Crystal Structure and Protium Absorption Properties of Ti–Cr–X Alloys*1

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This paper aims to develop the vanadium free Ti–Cr–X BCC solid solution alloys with high protium content. The effects of additional elements such as Mo, W, Nb and Ta to the phase formation on the Ti–Cr alloys were studied. It was found that Mo-added heat-treated alloys had the flattened plateau regions with the capacity of more than 2.2 mass% protium with maximum of 3.6 mass% protium content, which is equal to that of Ti–Cr–V alloys. It was found that the Ti–Cr–Mo alloys with BCC structure transformed to protide phase with BCC or FCC structure. The plateau pressure of the Ti–Cr–Mo alloys increased with increasing Mo content, but the lattice parameters decreased. Therefore, it is difficult to obtain only BCC solid solution phase at high temperature in narrow range:

Keywords: protium storage alloys, titanium-chromium-molybdenum alloys, body centered cubic phase, heat-treatment

1. Introduction

Recent strong demands for the hydrogen fuel cell (FC) as the emission-free vehicles urge to develop protium absorbing alloys with high capacity as hydrogen storage tank. Since they have advantages as compactness, free-shape and safety storage of hydrogen energy. However, the protium capacity of the presently used MmNi5 based alloys does not exceed 1.2 mass% protium content, which is insufficient for using as hydrogen storage tank. The strong candidate for the purpose will be body centered cubic (BCC) solid solution alloys, which is named as Laves phase related the BCC alloys.1–4)

Tominaga et al.5) reported that Ti–Cr–V solid solution alloys with a BCC structure exhibit an effective protium capacity of 2.6 mass% protium. The optimum heat-treatment conditions for the alloy were reported to be annealing at 1573 K for 1 min, and then quenching in water. Okada et al.6) reported that the Ti–Cr–V alloys with low V content (5–7.5 at% V) yield the high capacity of nearly 3 mass% protium, which is the highest value at 313 K reported so far. The optimum composition of the Ti–Cr–V alloys was also discussed and the alloys with Ti/Cr ratio of 2/3 have the plateau region in the PCT curve around 0.1 MPa (1 atm) with highest capacity at 313 K. The alloys will be promising since it contains a low amount of the expensive V element. Since the BCC alloys with low content of V exhibit high capacities comparable to pure vanadium or V-based alloys, it is expected that V free Ti–Cr alloys with a BCC structure may exhibit a high capacity. But Ti–60Cr alloys (Ti/Cr = 2/3) have Laves phase as equilibrium phase in the range of room temperature–1630 K and BCC solid solution phase at high temperature in narrow range of 1630 K–1700 K. Therefore it is difficult to obtain only BCC phase freezing from high temperature in the binary alloys, so that it is necessary to stabilize the BCC phase in Ti–Cr binary phase diagram by adding some BCC-forming elements such Mo, W, Nb, and Ta. Then, the purpose of the present study is to investigate the formation of BCC phase in the Ti–Cr–X alloys (X=Mo, W, Nb, Ta) and their protium absorption-desorption properties.

2. Experimental Procedures

The alloys were prepared from raw materials 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%; Cr > 99.99 at%; and V, Mo, W, Nb, Ta > 99.99 at%. In our previous study, The Mo or W added Ti–Cr–V alloys have mainly BCC phase. But Mo or W unmelted additives were remained in the alloys with the addition of more than 10%Mo or 5%W, respectively. The melting point of Mo, W, Nb and Ta is high temperature such as 2883 K, 3683 K, 2741 K and 3269 K respectively. Therefore, at first Cr–X alloys (X=Mo, W, Nb, Ta) were melted, and then Ti–Cr–X alloys were prepared. Sample ingots were remelted three times to ensure their homogeneity. Some samples were annealed at 1673 K for 1 min, and quenched into iced water. Crystal structures and lattice parameters were studied by X-ray diffractometer (XRD) using Cu-Kα radiation (Philips, X’pert System). Hydrogenated sample for the XRD experiment was prepared by pressurizing the alloys on 0.1 MPa hydrogen gas and soaking protium absorbed alloys in ethanol to confine the protium in the sample.

PCT curves were measured with a Sieverts-type apparatus at 313 K. Each sample was put into a vessel and was evacuated at 313 K for 2 h, using a rotary vacuum pump. The alloys absorb protium fully at first hydrogen charge process, so initial activation treatments were unnecessary. Hydrogen was introduced gradually into the vessel up to a pressure of 10 MPa. The third cycle of the PCT curve is shown as the protium absorption-desorption property in this study.

3. Results and Discussion

Figure 1 shows XRD patterns of cast state and heat-treated Ti–60Cr alloys, and Ti–56.5Cr–2.5X heat-treated alloys (X=V, Mo, W, Nb, Ta). It was shown that main phase of...
the binary alloys were C14-type Laves phase, and BCC phase is appeared in heat-treated alloys. All Ti–56.5Cr–2.5X alloys in as-cast state consist of only Laves phase, but the Ti–56.5Cr–2.5V, Ti–56.5Cr–2.5Mo and Ti–56.5Cr–2.5W heat-treated alloys contain only BCC solid solution phase. The Laves phase was observed with small amount of secondary BCC phase in the Ti–56.5Cr–2.5Nb and Ti–56.5Cr–2.5Ta alloys. It was found that the addition of V, Mo or W element to the Ti–Cr alloys had an effect to form BCC phase in the alloys. Figure 2 shows PCT curves of Ti–60Cr and Ti–56.5Cr–2.5X heat-treated alloys at desorption process. The protium contents of the alloys at 10 MPa hydrogen increased with V, Mo or W addition, and V and Mo added alloys exhibited the flattened plateau regions and the capacities of 3.6 mass% protium. It was found that Mo acts as BCC former similar to V element in the Ti–Cr alloys. The Ta added alloy had no plateau region in pressure range of this study, since it consists of mostly C14 type laves phase. It was found the capacity of the alloys would be related with the ability of formation BCC phase, and it is not necessary to include V, which knows as expensive element, by containing Mo element. Mo could possibly replace V in the Ti–Cr BCC solid solution alloys.

Figure 3 shows XRD patterns of Ti–56.5Cr–2.5Mo heat-treated alloy in various hydrogenated stages: A) as-prepared state (0 mass%; H/M = 0), B) hydrogenated stage at 0.1 MPa for absorption process (1.1 mass%; H/M = 0.6) and C) at desorption process (3.3 mass%; H/M = 1.7). The virgin sample had BCC phase and a lattice constant of the sample was 0.304 nm. The hydrogenated sample (B) with lower protium content than that of plateau region had also BCC phase (0.314 nm). The XRD pattern of hydrogenated sample (C) with higher protium content than plateau region showed FCC phase (0.428 nm). Considerations of BCT unit cell in FCC lattice structure(c), lattice parameters of a-axis and c-axis were 0.303 nm and 0.428 nm respectively. The variation of these lattice parameters was different from that of vanadium hydrogenation. Vanadium has two hydrides, VH$_{1.1}$ and VH$_2$, which had different structures of BCT and FCC respectively.

Figure 4 shows PCT curves of Ti–(60–x)Cr–xMo heat-treated alloys (x = 0, 0.5, 1.0, 2.0, 2.5) at desorption process. XRD study showed that the alloys containing more than 1.0 at%Mo consist of mainly the BCC phase, whereas the alloys without and with 0.5Mo contained a large amount of Laves phase in addition to the BCC phase. Ti–Cr–(1.0–2.5)Mo alloys with only the BCC phase yield the highest capacity of about 3.6 mass% protium and had flat plateau regions with the capacity of about 2.2 mass% protium. The plateau pressure of the alloys containing more than 1.0 at%Mo increased with increasing of Mo content in the alloys.
Figure 5 shows XRD patterns of Ti-(60 – x)Cr-xMo as-cast alloys \((x = 2.5, 5, 10, 20, 30, 50)\). The alloys containing less than 2.5 at%Mo consists of only the Laves phase as mentioned earlier whereas the 5.0Mo alloy contained small amounts of secondary Laves phase in addition to the BCC phase as main phase. The as-cast state alloys with more than 10 at%Mo had only the BCC phase. Figure 6 shows the corresponding PCT curves of these alloys. The all curves of the alloys showed absorption-desorption hysteresis loops and sloped plateau regions, even the curve of Ti–10Cr–50Mo alloys had small hysteresis loops and the capacity of 1.1 mass% protium. The protium absorbing amount decrease with increasing Mo content in the alloys.

Figure 7 shows PCT curves of Ti-(60 – x)Cr-xMo heat-treated alloys \((x = 2.5, 5, 10, 20, 30, 50)\). Only BCC phase were observed in all heat-treated alloys. The slope of the plateau region in these alloys decreased after heat-treatment except for the alloy containing 50 at%Mo. The 50Mo alloy did not change the shape of the curve by heat-treatment at 1673 K for 1 min, because it was expected that the annealing temperature was too low to homogenize the alloy or the time of the annealing was too short. The capacity of the alloys decreased with increasing Mo content and the pressure of the plateau increased. However, XRD study showed that the lattice parameters of the phase in the alloys increased with increasing Mo content. For example, the 2.5, 5, 10, 20, 30 and 50Mo alloys had the lattice parameters 0.302, 0.305, 0.306, 0.308, 0.311 and 0.315 nm, respectively. This is because the atomic radius of Mo is larger than that of Cr. Figure 8 shows the corresponding PCT curves with the horizontal axis described by H/M ratio at desorption process in these alloys. The H/M ratio of the alloy with less than 10 at%Mo was 1.8 at 10 MPa hydrogen pressure and was unchanged with Mo content. The ratio of H/M of the alloy with more than 20 at%Mo decreased with increasing the content of Mo.

4. Conclusions

The protium absorption desorption properties of Ti–Cr–X alloys (X=Mo, W, Nb, Ta) were investigated and the following conclusions were made.
The addition of V, Mo or W element to Ti–Cr alloys stabilizes BCC phase. The effects of Mo addition to Ti–Cr alloys give not only flattened plateau regions and also the capacities of 3.6 mass% protium similar to Ti–Cr–V alloys.

The phase change in the Ti–Cr–Mo alloys during the hydrogenation process was studied. BCC structure was formed at the ratio of H/M = 0.6 or below, then, a FCC structure appeared at higher protium concentration region passing the plateau region.

The as-cast state alloys with more than 10 at%Mo consist of only the BCC phase. The all curves in the PCT measurements of the alloys showed absorption-desorption hysteresis loops and sloped plateau regions, and they are flattened by heat-treatment. The curve of Ti–10Cr–50Mo alloys show small hysteresis loops and the capacity of 1.1 mass% protium.

The highest value of the capacity in this study yields 3.6 mass% protium of Ti–Cr–(1.0–2.5)Mo. However, it was found that the protium content in the alloys containing more than 2.5 at% Mo decreases with increasing Mo content and the plateau pressure increased, but there is no change in the H/M ratio of the alloy with less than 10 at% Mo content. The lattice parameters of the BCC phase in the Ti–Cr–Mo alloys increase with increasing Mo content.

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