Alloying Effects on the Phase Stability of Hydrides Formed in Vanadium Alloys

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The alloying effects on the stability of vanadium hydrides have been investigated systematically for binary V–M and ternary V–Ti–M alloys, where M’s are various alloying elements. The PCT curves for the β phase (V2H or VH) are measured at low hydrogen pressures using an electrochemical method. On the other hand, for the γ phase (VH2), the PCT curves are measured at high hydrogen pressures using an ordinary Sieverts-type apparatus. It is found that the phase stability of vanadium hydrides is affected strongly by the presence of a small amount of elements added to vanadium metal. 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 in the periodic table, Fe, Ru and Os, are added to vanadium metal. On the other hand, the stability of the β phase changes monotonously following the order of elements in the periodic table. Also, the efficiency of alloying element in modifying the hydride stability is found to be different between the β1 phase (V2H) and the β2 phase (VH). In addition, it is shown that the logarithm of the plateau pressures for the β1 and the γ phases change almost linearly with the amount of alloying element in the alloy. Using this linear relationship for the γ phase, the second plateau pressures of ternary V–Ti–Ru and V–Ti–Cr alloys can be estimated quantitatively in the wide compositional range.

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1. Introduction

Vanadium metal with a bcc crystal structure is one of the promising hydrogen storage materials with a high capacity. It absorbs hydrogen and forms first the β1 phase (V2H low-temperature phase). Then, as the hydrogenation proceeds, the first order phase transition from the β1 phase to the β2 phase (V2H high-temperature phase or VH) takes place. Finally, the γ phase (VH2) is formed when it is fully hydrogenated. As a result, there exist two plateaus in the PCT curve of the V–H system. Here, the first plateau corresponds to the coexistence of the α phase (hydrogen solid solution phase) and the β1 phase;

\[ 2V(\alpha) + 1/2H_2 \rightleftharpoons V_2H(\beta_1). \] (1)

However, the β1 phase is so stable that the first plateau pressure for this hydride formation is as low as 0.1 Pa at moderate temperatures. Therefore, the hydrogen desorption reaction from the β1 phase never occurs in the moderate conditions, for example, at room temperature.

On the other hand, the second plateau corresponds to the coexistence of the β2 phase (VH) and the γ phase;

\[ VH(\beta_2) + 1/2H_2 \rightleftharpoons VH_2(\gamma). \] (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 a half amount of hydrogen absorbed in vanadium metal can be used in the subsequent hydrogen absorption and desorption processes. 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.

Recently, we have calculated the electronic structures of vanadium hydrides, V2H, VH and VH2, which contain various alloying elements in order to understand the alloying effects on the stability of these hydrides in view of chemical bond between atoms. In addition, the stability of the γ phase has been investigated experimentally for binary V–1 mol%M and V–3 mol%M alloys where M’s are various alloying elements including 3d-, 4d-, 5d-transition metals and some non-transition metals. It is found that the stability of the γ phase is modified largely by the addition of a small amount of alloying elements, M. Also, the plateau pressure changes in a systematic way following the order of elements in the periodic table. For example, the plateau pressure is high for the group 8 elements such as Fe, Ru and Os.

On the other hand, to the best of our knowledge, there have been no systematic investigations concerning the alloying effects on the hydriding properties of the β phase. This is mainly due to the experimental difficulties in conducting the PCT measurement at low hydrogen pressures. Recently, we have developed a new electrochemical method for measuring PCT curves at low hydrogen pressures. In this study, focusing our attention on the alloying effects on the stability of the β phase, a systematic investigation has been performed experimentally at low hydrogen pressures. Also, the hydriding properties of ternary V–Ti–M alloys have been studied in order to investigate the effects of third elements on the stability of the γ phase at low hydrogen pressures.

2. Experimental Procedure

2.1 PCT measurement at low hydrogen pressures

The PCT curves are measured for the β phase at low hydrogen pressures by an electrochemical method using the electrodes made of Pd membrane. The schematic illustration of
the electrochemical cell used in this study is shown in Fig. 1. The Pd capsule is used for the sample cell (denoted by W in Fig. 1) so as to avoid the reaction of the sample in the cell with the electrolyte of H₃PO₄ aqueous solution. It also works as a hydrogen permeable membrane to attain the partial equilibrium on hydrogen between the sample and the electrolyte. It is noted that the sample in the cell reacts with gaseous hydrogen in this method. This is in contrast to the standard electrochemical method in which the sample reacts with the hydrogen ion in the electrolyte.

The hydrogen pressures are measured using the following hydrogen concentration cell between the reference electrode (denoted by R in Fig. 1) and the sample electrode; 8)

\[
\begin{align*}
P_{\text{H}_2}^{\text{(Reference)}} & \quad \text{Pd} - \text{H}^+ \quad \text{H}_3\text{PO}_4 \quad (\text{H}^+) \quad \text{Pd} - \text{H} \quad P_{\text{H}_2}^{\text{(Sample)}} \\
\end{align*}
\]

After the partial equilibrium is achieved, the hydrogen pressure can be estimated from the electromotive force, \(E\), between the standard and the sample electrodes following the Nernst’s equation,

\[
E = -\frac{RT}{2F} \ln \frac{P_{\text{H}_2}^{\text{(Reference)}}}{P_{\text{H}_2}^{\text{(Sample)}}},
\]

where \(R\) is the gas constant, \(F\) is the Faraday constant, \(P_{\text{H}_2}^{\text{(Reference)}}\) and \(P_{\text{H}_2}^{\text{(Sample)}}\) are the partial pressures of hydrogen at the reference and the sample electrode, respectively. The standard gas of Ar–H₂ (99:1) is used as the gas in the reference electrode and also as the hydrogen source of the counter electrode (denoted by C in Fig. 1). Hydrogen is introduced into the sample cell by the electrolysis charging method.

2.2 Sample preparation

The purity of raw materials used in this experiment is 99.9 mol% for vanadium and better than 99.9 mol% for 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 they are polished mechanically and chemically to remove surface oxide layers. Then the rod specimen is activated following the procedure reported in a previous study. After the specimen is fully activated, it is hydrogenated again at room temperature by introducing hydrogen of 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. Finally, hydrogen in the specimen is released by holding the Pd capsule at 673 K in vacuum of about \(5 \times 10^{-4}\) Pa for more than 21.6 ks. The PCT curves for the \(\beta\) phase are measured in the course of hydrogenation at 343 K.

On the other hand, for the \(\gamma\) phase, the PCT curves are measured at high hydrogen pressures using an ordinary Sieverts-type apparatus. The specimens are prepared and activated by the same way described in Ref. 7). The PCT curves are measured at 313 K.

3. Results and Discussion

3.1 Alloying effects on the stability of the \(\beta\) phase

3.1.1 Binary V–M alloys

The PCT curves of binary V–M alloys are measured in the course of hydrogenation at low hydrogen pressures at 343 K, and the results are shown in Fig. 2 for V–3 mol%M alloys, and in Fig. 3 for V–6 mol%M and V–10 mol%Ti alloys. As is evident from these figures, a plateau is observed in each PCT curve at the region, \(H/M < 0.5\), despite that its slope tends to become steeper as the amount of alloying element increases. Also, the PCT curve shows an inflection point around \(H/M = 0.6\), which is considered to be associated with the phase transition from the \(\beta_1\) phase to the \(\beta_2\) phase.

The equilibrium hydrogen pressures at \(H/M = 0.25\) and 0.6 are defined as \(P_1\) and \(P_2\), respectively. For V–3 mol%M alloys, the changes in the values of \(P_1\) and \(P_2\) with alloying elements are summarized in Fig. 4. As shown in this figure, both the values of \(P_1\) and \(P_2\) change monotonously following the order of the element, M, in the periodic table. For exam-
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3.1. Binary V–M Alloys

3.1.1. Hydrogen Pressure Changes

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Fig. 3 PCT curves at low hydrogen pressures measured in the course of hydrogenation of V–6 mol%M and V–10 mol%Ti alloys at 343 K.

Fig. 4 Changes in the equilibrium hydrogen pressures of V–3 mol%M alloys at H/M = 0.25 (P₁) and 0.6 (P₂) with alloying element, M.

Fig. 5 Change in the equilibrium hydrogen pressures, P₁, with the amount of alloying elements, M, in binary V–M alloys.

Fig. 6 PCT curves of V–x mol%Ti–x mol%Cr (x = 0, 10, 20) alloys measured in the course of hydrogenation at 343 K.

Fig. 7 PCT curves for V–10 mol%Ti–x mol%Cr (x = 0, 10, 20) alloys measured at high hydrogen pressures.
pressures in the course of hydrogenation at 343 K. As shown in this figure, the width of the plateau region expands to some extent with increasing Cr content in the alloy. This is because the starting position of each plateau shifts toward the lower H/M side with increasing Cr content, but the ending position falls in the almost same H/M region, regardless of the alloy composition. From both the results shown in Figs. 7 and 8, it can be said that the increase in the effective capacity of hydrogen in the V–10 mol%Ti–20 mol%Cr alloy is attributable mainly to the destabilization of the β phase. Similar results are also obtained in the ternary V–Ti–Ru alloys.

3.2 Alloying effects on the stability of the γ phase

3.2.1 Effect of third element into binary V–M alloys

The PCT curves are measured for V–1 mol%Ti–1 mol%M alloys at high hydrogen pressures in order to investigate the effects of third elements on the stability of the γ phase. The plateau pressure measured during the hydrogen desorption at 313 K is shown in Fig. 9. For comparison, the results of the plateau pressures for binary V–1 mol%M alloys are also presented in this figure. As shown in Fig. 9, the plateau pressure curves of these binary and ternary alloys are almost parallel to each other, despite that they change largely by the addition of a small amount of alloying elements, M. This result indicates that the Ti addition into the binary V–1 mol%M alloys lowers the plateau pressure, but it works independently of M. In other words, Ti and M seems to operate independently to the phase stability of the γ phase.

Such an independent effect of Ti from other alloying elements can also be seen in the ternary alloys containing a large amount of alloying elements. As an example, the experimental results of the plateau pressures for ternary V–x mol%Ti–y mol%M alloys (x = 0–30, y = 0–13) are shown in Fig. 10 by using solid circles. It is evident from this figure that
measured plateau pressure changes almost linearly with the amount of Ru in the alloy. Also, the slope of each line drawn at the constant Ti composition is nearly same in the wide range of the Ti composition from 0 to 30 mol%. Similar results are also obtained for a ternary V–Ti–Cr system as shown in Fig. 11.

3.2.2 Prediction of the plateau pressure of V–Ti–M ternary system

The changes in the plateau pressure with the amount of alloying elements are examined for binary V–M alloys, and the results are shown in Fig. 12. As shown in this figure, the logarithm of plateau pressure changes almost linearly with the amount of alloying element added into vanadium metal except for some elements such as Zr. Similar linearity can also be seen in the ternary V–10%Ti–M system as shown in Fig. 13.

From these results, it is expected that the plateau pressure for the γ phase can be estimated from the results of dilute binary alloys. Then, for V–x mol%Ti–y mol%Ru alloys, the plateau pressures are calculated using an equation,

\[ \log P = \log P_V + (x \cdot \Delta P_{Ti} + y \cdot \Delta P_{Ru}) \]  

where, \( P_V \) is the plateau pressure for pure vanadium and \( \Delta P_M \) is the slope of the plateau pressure change with the M content shown in Fig. 12 (in the present case, M = Ti or Ru). The calculated plateau pressures for various V–Ti–Ru alloys are shown in Fig. 10 by using open circles. Surprisingly, the plateau pressure estimated from the dilute binary system is very similar to the experimental value for the concentrated ternary alloys. Similar results are also obtained for the ternary V–Ti–Cr system as shown in Fig. 11.

The further comparison is performed using previous experimental data for more concentrated V–Ti–Cr alloys, in which the plateau pressure is measured during the hydrogen desorption at 313 K.9, 10 All the alloys shown in Fig. 14 are heat treated at either 1573 K for 3.6 ks or 1673 K for 60 s, so that they have a bcc crystal structure. It is surprising that the calculated value of the plateau pressure is very similar to the measured one, even in the case when the alloy contains a very limited amount of vanadium (e.g., 5 mol%V in V–37.5Ti–57.5Cr alloy).
4. Conclusion

The alloying effects on the phase stability of the hydrides formed in various binary V–M and ternary V–Ti–M alloys have been investigated experimentally.

It is found that the stability of the vanadium hydrides changes largely with a small amount of alloying elements, M. Also, the alloying effects on the hydride stability are different between the $\beta$ phase and the $\gamma$ phases. In addition, it is shown that the efficiency of alloying elements in modifying the stability is different between the $\beta_1$ and the $\beta_2$ phases.

The logarithms of the plateau pressure for the $\beta_1$ phase and for the $\gamma$ phase change almost linearly with the alloy composition in most cases. Using this linear relationship observed in the dilute binary V–M alloys, the plateau pressures can be estimated quantitatively even in the concentrated ternary V–Ti–Ru and V–Ti–Cr alloys.

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