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Alloying effects on the stability of vanadium hydrides

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Abstract

The alloying effects on the stability of the γ phase (VH_2) and the β phase (VH or V_2H) was investigated experimentally in binary V-1mol%M and V-3mol%M alloys, where M represents various alloying elements. It was found that the stability of the γ phase is dependent largely on the alloying elements, and changes systematically following the order of elements in the periodic table. On the other hand, two endothermic peaks are observed in the course of hydrogen desorption from the β phase in the DSC experiments. They are attributable to the onset of the successive transformations of the β phase to the bcc(α) phase containing hydrogen and then of this bcc(α) phase to the hydrogen-free bcc vanadium. Both the peak profile and the peak temperature vary significantly with alloying elements, M, indicating that the hydrogen desorption from the β phase is strongly modified by alloying. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Hydrogen storage alloys; Vanadium hydride; Alloying effects; Hydride stability

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1. Introduction

Vanadium metal with the bcc crystal structure is one of the promising hydrogen storage materials with a high capacity. It absorbs hydrogen and first forms the β phase (VH or V_2H) and then the γ phase (VH_2) [1]. The β phase is so stable that its hydrogen desorption reaction never occurs under moderate conditions [2]. On the other hand, the γ phase is not as stable as the β phase and its hydrogen absorption and desorption reaction, $VH + 1/2H_2 \rightleftarrows VH_2$, occurs at moderate temperatures and pressures. As a result, only about a half of the amount of the 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.

It is known that the stability of the γ phase changes significantly with alloying elements [1,3–5]. However, such alloying effects have been investigated for only a limited number of elements (e.g. the 3d transition metals). Also, to our knowledge, there have been no systematic investigations of the alloying effects on the hydriding properties of the β phase. In this study, focusing our attention on the alloying effects on the stability of the γ- and β-phases, a systematic investigation has been carried out with vanadium containing a variety of elements, M, where M represents the 3d-, 4d- and 5d-transition metals and some non-transition metals.

2. Experimental

The purity of the raw materials used in this experiment is 99.9mol% for vanadium and more than 99.9mol% for most alloying elements except for Zr (99.6mol%). About 10 g buttons of V-1mol%M and V-3mol%M alloys were arc-melted and then homogenized at 1373 K for 86.4 ks in a high purity argon gas atmosphere. These button specimens are first cold rolled so that the thickness is reduced to about 0.5 mm, and then cut into a plate of 30 mm in length×3 mm in width. Subsequently, they are polished mechanically and chemically to remove surface oxide layers. Then the specimen is treated so as to activate the surface for hydrogenation, following the procedure reported in a previous study [1]. Namely, the plate specimen is set into a capsule in the Sieverts-type apparatus. The capsule is first evacuated at room temperature for 1.8 ks and then heated up to 723 K in vacuum. Subsequently, hydrogen of about 5 MPa is introduced into the capsule, while holding it in this condition for 1.8 ks. Then, it is slowly cooled down to room temperature, followed by increasing the hydrogen pressure in the capsule to about 10

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MPa. This activation procedure is repeated 4 or 5 times. Finally, hydrogen in the specimen is released as much as possible by holding it at 723 K in vacuum of about 5×10^{-4} Pa for more than 14.4 ks, and then it is cooled to 313 K for the measurements.

The pressure–composition–isotherm (PCT) measurements are then performed at 313 K using the Sieverts-type apparatus in order to evaluate the stability of the γ phase. Also, differential scanning calorimetry (DSC) measurements are carried out with a constant heating rate of 10 K/s in vacuum in order to trace the desorption process of hydrogen from the β phase. Here, every specimen used for the DSC measurements is the one used for the PCT measurements, where the β phase is retained as explained later. Each of the phases formed in the specimen during the heat-up in vacuum are identified by the X-ray diffraction (XRD) method with a filtered Cu Kα radiation.

3. Results and discussion

3.1. Alloying effects on the stability of γ phase

For a variety of V-1mol%M alloys, the PCT curves are measured at 313 K. A relatively large hysteresis is observed in each PCT curve, in agreement with the previous experiment for pure vanadium [6]. The PCT curves measured in the course of hydrogen desorption are shown in Fig. 1(a)–(d). Here, the result of V-1mol%Mn alloy is not shown because it is difficult to prepare a specimen having the desired Mn concentration. As shown in Fig. 1, a plateau is seen in most alloys. However, in case of V-1mol%Pt alloy, such a plateau is not observed probably due to difficulty in hydrogenating the alloy. This leads to the lowering of the hydrogen content absorbed in the alloy, H/M, and inevitably to the narrowing of the plateau region in the PCT curve.

The value of the pressure at the centre of each plateau is referred to as the plateau pressure and all the results of plateau pressures are summarized in Fig. 2(a). For comparison, previous results for V-$x$mol%M alloys ($x = 0.90$–1.06) reported by Reilly and Wiswall [1] are also shown in the figure. The present results for V-1mol%M alloys are quite similar to the previous results [1], although the plateau pressure is slightly lower in the present experiment. As is evident from this figure, the stability of the γ phase is strongly dependent on the alloying elements, despite the fact that the alloy composition is very low, 1mol%. 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, Fe, Ru and Os, in the periodic table. The change

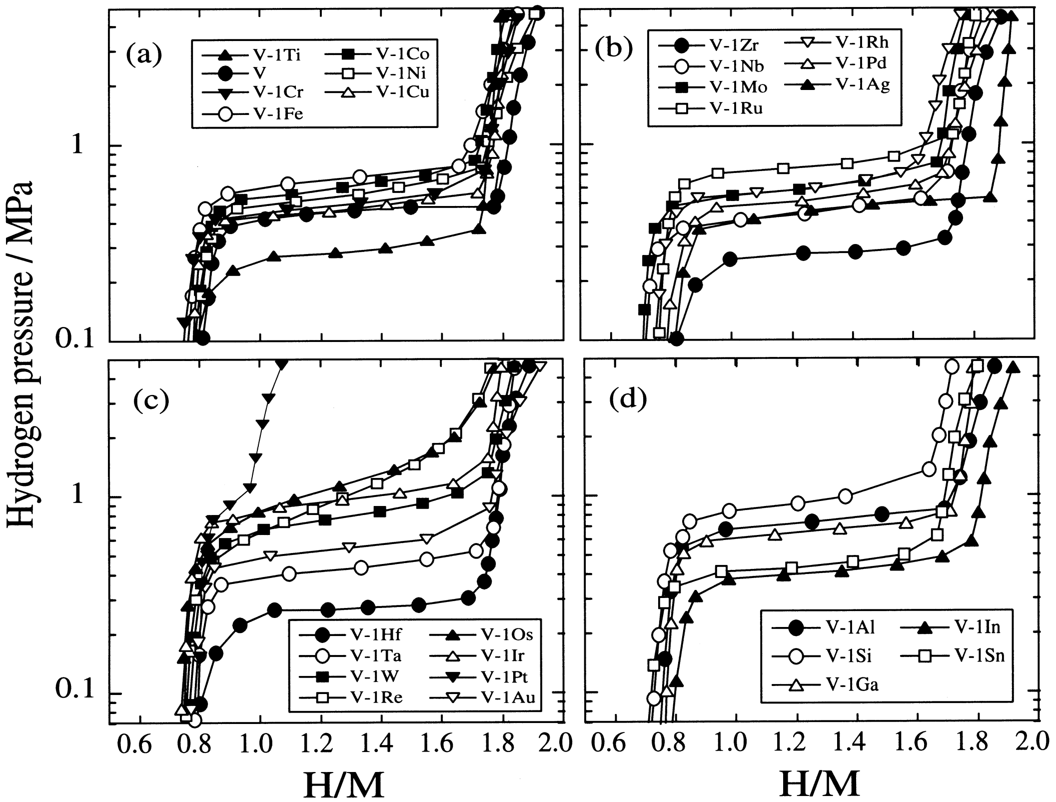

Fig. 1. PCT curves measured at 313 K in the course of hydrogen desorption of V-1mol%M alloys, where M represents (a) 3d transition metals, (b) 4d transition metals, (c) 5d transition metals and (d) non-transition metals.

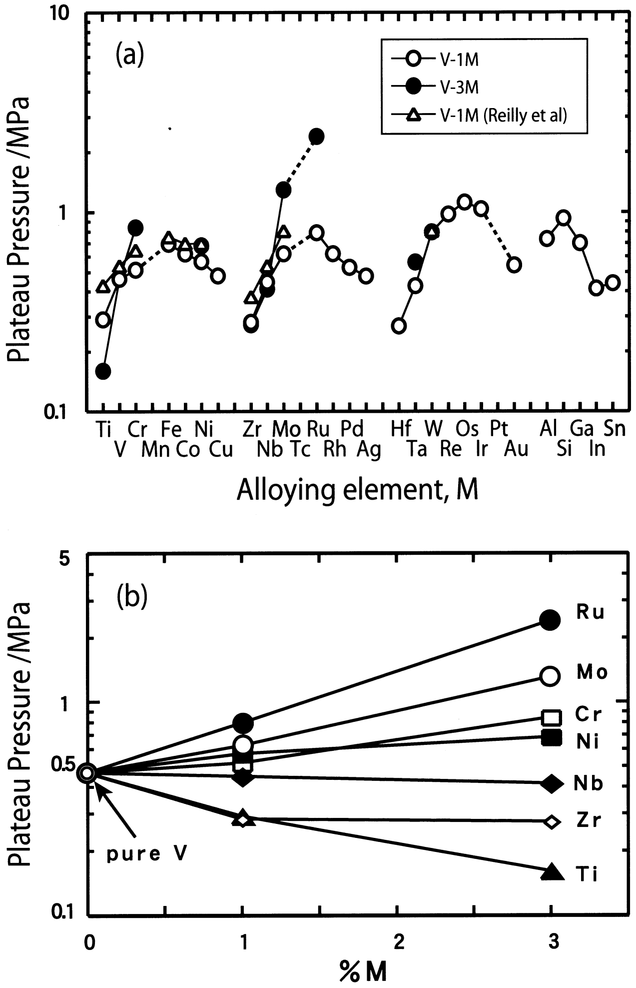

Fig. 2. (a) Plateau pressures measured at 313 K for V-1mol%M and V-3mol%M alloys and (b) the changes in the plateau pressure with the amount of alloying elements.

in the plateau pressure with the amount of alloying elements are examined by comparing the results between V-1mol%M and V-3mol%M alloys and the result is shown in Fig. 2(b). As shown in this figure, the logarithm of plateau pressure changes almost linearly with the amount of alloying element added into vanadium, except for the case of Zr.

The plateau pressure may be high in those elements which possess the small atomic radius or the high electronegativity. However, it is still difficult to understand the measured change in the plateau pressure with alloying elements in terms of either the atomic radius or the electronegativity. In fact, according to a least squares analysis, the correlation coefficient is about 0.45 between the plateau pressure and the atomic radius and about 0.66 between the plateau pressure and the electronegativity. An electronic approach is now in progress to help with the understanding of this plateau pressure change with alloying elements in vanadium [7].

3.2. Alloying effects on the stability of β phase

The desorption of hydrogen from the β phase is analyzed using the DSC under vacuum conditions. After the PCT measurements, the specimens are taken out from the capsule and used for the DSC measurements. The β phase is retained in every specimen after the PCT experiment is completed at 313 K in the hydrogen desorption process. A DSC profile obtained by heating up the β phase of pure V is shown in Fig. 3(a). The two endothermic peaks, P_1 and P_2, are observed clearly in the hydrogen desorption process of the β phase.

To examine the reason why these two peaks appear in the DSC curve, the XRD experiments are performed with the specimens quenched from 463, 563 and 773 K as indicated by a, b and c in Fig. 3(a), respectively. The measured XRD patterns are shown in Fig. 3(b). Only a low temperature phase, V_2H, is observed in the specimen quenched from a, the temperature below the first peak, P_1. On the other hand, a bcc vanadium phase is observed in the specimen quenched from b and c. From these results, it

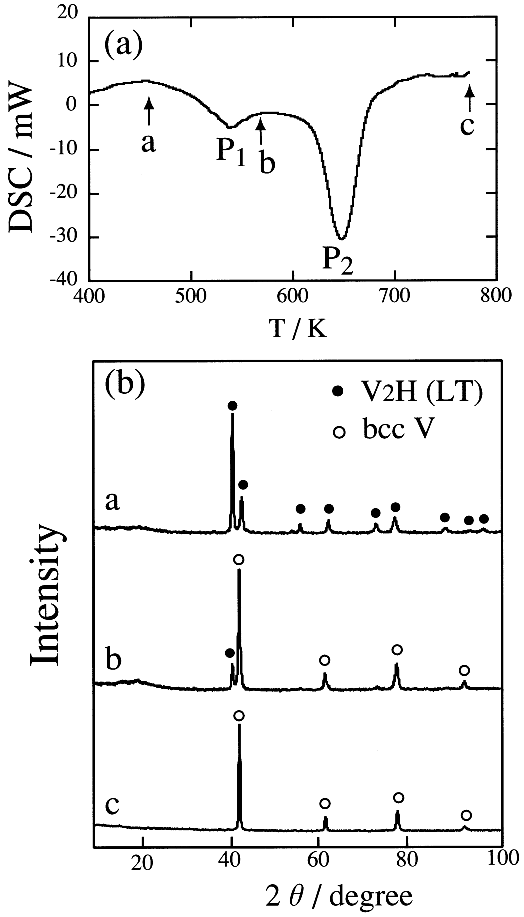

Fig. 3. (a) DSC profile obtained by heating the β phase of pure V in vacuum condition and (b) X-ray diffraction patterns from the specimens quenched from 463, 563 and 773 K.

is evident that the low temperature peak, P_1, appears due to the transformation of the β phase to the bcc(α) phase containing hydrogen. Also, the high temperature peak, P_2, may originate from the transformation of this bcc(α) phase to the hydrogen-free bcc vanadium, since hydrogen is released readily from vanadium at temperatures as high as 723 K.

A series of the DSC profiles is shown in Fig. 4 for V-3mol%M alloys. For comparison, the DSC profile for pure V (Fig. 3(a)) is shown here again. It is found that the shape and the position of the two endothermic peaks, P_1 and P_2, change significantly with alloying elements, M. For example, in case of Mn, Mo and W, the low temperature peak, P_1, seems to have disappeared. Also, in the case of Mn, Fe, Co, Ni, Rh, Pd, W and Re, the high temperature peak, P_2, shifts to the higher temperature side, as compared to the P_2 peak observed in pure V system. It is interesting to note that all these elements except for Pd are known as the non hydride-forming elements.

There may be two reasons for the changes in the shape and the position of these peaks with alloying elements. One is the modification of the β phase stability by alloying, and the other is the change in the kinetics of the hydrogen desorption reaction by alloying. For example, according to the XRD experiment for the V-3mol%W alloy, the low temperature phase, V_2H, still remains in the specimen quenched from 563 K, in accordance with the result of the disappearance of the P_1 peak in the DSC curve shown in Fig. 4. However, the V_2H phase is no longer present in the specimen when it is held at 563 K for 0.6 ks, but instead only the bcc phase is observed in it. These results imply that the kinetics of the hydrogen desorption reaction may be affected by the presence of a small amount of W in vanadium. Also the alloying effect on the β phase stability may be important in understanding the appearance of these peaks in the DSC curve. But the details remain unclear at the moment. To account for this, another study is now in progress using an electrochemical method.

4. Conclusion

The stability change of the γ phase (VH_2) and the β phase (VH or V_2H) with alloying elements, M, was investigated experimentally in binary V-1mol%M and V-3mol%M alloys. It was found that the stability of the γ phase is modified largely by the addition of a small amount of alloying elements, M. It changes in a systematic way following the order of elements, M, in the periodic table. Also, from a series of the DSC experiments, it was shown that alloying elements strongly affect the hydrogen desorption process from the β phase. However, it is still unknown whether the alloying can bring about a solution to the α(bcc)/β desorption problem at room temperature.

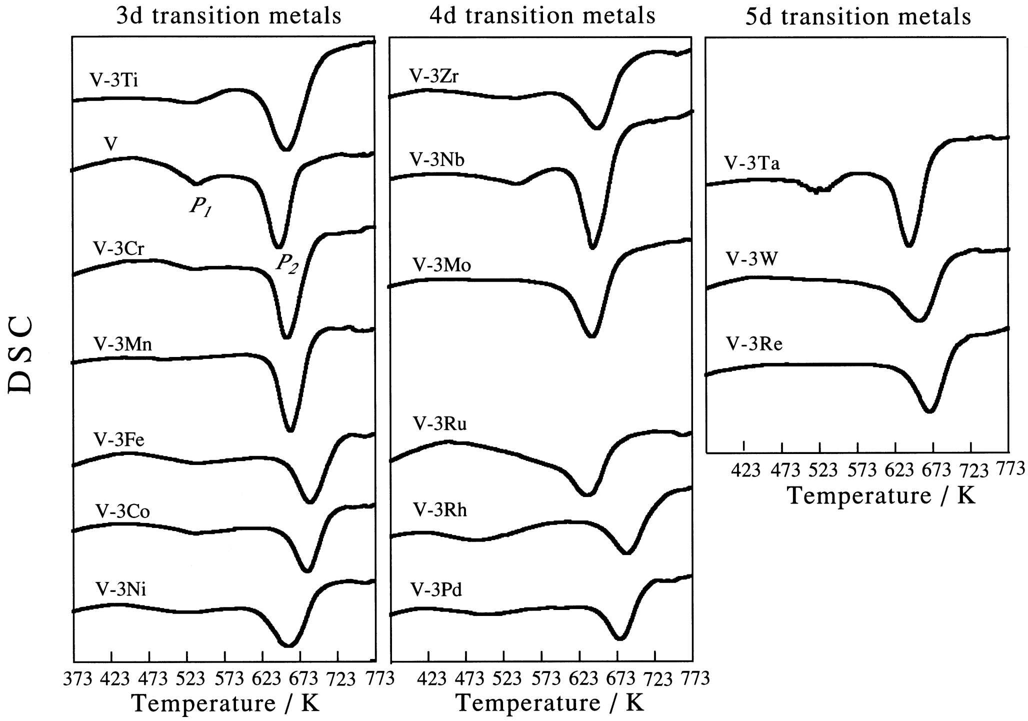

Fig. 4. DSC profiles for a variety of V-3mol%M alloys.

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