

Hydrogen Absorption by Laves Phase Related BCC Solid Solution Alloys

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Abstract

We propose a new concept of hydrogen absorbing alloy, "Laves phase related BCC solid solution". It was firstly found among the phases formed in multicomponent nominal AB_2 alloys which consisted of Zr and Ti for the A metal site and 5A, 6A and 7A transition metals for the B metal sites. In these alloys a BCC solid solution often coexisted with a Laves phase. It showed stability of hydrides and reaction kinetics almost identical to intermetallics such as Laves phase alloys. We prepared an almost pure "Laves phase related BCC solid solution" and found that it had a large hydrogen capacity (more than 2 mass%) and fast hydrogen absorption and desorption kinetics at ambient temperature and pressure. This new hydrogen absorbing alloy may open a new era of hydrogen related application such as hydrogen vehicles.

1. Introduction

Hydrogen absorbing alloys are commercially used for the electrode of Ni-hydrogen batteries since 1990¹. In 1996, the amount of alloys produced was worth about 10 billion yen (80 million US \$). It is a great success of a new

material which was found in the late 1960's. The alloy used for commercial Ni-hydrogen battery is basically a $LaNi_5$ based one. The capacity of the alloy presently used for batteries is not large enough.

Recently polymer electrolyte fuel cell which is lighter than other fuel cells and works below 373K

was developed especially for the emission-free vehicles. Using hydrogen absorbing alloy as the on-board hydrogen tank is one of the ideal methods of hydrogen supply to fuel cell because compactness and safety are key issues for on-board application. However, on intermetallic hydrogen absorbing alloy of capacity more than 2 mass% working at room temperature has been reported so far. In these two major application fields of hydrogen absorbing alloys, increasing of hydrogen capacity is strongly desired but conventional alloys do not reach more than 2 mass% at room temperature.

Body centered cubic(BCC) metals and alloys intrinsically have a large hydrogen capacity but they have not been used for any application so far. Even studies on hydride formation in BCC alloys were fewer than those of intermetallics such as AB_5 and AB_2 alloys¹⁻¹⁸. In this review, I will introduce new BCC alloys developed from a new concept, "Laves phase related BCC solid solution", proposed by the authors. The hydrogen capacity of this new generation BCC alloy reached 2.2 mass%. The microstructure and crystal structure of Laves phase related BCC alloys will be discussed.

2. Characteristics of pct Diagrams of BCC Metals and Alloys

Fig. 1 shows the pct diagram of vanadium¹⁹ which is one of typical hydrogen absorbing BCC metals. Vanadium has two plateaus with different equilibrium pressures. Fig. 1 shows only the plateau between VH_{-1} and VH_{-2} . Papathanasso-

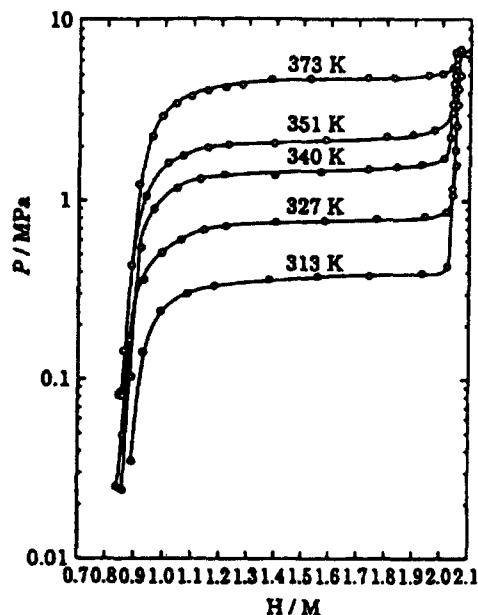


Fig. 1 Pct diagrams of VH_{-1} - VH_{-2} system¹

poulos and Wenzl²⁰ measured both equilibrium pressures. The lower desorption equilibrium pressure was 0.1 Pa at 353 K, while the higher one was about 10^5 Pa at 263 K. BCC metals and alloys generally show two plateaus in their pct diagrams. Their plateau region commonly exhibits a slope. The slope in the plateau region and the pressure difference between the two plateaus is undesirable for application of metal hydrides. Reported disadvantages of BCC metals and alloys as hydrogen absorbers were slow kinetics, difficulties in activation and the slope in the plateau. Therefore, even though BCC alloys have an intrinsic large hydrogen capacity, studies on their hydrogen absorption properties were limited.

One et al. studied the hydrogen absorbing properties of Ti-V alloys in which Ti and V form

a BCC solid solution in any ratio of two constituting metals². They mentioned that it took a long time to reach the equilibrium pressure in the case of the $Ti_{0.4}V_{0.6}$ alloy when they measured the pct diagram. Because of this slow kinetics, the plots on the pct diagram did not show the real equilibrium under standard experimental conditions. The reaction rate of these alloys seems to be slow and are not suitable for application.

Nomura and Akiba²¹ reported the hydrogen absorbing properties of the V-Ti-Fe system. Their objective was the development of high capacity hydrogen absorbers to recover hydrogen gas from a fusion reactor. Expected working temperatures were 573 K for desorption and 253 K for absorption. They found that a BCC alloy with a composition of $Ti_{0.435}V_{0.490}Fe_{0.075}$ absorbed a large amount of hydrogen. They indicate that the effective capacity for recovery usage is about 2.4 mass% which is almost twice that of conventional intermetallic hydrides such as $LaNi_5$.

Tsukahara et al.^{13, 15-18} reported on V-based multiphase alloys for electrodes of Ni-metal hydride battery. $TiV_3Ni_{0.56}$ consisted of two phases with different functions¹³. One was Ti-V based solid solution with a BCC structure which absorbed a large amount of hydrogen. The other was a TiNi based compound with a BCC structure which formed 3-D network to collect electrons and worked as a catalyst. They also reported another combination of phases in $TiV_3Ni_{0.56}Hf_x$ ($x=0.046, 0.24$)¹⁷. This alloy consisted mainly of a BCC solid solution and also of a C14 Laves phase. They found cracking mainly in and around the intermetallic

phase after five charge-discharge cycles. As a result, the reaction rate was improved because many cracks increased the fresh surface area of alloys. They explained that the combined effect of the two phases provided a higher electrode capacity than single phase intermetallics¹³. This is one of the ideal solutions to improve the poor kinetics of BCC hydrogen absorbers. An intermetallic phase which shows fast kinetics assists the hydride formation in the coexisting BCC phase.

3. Laves Phase Related BCC Solid Solution

3.1 Crystal structure analysis of AB_2 alloys by the Rietveld method

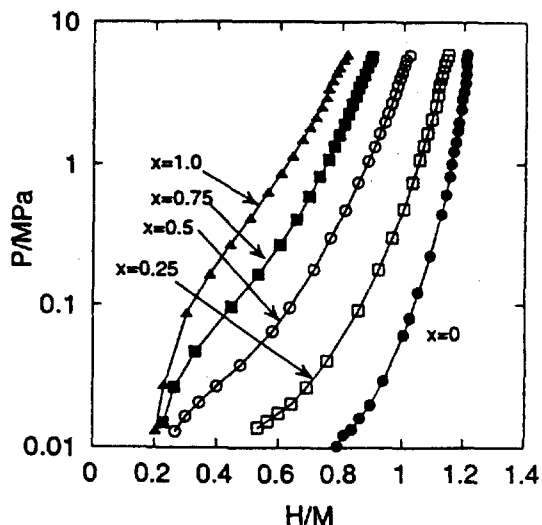
Zr based AB_2 alloys were intensively studied for electrode application²². They contain Zr and Ti in the A metal site and V, Cr, Mn, Co, Ni, etc. in the B metal site. We analyzed crystal structures of $Zr_{1-x}A_xM_2$ ($A=Ti, Nb, Hf, M=V_{0.5}Ni_{1.1}Mn_{0.2}Fe_{0.2}$)²² and $Zr_{1-x}Ti_xMn_{2-y}V_y$ ^{23, 24}. From Rietveld refinement using X-ray diffraction data, we found that many of these alloys studied were multiphase. Tables 1 and 2 list the phase abundance of the alloys $Zr_{1-x}A_xM_2$ ($A=Ti, Nb, Hf, M=V_{0.5}Ni_{1.1}Mn_{0.2}Fe_{0.2}$)²² and $Zr_{1-x}Ti_xMn_{2-y}V_y$ ^{23, 24}, respectively. It is worth noting that many of nominal AB_2 alloys studied consist of more than two phases²⁵. Because most of X-ray diffraction peaks from the C15 phase overlap with those of the C14 phase, it is therefore difficult to distinguish the peaks of the C15 phase from the diffraction pattern without the Rietveld

Table 1 Phase Abundance of $Zr_{1-x}A_xM_2$ ($M_2=V_{0.5}Ni_{1.1}Mn_{0.2}Fe_{0.2}$)

Alloys	phase	abundance(%)
ZrM_2	C14	57
	C15	43
$Zr_{0.75}Ti_{0.25}M_2$	C14	91
	C15	9
$Zr_{0.5}Ti_{0.5}M_2$	C14	100
$Zr_{0.25}Ti_{0.75}M_2$	C14	87
	BCC	13
TiM_2	BCC	100
$Zr_{0.75}Nb_{0.25}M_2$	C14	74
	C15	26
$Zr_{0.5}Nb_{0.5}M_2$	C14	79
	C15	21
$Zr_{0.25}Nb_{0.75}M_2$	C14	90
	C15	10
NbM_2	C14	100
$Zr_{0.75}Hf_{0.25}M_2$	C14	77
	C15	23
$Zr_{0.5}Hf_{0.5}M_2$	C14	85
	C15	15
$Zr_{0.25}Hf_{0.75}M_2$	C14	81
	C15	19
HfM_2	C14	87
	C15	13

Table 2 Phase Abundance of $Zr_{1-x}Ti_xMn_2-yV_y$

Alloys	phase	abundance(%)
$ZrMn_2$	C14	100
$ZrVMn$	C14	72
	C15	13
	Zr_3V_3O	15
	C15	63
ZrV_2	Zr_3V_3O	27
	BCC	10
	C14	100
$Zr_{0.5}Ti_{0.5}Mn_2$	C14	83
	Zr_3V_3O	7
	BCC	10
$Zr_{0.5}Ti_{0.5}V_2$	BCC	57
	Zr_3V_3O	43
	C14	100
$TiMn_2$	C14	100
$TiVMn$	BCC	100
TiV_2	BCC	100

Fig. 2 Pct diagram of the $Zr_{1-x}Ti_xM_2-H_2$ system

method. We found four phases such as C14 and C15 phases, BCC solid solution and Zr_3V_3O in the alloys studied using X-ray Rietveld analysis. It is interesting that all these phases including the oxide phase absorb hydrogen. Fig. 2 shows the pct diagram of the $Zr_{1-x}Ti_xM_2-H_2$ system²². Multiphase alloys ($x=0, 0.25, 0.75$) show smooth isotherms like the single phase alloys ($x=0.5, 1.0$). Pure BCC phase, TiM_2 , differs in the shape of the isotherm. All the multiphase alloys in the present work show smooth pct diagrams without any kink or step, this indicates that the multiphase alloys behave like a single phase alloy in hydrogen absorption-desorption.

3.2 The concept of Laves phase related BCC solid solution

I show the complexity of some AB_2 alloys in their phase composition and elemental distribution.

These alloys which have a nominal AB_2 composition cannot be categorized as a simple Laves phase. We name this kind of AB_2 -type alloys "Laves phases related multiphase alloys"²⁶. Some alloys studied contain a BCC solid solution phase which can absorb hydrogen as shown in Fig. 2. In addition, we found that this BCC phase behaves like a coexisting Laves phase. The BCC solid solution phase which appears with the Laves phases is also a promising candidate for a hydrogen absorbing alloy. Therefore, we name this type of BCC phase "Laves phase related BCC solid solution" to distinguish it from a simple BCC phase such as that in the Ti-V system.

Nominal AB_2 multicomponent alloys such as "Laves phases related multiphase alloys" are being developed for battery and heat pump application. These alloys usually contain Zr and Ti in the A metal site and 5A, 6A, 7A and 8A transition elements for the B metal site^{25, 27}. From binary phase diagrams, we learn that both Zr and Ti form BCC solid solutions with 5A, 6A and 7A metals in the same row of the periodic table in a wide range of atomic ratio. The Ti-V system forms a BCC solid solution at any ratio of both metals. In the Ti-Mn system, a BCC exists in Ti composition of 0~30 at% and the $TiMn_2$ C14 Laves phase has a wide solubility range. Particularly, the Ti-Cr binary phase diagram indicates that at the $TiCr_2$ composition three Laves phases and a BCC solid solution appear at different temperatures (Fig. 3). Therefore, it can be understood that the Laves and BCC phases are readily and simultaneously formed in Zr or Ti based "Laves phases related multiphase alloys".

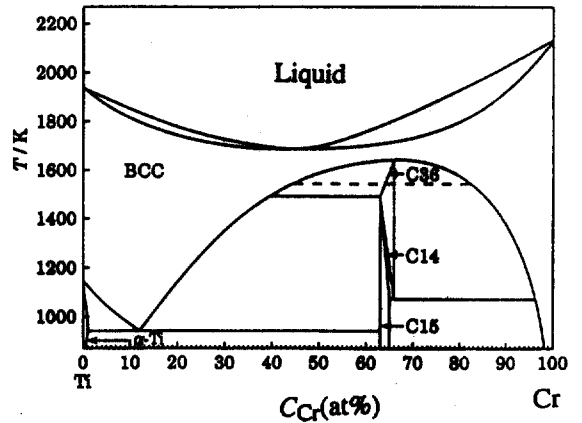


Fig. 3 Ti-Cr binary phase diagram

The simplest expression of Miedema's rule of reversed stability is "less stable alloys form more stable hydrides"²⁷. Difference in stability of Laves phases and the BCC phase in "Laves phases related multiphase alloys" seems to be small, because one phase transfers readily to another by changing the composition or temperature as mentioned above. Therefore, the stability of hydrides of these phases is expected to be similar and, as a result, the pct diagram of the multiphase of these phases is expected to be similar and, as a result, the pct diagram of the multiphase alloys becomes smooth.

In Laves phases related multiphase alloys, there are many ways of controlling microstructure and morphology in order to design their hydriding property, which is one of the advantages of these materials. In addition, Laves phase related BCC solid solutions are expected to absorb hydrogen up to two H per metal atom. Large hydrogen capacity is another and important feature of this kind of alloys.

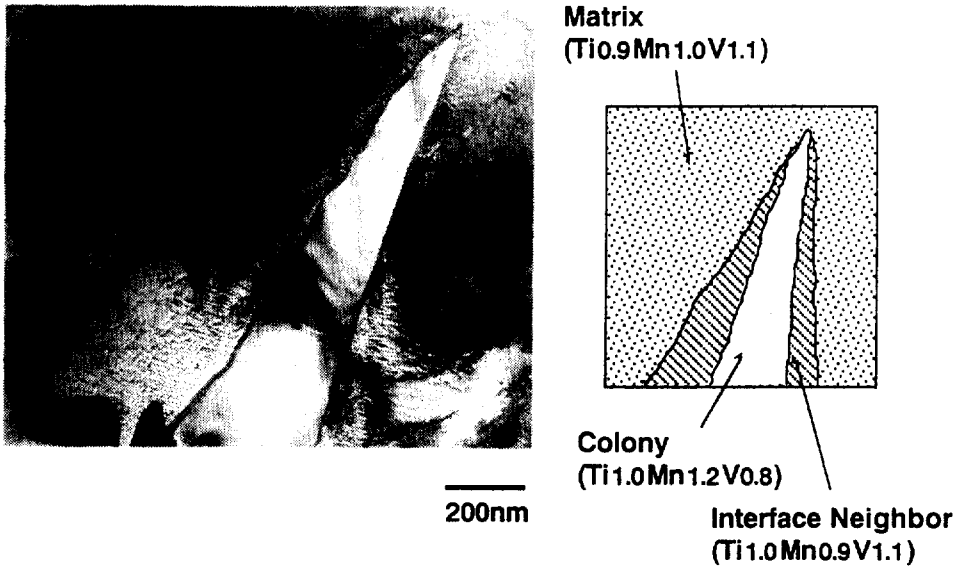
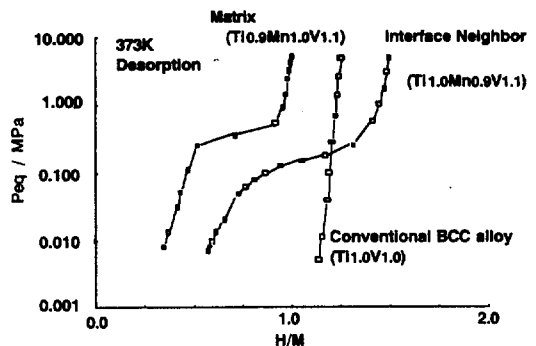


Fig. 4 TEM microstructure of TiMnV

4. Development of Laves Phase Related BCC Alloys

Fig. 4 shows the TEM microstructure observation of the area adjacent to the BCC/C14 interface in TiMnV²⁸. A very fine lamellar structure (10 nm thickness) was found. The crystal structure of both phases in this lamellar region was BCC, and it has the same crystal orientation that of the BCC matrix phase. Because the selected area diffraction pattern of the matrix phase showed satellites induced by lattice strain in the fine spinodal decomposition structure, it was concluded that these lamella structures adjacent to the BCC/C14 interface were modulated structures formed by spinodal decomposition.

The width of the lamellar structure region near the interface is about 200 nm, and the fraction of this phase in the TiMnV is small, so this phase

Fig. 5 PCT diagrams of Ti_{1.0}Mn_{0.9}V_{1.1}

cannot affect the hydrogen desorbing property of TiMnV. The composition of this adjacent interface phase was analyzed by EDX and was found to be Ti_{1.0}Mn_{0.9}V_{1.1}. An alloy with the composition identical to this interface neighbor alloy was fabricated. Fig. 5 shows the pct diagrams of Ti_{1.0}Mn_{0.9}V_{1.1}, which has a capacity 1.5~2 times larger than that of the matrix alloy,

$Ti_{0.9}Mn_{1.0}V_{1.1}$. Further, the plateau region is wide in the case of $Ti_{1.0}Mn_{0.9}V_{1.1}$. These are remarkable improvements over the conventional BCC hydrogen absorbing alloy, because, in general, a conventional BCC alloy such as TiV can not desorb hydrogen under ambient conditions.

5. New Approaches to Alloy Design

As mentioned before, increase in capacity can not be expected from the interaction between C14 and BCC phases in micro-composite multiphase alloys. However, if we regard the formation of the high capacity interface phase as the interaction between the two phases, the capacity can be increased by alloy design and heat treatment that control the fraction of the high capacity interface phase.

The alloy with the interface phase composition, $Ti_{1.0}Mn_{0.9}V_{1.1}$, which was prepared after TEM observation, has the nano-scale lamellar microstructure. This is the same as the interface phase in Fig. 4. Though the mechanism responsible for increasing the 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 coherent interfaces, such as modulation of composition or lattice strain.

Two BCC alloys corresponding to the matrix and the phase adjacent to the BCC/C14 interface, whose compositions were determined following the structural analysis of TiMnV, showed a large capacity and good desorption properties. In the present work we found that in the process of alloy

preparation by the are-melting method, stable phases with different compositions were precipitated. Each phase could be prepared as an almost pure alloy according to the composition obtained from the results of EDX. Hydrogenation properties of these phases were investigated. Thus we found that Laves phase related BCC solid solutions show a flat plateau, fast kinetics and easiness in activation. This provides us with a new way to find a novel hydrogen absorbing phase by studying the constituent phases in multiphase alloys which desorb hydrogen under ambient conditions. The new approach shown here is effective to find phases with a larger hydrogen capacity than those previously reported.

6. Conclusion

We introduced a new concept in development of hydrogen absorbing BCC alloys. These new alloys were named "Laves phase related BCC solid solutions" because these phases were co-precipitated with a Laves phase in multiphase AB_2 alloys and showed identical hydrogenation behavior to the coexisting Laves phase. We separately prepared an almost pure Laves phase related BCC solid solution and found that it absorbed a large amount of hydrogen with a flat plateau and fast kinetics.

It also provides us a new approach to find a novel hydrogen absorbing alloy.

Acknowledgment

The authors would like to thank Dr. Pascal

Tessier for his editorial comments.

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