Isotope Effects on Protium and Deuterium Absorption Properties in Ti-56 at%Cr-20 at%V Alloy

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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 BCC structure are regarded as one of the candidates for hydrogen storage tanks.1 Since the Ti-Cr-V alloys show the capacity of nearly 3 mass% at 373 K, a lot of works, such as the additions of other elements,2–7) the effects of heat-treatment and composition,8–12) V free Ti-Cr alloys,13–16) cyclic properties17–19) and the effects on hysteresis,20) have been reported in improving the properties.

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. The protide is defined as a compound of protium, namely, a hydride hereafter. 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 the Ti-Cr-V alloys, it is quite important to know how to decrease the regions of stable protides. The present authors reported that decreasing the V content and increasing the Cr content turned out to shift the beginning of the plateau regions to the low protium concentration, and higher protium desorption capacity was achieved by increasing the Cr content and controlling measurement temperature in order to control the desorption plateau pressure near atmospheric pressure for the alloys containing less than 40 at%V (at% is abbreviated hereafter).21–24) However, the Cr-rich alloys, e.g. Ti-Cr-20V alloys containing more than 56 at%Cr, were found to absorb up to H/M = 1 because of the formation of the mono-protides.23,24) On the basis of these results, the present authors reported the region with the higher protium desorption capacity (about 2.6 mass%; 9-0.01 MPa) in the Ti-Cr-V alloys.24)

Moreover, the present authors reported that the appearance region of the mono-dueteride was more Cr-rich compositions than that of the mono-protides.25) For example, Ti-Cr-20V alloys containing more than 60 at%Cr absorb deuterium up to D/M = 1. Therefore, Ti-56Cr-20V alloy absorbs protium up to H/M = 1, but deuterium up to D/M = 2. As higher protium desorption capacity is achieved by increasing the Cr content in the region of the di-protide, there is some possibility of increasing the protium desorption capacity in Ti-Cr-V alloys using the isotope effects on absorption-desorption properties of the Ti-56 at%Cr-20 at%V alloy. This paper aims to clarify the isotope effects on protium and deuterium absorption properties in the Ti-56 at%Cr-20 at%V alloy. It was found that the memory effect for the absorption plateau pressure appears only once when deuterium was absorbed after desorbing protium, and the memory effect for the absorption capacity appears when protium was absorbed after desorbing deuterium. The protium desorption capacity after deuterium treatment, namely, after desorbing deuterium showed twice as high as that without deuterium treatment in the Ti-56 at%Cr-20 at%V alloy. Increasing protium desorption capacity for deuterium treatment was caused by increasing di-protide formation and decreasing mono-protide formation.

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Sieverts-type apparatus. The purities of the hydrogen gas and the deuterium gas were 99.99999 mass% and 99.6 mass%, respectively. The PCT curves of hydrogen were measured from 0.01 to 10 MPa, and those of deuterium were measured from 0.01 to 3 MPa. The zero points of PCT curves were the points before activation for the first cycle and the points after evacuation for 1 h at the measurement temperature by the rotary pump for the cycles after the second cycle if the descriptions are not given in particular.

3. Results and Discussion

3.1 Deuterium storage properties after absorbing protium

It has been found by XRD that the Ti-56Cr-20V alloy has a BCC single phase.

Figure 1 shows PCT curves in absorbing protium and deuterium for the first cycle at 244 K for the Ti-56Cr-20V alloy. As can be seen, the Ti-56Cr-20V alloy absorbs protium up to \( H/M = 1 \), but deuterium up to \( D/M = 2 \). The plateau pressure of deuterium is normally lower than that of protium.

Figure 2 shows PCT curves in absorbing protium at the first cycle and deuterium at the second and the third cycles. It is difficult to compare the first cycle curve with the second and third cycle curves, because the zero point of the first cycle curve was the point before activation, but those of the second and the third cycle curves were the points after evacuation for 1 h at the measurement temperature by the rotary pump. Thus, the zero point of the first cycle curve was shifted from the point before activation to that after evacuation. It is rather surprising that the plateau pressure in absorbing deuterium after desorbing protium, namely, that for the second cycle show as high as the protium absorption plateau pressure for the first cycle. However, the deuterium absorption and desorption plateau pressures for the third cycle showed as high as those at the first cycle shown in Fig. 1. This means that absorbed protium at the first cycle has some influence on the plateau pressure of the second cycle of absorbing deuterium.

As these results, it was found that the memory effect for the absorption plateau pressure appears only once when deuterium was absorbed after desorbing protium.

3.2 Protium storage properties after absorbing deuterium

Figure 3 shows PCT curves in absorbing deuterium at the first cycle and protium at the second cycle. It is difficult to compare the first cycle curves with the second cycle curves,
because the zero point of the first cycle curves was the point before activation, but that of the second cycle curves was the points after evacuation for 1 h at the measurement temperature by the rotary pump. Thus, the zero point of the second cycle curves was shifted from the point after evacuation to that before activation. The capacity in absorbing protium after desorbing deuterium, namely, that for the second cycle showed as high as the deuterium absorption capacity that exhibits about $D/M = 2$. Thus, it was found that the memory effect for the absorption capacity appears when protium was absorbed after desorbing deuterium.

Figure 4 shows PCT curves in absorbing protium at the second cycle without deuterium treatment, namely, after desorbing protium, and after deuterium treatment, namely, after desorbing deuterium.

Figure 5 shows XRD patterns of the protides after deuterium treatment and without deuterium treatment. The protides after deuterium treatment and without deuterium treatment were measured at the (A)-point and the (B)-point shown in Fig. 4, respectively. Each sample has the diffracted peaks from the BCC phase that is considered to be the structure before the plateau region. Thus, the diffracted peaks from the BCC phase are not indexed. The sample at the (A)-point after deuterium treatment consists mostly of a FCC phase and has a small quantity of a hcp phase. These FCC and hcp phases are considered to be a di-protide and a mono-protide, respectively. However, some Bragg peaks cannot be identified. These results show that increasing protium desorption capacity for deuterium treatment is caused by increasing di-protide formation and decreasing mono-protide formation.

Figure 6 shows PCT curves at 10th, 11th and 22th cycles in absorbing deuterium from the first cycle to the 10th cycle and protium from the 11th cycle to 22th cycle. Though absorption and desorption of deuterium were repeated, the memory effect for the absorption capacity appeared when protium was absorbed.
absorbed. Furthermore, it was found that the memory effect for the absorption capacity doesn’t disappear even though absorption and desorption of protium were repeated. This result differs in durability from the memory effect for the absorption plateau pressure in absorbing deuterium after desorbing protium.

3.3 The Effects of the Desorption Capacity on the Memory Effects

Figure 7 shows PCT curves in absorbing protium at the first cycle, deuterium at the second cycle after evacuation at 673 K for 1 h and protium at the third cycle after evacuation at 673 K for 1 h. It is considered that almost all protium and deuterium in the alloy were desorbed by evacuation at 673 K for 1 h. The memory effect for the absorption plateau pressure disappeared when deuterium was absorbed after almost all protium was desorbed by evacuation at 673 K for 1 h. However, it was found that the memory effect for the absorption capacity appears though protium was absorbed after almost all deuterium was desorbed by evacuation at 673 K for 1 h.

Figure 8 shows a XRD pattern of the protides that were measured at the (A)-point shown in Fig. 7. The diffracted peaks from the BCC phase that is considered to be the structure before the plateau region are not indexed. The majority of the protides shown in Fig. 8 consists of the FCC phase that is the di-protide, and a small quantity of the hcp phase that is the mono-protide was observed. Thus, it is considered that the memory effect for the absorption capacity in absorbing protium after desorbing deuterium, namely, deuterium treatment has durability.

As these results, it is presumed that the memory effect for the absorption plateau pressure is a consequence of residual protium in the alloys. On the other hand, the memory effect for the absorption capacity is presumed to be a consequence of residual lattice strain or defects in the alloys. Thus, it is considered that there is some possibility of increasing the protium capacity if residual lattice strain or defects, that lead to a protide with high protium capacity, are induced in other alloys.

4. Conclusions

The isotope effects on protium and deuterium absorption properties in the Ti-56Cr-20V alloy have been investigated, and the following conclusions have been derived.

(1) It was found that the memory effect for the absorption plateau pressure appears only once when deuterium was absorbed after desorbing protium. However, this memory effect disappeared when deuterium was absorbed after almost all protium was desorbed. It was presumed that this memory effect is a consequence of residual protium in the alloys.

(2) It was found that the memory effect for the absorption capacity appears when protium was absorbed after desorbing deuterium. It was considered that this memory effect has durability. This memory effect was presumed to be a consequence of residual lattice strain or defects in the alloys.

(3) It was found that the protium desorption capacity after deuterium treatment shows twice as high as that without deuterium treatment in the Ti-56Cr-20V alloy. Increasing protium desorption capacity for deuterium treatment was caused by increasing di-protide formation and decreasing mono-protide formation. It is considered that there is some possibility of increasing the protium capacity if residual lattice strain or defects, that lead to a protide with high protium capacity, are induced in other alloys.

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