Effect of Absorption-Desorption Cycles on Structure and Stability of Protides in Ti–Cr–V Alloys *¹

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Ti–Cr–V alloys with a BCC structure have high protium capacities, but it is known that the cyclic properties for the alloys change with varying V content. In this paper, the cyclic properties of the Ti–Cr–V alloys are investigated in view of the crystal structure of the β protide phase, which was measured at the point after desorbing at the plateau region and the thermal stability of the γ protide phase, which was measured at the point immediately before desorbing at the desorption region. It was found that the crystal structure of the β phase was changed from BCC phase to BCT phase and the c/a increased with increasing the cycle number. This difference of the crystal structure of the β phase suggests that the lattice can't gradually contract to a -axis direction at absorbing process with increasing the cycle number. Furthermore, it was found that the absorption-desorption cycle process causes the declined slope of the ΔH plots due to existence of the different γ protides of different thermal stabilities. Namely, this result suggests that site energies of protium in the lattice have a distribution after absorption-desorption cycles.

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1. Introduction

Protium (hydrogen atom) storage alloys are proposed to be used as hydrogen storage tanks for fuel-cell automobiles. Ti–Cr–V alloys with a BCC structure, which are known to have about 3 mass% effective protium capacity with desorbing at 373 K, are regarded as one of the candidates for the media of hydrogen storage tanks.^{1–14} In view of practical use of the alloys, it is important to know absorption-desorption cyclic properties and heat balance associated with protium absorption-desorption process.

Shirasaki *et al.* in our group reported that the particle size of the Ti–Cr–V alloy after 50th cycle became small with decreasing V content.¹⁵ In their report, there are no studies on the crystal structure and the thermal stability of the protide phases. Thus, the cyclic properties were investigated in terms of the crystal structure and the thermal stability of the protide phases in this study. It is known that the magnitudes of the enthalpy changes ΔH for AB₅ type alloys are constant throughout the plateau region.¹⁶ However, there are few reports about ΔH on the BCC solid solution type alloys.

Therefore, the purpose of this study is to examine the crystal structure changes and the thermal stability changes of the protide phases for the Ti–Cr–V alloys with increasing the absorption-desorption cycles.

2. Experimental Procedures

Ti–Cr–V 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%. Samples were remelted five times to en-

sure their homogeneity. Heat-treatment was carried out under an Ar atmosphere. The samples were annealed at 1673 K for 1 h, and then quenched into iced-water.

Crystal structures were determined by X-ray diffractometer (XRD) with Cu–K α radiation. The Pressure-Composition-isotherms (PCT curves) were measured with a Sieverts-type apparatus at 293–353 K for Ti:Cr = 2:3 alloys, at 363–423 K for Ti:Cr = 1:1 alloys, at 423–523 K for Ti:Cr = 3:2 alloys respectively. The magnitudes of the enthalpy changes ΔH for the plateau versus protium concentration were determined from the van't Hoff plots. The magnitudes of the ΔH were evaluated in 1st cycle (after dehydrogenation following activated treatment) and 31th cycle for all alloys. The dehydrogenation treatment were performed for the purpose of appearing the original plateau pressure of the alloys that are independent of cooling rate in the condition at 673 K for 1 h for Ti:Cr = 2:3, 1:1 alloys and at 773 K for 1 h for Ti:Cr = 3:2 alloy.

The effective protium capacity was defined as a difference between protium absorbing capacity at hydrogen gas pressure of 7 MPa and that at 0.01 MPa in desorbing process. The hysteresis factor was defined as $\ln(P_a/P_d)$, where P_a is the plateau pressure in absorption process and P_d is the plateau pressure in desorption process.

3. Results and Discussion

3.1 Effect of cycles on the crystal structure of β protide phase

It has been found by XRD that all studied alloys has a BCC single phase.

Figure 1 shows P-C isotherms for Ti–Cr–20 at% V (Ti:Cr = 2:3) alloy (at% is abbreviated hereafter) in 1st, 31th and 101th cycle. The maximum protium absorption capacity for 1st cycle shows about 3.6 mass% protium. The effective pro-

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Fig. 1 P-C isotherms at 323 K for Ti–Cr–20V (Ti:Cr = 2:3) alloy from 1st to 101th cycle. $C_{\text{effec.}}$ is represented as effective protium capacity.

Fig. 2 XRD patterns of several protide phases for the Ti–Cr–20V (Ti:Cr = 2:3) alloy at 1st cycle.

tium desorption capacity, $C_{\text{effec.}}$, for 1st cycle shows about 2.4mass% protium. However, the effective protium desorption capacity decreased with increasing the absorption-desorption cycle number as follows: 31th; 2.1 mass%, 101th; 2.0 mass%. Furthermore, the shape of the P-C isotherms for the alloy was changed and the hysteresis factor, $\ln(P_a/P_d)$, decreased with increasing the cycle number as follows: 1st; 1.27, 31th; 0.73, 101th; 0.58.

Figure 2 shows XRD patterns of several protide phases for the Ti–Cr–20V (Ti:Cr = 2:3) alloy. The protide phases were

Fig. 3 (a) XRD patterns of β protide phase (b) XRD patterns of γ protide phase for the Ti–Cr–20V (Ti:Cr = 2:3) alloy from 1st to 101th cycle.

measured by XRD at two points of P-C isotherms as follows: β phase was measured at the point after desorbing at the desorption plateau region, γ phase was measured at the point immediately before desorbing at the desorption plateau region. The crystal structure of the β phase was BCC single phase and the crystal structure of the γ phase was FCC single phase at 1st cycle. Figure 3(a) shows XRD of the β protide phases for the Ti–Cr–20V (Ti:Cr = 2:3) alloy from 1st to 101th cycle. It was found that the crystal structure of the β phase was changed from BCC phase to BCT phase and the c/a increased with increasing the cycle number. Figure 3(b) shows XRD of the γ protide phases for the Ti–Cr–20V (Ti:Cr = 2:3) alloy from 1st to 101th cycle. It was found that the γ phase was maintained as FCC phase and the lattice parameter was almost constant with increasing the cycle number. Figure 4 shows lattice parameter changes and the schematic illustration of the crystal structures for several protide phases shown in Fig. 3. The γ phase are considered to be a BCT unit cell in two FCC unit cells. As shown in Fig. 4, the $\beta \rightleftharpoons \gamma$ transformation in 1st cycle was BCC(β) $\rightleftharpoons$ FCC(γ) transformation, thus the lattice must contract along a -axis direction at absorbing process and expand along a -axis direction at desorbing process as opposed to c -axis direction. With increasing the cycle number, however, the $\beta \rightleftharpoons \gamma$ transformation in 101th cycle was BCT(β) $\rightleftharpoons$ FCC(γ) transformation. This difference of the $\beta \rightleftharpoons \gamma$ transformation suggests that the lattice can't gradually contract along a -axis direction at absorbing process with increasing the cycle number. We reported that the magnitudes of the lattice parameter changes to a -axis direction appear to be correlation with the hysteresis factor shown in Fig. 1.¹⁷⁾ Namely, the major reason of the decrease

Fig. 4 Lattice parameter changes and schematic illustration with the $\beta \rightleftharpoons \gamma$ transformation for the Ti-Cr-20V (Ti:Cr = 2:3) alloy from 1st to 101th cycle.

Fig. 5 P-C isotherms at 483 K for the Ti-Cr-20V (Ti:Cr = 3:2) alloy from 1st to 31th cycle and 32th cycle after dehydrogenation following 31th cycle.

of the hysteresis factor with increasing the cycle number is considered to be such that the lattice hardly contracts along a -axis direction when BCT(β) $\rightarrow$ FCC(γ) transformation takes place at absorbing process.

Figure 5 shows P-C isotherms for the Ti-Cr-20V (Ti:Cr = 3:2) alloy from 1st to 31th cycle and 32th cycle after dehydrogenation following 31th cycle. The dehydrogenation treatment was performed in the condition of evacuation by rotary pump at 773 K for 1 h. The plateau of the P-C isotherms in

Fig. 6 XRD patterns of the β protide phase in several cycle numbers and after dehydrogenation for the Ti-Cr-20V (Ti:Cr = 3:2) alloy.

31th cycle remarkably inclined in comparing with the plateau for the Ti-Cr-20V (Ti:Cr = 2:3) alloy in same cycle as shown in Fig. 1. Furthermore, the hysteresis of the P-C isotherms in 31th cycle was very small as shown in Fig. 5. However, it was found that the plateau pressure and the hysteresis of the P-C isotherms in 32th cycle after dehydrogenation following 31th cycle were recovered. The increment of the plateau pressure by dehydrogenation may be that some accumulated lattice defects induced by absorption-desorption cycles were annealed out. Figure 6 shows XRD patterns of the β phase in several cycle numbers corresponding to the P-C isotherms shown in Fig. 5. The crystal structure of the β phase in 31th cycle was BCT phase. On the other hand, it was found that the crystal structure of the β phase in 32th cycle after dehydrogenation following 31th cycle returned to be a BCC phase. The major reasons of this result are considered as follows: dehydrogenation treatment decreases some amount of defects as well as complete desorption of protium. Although it is unclear which factor dominates to determine the crystal structure, some amount of defects still remains in the alloy as shown in Fig. 6, where the diffracted peak in 32th cycle was broad as before. BCC structure may be appeared by complete desorption of protium. Therefore, these result suggests that the recovery of the hysteresis in 32th cycle originates in the BCC(β) $\rightleftharpoons$ FCC(γ) transformation.

3.2 Effect of cycles on the thermal stability of γ protide phase

Figure 7 shows the magnitudes of the enthalpy changes ΔH at desorption process versus protium concentration throughout the plateau region of the P-C isotherms for the Ti-Cr-20V (Ti:Cr = 2:3, 1:1, 3:2) alloys. The zero point of protium concentration is fixed to be the same point in several cycles. The magnitudes of ΔH increased with increasing

Fig. 7 Enthalpy changes at desorption process ΔH versus protium concentration throughout the plateau region of the P-C isotherms for the Ti–Cr–20V (Ti:Cr = 2:3, 1:1, 3:2) alloys.

Fig. 8 Enthalpy changes ΔH versus protium concentration throughout the plateau region of the P-C isotherms for the as-cast and heat-treated Ti–Cr–20V (Ti:Cr = 2:3) alloys.

Ti content in 1st cycle as follows; $\Delta H = 41.4 \text{ kJ/mol H}_2$ (Ti:Cr = 2:3), $\Delta H = 52.5 \text{ kJ/mol H}_2$ (Ti:Cr = 1:1), $\Delta H = 64.6 \text{ kJ/mol H}_2$ (Ti:Cr = 3:2). Furthermore, it was found that the magnitudes of ΔH were almost constant throughout the plateau region in 1st cycle, while the magnitudes of ΔH in 31th cycle reduce with increasing protium concentration. This tendency is remarkable with increasing Ti content and the measurement temperature of the P-C isotherms. The 30th absorption-desorption cycle process cause the declined slope of the ΔH plots due to existence of the different γ protides of different stabilities. Namely, this result suggests that the energies of protium for occupying crystal sites have a distribution after 30th cycles, because the ΔH plots for as-cast alloy declines compared with the flat ΔH plots for heat-treated alloy as shown in Fig. 8. This result for as cast alloy in Fig. 8 is due to the inhomogeneous distribution of the constituent atoms, namely that protium occupies Ti-rich interstitial sites at low protium concentration, while protium gradually occupies Cr-rich interstitial sites with increasing protium concentration.

It is known to improve the cyclic properties with increasing V content for the Ti–Cr–V alloys in our recent work.¹⁵⁾ Thus, to investigate the slope of ΔH plots after 30th cycles for V-rich alloys, the magnitudes of ΔH for the Ti–Cr– x V (Ti:Cr = 2:3; $x = 20, 40, 60, 80$) alloy in 31th cycle was examined as shown in Fig. 9. It was found that the ΔH plots in 31th cycle become flat with increasing V content. Therefore, the slope of ΔH plots is considered as one of factors to evaluate the cyclic property for protium storage alloys.

Fig. 9 Enthalpy changes at desorption process ΔH versus protium concentration throughout the plateau region of the P-C isotherms for the Ti–Cr– x V (Ti:Cr = 2:3; $x = 20, 40, 60, 80$) alloys in 31th cycle.

4. Conclusions

Effect of the absorption-desorption cycles on the structure and the stability of protides in the Ti–Cr–V alloys have been investigated and the following conclusions have been derived.

(1) The crystal structure of the β protide phase was changed from BCC phase to BCT phase and the c/a increased with increasing the cycle number.

(2) The absorption-desorption cycle process causes the declined slope of the ΔH plots due to existence of the different γ protides of different thermal stabilities.

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