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Protium absorption properties of Ti–V–Cr–Mn alloys with a b.c.c. structure

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Abstract

The protium absorption–desorption properties of Ti–V–Cr–Mn alloys were studied by varying the contents of Mn, Ti and V in the alloys. It was found that Mn addition of <10 at% was effective in improving the slope of the plateau region without any reduction of the protium absorption–desorption capacity. For Ti–V–Cr–Mn alloys, the α-Ti phase, which does not contribute to the protium storage capacity, appeared along grain boundaries during heat treatment. The formation of the α-Ti phase was found to be suppressed by reducing the Ti content and increasing the V content. By inhibiting the appearance of the α-Ti phase along the grain boundary, the protium absorption–desorption capacity of Ti–xV–Cr–Mn ($x=45$, 55; Ti/Cr/Mn = 24:31:10) heat-treated alloys exhibited 2.7 mass% H, the highest value reported so far.

Keywords: Hydrogen storage alloy; Titanium–vanadium–chromium–manganese alloys; b.c.c. phase; Heat treatment

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1. Introduction

Protium (hydrogen atom) storage alloys are considered to be promising candidates for use as hydrogen storage tanks for fuel-cell automobiles. According to the WE-NET (International Clean Energy Network Using Hydrogen Conversion) program in Japan, the alloys are required to have an effective protium capacity of 3 mass% below 373 K. However, at present, $LaNi_5$-type protium storage alloys cannot achieve this objective, since they absorb a maximum value of 1.4 mass% [1].

Vanadium-based solid solutions with a b.c.c. structure are regarded as candidates, since vanadium itself can absorb about 3.8 mass% protium. However, only half of the absorbed protium can be desorbed at room temperature [2]. Iba et al. reported that a Ti–40 at% V–35 at% Cr alloy (at% is omitted below) with a b.c.c. structure exhibited an effective protium capacity of 2.4 mass% [3–6]. The present authors also reported that a Ti–35V–40Cr alloy annealed at 1573 K for 1 min exhibited a capacity of 2.6 mass% H [7]. In addition, the present authors also reported that Ti–V–Cr alloys with added Mn form b.c.c. solid solutions readily and exhibit about 2.6 mass% protium absorption–desorption capacity, as high as that without Mn [8].

Thus, the purpose of this study was to investigate further the protium absorption–desorption properties of Ti–V–Cr–Mn alloys by varying the contents of Mn, Ti and V in the alloys and, if possible, to improve the desorption protium capacity.

2. Experimental

The alloys were prepared by arc-melting on a water-cooled copper hearth under an Ar atmosphere. The purities of the raw materials were as follows: Ti, Cr >99.99 mass%; V >99.95 mass%; Mn >99.9 mass%. Samples were remelted three times to ensure homogeneity. Heat treatment was carried out in a vacuum-sealed quartz tube. The sealed samples were heated at a rate of 400 K/h to 1573 K, annealed for 1 min, and then quenched in iced water.

Crystal structures were studied using an X-ray diffractometer (XRD) with Cu Kα radiation. The microstructures were examined by optical microscopy. The pressure composition isotherms (PCT curves) were measured at 313 K using a Sieverts-type apparatus. Each sample was placed in a vessel and evacuated for 2 h using a rotary pump. Hydrogen was introduced gradually into the vessel up to a pressure of 10 MPa for the absorption process, and then evacuated gradually below 0.005 MPa for the desorption

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process. At the end of each measurement cycle, the vessel was evacuated for 2 h. The first two cycles were used to activate the samples, and the third cycle was evaluated as the protium absorption–desorption property of the Ti–Cr–V–Mn alloys. Thus, the PCT curves and protium storage capacities presented in this study were taken from the data for the third cycle.

3. Results and discussion

3.1. Effect of Mn addition and heat treatment on the phase composition and protium storage properties

Fig. 1 shows PCT curves for Ti–35V–(37 − *x*)Cr–*x*Mn ($x = 0$, 5, 10, and 15) heat-treated alloys. The slope of the desorption plateau region decreases with increasing Mn content (x). Except for the sample with added Mn at $x = 15$, the protium absorption–desorption capacity of 2.6 mass% seems to be almost the same as that for the Ti–35V–37Cr ternary alloy without Mn. However, $x = 15$ significantly decreases the protium absorption–desorption capacity. Consequently, it is possible to state that the addition of Mn below $x = 10$ is effective in improving the absorption–desorption characteristics.

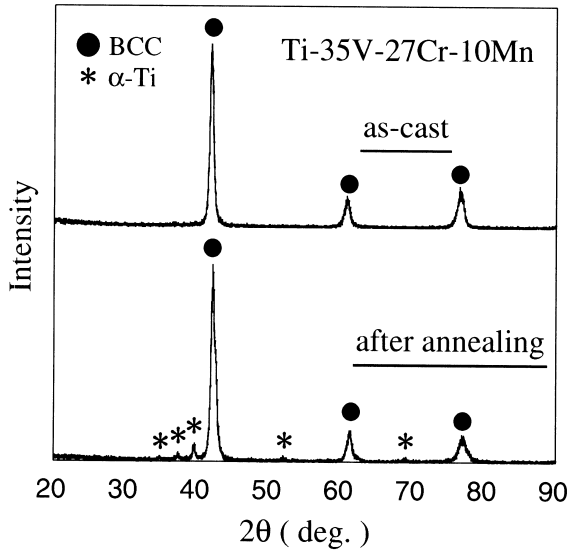

Fig. 2. XRD patterns of Ti–35V–27Cr–10Mn alloys in the as-cast state and after heat treatment.

X-ray diffraction studies showed that the Ti–35V–(37 − *x*)Cr–*x*Mn heat-treated alloys consisted mostly of b.c.c. solid solution and had a small quantity of the α-Ti phase. Fig. 2 shows XRD patterns of the Ti–35V–27Cr–10Mn alloy in the as-cast state and after heat treatment. As can be seen, the as-cast alloy has a b.c.c. single phase, but the heat-treated alloy also contained a small quantity of the α-Ti phase. Fig. 3 shows the corresponding optical micrographs of the Ti–35V–27Cr–10Mn alloy in the as-cast state and after heat treatment. The dark phase along grain boundaries is clearly observed in the heat-treated sample, but is not clearly seen in the as-cast sample. This phase with dark contrast along grain boundaries seems to be the α-Ti phase detected by XRD (Fig. 2). This result suggests that the α-Ti phase appears along grain boundaries during heat treatment. The reason why α-Ti appears during heat

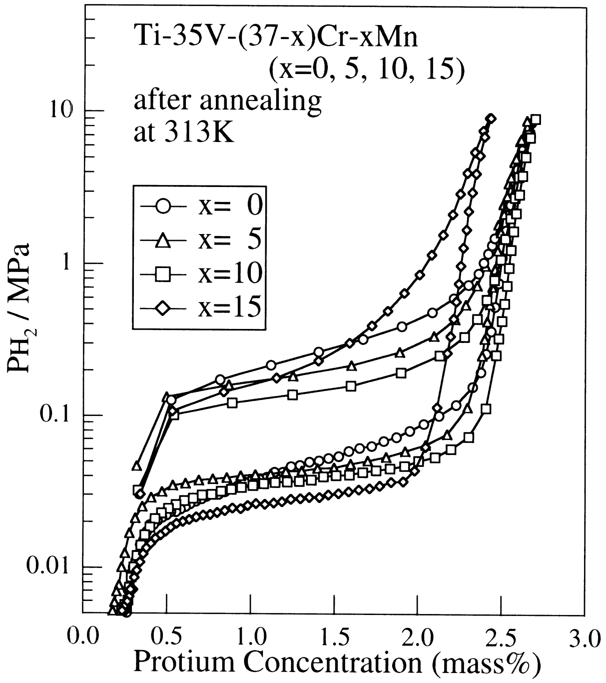

Fig. 1. PCT curves for Ti–35V–(37 − *x*)Cr–*x*Mn ($x = 0$, 5, 10, and 15) heat-treated alloys.

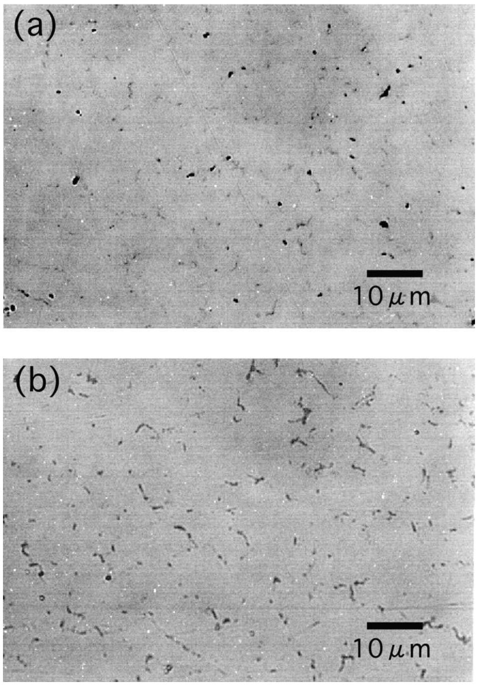

Fig. 3. Optical micrographs of Ti–35V–27Cr–10Mn alloys (a) in the as-cast state and (b) after heat treatment.

treatment may be oxygen intrusion into the sample stabilizing the α-Ti phase because of the large solubility of oxygen in α-Ti [9].

It is known that titanium does not react with hydrogen gas at room temperature and needs to be heated to 723 K to absorb protium. The α-Ti phase therefore seems not to react with hydrogen gas and does not contribute to the protium storage capacity. Thus, inhibition of α-Ti phase formation along the grain boundaries is required to achieve a higher protium absorption–desorption capacity.

3.2. Effect of Ti content on the phase composition and protium storage properties

Since the main element of the α-Ti phase along grain boundaries is titanium, its content in Ti–V–Cr–Mn heat-treated alloys is considered to affect the appearances of the α-Ti phase along grain boundaries.

Fig. 4 shows XRD patterns of Cr–*x*Ti–35V–10Mn (x = 24, 26, 28) heat-treated alloys. As can be seen, the quantity of α-Ti phase increases with Ti content (x). The PCT curves for the Cr–*x*Ti–35V–10Mn ($x = 24$, 26, 28) heat-treated alloys are shown in Fig. 5. The plateau pressure decreases with increasing Ti content, since the Ti atom has a larger radius than the other elements. It is generally known that the protium absorption–desorption capacity decreases with increasing plateau pressure due to the slope of the absorption curves. However, no decrease in the protium absorption–desorption capacity with increasing plateau pressure was observed for these alloys. On the contrary, the protium absorption–desorption capacity of the samples with $x = 24$ and 26 was higher than that for the sample with $x = 28$, which had the lowest plateau pressure. This is considered to be caused by the existence of a small quantity of α-Ti in alloys with a lower Ti content.

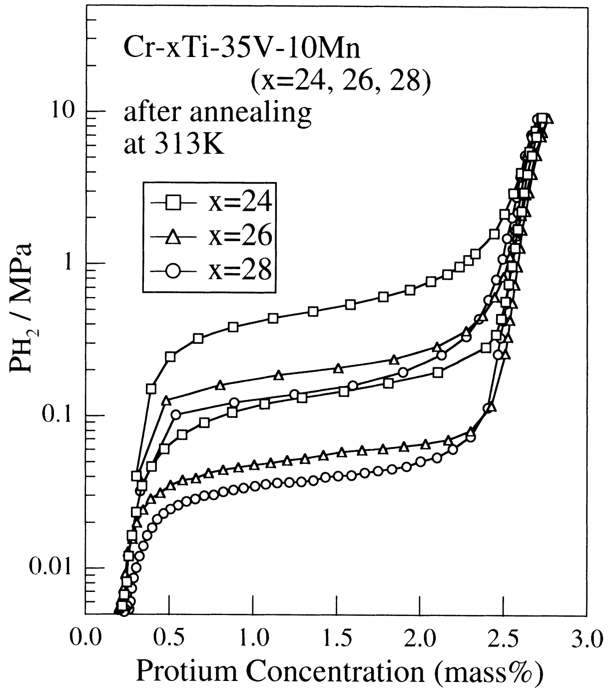

Fig. 5. PCT curves of Cr–*x*Ti–35V–10Mn ($x = 24$, 26, 28) heat-treated alloys.

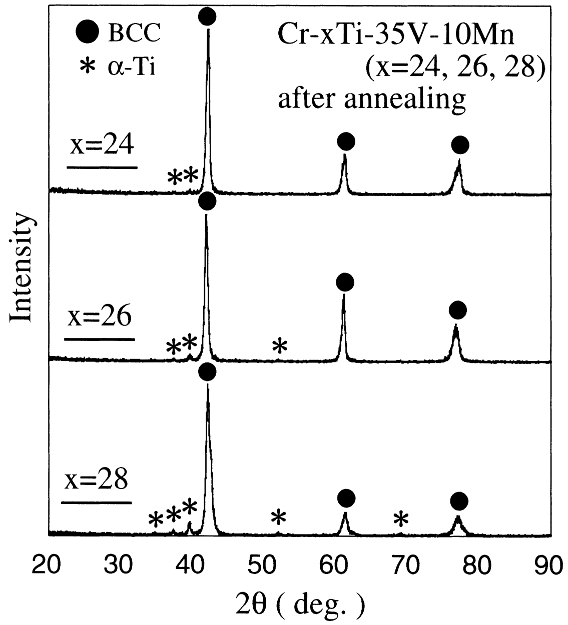

Fig. 4. XRD patterns of Cr–*x*Ti–35V–10Mn ($x = 24$, 26, 28) heat-treated alloys.

3.3. Effect of V content on the phase composition and protium storage properties

It was found that a decrease in the Ti content is effective in suppressing the formation of the α-Ti phase and for increasing the protium absorption–desorption capacity. However, reducing the Ti content too much is considered to increase the plateau pressure exceedingly and to cause a decrease of the protium absorption–desorption capacity. Thus, the effect of V content, which affects the stability of the b.c.c. phase, on the phases present and on the protium storage properties of Ti–V–Cr–Mn heat-treated alloys was studied.

Fig. 6 shows XRD patterns of Ti–*x*V–Cr–Mn ($x = 35$, 45, 55) heat-treated alloys. Since varying the Ti, Cr, and Mn ratio varies the plateau pressure, it was fixed at Ti/Cr/Mn=24:31:10. As can be seen, the sample with $x = 35$ consists mostly of a b.c.c. solid solution and has a small quantity of the α-Ti phase. On the other hand, the samples with $x = 45$ and 55 have a b.c.c. single phase. This result suggests that increasing the V content is effective in suppressing the formation of the α-Ti phase.

The PCT curves for the Ti–*x*V–Cr–Mn ($x = 35$, 45, 55) heat-treated alloys are shown in Fig. 7. Each alloy has a usable desorption plateau pressure near atmospheric pres-

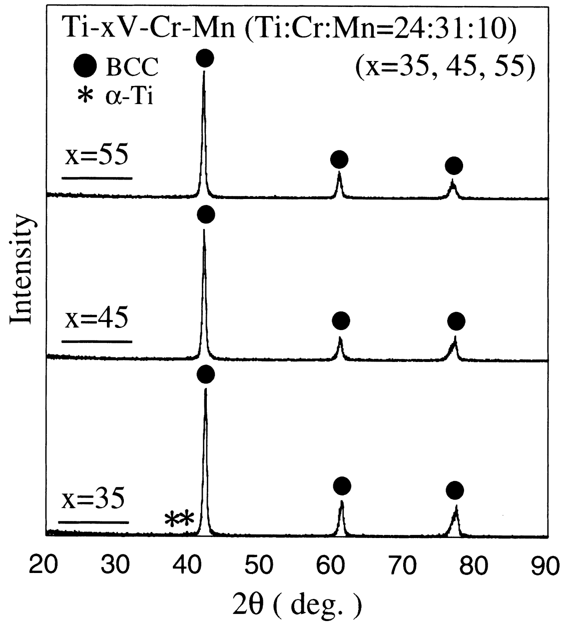

Fig. 6. XRD patterns of Ti–*x*V–Cr–Mn ($x=35$, 45, 55) heat-treated alloys.

sure, and shows about 2.7 mass% protium absorption–desorption capacity. The effective protium desorption capacity (7–0.01 MPa) shows 2.44 mass% H for the sample with $x=35$ and 2.47 mass% H for the samples with $x=45$ and 55. The reason that the samples with $x=45$ and 55 have a higher effective protium desorption capacity than the sample with $x=35$ seems to be suppression of the formation of the α-Ti phase on increasing the V content.

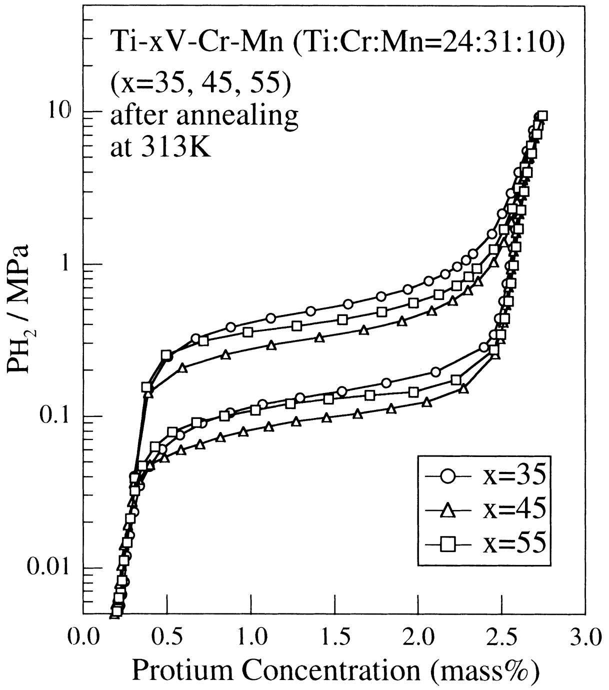

Fig. 7. PCT curves of Ti–*x*V–Cr–Mn ($x=35$, 45, 55) heat-treated alloys.

4. Conclusions

The protium absorption–desorption properties of Ti–V–Cr–Mn alloys have been investigated. It was found that Mn addition of <10 at% was effective in improving the slope of the plateau region without reducing the protium absorption–desorption capacity.

For Ti–V–Cr–Mn alloys, the α-Ti phase, which does not contribute to the protium storage capacity, appeared along grain boundaries during heat treatment. The formation of the α-Ti phase was found to be suppressed by decreasing the Ti content and increasing the V content. By inhibiting α-Ti phase formation along grain boundaries, the protium absorption–desorption capacity of Ti–*x*V–Cr–Mn ($x=45$ and 55; Ti/Cr/Mn = 24:31:10) heat-treated alloys exhibited 2.7 mass% H. In addition, these alloys exhibited an effective protium desorption capacity of 2.47 mass% (7–0.01 MPa) with a usable desorption plateau pressure near atmospheric pressure.

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