni–MH battery. In the AB_2 alloy, property control is rather easy, but the reported capacities are less than double that of the AB_5 alloy. Therefore, we do not believe that the AB_2 alloys have enough capacity for application as new energy carriers.

On the other hand, the third generation alloys, such as the Ti-based solid solution with body centered cubic (bcc) structure or the magnesium-based alloys, have been known to have a large capacity, even prior to the discovery of $LaNi_5$. However, there has been little investigation of these alloys [6–8] and they have never been commercialized.

The development of hydrogen-absorbing alloys has generally been done via the survey of metal combinations, to find a binary alloy which can absorb hydrogen at ambient temperature and pressure. The hydriding properties are then usually controlled with the substitution of a third or fourth metal for the binary alloy, forming a pseudo-binary system.

In order to identify new large capacity alloys for application as a new energy carrier, we attempted to establish a new investigation methodology. This methodology focused on the development of a multi-phase hydrogen-absorbing alloy instead of the usual single-phase variety. Two possibilities for identifying enlarged capacity in a multi-phase alloy design were proposed.

(1) The effect of the interface and interaction of each phase in creating a capacity larger than the linear combination of the end member phases.

(2) Identifying an alloy with a new composition and structure, found as a constituent in a phase of multiphase alloys.

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Table 1
Conventional hydrogen-absorbing alloys

	Type	Alloy	Capacity		Condition (Pressure, Temp.)	Reaction rate	Activation condition	Resistance
			H/M	wt.%				
1	AB_5	$LaNi_5$ $MmNi_5$	1.0	0.8–1.2	Mild	High	Mild	High
2	AB_2 (Laves)	$ZrMn_2$ $TiMn_2$ ZrV_2	1.3	1.5–2.0	Hard	High	Mild	Low
3	A*x*B*y* (bcc) (Mg)	V, Nb Ti–V Mg–Ni	2.0	3.0–7.6	Hard	Low	Hard	High

Through our work, these two possibilities were demonstrated in an alloy system whose end member phases are established hydrogen-absorbing alloys, and these approaches were proposed as new methods for alloy design.

2. Experimental

2.1. Alloy design

The alloy system selected for the first multiphase experiment was Zr–Ti–Mn–V [9–11]. The Zr–Ti–Mn–V phase map in Fig. 1a shows the area where the Laves phases and the bcc phase coexist. The Laves phase shows favourable hydrogen-absorbing properties, and the bcc phase shows a large capacity. Fig. 1b show the simulated capacity on the $Zr_{1-x}Ti_xMnV$ line in the multiphase region. These capacities were calculated from a linear combination of the nominal or observed capacities of the constituent phases, and the weight fraction was obtained by X-ray Rietveld analysis. The calculated capacity increased with Ti content and bcc phase fraction. Therefore, in this simulation the TiMnV alloy had the largest capacity.

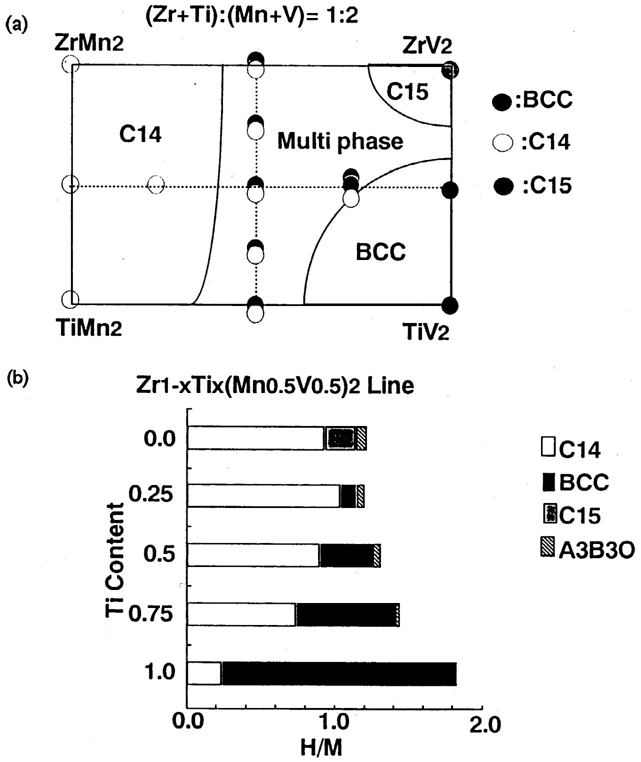

Fig. 1. Zr–Ti–Mn–V system: (a) Phase map, (b) Capacity simulation.

2.2. Equipment

The transmission electron microscope (TEM) and attached EDX were used for the analysis of alloy structure. X-ray powder diffraction data were refined by the Rietveld method. The initial structure model, based on information from the TEM observation, was adopted for the refinement of the structural parameters, and the weight fraction of the various phases by using the RIETAN-94 [12] program. The capacity and pressure-composition (PC) isotherms were measured with a conventional constant volume apparatus.

3. Results and discussion

3.1. The linear combination method for simulation of PC-isotherms (micro-composite multiphase)

The results of optical micrography and structure analysis observations of TiMnV are shown schematically in Fig. 2. Crystallized colonies were found in as-cast TiMnV. TEM observation showed that the matrix is bcc and the colony has a C14 Laves phase structure. Using Rietveld analysis, the weight fraction of the bcc and C14 phases was determined to be 78% and 22%, respectively. EDX analysis showed that each phase contained three elements (Ti, Mn and V), and that slight differences in composition changed the crystal structure drastically. Two TiMnV end-member alloys were prepared based on the EDX results, and the PC isotherms of these alloys were measured. As

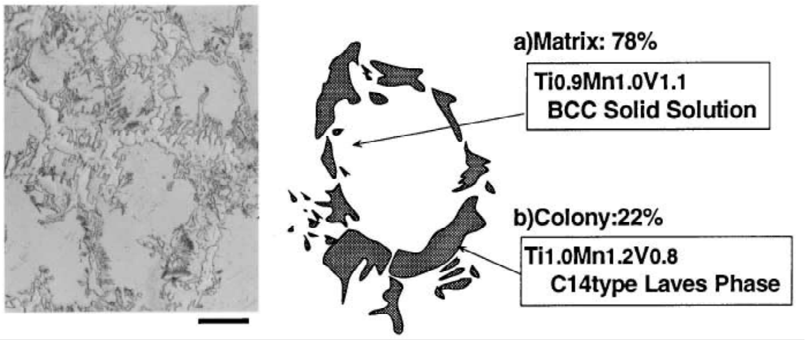

Fig. 2. Microstructure of TiMnV.

shown in Fig. 3, the result as calculated by linear combination of the end-member alloys [1], correlate with the PC isotherm measurement for TiMnV. This calculation can be written as:

$$X_{\mathrm{TiMnV}} = 0.78{*}X_{\mathrm{BCC}} + 0.22{*}X_{\mathrm{C14}} \tag{1}$$

where X is the capacity at the pressure measured in the PC isotherms, and the coefficients 0.78 and 0.22 are the weight fraction of the bcc and C14 end-member phases, respectively, as determined by Rietveld analysis. This result suggests that an increase of capacity cannot be expected in a multiphase alloy consisting of micron size phases.

The hydriding property of the bcc phase alloy $Ti_{0.9}Mn_{1.0}V_{1.1}$, one of the end-member phases of TiMnV, is suitable for hydrogen storage, as shown in Fig. 3. The desorption plateau in the isotherm of $Ti_{0.9}Mn_{1.0}V_{1.1}$ is fairly flat. This is a great improvement over conventional bcc alloys, whose desorbing properties are considered to be difficult to control. However, maximum capacity decreases to only half of the ideal capacity, $H/M = 2.0$, calculated from the number of hydrogen interstitial sites of the bcc structure. Therefore, the structure of the bcc region in TiMnV was investigated in order to determine the reason for the desorbing property improvement, and to determine how to increase the hydrogen capacity.

3.2. Nanocomposite interface

Fig. 4 shows the TEM microstructure observation of the area adjacent to the bcc/C14 interface in TiMnV. At the 10 nm scale, a very fine lamellar structure was found. The crystal structures of both phases in this lamellar region were bcc, with the same cell parameters as the bcc matrix phase. Because the diffraction pattern of the matrix phase in the selected area showed satellite reflections induced from lattice strain of the fine spinodal decomposition structure, it was concluded that these lamellar structures adjacent to the bcc/C14 interface were modulated by spinodal decomposition.

The width of the lamellar structure region near the interface is 200 nm, and the fraction of this phase in the TiMnV alloy is small, so this phase cannot affect the hydrogen desorbing property of TiMnV. The composition of this interface adjacent phase was analyzed by EDX and was found to be $Ti_{1.0}Mn_{0.9}V_{1.1}$. An alloy with a composition identical to this interface neighbour alloy was fabricated. Fig. 5 shows the PC isotherms of

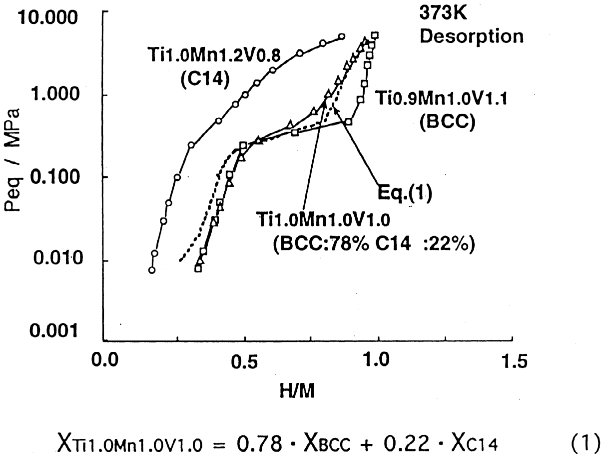

Fig. 3. Linear combination of capacity on PC isotherms.

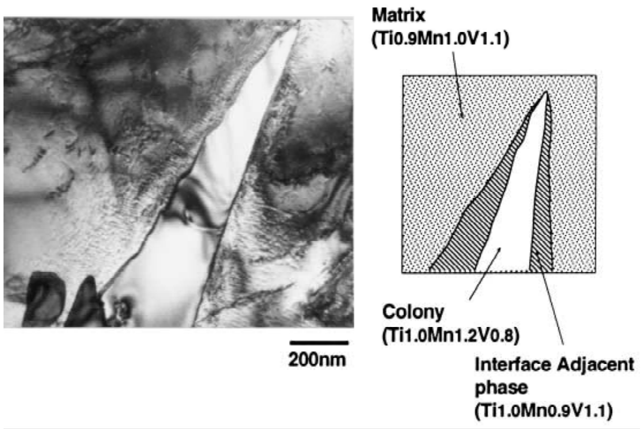

Fig. 4. TEM microstructure of TiMnV.

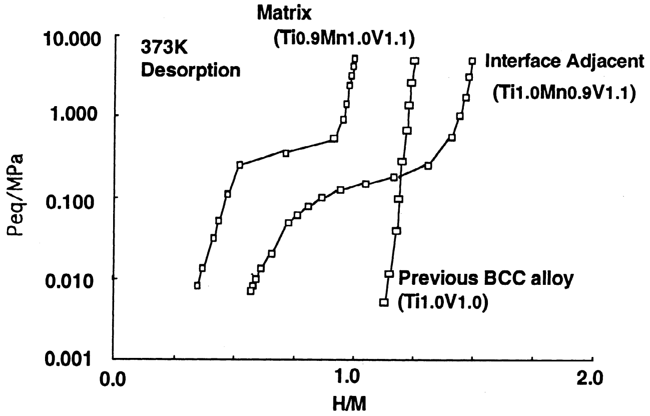

Fig. 5. PC isotherms of interface adjacent alloy.

$Ti_{1.0}Mn_{0.9}V_{1.1}$, which has a capacity 1.5–2 times larger than that of the matrix alloy, $Ti_{0.9}Mn_{1.0}V_{1.1}$. Furthermore, the plateau region is large for $Ti_{1.0}Mn_{0.9}V_{1.1}$. These are remarkable improvements in the conventional bcc hydrogen-absorbing alloy, because, in general, a conventional bcc alloy such as TiV cannot desorb hydrogen under ambient conditions.

3.3. New approaches to alloy design

3.3.1. The effect of multiphase composite

As shown in Section 3.1, an increase of capacity cannot be expected from the interaction between C14 and bcc phases in a micro-composite multiphase alloy. However, if we regard the information presented on the high capacity interface phase as the interaction between the two phases, capacity can be increased by an alloy design and heat treatment that controls the fraction of the high capacity interface phase.

The alloy of the interface phase composition, $Ti_{1.0}Mn_{0.9}V_{1.1}$, which was prepared after TEM observation, is covered with the nano-scale lamellar structure. This is the same as the interface phase in Fig. 4. Though the mechanism responsible for increasing hydrogen capacity in this structure is not clear, the high capacity is considered to be caused by the interactions of these nano-composite phases through a coherent interface, such as modulation of composition or lattice strain.

3.3.2. New alloy design

Two alloys of bcc structure (matrix and phase adjacent to the bcc/C14 interface), whose compositions were determined by the structural analysis of TiMnV, showed large capacity and good desorbing properties. Miedema's rule of reversed stability [13], which is applied to the development of hydrogen-absorbing alloys, states that 'the less stable hydride forms the more stable alloys.' Because each end member phase forms as the stable one in its preparation process, these phases seem to have similar stabilities, and, therefore, their hydrides also seem to have similar stabilities. In Zr–Ti–Mn–V multiphase alloys, the step on the PC isotherms which indicates a difference in stability of the constituting hydride phases has not been observed. It clearly shows that the constituting phases in the multiphase alloy have almost identical stabilities both in the alloy and the hydride. This provides a new way to find novel hydrogen-absorbing phases as one of the end members in a multiphase alloy which desorbs hydrogen under ambient conditions. The new approach to design a hydrogen-absorbing alloy as shown here was effective to find phases with a larger hydrogen capacity than previously reported.

4. Conclusion

(1) The capacity of TiMnV at a given pressure agreed with the one calculated by the linear combination method from the capacity and weight fraction of its constituent phases. This result indicates that an increase in capacity cannot be expected from multiphase alloys with micron-size structure.

(2) A new phase, with nano-composite structure, was found adjacent to the interface of the end members. The alloy with this composition showed a large capacity and good desorbing properties. It should be emphasized that micron-scale structures are not easily improved, but that nano-scale structures have much more room for improvement.

These results show the effectiveness of the proposed new alloy design method; a new structure and composition can be found in the end-member phases by metallographic analysis of multiphase alloys.

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