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Ti–Cr–X protium absorbing alloys with high protium content for fuel-cell

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Abstract

The effects of additional elements to the Ti–Cr alloys on their protium absorption–desorption properties were investigated. Although Ti–Cr alloys with a b.c.c. structure is expected to exhibit a high protium content, it is difficult to obtain single b.c.c. phase quenching from the high temperature. The effects of additional elements such as V, Mo, W, Nb, Ta, Ru, Rh, Re, Os, Ir etc. on stabilizing b.c.c. phase in the alloys were investigated. Then, it was found that the additions of V, Mo, W, Ru, Rh, Re, Os, Ir effectively stabilized b.c.c. phases. But the addition of Nb and Ta preferentially formed Laves phases. Specially, the addition of Mo and Ru is effective to stabilize the b.c.c. phases with high protium content. The Ti–Cr–(1~2.5%)Mo alloys show almost same capacity of protium as that reported in Ti–Cr–(5–7.5)V alloys. The addition of Ru to Ti–Cr alloys also shows the capacity of 3.0 mass% protium. These V-free Ti–Cr alloys will be also suitable for the future applications.

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Keywords: Hydrogen absorbing alloys; BCC hydrogen absorbing alloys; Ti–Cr–Mo alloys; Ti–Cr–Ru alloys; High hydrogen content; V-free Ti–Cr alloys; Hydrogen alloys tanks for fuel cell

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1. Introduction

Recently, polymer electrolyte fuel cell (PEFC) was developed especially for the emission-free vehicles. Using protium(hydrogen atom) absorbing alloy as protium tank on FC-cars is one of the ideal methods of hydrogen supply to fuel cell because of their compactness and safety. But the protium capacity of presently used alloys such as $LaNi_5$ based alloys which have the capacity of 1.4 mass%, is insufficient for using as hydrogen tank. So, increasing of the capacity is a very important request. The strong candidate for this realization is Vanadium based solid solutions with a b.c.c. structure since they have capacities of more than 3.8 mass% working at room temperature, but they can desorb only about half of the absorbed protium [1].

Iba et al. [2–4] 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 et al. [2,5] also reported that a Ti–40at%V–35at%Cr (at% will be abbreviated hereafter) alloy with a b.c.c. structure could desorb about 2.4 mass% protium. Okada et al. [6–19] reported that the Ti–Cr–(10–20)%V b.c.c. heat-treated alloys can desorb about 2.4–2.6 mass% protium, and specially the alloys with low content (5–7%) of V exhibit high protium capacity of 2.8 mass% [9], and yield the high capacity of 3.0 mass% protium absorption capacity at 313 K following the evacuation at 368 K [10], which is the highest value at 313 K reported so far. Then it is expected that Ti–Cr–X alloys may have a high protium content, although it is well known that a b.c.c. single phase is hardly obtained by quenching from the high temperature in binary Ti–Cr alloys. Therefore, the present paper describes the development of the new protium absorbing Ti–Cr–X alloys with high capacity of protium. The effects of additional elements such as V, Mo, W, Nb, Ta, Ru, Rh, Re, Os, Ir etc. on stabilizing b.c.c. phase and their protium absorbing–desorbing properties in the Ti–Cr alloys were investigated.

2. Experimental details

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

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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 to the annealing temperature. The samples were annealed at 1173–1623 K for 1 min–50 h, and quenched into water. The additives (X) for stabilizing the b.c.c. phases in Ti–Cr alloys were selected as 5B(Nb, Ta), 6B(Mo, W) series elements and 7B (Re), and 8 series (Ru, Os, Rh, Ir) elements in periodic table, in referring the Cr–X, and Ti–X binary phase diagram where X has some solubility with Ti and Cr.

Crystal structures and lattice parameters were studied by X-ray diffractometer (XRD) using Cu Kα radiation. The microstructures were observed by scanning electron microscopy with an energy dispersive X-ray spectrometer.

Pressure–composition–temperature (*P–C–T*) curves were measured using a Sieverts-type apparatus. The protium absorption–desorption property and protium capacities were defined by the third cycle of *P–C–T* curve. The origin of the horizontal axis was fixed on zero capacity after activation.

3. Results and discussion

3.1. Ti–Cr–X alloys (X=V, Mo, W, Nb, Ta)

Fig. 1 shows the X-ray diffraction patterns of Ti–58.5Cr–2.5X alloys and Ti–60Cr alloys heat-treated at 1673 K for 1 min. It was found that the alloys with 2.5 at%Mo, W or V consist of mainly b.c.c. phase, but the alloys with 2.5 at%Nb or Ta and without additives mostly contain C14-type Laves phase besides b.c.c. phases. Thus the addition of Mo or W to Ti–Cr alloys is effective for obtaining a b.c.c. single phase. Fig. 2 shows the corresponding (*P–C–T*) curves of the alloys. Ti–Cr–2.5%Mo alloys with only b.c.c. phase yield the absorbing capacity of 3.6 mass% protium, which is almost the same value as that of the alloys with 2.5%V. Although the alloy with W consists of only b.c.c. phase, the absorbing capacity is around 3.3 mass% because of its heavy atomic weight. The alloys without any additives and with Nb, or Ta, which contained Laves phase show the low absorbing capacity. Then the addition of Mo turned out to be most effective. In the next section, the optimum amount of Mo is studied.

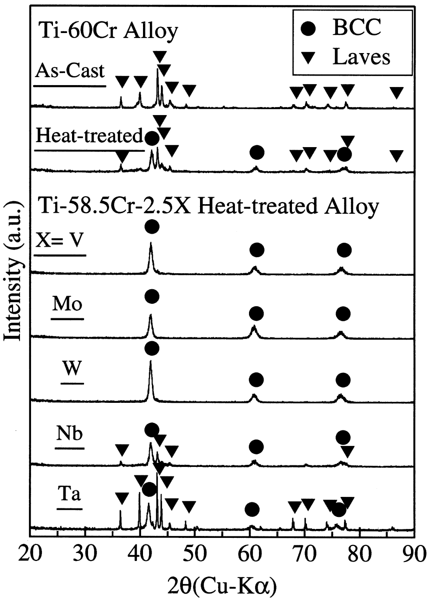

Fig. 1. X-ray diffraction patterns of Ti–58.5Cr–2.5X alloys and Ti–60Cr alloys heat-treated at 1673 K for 1 min.

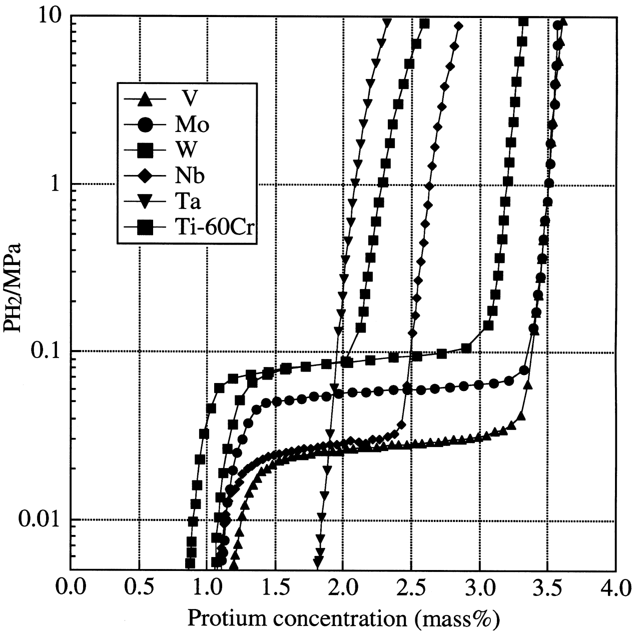

Fig. 2. Corresponding (*P–C–T*) curves of the alloys shown in Fig. 1.

3.2. Ti–Cr–Mo alloys

Fig. 3(a) shows the X-ray diffraction patterns of Ti–Cr–(1–50)at%Mo alloys heat-treated at 1673 K for 1 min. It was found that the alloys with more than 2.5 at%Mo consist of mainly b.c.c. phase, but the alloys with 1 at%Mo contain C14-type Laves phase besides b.c.c. phase. The lattice parameter of the alloys increases with increasing Mo content because of the larger atomic radius of Mo than that of Ti and Cr. Fig. 3(b) shows the corresponding (*P–C–T*) curves of the alloys. The absorbing capacity becomes maximum when the Mo content is 2.5%Mo, and it decreases with increasing Mo content. The plateau pressures of the alloys increased with increasing Mo content. Generally, it is known that plateau pressure becomes higher as the lattice parameter decreases. But in the Ti–Cr–Mo alloys the plateau pressures increased with increasing lattice parameters. Fig. 4 shows the same (*P–C–T*) curves of the alloys, which is redrawn with pressure versus H/M. The alloys with (2.5–10)%Mo absorb the

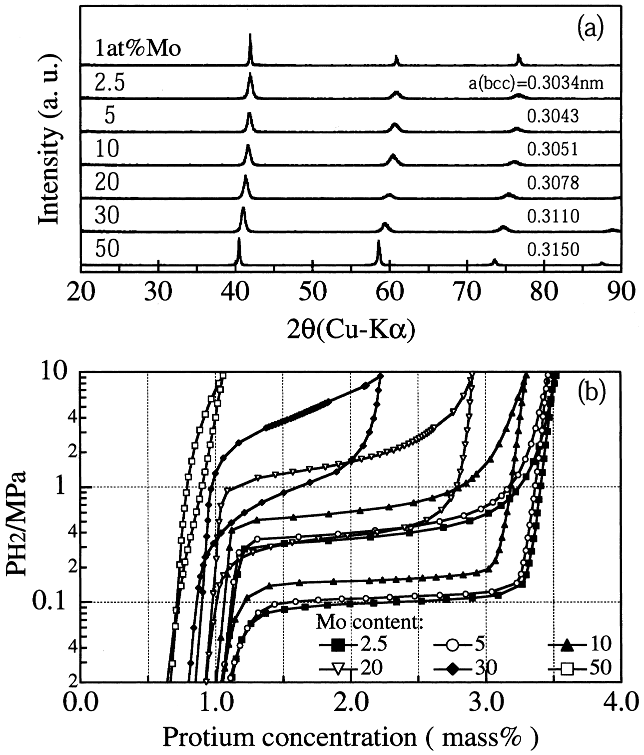

Fig. 3. (a) XRD patterns of Ti–Cr–(1–50)at%Mo alloys heat-treated at 1673 K for 1 min, (b) their corresponding (P–C–T) curves.

protium up to 1.8 of H/M, but absorbed capacities of the alloys with more than 20%Mo decrease with increasing Mo content. This means that total absorbed mass% of protium decreases with increasing Mo content because of the heavy atomic weight although the alloys with less than 10% Mo are capable of absorbing the same amount of protium up to 1.8 H/M. Then it can be said that the optimum additional amount of Mo to Ti–Cr alloys could be 2.5at%, which yields the high capacity of 2.8 mass% protium at 313 K.

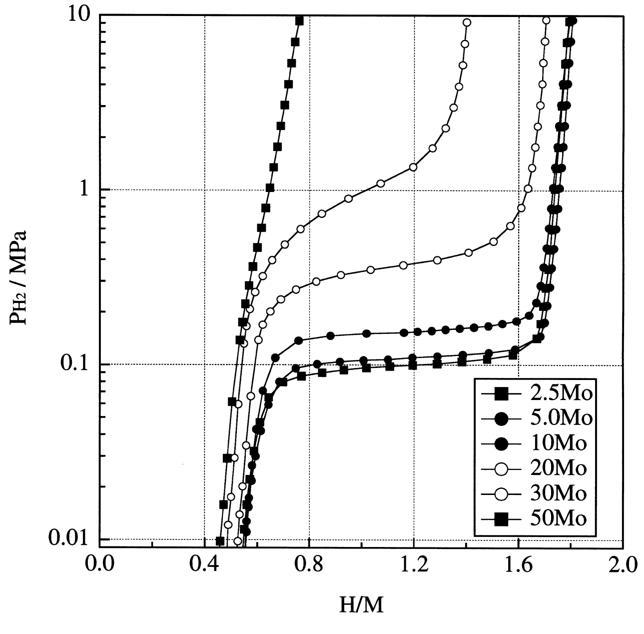

Fig. 4. Same (P–C–T) curves shown in Fig. 3(b), which is redrawn with pressure versus H/M.

3.3. Ti–Cr–X alloys (X=Ru, Rh, Re, Os, Ir)

In the next study, 7B (Re), and 8 series (Ru, Os, Rh, Ir) elements in the periodic table, are chosen for the additional elements because they have some solubility with Ti and Cr, in referring the Cr–X, and Ti–X binary phase diagrams. Fig. 5(a) and (b) show the X-ray diffraction patterns of Ti–56%Cr–2.0%X (X=Ru, Rh, Re, Os, Ir) alloys (a) in as-cast state and (b) after heat-treatment at 1673 K for 10 min. It was found that all alloys with the addition of 2.0% X consist of mainly b.c.c. phase after heat-treatment, although they mostly contain the C14-type Laves in as-cast state except the alloy with 2.0at% Ru where strong b.c.c. diffracted peaks were observed. Thus, it should be stressed that the addition of Ru to Ti–Cr alloys is most effective for obtaining a b.c.c. single phase among the selected additional elements. Fig. 6 shows the corresponding (P–C–T) curves of the heat-treated alloys. The plateau pressures of the alloys with the additional elements become higher in the order of Ir>Os>Ru>Re>Rh, although the lattice parameter of the b.c.c. phases are almost unchanged. The alloys with Rh and Ru show the maximum absorbed protium of 3.5 mass%. Since the alloys with Ru contained some amount of b.c.c. phases in as-cast state, it is expected that small additions of Ru may be more effective to stabilize b.c.c. phases than that of Rh. Then Ru was chosen for further studies.

3.4. Ti–Cr–Ru alloys

Fig. 7 shows the X-ray diffraction patterns of Ti–Cr–(1–5)at%Ru alloys heat-treated at 1673 K for 10 min. The alloys with more than 1.0at%Ru consist of mainly b.c.c. phases. The lattice parameter of the alloys remains unchanged with increasing Ru content, probably because atomic radius of Ru (0.138 nm) is between that of Ti (0.147 nm) and Cr (0.130 nm). Fig. 8 shows the corresponding (P–C–T) curves of the alloys. The absorbing capacity becomes maximum when the Ru content is 1.0%Ru, and it decreases with increasing Ru content. The plateau pressures of the alloys increased with increasing Ru content, although the lattice parameter of the alloys remains unchanged with varying Ru content.

Fig. 9 shows the X-ray diffraction patterns of Ti–56%Cr–2at%Ru alloys heat-treated at 1723–1523 K for 10 min. The alloy heat-treated above 1673 K consists of b.c.c. phase, but the heat-treated alloy below 1623 K contains Laves phases besides b.c.c. phases. Fig. 10 shows the corresponding (P–C–T) curves of the Ti–56%Cr–2at%Ru alloys. The absorption–desorption capacity becomes maxi-

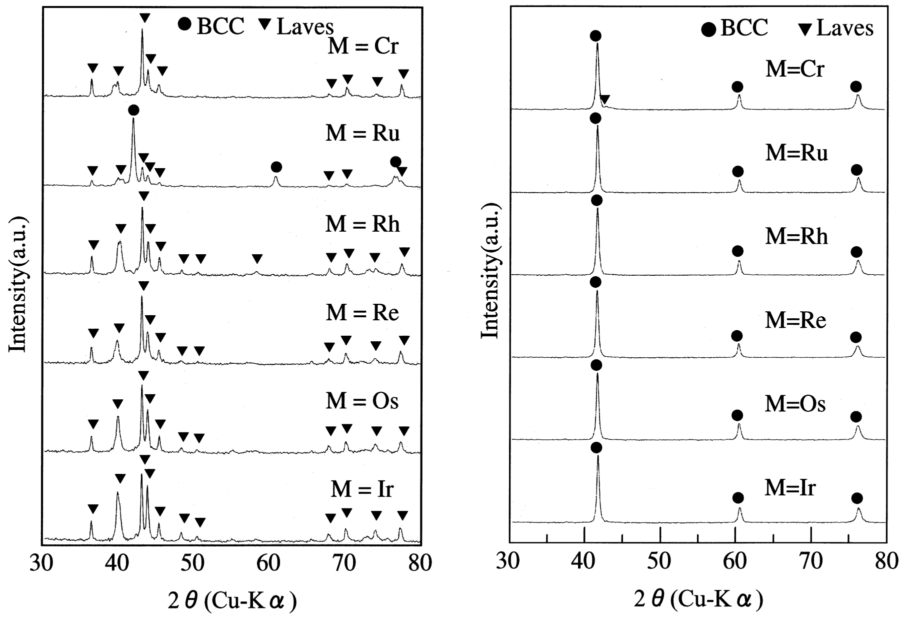

Fig. 5. XRD patterns of Ti–56%Cr–2.0%X (X=Ru, Rh, Re, Os, Ir) alloys (a) in as-cast state and (b) after heat-treatment at 1673 K for 10 min.

mum when the heat-treatment temperature is above 1673 K where the alloy has a b.c.c. single phase. The alloy heat-treated below 1623 K shows lower capacities, where the alloy contained Laves phases. Fig. 11 shows the (*P*–*C*–*T*) curve of the Ti–56%Cr–2at%Ru alloy measured at 293 K after evacuation at 373 K for 30 h, and yield the high capacity of 3.0 mass% protium.

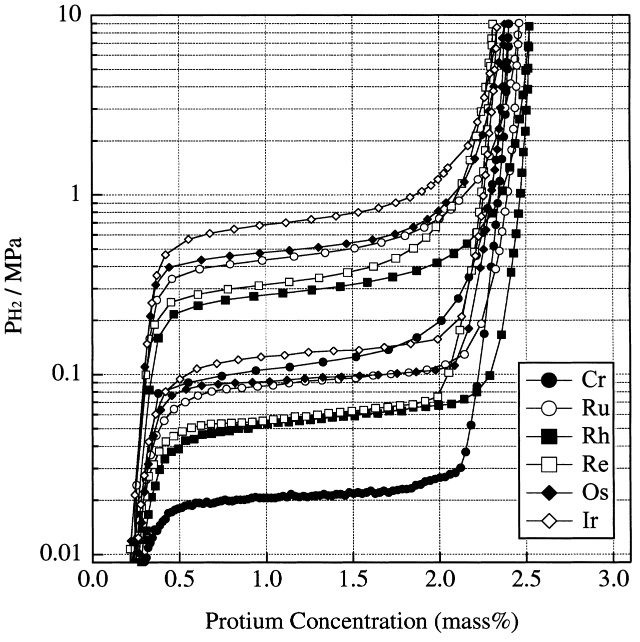

Fig. 6. Corresponding (*P*–*C*–*T*) curves of the heat-treated alloys shown in Fig. 5(b).

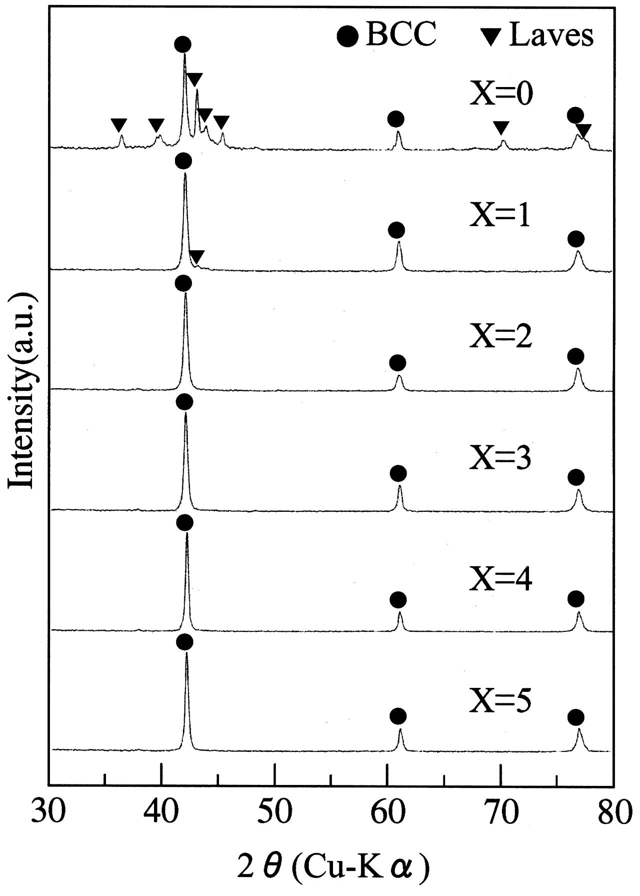

Fig. 7. XRD patterns of Ti–Cr–(1–5)at%Ru alloys heat-treated at 1673 K for 10 min.

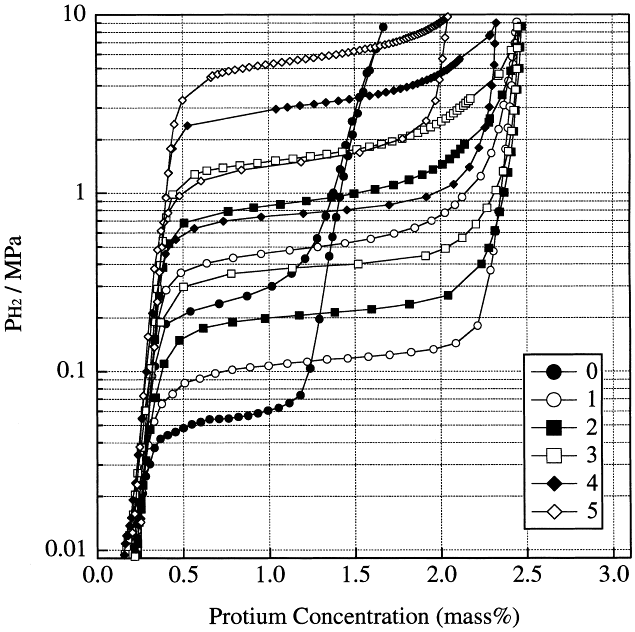

Fig. 8. Corresponding (*P–C–T*) curves of the alloys shown in Fig. 7.

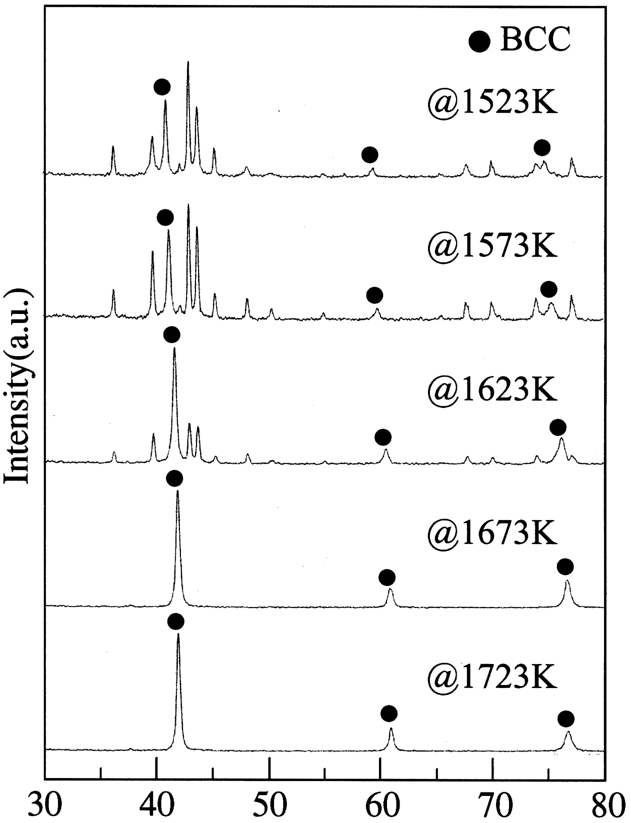

Fig. 9. X-ray diffraction patterns of Ti–56%Cr–2at%Ru alloys heat-treated at 1723–1523 K for 10 min.

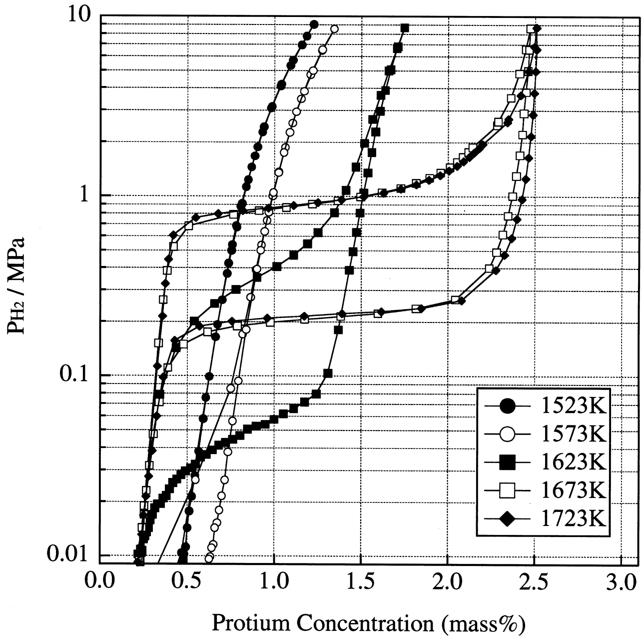

Fig. 10. Corresponding (*P–C–T*) curves of the Ti–56%Cr–2at%Ru alloys.

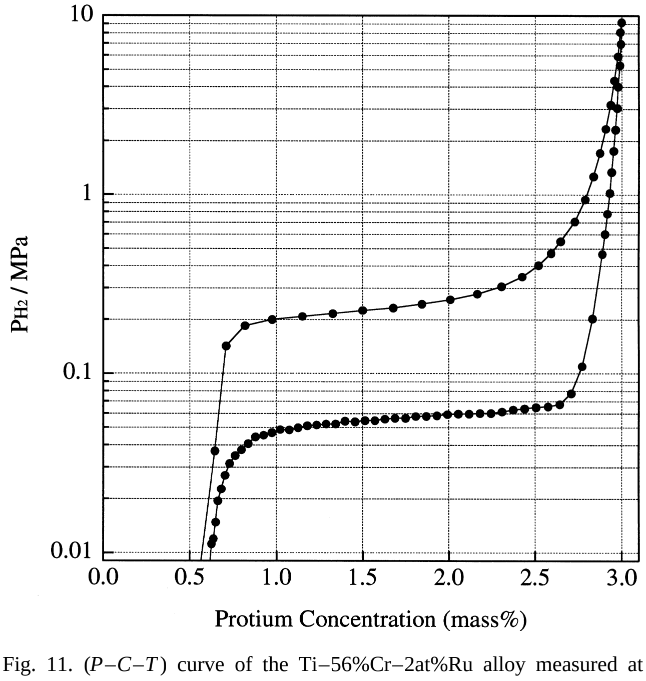

Fig. 11. (*P–C–T*) curve of the Ti–56%Cr–2at%Ru alloy measured at 313 K after evacuation at 368 K for 2 h.

As a summary, the addition of Ru or Mo to Ti–Cr alloys stabilizes the b.c.c. phase, and yields the highest capacity of 2.8 mass% protium, which is almost the same as that of the reported Ti–Cr–5%V alloys. This value could be the highest value at 313 K reported so far. These V-free Ti–Cr alloys will be also potential candidates for further development of higher capacity protium absorbing alloys in the future.

4. Conclusions

V-free Ti–Cr–X alloys with high protium capacity are developed, and the following conclusions were made.

(1) The addition of Mo and W to Ti–Cr alloys stabilizes the b.c.c. phases, but one of Nb and Ta forms Laves phase. The alloys with more than 2.5at%Mo consist of mainly b.c.c. phases, and their absorbing capacity decreases with increasing Mo content. The plateau pressures of the alloys increased with increasing Mo content. The optimum Mo content turned out to be 2.5%Mo. The Ti–Cr–2.5at%Mo b.c.c. alloys exhibited protium desorption capacities of about 2.8 mass%H at 313 K.

(2) The addition of 2.0%X (X=Ru, Rh, Re, Os, Ir) to the Ti–Cr alloys forms mainly b.c.c. phase after heat-treatment, although the alloys mostly contain the C14-type Laves in as-cast state except the alloy with 2.0at%Ru where b.c.c. phases were observed. The plateau pressures of the (P–C–T) curves for the alloys with the additional elements become higher in the order of Ir>Os>Ru>Re>Rh, although the lattice parameter of the b.c.c. phases are almost unchanged. The alloys with Rh and Ru show the maximum absorbed protium of 3.5 mass%.

(3) The Ti–Cr–(1–5)at%Ru heat-treated alloys with more than 1.0at%Ru consist of mainly b.c.c. phases, where the lattice parameter of the alloys remains unchanged. The absorbing capacity of the alloys decreases, and the plateau pressures of the alloys increased with increasing Ru content. The Ti–Cr–1.0at%Ru alloy show the high protium capacity of nearly 3.0 mass%, which is almost the same capacity of protium as that reported in Ti–Cr–(5–7.5)V alloys.

Acknowledgements

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