

# Protium absorption properties and protide formations of Ti–Cr–V alloys

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## Abstract

Ti–Cr–V alloys are known to absorb about 3.8 mass% (H/M=2) of protium (hydrogen atom), but to desorb about 2.4 mass%. This paper aims to clarify protium absorption properties and protide formations of Ti–Cr–V alloys. It was found that higher protium desorption capacity was achieved by increasing Cr content and controlling measurement temperature in order to control the desorption plateau pressure near atmospheric pressure for the alloys with less than 40 at% V content. However, Cr-rich alloys were found to absorb up to H/M=1 because of the formation of the mono-protides. The region with higher protium desorption capacity was obtained. The lattice parameters of the alloys and the enthalpy changes for di-protide formation were estimated from the compositions of the alloys. Moreover, estimated enthalpy changes for di-protide formation and the lattice parameters of the alloys were found to be generally constant on the limited line between appearance of regions of mono- and di-protides.

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## 1. Introduction

Protium (hydrogen atom) storage alloys are considered to be used as hydrogen storage tanks for fuel-cell automobiles. Ti–Cr–V alloys with a b.c.c. structure are regarded as one of the candidates for hydrogen storage tanks [1,2].

Iba et al. reported that a Ti–40at%V–35at%Cr alloy (at% is abbreviated hereafter) with a b.c.c. crystal structure exhibited an effective protium capacity of 2.4 mass% [3,4]. The present authors also reported that a Ti–35V–40Cr alloy annealed at 1573 K for 1 min exhibited a 2.6 mass%H capacity [5], and that Mn-added Ti–V–Cr alloys formed b.c.c. solid solutions easily and exhibited about 2.7 mass% protium absorption–desorption capacity as high as that without Mn [6,7]. In addition, the present authors reported that Ti–V–Cr alloys with low vanadium content of 5–7.5 at% after heat-treatment at 1673 K exhibited a 2.8 mass%H capacity [8] and yielded the high capacity of 3.0 mass% protium absorption (–10 MPa) at 313 K following evacuation at 368 K [9].

Ti–Cr–V alloys absorb protium up to H/M=2 (about 3.7 mass% of protium), but desorb about 2.4 mass% from

the viewpoint of protium desorption capacity (9–0.01 MPa) through forming stable protides in low hydrogen pressure regions [10–12]. The protium desorption capacity (9–0.01 MPa) is defined as the difference between the protium concentration at 9 MPa and that at 0.01 MPa in the desorption process. In further increasing desorption capacity of Ti–Cr–V alloys, it will be quite important to know how to decrease the regions of stable protides. Thus, the purpose of this study is to investigate protium absorption properties and protide formations in a wide compositional range of Ti–Cr–V alloys.

## 2. Experimental procedures

The alloys were prepared by arc-melting, annealed for 1 h at 1673 K, and then quenched into iced water. Details of the preparation methods have been described elsewhere [11].

Crystal structures were studied by X-ray diffraction (XRD) using Cu K $\alpha$  radiation. The XRD samples for studying the structure of protides were prepared by treating in acetone to keep the conditions for absorbing protium. The pressure composition isotherms (PCT curves) were measured using a Sieverts-type apparatus. Pure V metal and 80 at% V alloy were activated by repeating the following process three times: holding under a hydrogen

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pressure of 7 MPa for 30 min at 673 K and then evacuating by rotary pump for 30 min at room temperature. The zero points of the PCT curves were the points after dehydrogenation at 673 K for the pure V metal and the 80 at% V alloy and the points before activation for the others. PCT curves presented in this study were taken from the first cycle data.

### 3. Results and discussion

#### 3.1. The protium storage properties in Ti–Cr–V alloys

It has been found by XRD that all studied alloys have a b.c.c. single phase.

Fig. 1 shows PCT curves (desorption process) at 313 K for the pure V metal and Ti–Cr– $x$ V (Ti/Cr=2:3;  $x$ =80 to 5) alloys. To examine the influence of the V content, the ratio of Ti and Cr was fixed at Ti/Cr=2:3. The alloys with  $x$  (V content)=40, 20 and 5 have wider plateau regions than the others with Ti/Cr=2:3, and show about 2.5 mass% protium desorption capacity (9–0.01 MPa). Thus, higher protium desorption capacity (9–0.01 MPa) is considered to be achieved for the alloys with less than 40 at% V content.

Fig. 2 shows PCT curves for the Ti– $x$ Cr–20V ( $x$ =32, 48 and 52) alloys. To examine the influence of the ratio of Ti and Cr, the V content was fixed at 20 at% and measurement temperature was controlled in order to control the desorption plateau pressure near atmospheric pressure. The protium desorption capacity increases with increasing Cr content because of decreasing the regions of stable protides in low hydrogen pressure regions (–0.01 MPa). The alloy

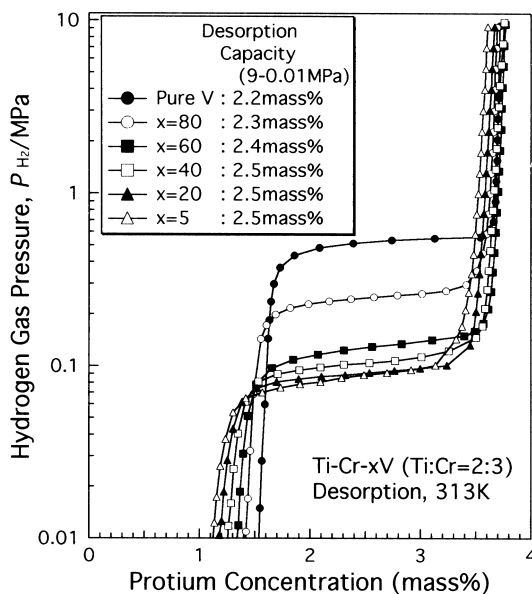


Fig. 1. PCT curves (desorption process) at 313 K for the pure V metal and Ti–Cr– $x$ V (Ti/Cr=2:3;  $x$ =80 to 5) alloys.

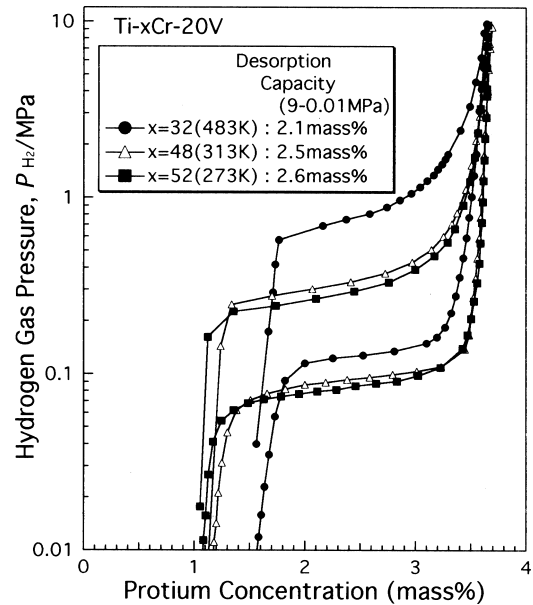


Fig. 2. PCT curves for the Ti– $x$ Cr–20V ( $x$ =32, 48 and 52) alloys.

with 52 at% Cr content has 2.6 mass% protium desorption capacity (9–0.01 MPa). Therefore, higher protium desorption capacity (9–0.01 MPa) is considered to be achieved by increasing Cr content and controlling measurement temperature in order to control the desorption plateau pressure near atmospheric pressure.

#### 3.2. The protide formations in Ti–Cr–V alloys

Fig. 3 shows PCT curves (absorption process) at 273 K for the Ti– $x$ Cr–20V ( $x$ =52 to 62) alloys. It was found that

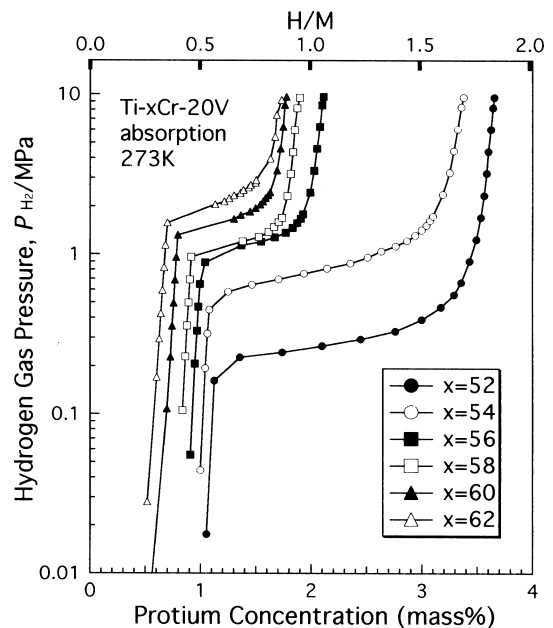


Fig. 3. PCT curves (absorption process) at 273 K for the Ti– $x$ Cr–20V ( $x$ =52 to 62) alloys.

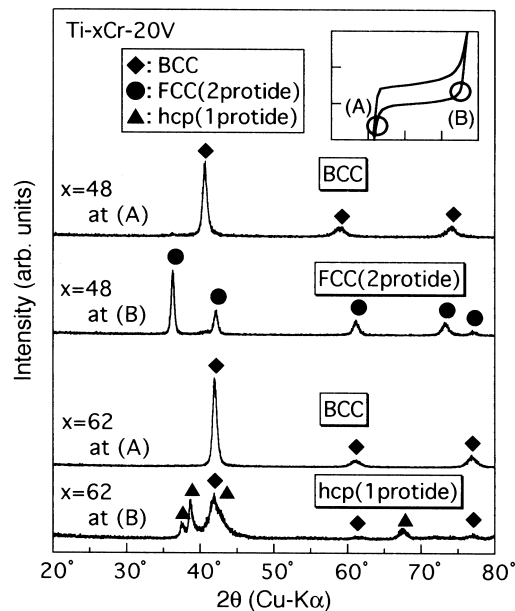


Fig. 4. XRD patterns of the protides for the Ti–xCr–20V ( $x=48$  and  $62$ ) alloys. The protides were measured at two points on the PCT curves as follows: (A)-points are the points after desorbing in the desorption plateau region; (B)-points are the points immediately before desorbing in the desorption plateau region.

the alloys with more than 56 at% Cr content absorb protium up to  $H/M=1$ . Fig. 4 shows XRD patterns of the protides for the Ti–xCr–20V ( $x=48$  and  $62$ ) alloys. The protides were measured at two points on the PCT curves as follows: (A)-points are the points after desorbing at the desorption plateau region; (B)-points are the points immediately before desorbing at the desorption plateau region. The protides at (A)-points for both alloys have B.C.C. single phases. The present authors reported that the protides at (A)-points for the alloys with more than 70 at% V content had the B.C.T. single phases [13]. The protide at (B)-point for the 48 at% Cr alloy that absorbed about  $H/M=2$  has a F.C.C. single phase. This F.C.C. phase is considered to be di-protide, judging from the absorbed protium concentration. The protide at (B)-point for the 62 at% Cr alloy has a B.C.C. phase and a h.c.p. phase. This B.C.C. phase is considered to be the protide at (A)-point because the protide at (B)-point for the 62 at% Cr alloy was unstable at room temperature and considered to desorb a part of protium. Therefore, it is considered that the protide at (B)-point for the 62 at% Cr alloy has the h.c.p. single phase and this h.c.p. phase is the mono-protide, judging from the absorbed protium concentration.

The present authors investigated the effects of compositions on formation of 1,2 protides in Ti–Cr–V alloys [11]. Fig. 5 shows the appearance of regions of 1,2 protides in Ti–Cr–V ternary alloys. It was found that the limited line between appearance of regions of mono- and di-protides is a straight line. V-rich alloys and Cr-rich alloys in the region of mono-protides were considered to

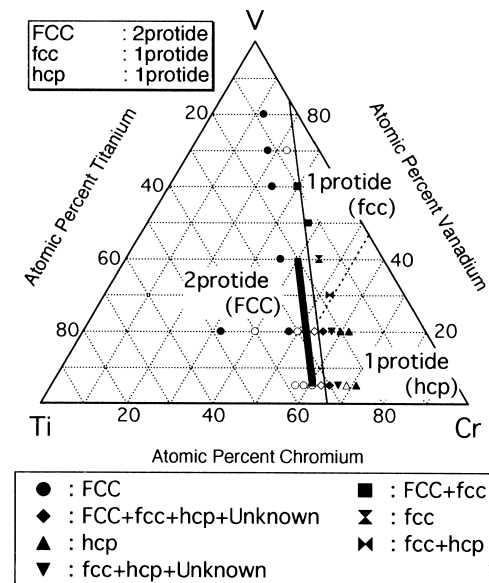


Fig. 5. The appearance of regions of 1,2 protides in Ti–Cr–V alloys. Open symbols are presumed from the PCT curves. The region of the boldest line is considered to achieve higher protium desorption capacity (about 2.6 mass%; 9–0.01 MPa).

form mono-protides with a f.c.c. structure and h.c.p. structure, respectively. The mono-protide with the f.c.c. structure was different from the di-protide with the F.C.C. structure in the lattice parameters [11]. Higher protium desorption capacity (9–0.01 MPa) was considered to be achieved by increasing Cr content for the alloy with less than 40 at% V content. However, the alloys in the mono-protides regions absorb protium up to  $H/M=1$ , and the alloys with a B.C.C. single phase are hardly prepared for the compositions with less than 5 at% V content. Thus, the region with higher protium desorption capacity (about 2.6 mass%; 9–0.01 MPa) is considered to be shown by the boldest line in Fig. 5. This region is Cr-rich from the region reported by Cho et al. [14]. This result is considered because measurement temperature was controlled in order to control the desorption plateau pressure near atmospheric pressure in this study.

### 3.3. The lattice parameters and the enthalpy changes for di-protide formation in Ti–Cr–V alloys

Fig. 6 shows the lattice parameters of Ti–Cr–V alloys. The metallic radii of each element were reported as follows: Ti=1.44–1.47 Å; Cr=1.25 Å; V=1.31 Å [15]. Titanium has the width to metallic radii because of allotropic transformations. When the titanium metallic radius is 1.42 Å with the assumption that the lattice parameters are linearly proportional to the compositions, the calculated lattice parameters shown by broken lines in Fig. 6 were found to be in good agreement with the observed parameters.

The present authors reported the enthalpy changes for

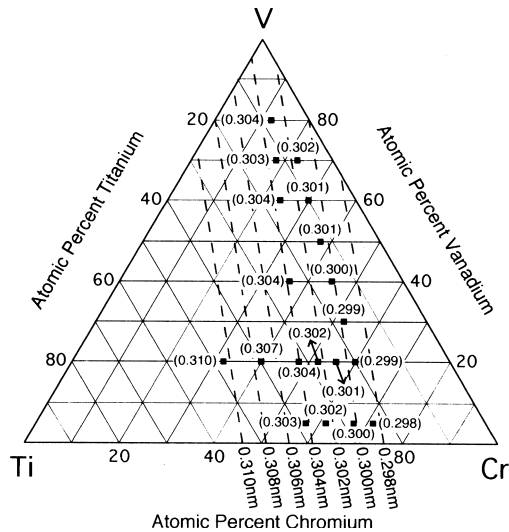


Fig. 6. The lattice parameters of Ti–Cr–V alloys. The broken lines show the calculated lattice parameters.

di-protide formation of  $x\text{Ti–Cr–}20\text{V}$  ( $x=32, 40, 48$ ) alloys [16]. Fig. 7 shows the enthalpy changes for di-protide formation of  $x\text{Ti–Cr–}20\text{V}$  ( $x=32, 40, 48$ ) alloys versus Ti content. It was found that the enthalpy changes for di-protide formation are linearly proportional to Ti content. The enthalpy change for di-protide formation in Ti–20V alloy from the approximate value in Fig. 7 is  $-110.8$  kJ/mol  $\text{H}_2$ . On the other hand, it is reported that the standard enthalpies of formation of  $\text{TiH}_{1.97}$  and  $\text{VH}_{2.0}$  are  $-125.2$  and  $-40.2$  kJ/mol  $\text{H}_2$ , respectively [17]. We assumed that the law of mixture can be applied to the system, and that the enthalpy changes were linearly proportional to the compositions for Ti–Cr–V alloys. The calculated value for the Ti–20V alloy is  $-108.2$  kJ/mol  $\text{H}_2$ . It is almost equal to the value from Fig. 7. Therefore, it can be said that the estimated values of the enthalpy

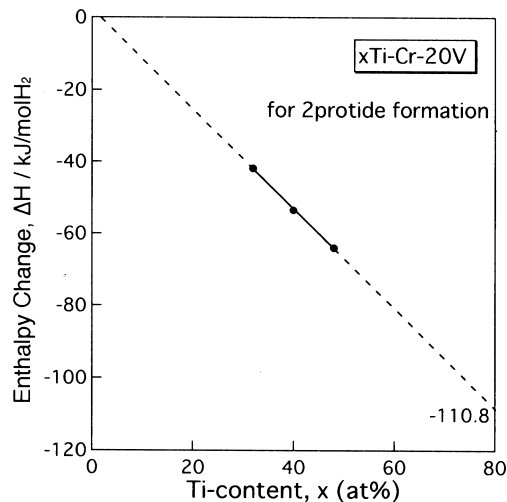


Fig. 7. The enthalpy changes for di-protide formation of  $x\text{Ti–Cr–}20\text{V}$  ( $x=32, 40, 48$ ) alloys versus Ti content.

changes for di-protide formation in Ti–Cr–V alloys could be reasonable.

Estimated enthalpy changes for di-protide formation and the lattice parameters of the alloys were found to be generally constant ( $\Delta H = -32$  kJ/mol  $\text{H}_2$  and  $a = 0.301$  nm) on the limited line between the appearance of regions of mono- and di-protides shown in Fig. 5.

#### 4. Conclusions

Protium absorption properties and protide formations in Ti–Cr–V alloys have been investigated widely, and the following conclusions have been derived.

1. It was found that higher protium desorption capacity was achieved by increasing Cr content and controlling measurement temperature in order to control the desorption plateau pressure near atmospheric pressure for the alloys with less than 40 at% V content. However, Cr-rich alloys were found to absorb up to  $\text{H}/\text{M}=1$  because of the formation of the mono-protides. The region with the higher protium desorption capacity was obtained.
2. The lattice parameters of the alloys and the enthalpy changes for di-protide formation were estimated from the compositions of the alloys. Moreover, estimated enthalpy changes for di-protide formation and the lattice parameters of the alloys were found to be generally constant on the limited line between the appearance of regions of mono- and di-protides.

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#### References

- [1] T. Tamura, T. Kuriwa, T. Amemiya, T. Fuda, A. Kamegawa, H. Takamura, M. Okada, Mater. Trans. JIM 40 (1999) 431–434.
- [2] T. Kuriwa, T. Tamura, T. Amemiya, T. Fuda, A. Kamegawa, H. Takamura, M. Okada, J. Alloys Comp. 293–295 (1999) 433–436.
- [3] H. Iba, Ph.D. Dissertation, Tohoku University, Japan, 1997, in Japanese.
- [4] H. Iba, T. Mouri, M. Shionoya, E. Akiba, Mater. Jap. 36 (1997) 640–642, in Japanese.
- [5] Y. Tominaga, S. Nishimura, T. Amemiya, T. Fuda, T. Tamura, T. Kuriwa, A. Kamegawa, M. Okada, Mater. Trans. JIM 40 (1999) 871–874.
- [6] Y. Tominaga, K. Matsumoto, T. Fuda, T. Tamura, T. Kuriwa, A. Kamegawa, H. Takamura, M. Okada, Mater. Trans. JIM 41 (2000) 617–620.
- [7] T. Tamura, Y. Tominaga, K. Matsumoto, T. Fuda, T. Kuriwa, A.

- Kamegawa, H. Takamura, M. Okada, J. Alloys Comp. 330–332 (2002) 522–525.
- [8] M. Okada, T. Kuriwa, T. Tamura, H. Takamura, A. Kamegawa, J. Alloys Comp. 330–332 (2002) 511–516.
- [9] M. Okada, T. Kuriwa, T. Tamura, H. Takamura, A. Kamegawa, Metal. Mater. Korea 7 (2001) 67–72.
- [10] T. Tamura, A. Kamegawa, H. Takamura, M. Okada, Mater. Trans. 42 (2001) 1862–1865.
- [11] T. Tamura, A. Kamegawa, H. Takamura, M. Okada, Mater. Trans. 43 (2002) 410–413.
- [12] T. Tamura, M. Hatakeyama, T. Ebinuma, A. Kamegawa, H. Takamura, M. Okada, Mater. Trans. 43 (2002) 1120–1123.
- [13] T. Tamura, T. Kazumi, A. Kamegawa, H. Takamura, M. Okada, Mater. Trans. 43 (2002) 2753–2756.
- [14] S.W. Cho, C.S. Han, C.N. Park, E. Akiba, J. Alloys Comp. 288 (1999) 294–298.
- [15] L.V. Azaroff, Introduction to Solids, McGraw-Hill, New York, 1960, p. 441.
- [16] T. Kazumi, T. Tamura, A. Kamegawa, H. Takamura, M. Okada, Mater. Trans. 43 (2002) 2748–2752.
- [17] R. Wiswall, Hydrogen in metals II, in: G. Alefeld, J. Völkl (Eds.), Topics in Applied Physics, Vol. 29, Springer, Berlin, 1978, p. 209.