ELSEVIER

Journal of Alloys and Compounds 330–332 (2002) 511–516

Journal of
ALLOYS
AND COMPOUNDS

www.elsevier.com/locate/jallcom

Ti–V–Cr b.c.c. alloys with high protium content

M. Okada*, T. Kuriiwa, T. Tamura, H. Takamura, A. Kamegawa

Department of Materials Science, Graduate School of Engineering, Tohoku University, Aoba-ku 02, Sendai 980-8579, Japan

Abstract

The effects of composition and heat-treatment on the protium absorption–desorption properties of Ti–V–Cr alloys were investigated. It was found that the Ti–35V–40Cr alloy shows a 2.6 mass% protium capacity. The plateau pressure of the Ti–35V–*x*Cr alloys increased with decreasing lattice constants associated with increasing Cr content. The main phase of the as-cast Ti–*x*V–Cr (Cr/Ti=40/25) alloys containing more than 15%V was a b.c.c. phase. These b.c.c. alloys exhibited a 2.4 mass% protium capacity. Heat-treatment over 1673 K was effective on stabilizing the b.c.c. structure for the Ti–*x*V–Cr (Cr/Ti=2/3) alloys with low V content. The Ti–5V–57.5Cr alloy heat-treated at 1673 K for 1 h yields a high capacity of 2.8 mass% protium, which is the highest value at 313 K reported so far. The alloy is economically promising since it contains low amounts of expensive V metal.

Keywords: Ti–V–Cr alloys; Protium absorption–desorption properties

1. Introduction

Protium-absorption alloys, such as those based on $MmNi_5$, have been widely used as the negative electrode of secondary electric batteries. Typical $LaNi_5$ alloys have a protium capacity of nearly 1.4 mass%H. However, one of the future applications for protium absorbing alloys will be hydrogen tanks for fuel-cell automobiles, which will require the alloys with even greater protium capacities, for example, 3 mass%H operated at below 100°C according to Japanese WE-NET project.

Vanadium or vanadium-based solid-solutions with a b.c.c. structure are known to absorb about 3.8 mass% of protium. Vanadium has two hydrides, $VH_{\sim 1}$ and VH_2, which cause appearance of two plateau regions [1]. The low pressure plateau ($VH_{\sim 1}$) exists in the region of low pressure of 1 Pa at room temperature. This will be the reason why vanadium or vanadium-based solid-solutions can desorb only about half the absorbed protium at room temperature.

Recently, Iba and co-workers [2–5] reported that multi-phase Ti–V–Mn alloys consisting of Laves and b.c.c. solid-solution phases had good desorption capacities of nearly 2.1 mass%H. Akiba and co-workers [5–7] also reported that a Ti–40 at%V–35 at%Cr (at% will be abbreviated hereafter) alloy with a b.c.c. structure could desorb about 2.4 mass% protium. However, as far as we are aware, no systematic studies have yet been reported in establishing the relationship between the protium absorption properties and alloy composition of Ti–V–Cr alloys. Therefore, the present paper describes the development of the new protium absorbing Cr–Ti–V alloys with high capacity of protium.

2. Experimental

The alloys were prepared from elements by arc melting on a water-cooled copper hearth under pure argon atmosphere. The purity of the elements were as follows: Ti >99.6 at%; V 99.9 at%; and Cr >99.99 at%. Samples were remelted three times to ensure their homogeneity. Some samples were sealed in a quartz tube after evacuation for 1 h by rotary pump, and were then heated at a rate of 400 $K\,h^{-1}$ to the annealing temperature. The samples were annealed at 1173–1623 K for 1 min to 50 h and quenched into water.

Crystal structures and lattice parameters were studied by X-ray diffractometer (XRD) using Cu Kα radiation (Rigaku, RINT2000 System). The microstructures were observed by scanning electron microscopy (SEM, Hitachi S-530) with an energy dispersive X-ray spectrometer (EDX, Horiba EMAX-5770W).

Pressure–composition–temperature (P–C–T) curves were measured using a Sieverts-type apparatus. Initial activation treatments were as follows. Each sample was put into a vessel and was evacuated at 313 K for 2 h using a rotary vacuum pump. Hydrogen was introduced gradual-

---

*Corresponding author.

0925-8388/02/$ – see front matter
PII: S0925-8388(01)01647-4

ly into the vessel up to a pressure of 10 MPa, and then exposed to vacuum for 2 h. This process was repeated twice, which was regarded as activation treatment. The protium absorption–desorption property and protium capacities were defined by the 3rd cycle of P–C–T curve. The origin of the horizontal axis was fixed on zero capacity after activation as mentioned above. Then, low pressure (vacuum region) P–C–T curves were measured in 10^{-1}–10^{5} Pa, after the alloys were annealed at 673 K for 1 h in vacuum.

3. Results and discussion

3.1. Ti–V–Cr ternary alloys

Fig. 1 shows the P–C–T curves at desorption process of Ti–35V–*x*Cr (*x*=37, 40, 43) alloys in the as-cast state. The plateau pressures of these alloys increased with increasing Cr content. Generally, it is known that plateau pressure becomes higher as the lattice parameter decreases. From XRD analysis, the structures of these alloys were b.c.c. structure and these lattice parameters decreased with increasing Cr content. This is because the atomic radius of Cr is smaller than that of Ti and V. This result suggests that the plateau pressure can be controlled by the content ratio of Ti/Cr [8].

Fig. 2 shows P–C–T curves at desorption process of Ti–*x*V–Cr (Cr/Ti=40/25) (*x*=0, 5, 10, 15, 25, 35) alloys in as-cast state. The alloys containing more than 15 at% V with mainly b.c.c. phase exhibited a large protium absorption–desorption capacity of about 2.4 mass% H. X-ray diffraction indicated that the alloys with *x*=10 contain Laves phase, and they had a small protium capacity of less than 1.8 mass% H. The plateau region of these alloys was not observed at 313 K.

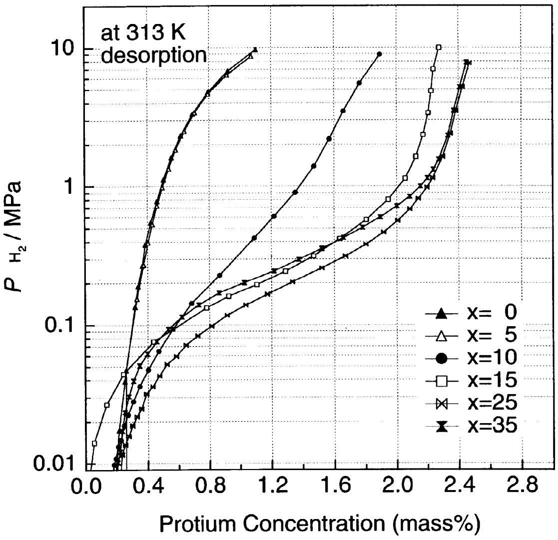

Fig. 2. P–C–T curves at desorption process of Ti–*x*V–Cr (Cr/Ti=40/25) (*x*=0, 5, 10, 15, 25, 35) alloys in as-cast state.

The cast-alloys shown in Figs. 1 and 2 exhibit sloped plateau regions in their P–C–T curves, which may be due to the inhomogeneous distribution of their constituents. In the next section, effects of heat-treatment will be discussed.

3.2. Optimizing of heat-treatment condition

Fig. 3 shows P–C–T curves at desorption process of Ti–35V–40Cr alloys with a single b.c.c. phase annealed at 1173–1623 K for 2 h. After annealing below 1373 K, the plateau region of alloys remained unchanged. However, after annealing above 1573 K, the plateau becomes flattened. This result suggests that the heat-treatment above 1573 K was an effective way of improving the flatness of the plateau region.

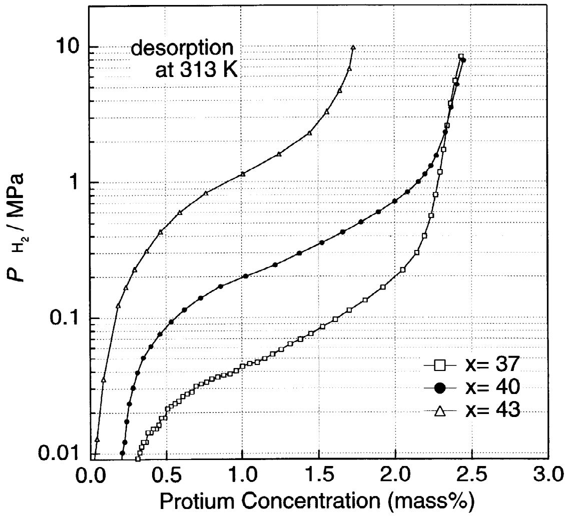

Fig. 1. P–C–T curves at desorption process of Ti–35V–*x*Cr (*x*=37, 40, 43) alloys in the as-cast state.

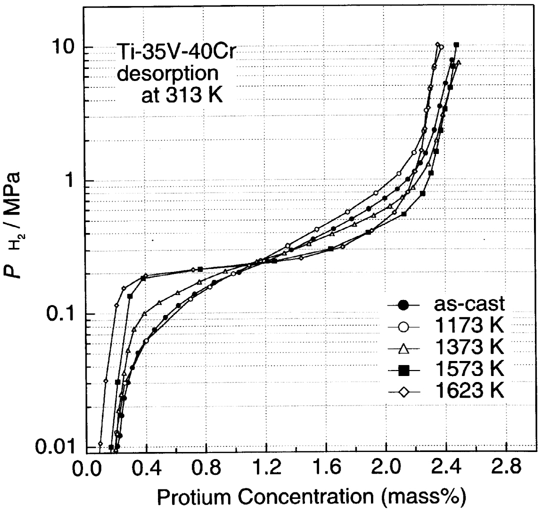

Fig. 3. P–C–T curves at desorption process of Ti–35V–40Cr alloys with a single b.c.c. phase annealed at 1173–1623 K for 2 h.

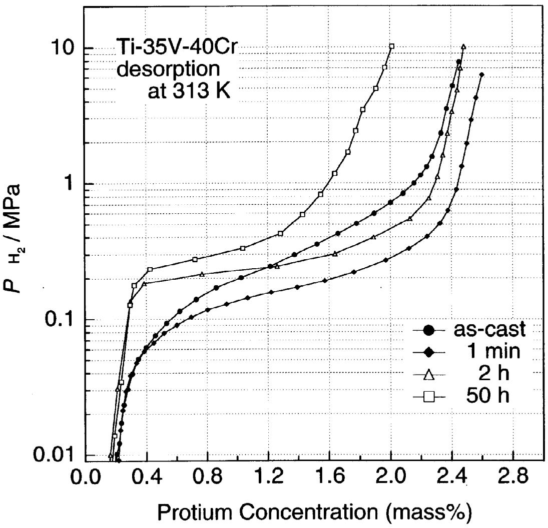

Fig. 4. P–C–T curves at desorption process of Ti–35V–40Cr alloys annealed at 1573 K for 1 min to 50 h.

P–C–T curves at desorption process of Ti–35V–40Cr alloys annealed at 1573 K for 1 min to 50 h are shown in Fig. 4. Heat-treated samples exhibited flat plateau region in their P–C–T curves. The sample annealed for 1 min showed the highest effective protium capacity of about 2.6 mass% H. However, this capacity decreased after annealing for longer times up to 50 h. The plateau pressure increased and the protium capacity decreased with increasing annealing time. Fig. 5 shows the corresponding SEM micrographs of these alloys. Two-phase microstructures were observed. The volume fraction of a minor dark phase increased with increasing annealing time. Table 1 shows the compositions of the main and minor phases analyzed by SEM-EDX. It was found that the Ti content of the minor dark phase was larger than that of the major phase. In the dark minor phase, Ti content increased with increasing annealing time. However, Ti content decreased in the major phase. For example, in the case of the sample annealed for 50 h, the Ti content of its minor phase increased from 53.6 to 95.6 at%, while that of major phase decreased from 24.9 to 11.0 at%. It seems that the reason why the plateau pressure increases with increasing annealing time is due to the decrease in the lattice constant of the main phase, which results from the decrease in Ti content. It was found that annealing at 1573 K for a short time was an effective method for flattening the plateau region and increasing the effective protium capacity.

It was shown that the Ti–10V–55.4Cr (Cr/Ti=40/25) alloy had b.c.c. and C14 Laves phases in the as-cast state. However, it may be possible to increase the volume fraction of b.c.c. phase by heat-treatment. Fig. 6 shows XRD patterns of the Ti–10V–55.4Cr alloy in the as-cast state (a) and after annealing at 1573 K for 1 min (b). After heat-treatment, the main phase of this alloy is the b.c.c. phase. This result suggests that annealing above 1573 K is

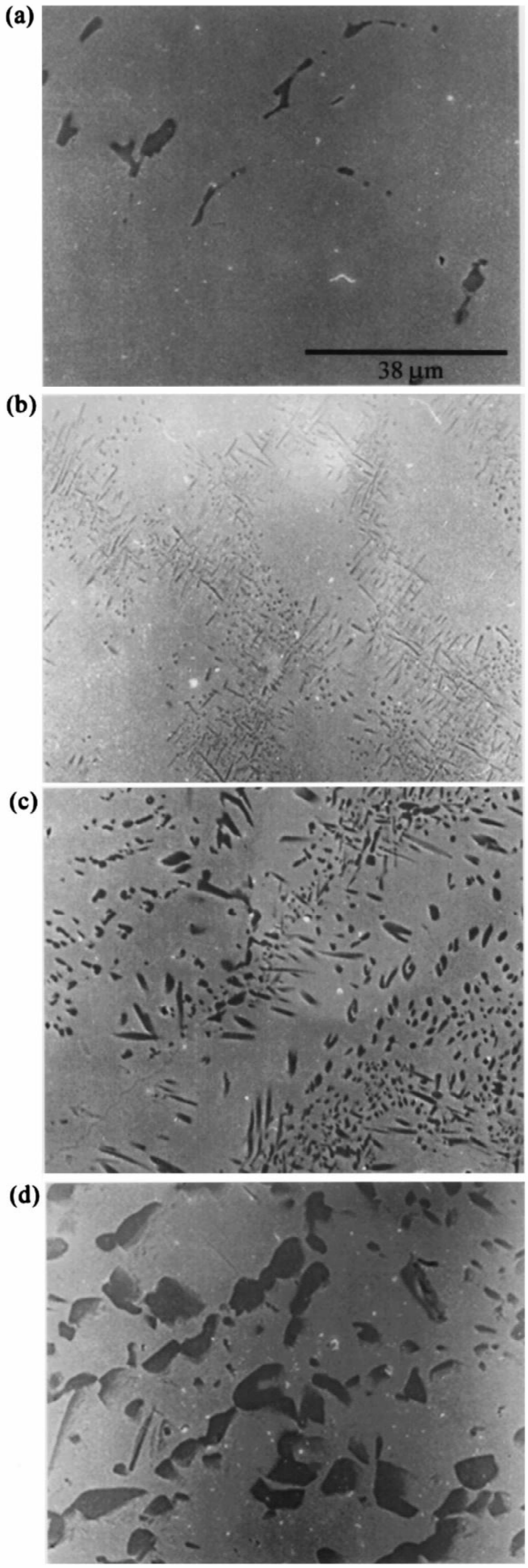

Fig. 5. Corresponding SEM micrographs of the alloys in the as-cast state (a) and after heat-treatment for 1 min (b), 2 h (c) and 50 h (d).

Table 1
EDX analysis of Ti–35V–40Cr alloys heat-treated at 1573 K for 1 min to 50 h

	Major phase composition (at%)			Minor phase composition (at%)		
	Ti	V	Cr	Ti	V	Cr
As-cast	24.9	34.8	40.4	53.6	20.6	25.8
Heat-treated: 1 min	20.8	37.0	43.8	57.4	19.4	23.1
2 h	19.1	37.0	43.8	54.6	21.5	24.0
50 h	11.0	41.2	47.9	95.6	3.1	1.3

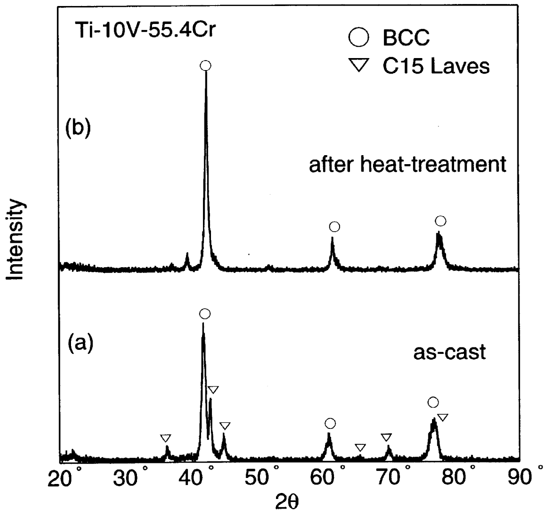

Fig. 6. XRD patterns of the Ti–10V–55.4Cr alloy in the as-cast state (a) and after annealing at 1573 K for 1 min (b).

effective in forming a b.c.c. phase even in alloys with low V contents.

Fig. 7 shows P–C–T curves of this alloy in the as-cast state (a) and after heat-treatment (b). The as-cast alloy, consisting of Laves phase and b.c.c. phase, showed less than about 1.8 mass% protium absorption and desorption capacity. However, after heat-treatment, it contained mainly a b.c.c. phase, and had a capacity greater than 2.6 mass% H. It was found that the heat-treated 10 at% V alloy had a higher effective protium capacity than the vanadium-based 40 at% V b.c.c. alloys reported by Iba [7].

3.3. Observations of P–C–T curves in low pressure region

The increment of protium capacity in V-based b.c.c. alloys will be realized by answering how to use some part of the stable vanadium mono-protride. The one possible way for that is to add some elements to the V-based alloys which destabilize vanadium mono-protride. The other way will be increasing the desorption temperature. However, there is no data on the stability of vanadium mono-protride since it may be difficult to measure the P–C–T curves in low pressure region of around 1 Pa. We set up the P–C–T measurements apparatus operated in low pressure range of nearly 10^{-1}–10^{5} Pa. Fig. 8 shows P–C–T curves at absorption process of Ti–*x*V–Cr (Ti/Cr=2/3) alloys measured at 313 K. The origin of the capacity axis of the curves was set to zero before activation treatment. It was found that there exists stable vanadium mono-protride in low pressure region below 10^{4} Pa. Fig. 9 shows P–C–T curves of the alloys in low pressure region (10^{-1}–10^{5} Pa)

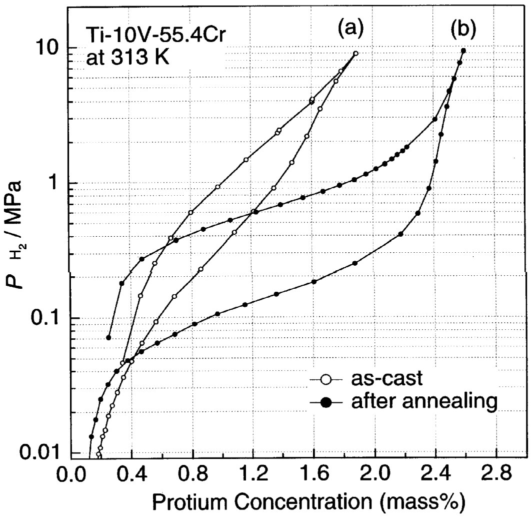

Fig. 7. P–C–T curves of this alloy in the as-cast state (a) and after heat-treatment (b).

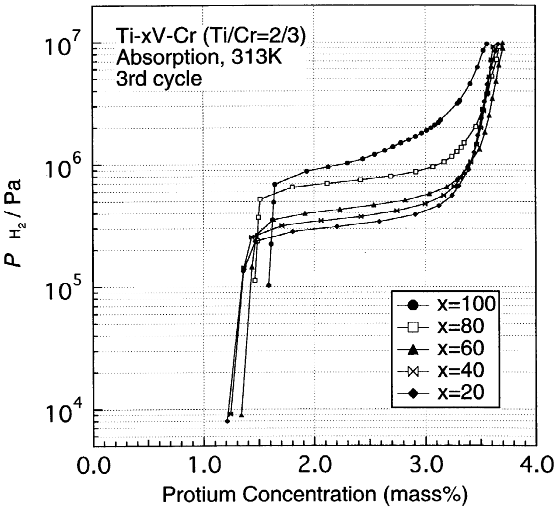

Fig. 8. P–C–T curves at absorption process of Ti–*x*V–Cr (Ti/Cr=2/3) alloys measured at 313 K.

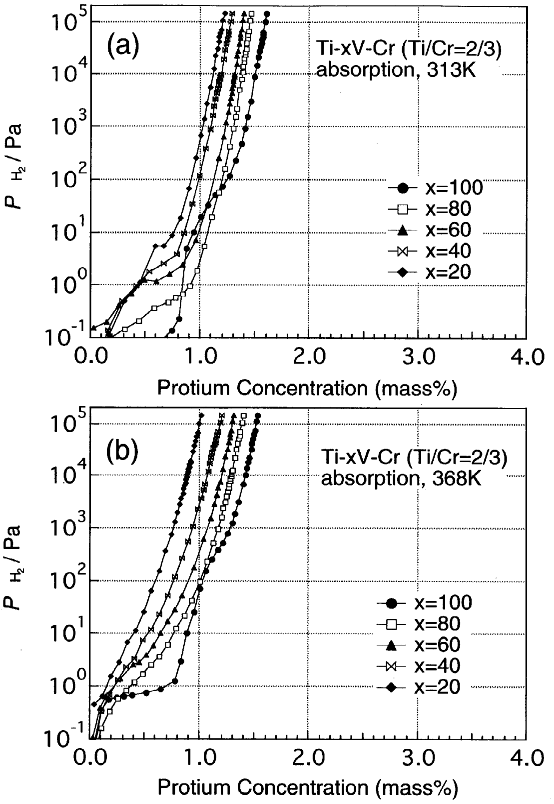

Fig. 9. P–C–T curves of the alloys in low pressure region (10^{-1}–10^5 Pa) measured at 313 and 368 K.

measured at 313 and 368 K. It was found that pure vanadium has a distinct plateau at 368 K although the plateau at 313 K would exist below the measurement pressure range. On decreasing vanadium content of the Ti–V–Cr alloys, the plateau region becomes unclear and declined. This means that vanadium mono-protride becomes unstable and starts to contribute to desorption of the protium at atmospheric pressure. In other words, the protium concentration at 10^5 Pa for the alloys decreases with decreasing V content, and higher content of protium can contribute to the practical usable pressure between 10^5 and 10^7 Pa. This would be the first observation that stable vanadium mono-protride becomes unstable by adding the other elements and starts to be usable in practical desorption pressure range.

3.4. Low vanadium contained alloys with high protium capacity

It may be possible to increase the protium capacity if the b.c.c. phase would be obtained for alloys with low V content. However, the alloys with less than 10 at% V contain Laves phase besides b.c.c. phase even after a heat-treatment at 1573 K, which is optimum for the studied alloys with V>10%. It is required for low V contained alloys to investigate the optimum heat-treatment temperatures.

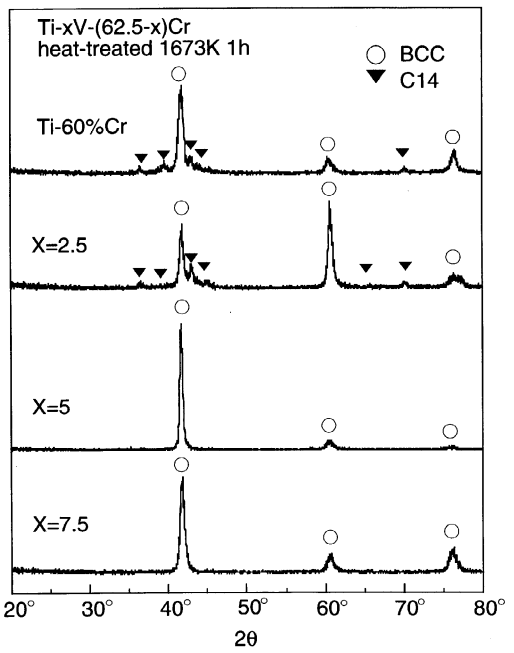

Fig. 10. XRD patterns of the Ti–*x*V–Cr (*x*=0–7.5) alloys after a heat-treatment at 1673 K for 1 h.

Fig. 10 shows XRD patterns of the Ti–*x*V–Cr (*x*=0–7.5) alloys after a heat-treatment at 1673 K for 1 h. It was found that the alloys containing more than 5 at% V consist of mainly b.c.c. phase. However, the alloys with less than 2.5 at% V contain C14-type Laves phase. Fig. 11 shows the corresponding P–C–T curves of the alloys. Ti–(5–7.5)V–Cr alloys with only b.c.c. phase yield the highest capacity of 2.8 mass% protium, which will be the highest value at 313 K reported so far. Since the vanadium is expensive metal, the developed alloys are economically suitable. This suggests that the b.c.c. alloys are potential candidates for further development of higher capacity protium absorbing alloys in the future.

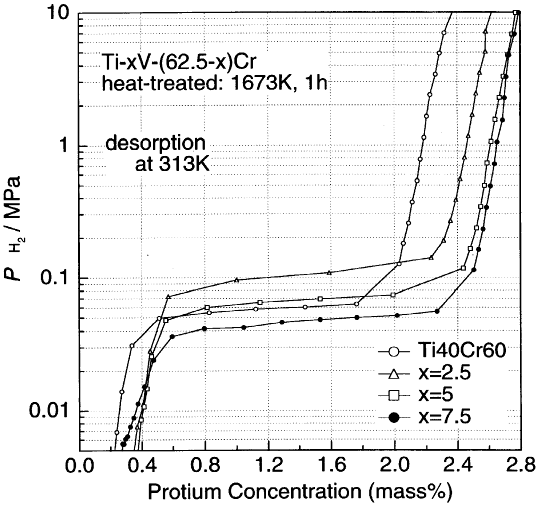

Fig. 11. Corresponding P–C–T curves of the alloys.

4. Conclusions

The protium capacity of Ti–V–Cr alloys containing less than 35 at% V were investigated and the following conclusions were made:

1. The plateau pressure of Ti–35V–xCr (x=37, 40, 43) alloys increased with decreasing lattice constants, resulting from increasing Cr content. For Ti–xV–Cr (Cr/Ti=40/25) (x=0–35) alloys, the main phase of the samples containing more than 15 at% V was a b.c.c. phase in the as-cast state. These b.c.c. alloys exhibited effective protium capacities of about 2.4 mass% H.
2. The optimum heat-treatment conditions for the Ti–35V–40Cr alloy was determined to be annealed at 1573 K for 1 min, and then quenched in water. After this heat-treatment, a Ti–35V–40Cr alloy had a 2.6 mass% protium capacity. Longer annealing time led to the increase in the amount of the Ti-rich phase, which decreased the protium capacity.
3. A Ti–10V–55.4Cr alloy, which consisted of Laves and b.c.c. phases in the as-cast state, contained mainly b.c.c. phase after heat-treatment, and had a protium capacity of more than 2.6 mass% H.
4. The P–C–T curves of the Ti–xV–Cr (Ti/Cr=2/3) alloys in the range of low pressure region of above 1 Pa were observed. It was found that vanadium mono-protride becomes unstable when decreasing the V content of the alloys, and starts to contribute to the usable protium desorption properties. This could be the first observation that the stable vanadium mono-protride becomes unstable by adding the other elements.
5. The amount of protium capacity of the Ti–xV–Cr alloys with low vanadium content of 5–7.5% after heat-treatment at 1673 K achieved 2.8 mass%, which will be the highest value at 313 K reported so far.

Acknowledgements

This work has been supported in part by a Grant-in-Aid for Scientific Research on Priority Area A of ‘New Protium Function’ from the Ministry of Education, Science, Sports and Culture.

References

[1] J.J. Reilly, R.H. Wiswall, Inorg. Chem. 9 (1970) 1678–1682.

[2] H. Iba, E. Akiba, J. Alloys Comp. 253 (1997) 21–24.

[3] H. Iba, E. Akiba, J. Alloys Comp. 231 (1995) 508–512.

[4] E. Akiba, H. Enoki, Mater. Jpn. (in Japanese) 37 (1998) 645.

[5] E. Akiba, H. Iba, Intermetallics 6 (1998) 461–470.

[6] H. Iba, T. Mouri, M. Shionoya, E. Akiba, Mater. Jpn. (in Japanese) 36 (1997) 640–642.

[7] H. Iba, PhD dissertation, Tohoku University Japan, 1997 (in Japanese).

[8] Y. Tominaga, S. Nishimura, T. Amemiya, T. Fuda, T. Tamura, T. Kuriiwa, A. Kamegawa, M. Okada, Mater. Trans. J. Inst. Metals 40 (1999) 871–874.