

Metallic Hydrides III: Body-Centered- Cubic Solid- Solution Alloys

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Abstract

Hydrogen-absorbing alloys with bcc (body-centered-cubic) structures, such as Ti-V-Mn, Ti-V-Cr, Ti-V-Cr-Mn, and Ti-Cr-(Mo, Ru), have been developed since 1993. These alloys have a higher hydrogen capacity (about 3.0 mass%) than conventional intermetallic hydrogen-absorbing alloys. Generally, bcc metals and alloys exhibit two plateaus in pressure–composition isotherms, but the lower plateau is far below atmospheric pressure at room temperature. Many efforts have been made to increase hydrogen capacity and raise the equilibrium pressure of this lower plateau. The crystal structure and morphology of Laves-phase-related bcc solid-solution alloys are reviewed.

Keywords: bcc structure, hydrogen storage, metallic hydrides, solid-solution alloys.

Introduction

Body-centered-cubic (bcc) metals and alloys intrinsically have a large hydrogen capacity, but they have not been used for any hydrogen-storage applications so far. Fewer studies have been done on hydride formation in bcc alloys than in intermetallics such as AB₅ and AB₂ alloys.^{1–7} In this article, we will review new bcc hydrogen-absorbing alloys based on a new concept, the Laves-phase-related bcc solid solution, as proposed by one of the authors. Recent progress on the materials development of these alloys and crystal structure analysis will be introduced.

Hydrogenation Properties of bcc Metals and Alloys

Figure 1 shows the pressure–composition (PC) isotherms of vanadium,⁷ one of the most studied hydrogen-absorbing bcc metals. Vanadium has two clear plateaus with remarkably different equilibrium pressures. Figure 1 shows only the plateau between monohydride (H/V ~ 1) and dihydride (H/V ~ 2). Papathanassopoulos and Wenzl⁸ measured both equilibrium pressures. The lower desorption equilibrium pressure was 10⁻¹ Pa at 353 K, while the higher one was about 10⁵ Pa at 263 K.

Body-centered-cubic metals and alloys generally show two plateaus in their PC isotherms. Their plateau region commonly exhibits a slope. The slope in the plateau region and the pressure difference between the two plateaus are undesirable for any hydrogen-storage applications. The reported disadvantages of bcc metals and alloys as hydrogen-absorbers include slow kinetics, difficulties in activation, and the slope in the PC plateau. Therefore, even though bcc alloys have an intrinsically large hydrogen capacity, studies on their hydrogen-absorption properties have been limited.

Libowitz and Maeland¹ found bcc solid-solution alloys that showed extremely rapid reaction kinetics with hydrogen. They are Ti-V-based alloys such as Ti-V-Fe, Ti-V-Mn, Ti-V-Co, Ti-V-Cr, and Ti-V-Ni.^{3,9,10} The alloys Ti₇₀V₃₀-10at.%M (M = Fe, Mn, Co, Cr, Ni) reacted rapidly with hydrogen in a glass apparatus at room temperature just after evacuation.⁹ Lynch et al.³ reported hydride formation in the Ti-V-Fe system with a bcc structure. They found that dihydride formation, as well as the lattice parameter, depends on alloy composition. This system showed a flat

plateau for the region of mono- and dihydrides. Nomura and Akiba¹¹ reported the hydrogen-absorbing properties of the Ti-V-Fe system. They indicated that the effective capacity for recovery usage is about 2.4 mass%, which is almost twice that of conventional intermetallic hydrides such as LaNi₅. Tsukahara et al.^{4,6} reported on V-based multiphase alloys for the electrodes in a nickel metal hydride battery. TiV₃Ni_{0.56} consisted of two phases that work differently as the electrode material.⁴ One was a Ti-V-based solid solution with a bcc structure that absorbed a large amount of hydrogen. Another was a TiNi-based compound with a bcc structure that formed a three-dimensional network to collect electrons and worked as a catalyst. They also reported another combination of phases in TiV₃Ni_{0.56}Hf_x (x = 0.046, 0.24).⁶ 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 the many cracks increased the fresh surface area of the alloy.

The Laves-Phase-Related bcc Solid Solution Concept

Nominal AB₂ multicomponent alloys developed for battery and heat-pump applications usually contain Zr and Ti in the

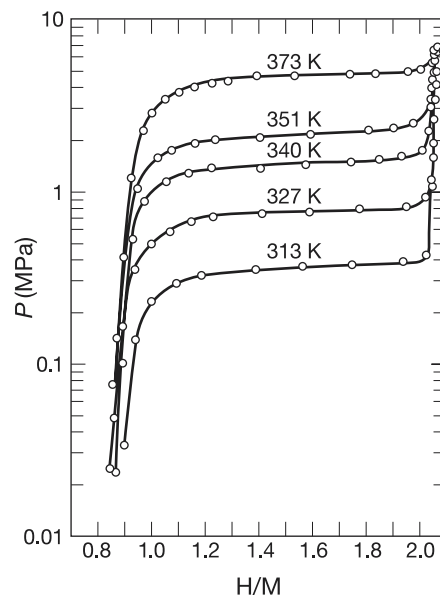


Figure 1. Pressure–composition (PC) isotherms of the vanadium monohydride–dihydride system.⁷ H/M is the hydrogen-to-metal ratio.

A metal site and transition elements in the B metal site.¹²⁻¹⁴ From binary phase diagrams, we learn that both Zr and Ti form bcc solid solutions with Group V, VI, and VII metals in the same row of the periodic table in a wide range of atomic ratios. The Ti-V system forms a bcc solid solution at any ratio of both metals. In the Ti-Mn system, a bcc solid solution exists when the Ti composition is 0–30 at.%, and the TiMn₂ C14 Laves phase has a wide solubility range. In particular, the Ti-Cr binary phase diagram indicates that in the TiCr₂ composition, three Laves phases and a bcc solid solution appear at different temperatures. Therefore, it can be understood that the Laves and bcc phases are readily and simultaneously formed in Zr- or Ti-based alloys. The simplest expression of Miedema's rule of reversed stability is *less stable alloys form more stable hydrides*.¹⁵ The difference in stability of Laves phases and the bcc phase in these Zr- or Ti-based alloys seems to be small, since one phase transfers readily to another by changing the composition or temperature, as previously mentioned. Therefore, the stability of hydrides of these phases is expected to be similar and, as a result, the PC isotherms of the multiphase alloys become smooth. One of the authors named this type of bcc phase the Laves-phase-related bcc solid solution in order to distinguish it from a simple bcc phase such as that in the Ti-V system.¹⁶ Iba and Akiba expanded this concept to pure bcc alloys that consisted mainly of Ti, V, Cr, and Mn and that show a higher hydrogen capacity than that of conventional alloys, as well as rapid reaction kinetics and ease in activation. They proposed Ti-V-Mn, Ti-V-Cr, and Ti-V-Cr-Mn alloys as the typical Laves-phase-related bcc solid-solution alloys.^{17,18} Figure 2 shows the PC isotherms of as-cast and heat-treated Ti₂₅Cr₃₅V₄₀.¹⁹ The width of the plateau reached about 2.2 mass% for the heat-treated alloy.

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

Morphology

Figure 3 shows a transmission electron microscopy (TEM) micrograph of the area adjacent to the bcc/C14 interface in the microstructure of a Ti-V-Mn alloy.¹⁸ A very fine lamellar structure (10 nm thick) was found. The crystal structure of both phases in this lamellar region was bcc, and it has

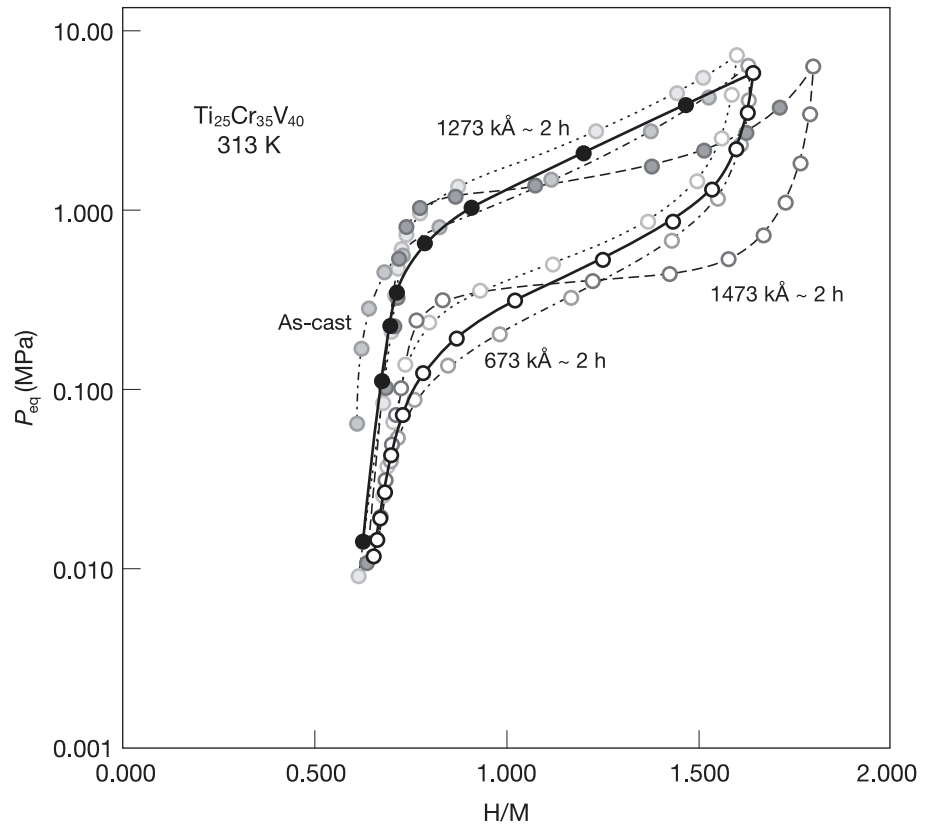


Figure 2. PC isotherms of as-cast and heat-treated Ti₂₅Cr₃₅V₄₀. Solid circles represent hydrogen equilibrium pressures at absorption; open circles represent hydrogen equilibrium pressures at desorption.

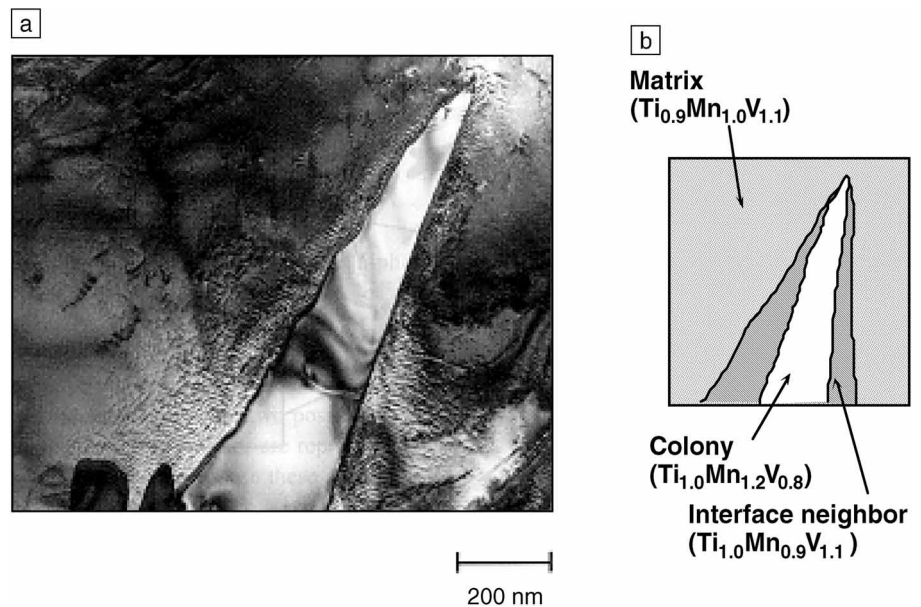


Figure 3. (a) Transmission electron micrograph of the Ti-V-Mn alloy and (b) schematic explanation of the image. Colony is the Laves phase, and interface neighbor is the modulated structure originated by spinodal decomposition.

the same crystal orientation as 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 lamellar structures adjacent to the bcc/C14 interface were modulated structures formed by spinodal decomposition.¹⁸ Iba and Akiba prepared the alloy with the composition of the lamellar region found in Figure 4 and obtained an almost-pure lamellar-structure phase 10 nm thick and 100–200 nm wide. This alloy absorbed more than 2.1 mass% of hydrogen, but the alloy without the lamellar structure absorbed less than 1.5 mass%.

A nanoscale lamellar structure found in the Ti-V-Mn alloy was also observed in the Ti-V-Cr alloys by TEM. This means that Laves-phase-related bcc alloys consist of a nanoscale modulated structure with two bcc phases that were originated by spinodal decomposition,²⁰ or ω transformation (involving a slight displacement of atoms in the bcc lattice), as recently proposed by Enoki et al.²¹ The coherent strain through the boundary between two bcc phases seems to be effective for hydrogen absorption and desorption, but the detailed mechanism is still under investigation.²⁰

Heat Treatment

In the Ti-V-Cr system, the phase diagram indicates the coexistence of bcc solid-solution and Laves phases.²² In addition, Ti-V-Cr alloys showed smaller hysteresis than Ti-Mn-V alloys, making them more suitable for on-board hydrogen storage in fuel-cell vehicles. We found that the lattice parameter of the bcc phase in the Ti-V-Cr system was in the 0.3020–0.3040-nm range.¹⁹ It is interesting to note that the alloys with these lattice parameters absorbed hydrogen at ambient pressure and temperature after only one activation cycle. The as-cast alloy had a sloping plateau, but the alloy treated at 1473 K showed a much flatter plateau. From the results of electron-probe microanalysis, the heat-treated alloys are well homogenized, but the Ti concentration in the as-cast alloy was observed to vary from place to place.²⁰

Okada et al. reported the PC isotherms of Ti₂₅V₃₅Cr₄₀ alloys annealed at 1573 K for periods of time from 1 min to 50 h.²³ Heat-treated samples exhibited a flat plateau region in their PC isotherms. The sample annealed for 1 min showed the highest effective hydrogen capacity, about 2.6 mass%. However, this capacity decreased after annealing for longer annealing times of up to 50 h. The plateau pressure increased and the hydrogen capacity decreased with increasing annealing time. In addition, heat

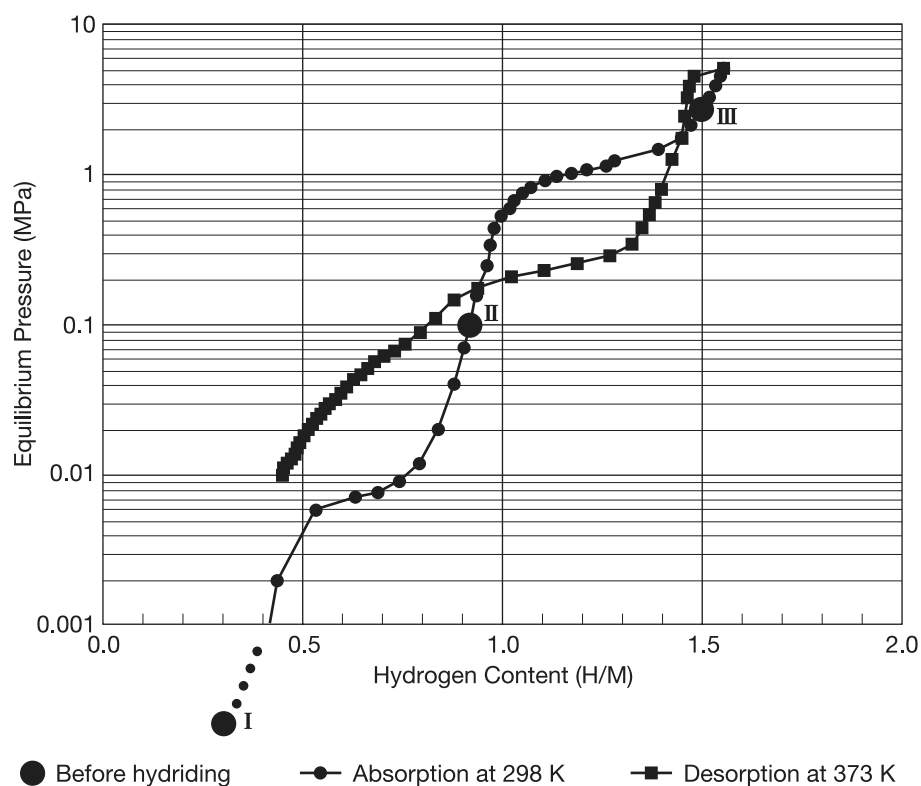


Figure 4. PC isotherms of as-cast Ti_{1.0}V_{1.1}V_{0.9} absorption at 298 K and desorption at 373 K.

treatment above 1573 K was effective in improving the flatness of the plateau region.

The as-cast Ti_{34.6}V₁₀Cr_{55.4} (Cr/Ti = 40/25) alloy contained bcc and C14 Laves phases.²³ However, it was found that after heat treatment over 1573 K, the main phase of this alloy was no longer the Laves phase, but rather the bcc phase with a minor α -Ti phase. This result suggests that annealing above 1573 K is effective in forming a bcc phase even in alloys with low V contents. The as-cast alloy, consisting of Laves and bcc phases, had a hydrogen capacity of <1.8 mass%, while after heat treatment, it had a capacity of >2.6 mass%.²³ It was found that the heat-treated 10 at.% V alloy had a higher effective hydrogen capacity than the vanadium-based 40 at.% V bcc alloys reported by Iba.¹⁹

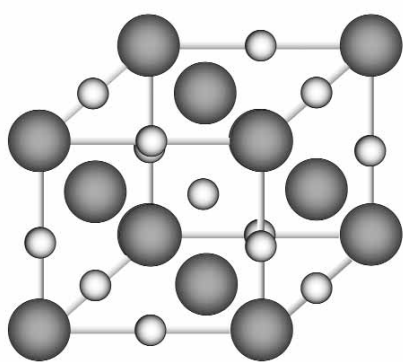
Crystal Structure of Mono- and Dihydrides of Ti-V-Mn bcc Alloys

Figure 4 shows PC isotherms of Ti₃₃V₃₇Mn₃₀.²⁴ It clearly shows two plateau regions in absorption. The lower plateau pressure was around 0.01 MPa, and the higher plateau pressure was around 1 MPa at 298 K. We found three kinds of hydrides in the x-ray diffraction (XRD) profiles of the hydride samples;²⁴ their hydrogen contents are indicated on the PC isotherms I,

II, and III shown in Figure 4. Hydride I has a bcc structure with a hydrogen-to-metal ratio (H/M) of less than 0.5, and hydride II has a pseudo-fcc structure. The hydrogen atom positions in the pseudo-fcc structure with H/M = 1 were investigated by neutron diffraction.²⁵

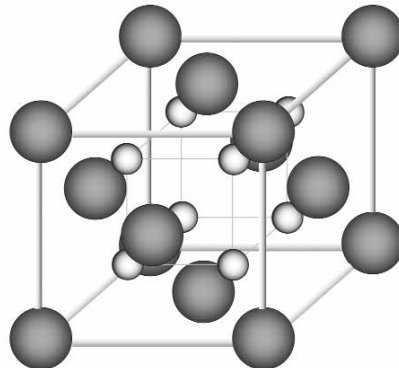
It was found that the structure of hydride II is a pseudo-NaCl and is distinguished from any hydrides formed from bcc solid-solution alloys that have been reported. Hydrogen atoms occupy the octahedral site in the pseudo-fcc lattice. The obtained tetragonal unit cell with $a = 0.29188(3)$ nm and $c = 0.37685(8)$ nm corresponds to a pseudo-fcc unit cell with $a = 0.413$ nm and $a' = 0.377$ nm. We confirmed that hydride III has the CaF₂-type structure in the present study.

Figure 5 shows the crystal structures of hydrides II and III. It is interesting to note that hydrogen atoms occupy the octahedral site in hydride II and the tetrahedral site in hydride III, while the metal sublattice of both hydrides is fcc. As far as the authors know, this is the first finding that NaCl-type interstitial hydride is formed from the bcc structure in transition metals and alloys. This NaCl-type hydride formation is being investigated by the authors because an intermediate hydride between



Monohydride

[Hydride (II)]



Dihydride

[Hydride (III)]

Figure 5. Crystal structures of mono- and dihydride of Ti-V-Mn alloys. Large spheres are metal atoms; small spheres are hydrogen atoms.

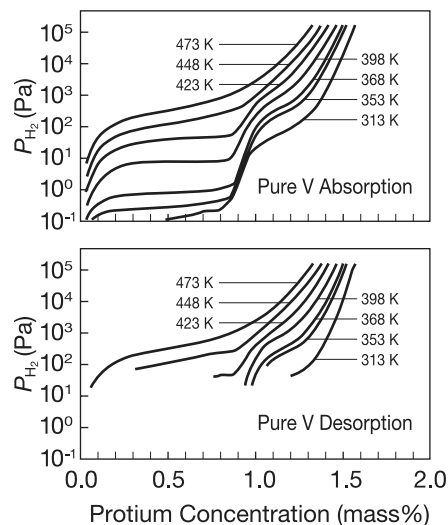


Figure 6. PC isotherms of Ti-Cr-xV ($x = 20\text{--}100$, $\text{Ti}/\text{Cr} = 2/3$) alloys measured in low-pressure region ($10^{-1}\text{--}10^5$ Pa).

a bcc alloy and a full hydride of $\text{H}/\text{M} = 2$ seems to be one of the materials needed to improve the hydrogen capacity of the alloy.

Materials Development of bcc Hydrogen-Absorbing Alloys Ti-V-Cr Ternary Alloys

Tominaga et al. reported the effects of alloy composition and heat treatment on hydrogen absorption-desorption properties of Ti-(0–35)at.%V-Cr alloys.²⁶ The alloys containing more than 15 at.% V with mainly bcc phase exhibited a hydrogen absorption-desorption capacity of about 2.4 mass%. However, XRD indicated that the alloys with a V content of less than 10% contain Laves phase, and they had a small hydrogen capacity of less than 1.8 mass%. These results suggest that the alloys containing a bcc phase as a main phase exhibit large hydrogen absorption-desorption capacities.

Pressure-Composition Isotherms in a Low-Pressure Range for Pure V or Ti-V-Cr Alloys

Increasing the hydrogen-storage capacity of V-based bcc alloys will require using some part of the stable vanadium monohydride. The one possible way is to add some elements to the V-based alloys to destabilize the vanadium monohydride. In order to measure the stability of vanadium monohydride, PC isotherms were measured in a low-pressure range ($10^{-1}\text{--}10^5$ Pa).

Figure 6 shows PC isotherms of the alloys in this low-pressure region measured at 313 K and 368 K. It was found that pure vanadium has a distinct plateau at 368 K;

the plateau at 313 K exists below the measured pressure range. On decreasing the vanadium content of the Ti-V-Cr alloys, the plateau region becomes less well defined and more sloping. This means that vanadium monohydride becomes unstable and starts to contribute to desorption of the hydrogen at atmospheric pressure. In other words, the hydrogen concentration at 10^5 Pa for the alloys decreases with decreasing V content, and a higher hydrogen content can contribute to a practical pressure between 10^5 Pa and 10^7 Pa. It is interesting to note that stable vanadium monohydride becomes unstable by adding the other elements, and that the instability starts in the practical desorption pressure range.

Low-Vanadium Alloys with High Hydrogen Capacity

Since vanadium monohydride becomes unstable with decreasing V content, higher hydrogen capacity is expected in the alloys with low V content. However, as mentioned previously, the alloys with low V content required optimization of the heat-treatment conditions. Okada et al. reported that Ti-(5–7.5)at.%V-Cr alloys, which consist of pure bcc phase, yield the highest hydrogen capacity, 3.0 mass%.²³ This is the highest value at 313 K reported so far. Since vanadium is expensive, the developed alloys with small V content are economical.

Ti-Cr-X (X = Mo, Ru) Alloys

Kamegawa et al.²⁷ reported that the Ti-Cr-(1–2.5)at.%Mo alloys show almost the same hydrogen capacities as those

reported in Ti-(5–7.5)at.%V-Cr alloys. Matsukawa et al.²⁸ also obtained a hydrogen capacity of 3.0 mass% by adding Ru to Ti-Cr alloys. These V-free Ti-Cr alloys will also be suitable for future applications.

Conclusions

In this article, we introduced a new concept of hydrogen-absorbing bcc alloys called Laves-phase-related bcc solid solutions, so named because they were found to have a Laves phase in multiphase AB_2 . The concept has been extended to the bcc alloys consisting of Ti, V, Cr, and Mn, which behave like conventional intermetallic hydrogen-absorbing alloys, but with a larger hydrogen capacity.

However, bcc alloys generally exhibit two plateaus in pressure-composition isotherms and only the higher-pressure plateau is applicable. Efforts have been made to increase the hydrogen capacity of these alloys by, for example, determining the crystal structure of a new monohydride phase and developing Ti-V-Cr-based alloys. By optimizing the chemical compositions and heat-treatment conditions, new materials with greater hydrogen-storage capacity can be synthesized.

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References

1. G.G. Libowitz and A.J. Maeland, *Mater. Sci. Forum* **30** (1988) p. 177.
2. S. Ono, K. Nomura, and Y. Ikeda, *J. Less-Common Met.* **72** (1980) p. 159.
3. J.F. Lynch, A.J. Maeland, and G.G. Libowitz, *Z. Phys Chem. NF* **145** (1985) p. S. 51.
4. M. Tsukahara, K. Takahashi, T. Mishima, T. Sakai, H. Miyamura, N. Kuriyama, and I. Uehanara, *J. Alloys Compd.* **224** (1995) p. 162.
5. T. Kabutomori, H. Takeda, Y. Wakisaka, and K. Ohnishi, *J. Alloys Compd.* **231** (1995) p. 528.
6. M. Tsukahara, K. Takahashi, T. Mishima, A. Isomura, and T. Sakai, *J. Alloys Compd.* **236** (1995) p. 151.
7. J.J. Reilly and R.H. Wiswall Jr., *Inorg. Chem.* **9** (1970) p. 1678.
8. K. Papatthanassopoulos and H. Wenzl, *J. Phys. F: Met. Phys.* **12** (1982) p. 1369.
9. A.J. Maeland, G.G. Libowitz, and J.F. Lynch, *J. Less-Common Met.* **104** (1984) p. 361.
10. A.J. Maeland, G.G. Libowitz, J.F. Lynch, and G. Rak, *J. Less-Common Met.* **104** (1984) p. 133.
11. K. Nomura and E. Akiba, *J. Alloys Compd.* **231** (1995) p. 513.
12. J. Huot, E. Akiba, T. Ogura, and Y. Ishido, *J. Alloys Compd.* **218** (1995) p. 101.
13. J. Huot, E. Akiba, and H. Iba, *J. Alloys Compd.* **228** (1995) p. 181.
14. H. Iba and E. Akiba, *J. Alloys Compd.* **231** (1995) p. 508.
15. H.H. van Mal, K.H.J. Buschow, and A.R. Miedema, *J. Less-Common Met.* **35** (1974) p. 65.
16. E. Akiba, J. Huot, and H. Iba, *Hydrogen and Metal Hydride Batteries*, edited by P.D. Bennett and T. Sakai (The Electrochemical Society, Proc. **94-27**, Pennington, NJ, 1994) p. 165.
17. H. Iba and E. Akiba, U.S. Patent No. 5,968,291 (October 19, 1999) and No. 6,153,032 (November 28, 2000).
18. H. Iba and E. Akiba, *J. Alloys Compd.* **253-254** (1997) p. 21.
19. H. Iba, Ph.D. thesis, Tohoku University, Sendai, Japan, 1997.
20. E. Akiba and H. Iba, *Intermetallics* **6** (1998) p. 461.
21. H. Enoki, Y. Nakamura, and E. Akiba, in *Proc. 4th Pacific Rim Int. Conf. on Advanced Materials and Processing*, edited by S. Hanada, Z. Zhong, S.W. Nam, and R.N. Wright (The Japan Institute of Metals, Sendai, 2001) p. 521.
22. E. Enomoto, *J. Phase Equilib.* **13** (1992) p. 195.
23. M. Okada, T. Kuriwa, T. Tamura, H. Takamura, and A. Kamegawa, *Met. Mater. Int.* **7** (2001) p. 67.
24. Y. Nakamura and E. Akiba, *J. Alloys Compd.* **311** (2000) p. 217.
25. Y. Nakamura, K. Oikawa, T. Kamiyama, and E. Akiba, *J. Alloys Compd.* **316** (2001) p. 284.
26. Y. Tominaga, S. Nishimura, T. Amemiya, T. Fuda, T. Tamura, T. Kuriwa, A. Kamegawa, and M. Okada, *Mater. Trans., JIM* **40** (1999) p. 871.
27. A. Kamegawa, T. Kuriwa, T. Tamura, H. Takamura, and M. Okada, *Mater. Trans., JIM* **43** (2002) p. 470.
28. A. Matsukawa, T. Iwamura, T. Chou, and S. Yamashita, in *Proc. of Spring Meeting of Japan Institute of Metals* (The Japan Institute of Metals, Sendai, 2001) p. 349. □

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