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Compositional dependence of hydriding properties of vanadium alloys at low hydrogen pressures

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Abstract

The alloying effects have been investigated experimentally on the hydriding properties of vanadium at low hydrogen pressures. The PCT curves for the β phase (V_2H or VH) are measured using an electrochemical method. It is found that the logarithm of the plateau pressure for the V_2H and the VH phases change almost linearly with the amount of alloying element in vanadium metal. Also, when the Ti/Cr compositional ratio is fixed at 1, the equilibrium hydrogen pressure increases for the V_2H phase but decreases for the VH phase with increasing total content of Ti and Cr. However, both the V_2H and the VH phases become unstable with decreasing Ti/Cr compositional ratio, so that the PCT curve shifts towards the lower H/M side and the second plateau region for the VH_2 phase existing at high hydrogen pressures spreads to some extent, which leads to the improvement in the effective hydrogen capacity of the alloy.

Keywords: Hydrogen storage materials; Vanadium hydride; V_2H; VH; Alloying effects; Hydride stability

1. Introduction

Vanadium metal with b.c.c. crystal structure is one of the promising hydrogen storage materials with a high capacity. When it absorbs hydrogen, the β_1 phase (V_2H low-temperature phase) is formed first. Then, as the hydrogenation proceeds, the first-order phase transition from the β_1 phase to the β_2 phase (V_2H high-temperature phase or VH) takes place in it [1]. Finally, the γ phase (VH_2) is formed when it is fully hydrogenated [2]. As a result, there exists two plateaus in the PCT curve of the V–H system. The first plateau corresponds to the coexistence of the following reaction between α phase (hydrogen solid solution phase) and the β_1 phase;

$$2V(\alpha) + 1/2\,H_2 \rightleftarrows V_2H(\beta_1) \tag{1}$$

The β_1 phase is so stable that the first plateau pressure for this hydride formation is as low as 0.1 Pa at moderate temperatures [3]. Therefore, the hydrogen desorption reaction from the β_1 phase never occurs at room temperature.

On the other hand, the second plateau corresponds to the following reaction between the β_2 phase (VH) and the γ phase;

$$VH(\beta_2) + 1/2\,H_2 \rightleftarrows VH_2(\gamma) \tag{2}$$

As the γ phase is not so stable, its hydrogen absorption and desorption reaction can take place at moderate temperatures and pressures. For this reason, only about half the amount of hydrogen absorbed in vanadium metal can be used in the subsequent hydrogen absorption and desorption processes [2]. This amount is, however, not enough for practical applications, so it would be desirable to increase the usable hydrogen capacity by controlling the stability of the vanadium hydrides by alloying. However, the alloying effects on the phase stability of vanadium hydrides still remain unclear, especially for the β phase. This is mainly due to the experimental difficulties in measuring PCT curves at low hydrogen pressures.

Recently, we have developed a new electrochemical method for measuring PCT curves at low hydrogen pressures [4]. Using this method, the alloying effects on the stability of the β phase have been investigated for V–3mol%M alloys, where M is a 3d transition metal. It is found that a small amount of alloying element, M,

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modifies largely the stability of the β phase, and the alloying effects on the hydride stability are different between the γ phase and the β phase. For example, the γ phase becomes most unstable when the Group 8 elements, Fe, Ru and Os, are added to vanadium [5]. On the other hand, the stability of the β phase changes monotonously following the order of elements in the periodic table [4].

In this study, focusing our attention on the alloying effects on the stability of the β phase, a systematic investigation has been carried out experimentally at low hydrogen pressures in order to understand the compositional dependence of hydriding properties of vanadium alloys in a concrete manner.

2. Experimental procedure

2.1. PCT measurement at low hydrogen pressures

The PCT curves are measured at low hydrogen pressures by a coulometric titration method using a electrochemical cell with the electrodes made of Pd membrane [4]. In this method, the hydrogen pressures are measured using the following hydrogen concentration cell between the reference and the working electrodes

$$\underset{\text{(Reference)}}{P_{H_2}{}^{\circ}}\;\Big|\;\text{Pd}-\underline{\text{H}}^{\circ}\;\Big|\;\underset{(\text{H}^{+})}{\text{H}_3\text{PO}_4}\;\Big|\;\text{Pd}-\underline{\text{H}}\;\Big|\;\underset{\text{(Sample)}}{P_{H_2}}\;\Big| \tag{3}$$

After the partial equilibrium is achieved, the hydrogen pressure can be estimated from the electromotive force, E, between the reference and the working electrodes following the Nernst's equation

$$E = -\frac{RT}{2F}\ln\frac{P_{H_2}}{P_{H_2}{}^{\circ}} \tag{4}$$

where R is the gas constant, F is the Faraday constant, $P_{H_2}{}^{\circ}$ and P_{H_2} are the partial pressures of hydrogen at the reference and the working electrode, respectively. Hydrogen is introduced into the sample cell by the electrolysis charging method. The detailed explanation for this method is given in Ref. [4].

2.2. Sample preparation

The purity of raw materials used in this experiment is 99.9mol% for vanadium and better than 99.9mol% for the other alloying elements. About 10 g buttons of binary V–M and ternary V–Ti–M alloys are arc-melted and then homogenized at 1373 K for 86.4 ks in a high purity argon gas atmosphere. The button specimen is cut into rods and subsequently polished mechanically and chemically to remove surface oxide layers. Then the rod specimen is activated following the procedure reported in a previous study [2]. After the specimen is fully activated, it is hydrogenated again at room temperature by introducing hydrogen at about 0.7 MPa. Then, the hydrogenated specimen is put into a Pd capsule under a highly purified argon gas atmosphere and completely sealed by welding both ends of the capsule in order to avoid the reaction of the sample in the cell with the electrolyte of H_3PO_4 aqueous solution. Finally, hydrogen in the specimen is released by holding the Pd capsule at 673 K in a vacuum of about 5×10^{-4} Pa for more than 21.6 ks. The PCT curves for the β phase are measured in the course of hydrogenation at 343 K.

On the other hand, for the γ phase, the PCT curves are measured at high hydrogen pressures in the course of hydrogenation at 314 K using an ordinary Sieverts-type apparatus.

3. Results and discussion

3.1. Alloying effects on the stability of the β phase

3.1.1. Binary V–M alloys

The PCT curves for V–6mol%M and V–10mol%Ti alloys are measured at low hydrogen pressures at 343 K, and the results are shown in Fig. 1. As is evident from this figure, a plateau is observed in each PCT curve at the region, $H/M<0.5$, although its slope is steep to some extent. Also, the PCT curve shows an inflection point around $H/M=0.6$, which is associated with the phase transition from the β_1 phase to the β_2 phase [1]. Here, the

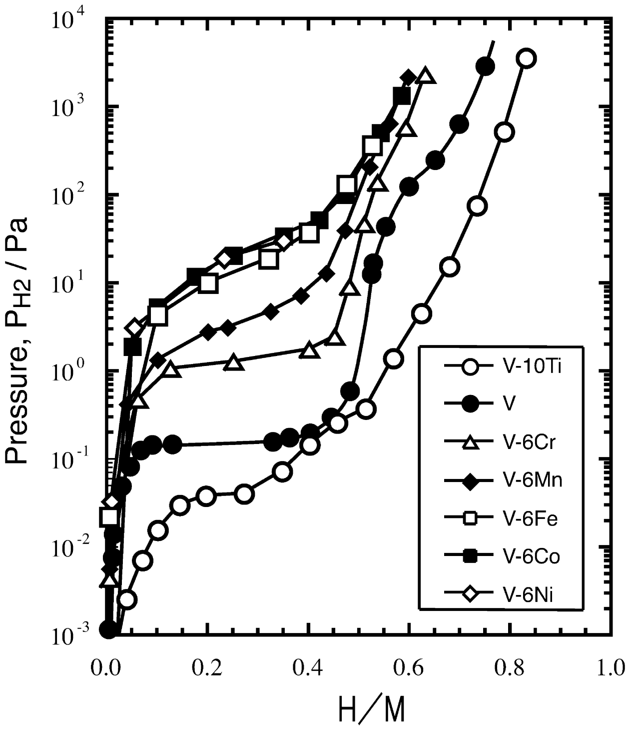

Fig. 1. PCT curves at low hydrogen pressures measured in the course of hydrogenation of V–6mol%M and V–10mol%Ti alloys at 343 K.

equilibrium hydrogen pressures at H/M = 0.25 and 0.6 are defined as P_1 and P_2, respectively.

Fig. 2 shows the changes in the values of P_1 and P_2 for V–6mol%M alloys with alloying element, M. For comparison, the results of V–10mol%Ti alloy are presented in this figure. It is apparent that both the values of P_1 and P_2 change monotonously following the order of the element, M, in the periodic table. Similar results are also obtained for V–3mol%M alloys as shown in Fig. 3 [4]. This trend of the hydrogen pressure change with M for the β phase is different from that of the second plateau pressure change for the γ phase [5]. For example, the second plateau pressure shows a peak when the Group 8 element, Fe (or Ru or Os), is added to vanadium metal [5]. Such a peak is not seen in the P_1 and P_2 curves shown in Figs. 2 and 3.

The changes in the values of P_1 and P_2 with the amount of alloying elements in the alloys are shown in Fig. 4(a) and (b), respectively. As is evident from this figure, the logarithm of the hydrogen pressures at H/M = 0.25 and 0.6

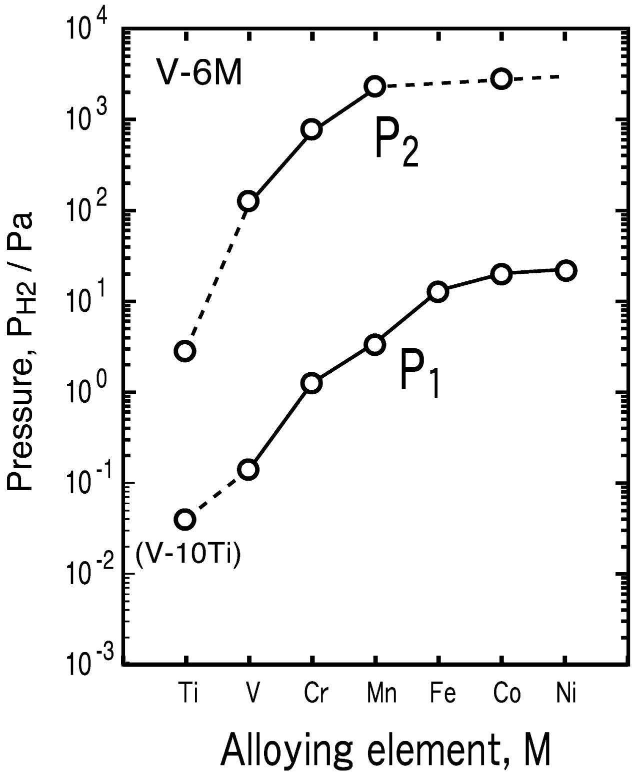

Fig. 2. Changes in the hydrogen pressure of V–6mol%M alloys at H/M = 0.25 (P_1) and 0.6 (P_2) with alloying element, M.

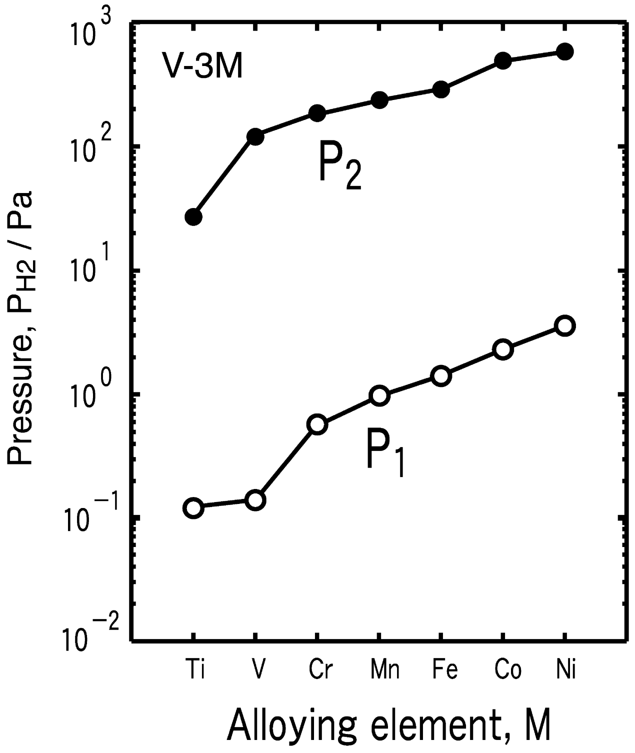

Fig. 3. Changes in the hydrogen pressures of V–3mol%M alloys at H/M = 0.25 (P_1) and 0.6 (P_2) with alloying element, M.

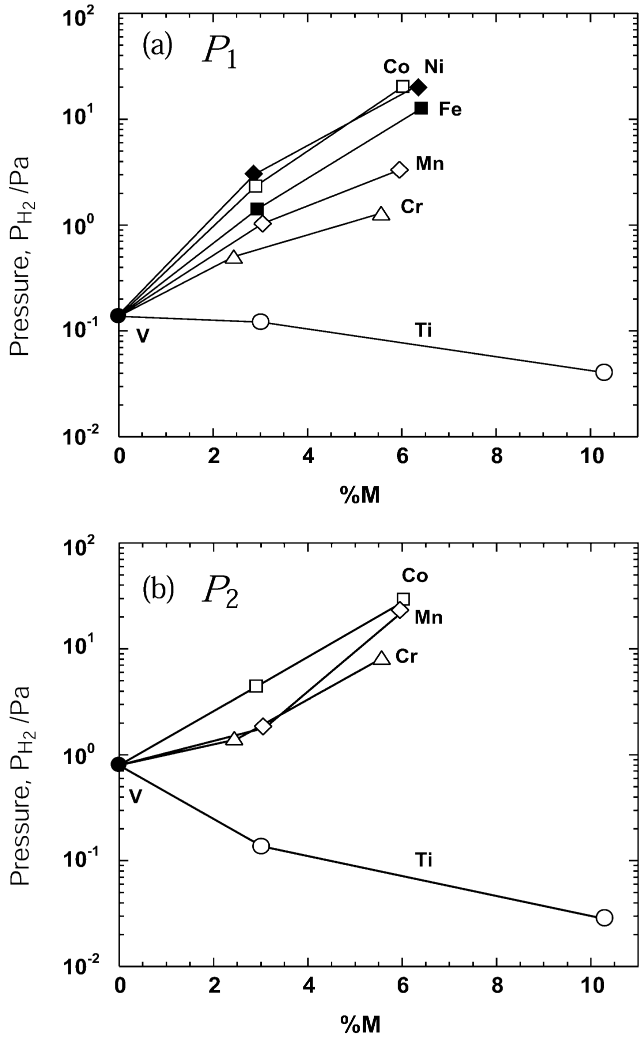

Fig. 4. Change in the hydrogen pressures at (a) H/M = 0.25 (P_1) and (b) H/M = 0.6 (P_2) with the amount of alloying elements, M, in binary V–M alloys.

change almost linearly with the amount of alloying element. Such a linear relationship is also obtained for the second plateau pressure for the γ phase at high hydrogen pressures [5].

3.1.2. Ternary V–Ti–M alloys

Here, it is noted that the efficiency in modifying P_1 and P_2 by alloying is dependent on the alloying elements, M. For example, as shown in Fig. 3, the addition of the hydride forming element, Ti, scarcely affects the equilibrium hydrogen pressure, P_1, but it significantly lowers the pressure, P_2. On the other hand, the addition of the hydride non-forming elements (e.g. Cr, Mn, Fe, Co, Ni), yields a larger change in P_1 than in P_2.

From these results, it may be expected that when both the hydride forming element (e.g. Ti) and the hydride non-forming element (e.g. Cr) are added to vanadium metal at the same time, the apparent stability of the β_2 phase has a chance to increase in some cases, even if the β_1 phase becomes unstable.

In fact, such a phenomenon is observed in the ternary V–Ti–Cr alloys. Fig. 5 shows the PCT curves of V–*x* mol%Ti–*x* mol%Cr (*x* = 0, 10, 20) alloys measured in the course of hydrogenation at 343 K. It is noted that all these alloys have the same Ti/Cr compositional ratio, Ti/Cr = 1. As is evident from this figure, the equilibrium hydrogen pressures for the β_1 phase increases but that for the β_2 phase decreases with increasing content of alloying elements. As a result, each curve ends at almost the same H/M position in Fig. 5. In this case, as shown in Fig. 6, the extent of the second plateau region existing at high hydrogen pressures is scarcely modified, despite the fact that the second plateau pressure changes largely depend on the alloy composition.

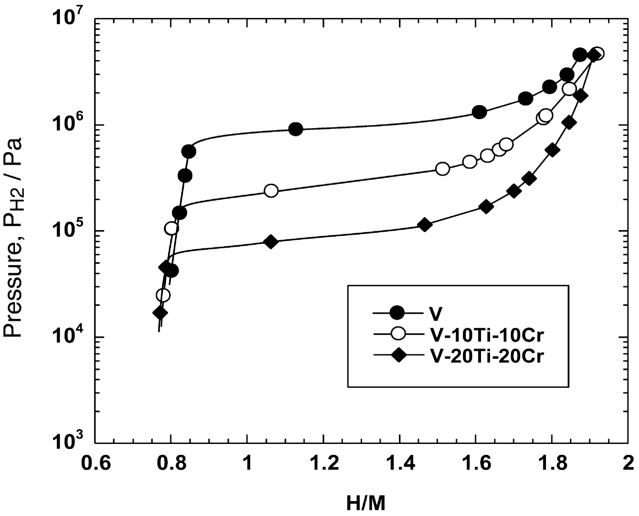

Fig. 6. PCT curves for V–*x* mol%Ti–*x* mol%Cr (*x* = 0, 10, 20) at high hydrogen pressures measured in the course of hydrogenation at 313 K.

On the other hand, the stabilities of both the β_1 and the β_2 phases can be modified by controlling the Ti/M compositional ratio in the ternary V–Ti–M alloys. Fig. 7

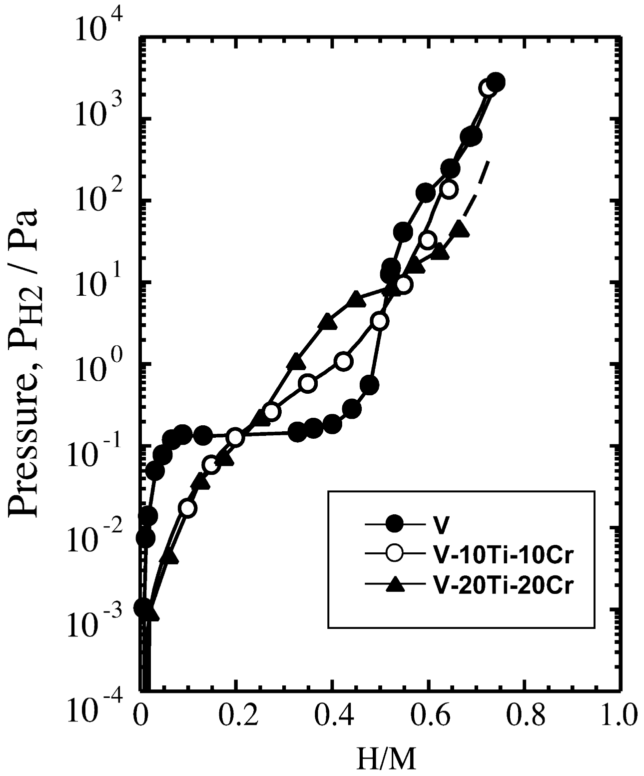

Fig. 5. PCT curves for V–*x* mol%Ti–*x* mol%Cr (*x* = 0, 10, 20) measured in the course of hydrogenation at 343 K.

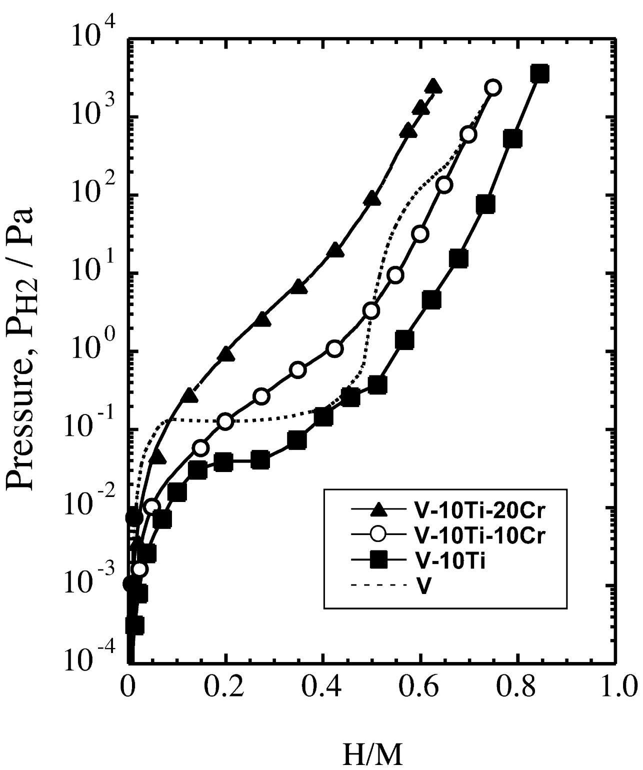

Fig. 7. PCT curves for V–10mol%Ti–*x* mol%Cr (*x* = 0, 10, 20) measured in the course of hydrogenation at 343 K.

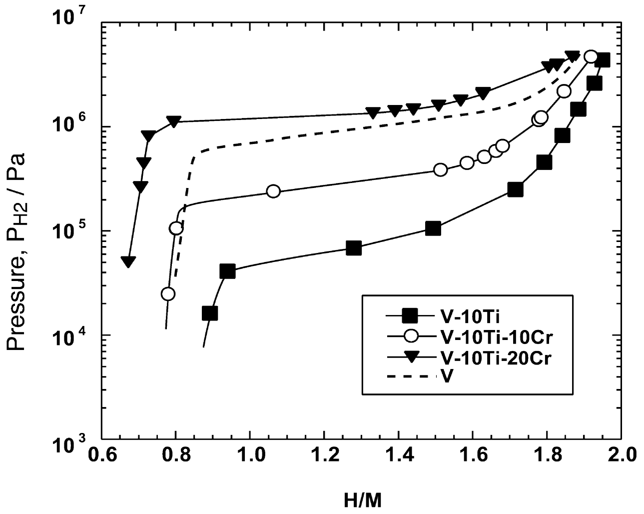

Fig. 8. PCT curves for V–10mol%Ti–*x* mol%Cr ($x=0$, 10, 20) at high hydrogen pressures measured in the course of hydrogenation at 313 K.

shows the PCT curves for V–10mol%Ti–*x* mol%Cr ($x=0$, 10, 20) alloys measured in the course of hydrogenation at 343 K. The Ti/Cr compositional ratios of these alloys are ∞, 1 and 0.5, respectively. As shown in this figure, the curve shifts toward the higher hydrogen pressure side when the Cr content increases. In other words, both the β_1 and the β_2 phases become unstable with decreasing Ti/Cr compositional ratio. As a result, the end position of the curve shown in Fig. 7 shifts towards the lower H/M side. This may cause the expansion of the second plateau region, which leads to the improvement in the effective hydrogen capacity of the alloy. In fact, as shown in Fig. 8, such a positive effect can be seen in the PCT curves of these alloys measured in the course of hydrogenation at 313 K, despite the fact that the second plateau pressure increases with decreasing Ti/Cr compositional ratio. Similar results are also obtained in ternary V–Ti–Ru alloys.

4. Conclusion

The alloying effects have been investigated experimentally on the stability of the β_1 (V_2H) and the β_2 (VH) phases formed in various binary V–M and ternary V–Ti–M alloys at low hydrogen pressures.

It is found that the logarithms of the plateau pressure for the β_1 and the β_2 phases change almost linearly with the amount of alloying element, M, in the binary alloys. It is also shown that the alloying efficiency in modifying the stability operates in a different way between the β_1 and the β_2 phases. In addition, it is shown that the hydrogen capacity is improved to some extent by controlling the stability of vanadium hydrides by the combinational use of alloying elements.

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